Advanced Proton Conducting Polymer Electrolytes for Electrochemical Capacitors

by

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Research on solid electrochemical energy storage devices aims to provide high performance, low cost, and safe operation solutions for emerging applications from flexible consumer electronics to microelectronics. Polymer electrolytes, minimizing device sealing and liquid electrolyte leakage, are key enablers for these next-generation technologies.

In this thesis, a novel proton-conducting polymer electrolyte system has been developed using heteropolyacids (HPAs) and polyvinyl alcohol for electrochemical capacitors. A thorough understanding of proton conduction mechanisms of HPAs together with the interactions among HPAs, additives, and polymer framework has been developed. Structure and chemical bonding of the electrolytes have been studied extensively to identify and elucidate key attributes affecting the electrolyte properties. Numerical models describing the proton conduction mechanism have been applied to differentiate those attributes.

The performance optimization of the polymer electrolytes through additives, polymer structural modifications, and synthesis of alternative HPAs has achieved several important milestones, including: (a) high proton mobility and proton density; (b) good ion accessibility at electrode/electrolyte interface; (c) wide electrochemical stability window; and (d) good environmental stability. Specifically, high proton mobility has been addressed by cross-linking the polymer framework to improve the water storage capability at normal-to-high humidity.
conditions (e.g. 50-80% RH) as well as by incorporating nano-fillers to enhance the water retention at normal humidity levels (e.g. 30-60% RH). High proton density has been reached by utilizing additional proton donors (i.e. acidic plasticizers) and by developing different HPAs. Good ion accessibility has been achieved through addition of plasticizers. Electrochemical stability window of the electrolyte system has also been investigated and expanded by utilizing HPAs with different heteroatoms. The optimized polymer electrolyte demonstrated even higher proton conductivity than pure HPAs and the enabled electrochemical capacitors have demonstrated an exceptionally high rate capability of 50 V s\(^{-1}\) in cyclic voltammograms and a 10 ms time constant in impedance analyses.
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<th>Description</th>
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<td>AC</td>
<td>alternating current</td>
</tr>
<tr>
<td>BWA</td>
<td>tungstoboric acid</td>
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<td>CNT</td>
<td>carbon nanotube</td>
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<td>CoWA</td>
<td>tungestocobaltic acid</td>
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<td>CPE</td>
<td>constant phase element</td>
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<td>CuWA</td>
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<td>cyclic voltammetry/cyclic voltammogram</td>
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<td>DSC</td>
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<td>EDLC</td>
<td>electrochemical double-layer capacitor</td>
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<td>fourier transform infrared spectroscopy</td>
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<td>FWHM</td>
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<td>HPA</td>
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<td>PVP</td>
<td>poly(vinylpyrrolidone)</td>
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<td>PWA</td>
<td>phosphotungstic acid</td>
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<td>RC</td>
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<tr>
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<tr>
<td>SPEEKK</td>
<td>sulfonated poly(ether ether ketone ketone)</td>
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<td>SWCNT</td>
<td>single-wall carbon nanotube</td>
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<tr>
<td>TMS</td>
<td>tetramethylsilane</td>
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<td>XRD</td>
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# List of Symbols and Units

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<td>area (m²)</td>
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<td>$C(\omega)$ or $C^*$</td>
<td>complex capacitance (F)</td>
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<tr>
<td>$C'$</td>
<td>real part of complex capacitance (F)</td>
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<tr>
<td>$C''$</td>
<td>imaginary part of complex capacitance (F)</td>
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<td>capacitance of vacuum (F)</td>
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<td>thickness (m)</td>
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<td>resistance (Ω) or gas constant (JK⁻¹mol⁻¹)</td>
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<tr>
<td>t</td>
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<td>$W_{wet}$</td>
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<td>imaginary part of complex impedance (Ω)</td>
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<td>change of potential in positive electrode (V)</td>
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<tr>
<td>$\Delta E_{-ve}$</td>
<td>change of potential in negative electrode (V)</td>
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<td>$\Delta R_L$</td>
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<td>$\varepsilon_r$ or $\varepsilon_r'$</td>
<td>dielectric constant (-)</td>
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<td>$\varepsilon_r, EP$</td>
<td>low frequency dielectric constant (-)</td>
</tr>
<tr>
<td>$\varepsilon_r, s$</td>
<td>static dielectric constant (-)</td>
</tr>
<tr>
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<td>Name</td>
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<td>-------------------------------------------</td>
</tr>
<tr>
<td>$\varepsilon''$</td>
<td>dielectric loss (-)</td>
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<td>$\theta$</td>
<td>impedance phase shift (deg.)</td>
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<tr>
<td>$\mu$</td>
<td>proton mobility (m$^2$V$^{-1}$s$^{-1}$)</td>
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<tr>
<td>$\pi$</td>
<td>pi (-)</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>conductivity (Sm$^{-1}$)</td>
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<tr>
<td>$\tau$</td>
<td>dielectric time constant (s)</td>
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<td>correlation time in Bloembergen-Purcell-Pound equation (s)</td>
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<td>$\tau_{EP}$</td>
<td>dielectric time constant with electrode polarization (s)</td>
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<td>$\tau_s$</td>
<td>static dielectric time constant (s)</td>
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<td>$\omega$</td>
<td>angular frequency (rads$^{-1}$)</td>
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</table>
1 Introduction

1.1 Motivation

Electrochemical capacitors (or supercapacitors) are electrochemical energy storage devices that can stand alone or complement batteries in hybrid systems to reach high power density and fast charge/discharge rates [1-7]. In industrial and automotive applications, supercapacitors mainly provide regenerative power and peak assist, while in consumer electronics, they are much smaller and can supplement or replace batteries. Recently small sized supercapacitors, often referred to as micro-supercapacitors, have emerged for on-chip applications such as powering micro-electromechanical systems and bio-sensors [8]. In addition, some high rate micro-supercapacitors have shown potential to replace electrolytic capacitors for alternating current (AC) line filtering with very small RC (resistor-capacitor) time constants [9].

In a traditional supercapacitor, an ion-permeable and electrically insulating separator film is sandwiched between two electrodes soaked with a liquid electrolyte. Since liquid electrolyte leakage is a potential safety issue, especially when the material is environmentally hazardous, efforts abound to replace liquid electrolytes with solid electrolytes for next-generation solid supercapacitors that are not only safer, but also offer high performance, light weight, and flexible form factors. A few application examples of solid supercapacitors are shown in Appendix A, which provide flexible power sources with smaller dimensions and higher power density.

In recent years, significant efforts have been dedicated to achieve thin and/or free-standing supercapacitor electrodes, leveraging carbon nanotube (CNT) films, graphene sheets, reduced graphene oxide, conducting polymer/carbon composites, or metal oxide/carbon composites [10-12]. At the same time, flexible substrates or supports have been investigated, including paper, textile, woven cotton, and fabrics [13]. Although these materials have led to an advance in flexible solid supercapacitors, commercialization of such devices still remains challenging. One of the main limitations is the availability of solid electrolytes.

Among solid electrolytes, polymer electrolytes are ideal for flexible solid supercapacitors. A polymer electrolyte enables different supercapacitor cell designs with minimum packaging (see Figure 1-1). Slim supercapacitor multi-cell modules can be constructed by inserting bi-polar
electrodes between terminal electrodes and the polymer electrolyte layers in a sandwiched cell. Interdigitated finger cell design is often used for 2D planar micro-supercapacitors while a coaxial structure provides more flexibility to be woven into wearable electronics.

**Figure 1-1**: Schematic of polymer electrolyte-enabled supercapacitors in flexible sandwiched cell configuration (left), interdigitated finger cell configuration (middle), and coaxial fiber cell configuration (right). Reproduced from Ref. [14] with permission from the Royal Society of Chemistry.

### 1.2 Objectives

A typical polymer electrolyte consists of an ionic conductor, a polymer matrix, and additives. As shown in Figure 1-2, a high performance polymer electrolyte for flexible solid devices such as supercapacitors should exhibit the following properties:

- high ionic conductivity for high power output,
- good ion accessibility at electrode-electrolyte interface for high capacitance,
- wide electrochemical stability window for maximum cell voltage, and
- high environmental and temperature stability for device safety and long service life.

Heteropolyacids (HPAs) have demonstrated high solid-state proton conductivity at room temperature [15-19]. However its conductivity and stability fluctuates significantly with relative humidity (RH). HPA powders also cannot form films and earlier studies relied on HPAs pressed into pellets, resulting in inhomogeneous particle contact [17, 18]. This issue can be addressed by developing HPA/polymer composite electrolytes that can leverage the excellent film forming capability of the polymer and the high proton conductivity of HPAs.
This research has been focusing on all the above attributes in order to develop HPA-poly(vinyl alcohol) (PVA) based polymer electrolytes and to understand the mechanisms leading to their performance and properties. The specific objectives of the study were to:

- develop a thorough understanding of the structural and chemical bonding of the electrolyte system and interactions between polymer, proton conductors, and additives,
- deduce the mechanism of proton conduction of HPA within the polymer electrolytes as well as its effect on conductivity, and
- optimize the HPA-PVA polymer electrolyte system to achieve fast proton transport as well as good stability and cyclability at ambient conditions;

1.3 Outline

High rate and power capabilities with good environmental stability are essential for solid supercapacitors. To push the polymer electrolyte material performance excellence, various approaches have been included in this thesis (Figure 1-3). Different generations of polymer electrolytes have been developed. Details on the electrolyte compositions are shown in Section 3.2.

This thesis is organized as follows: Chapter 2 reviews current proton-conducting polymer electrolytes and the enabled solid and/or flexible supercapacitors. This is followed by an introduction of HPAs and their related properties. Chapter 3 details the experimental methods and characterization techniques used in this work. Chapter 4-9 present the major results. A summary and outlook of this work is shown in Chapter 10.
Figure 1-3: Overview of various approaches included in this thesis to improve the respective polymer electrolyte properties.
2 Background*

2.1 Solid electrochemical capacitors

Solid supercapacitors can be categorized along various criteria as shown in Figure 2-1. Depending on the charge storage mechanism, supercapacitors can be divided into electrochemical double-layer capacitors (EDLCs) and pseudo-capacitors. While EDLCs store charge electrostatically at an electrode/electrolyte interface as charge separation, pseudo-capacitors store energy by charge transfer between electrode and electrolyte via faradaic reactions. Supercapacitors come in either symmetric (using identical electrodes) or asymmetric (using different electrodes) configurations. Asymmetric supercapacitors may consist of a double layer electrode and a pseudo-capacitive electrode or two different pseudo-capacitive electrodes.

\[ E = \frac{1}{2} CU^2 \]  

(1)

* Part of this section published as RSC Adv., 4, 33091-33113 (2014)
$$Q = CU$$ \hspace{1cm} (2)$$

where $C$ is cell capacitance and $U$ is cell voltage. The peak power ($P_{peak}$) is defined as [1]:

$$P_{peak} = \frac{U^2}{4R}$$ \hspace{1cm} (3)

where $R$ is the equivalent series resistance (ESR). Alternatively, power ($P$) in general can be calculated by the energy ($E$) released or stored during a discharge or charge period ($t$)

$$P = \frac{E}{t}$$ \hspace{1cm} (4)

For an EDLC, double-layer formed by solvated electrolytic ions at an electrode surface (Figure 2-2a). The double-layer capacitance is $ca.$ 15-30 $\mu$Fcm$^{-2}$ for a smooth metallic electrode in a liquid electrolyte solution [1]. It can be calculated by

$$C = \frac{\varepsilon_r \varepsilon_0 A}{d}$$ \hspace{1cm} (5)

where $\varepsilon_r$ is the electrolyte dielectric constant, $\varepsilon_0$ is the absolute dielectric permittivity of classical vacuum, $d$ is the effective thickness of the double layer and $A$ is the electrode surface area. Since EDLCs only utilize electrostatic charge accommodation with no charge transfer between electrode and electrolyte (Figure 2-2a), they are intrinsically high power devices with excellent cycle life in the order of $10^5$ to $10^6$ cycles [1, 2].

**Figure 2-2**: Schematic of two charge storage mechanisms in supercapacitors: (a) double-layer formation at an electrode/electrolyte interface; and (b) reversible redox reactions on a RuO$_2$ electrode.
Pseudo-capacitors store energy by charge transfer between the electrode and electrolyte via faradaic reactions. In contrast to batteries, reactions in pseudo-capacitors are limited to one or two monolayers of the electrode surface. Typically, pseudo-capacitors can achieve up to 100 times higher specific capacitance than EDLCs. Materials used as pseudo-capacitive electrodes tend to exhibit multiple oxidation states, such as transition metal oxides (e.g. RuO$_2$, MnO$_2$) and conducting polymers (e.g. polypyrrole, polyaniline). Figure 2-2b depicts these redox reactions using the example of a RuO$_2$ electrode, the current “gold-standard” pseudo-capacitive material with fast and highly reversible reactions. Adsorption of protons from the electrolyte is required for these reactions. Unlike EDLCs, where the capacitance is a constant and is independent of voltage; the charge transferred in faradaic reactions is voltage-dependent, and consequentially, the average capacitance over the cell voltage $C_{av}$ is often used

$$C_{av} = \frac{Q_{tot}}{U}$$

where $Q_{tot}$ is total charge change for the charge or discharge of a pseudo-capacitor. Due to this voltage-dependence, nonlinear curves will be observed in constant current charge/discharge tests. The selection of different regions from the curve can make a large difference in determining average capacitance. Therefore, the use of a proper voltage region is critical and needs to be standardized. For supercapacitor applications, proton-conducting polymer electrolytes are of special significance since they tend to have high ionic conductivity and many pseudo-capacitive electrodes require protons for their faradaic redox reactions. Although the ionic conductivity of polymer electrolytes is 100 to 1000 times less than that of liquid electrolytes, this is less problematic as a thin film polymer electrolyte can largely compensate for the reduction in ionic conductivity (attributed to the reduced electrolyte thickness). To date, proton-conducting polymer electrolytes for solid supercapacitors have not been discussed extensively albeit they are widely used for fuel cells. A major difference between proton-conducting polymer electrolytes in fuel cells and supercapacitors is their application temperature, as the latter are normally operated at ambient room temperature conditions.

### 2.2 Proton conduction mechanisms in polymer electrolytes

The study of proton conduction in solids started with the fact that ice conducts electricity [20, 21]. Subsequently, the study of proton-conducting materials and the investigation of proton
conductivity expanded to proton-conducting polymer electrolytes for applications below the boiling point of water and proton-conducting oxides for higher temperature applications. Table 2-1 summarizes the brief history of both polymeric and inorganic proton-conducting materials.

**Table 2-1:** Brief history of polymeric and inorganic proton-conducting materials. Reproduced from Ref. [14] with permission from the Royal Society of Chemistry.

<table>
<thead>
<tr>
<th>Year</th>
<th>Material</th>
<th>Application temperature</th>
<th>Reference</th>
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<tbody>
<tr>
<td>1806</td>
<td>Aqueous solutions</td>
<td>&lt;100 °C</td>
<td>[22]</td>
</tr>
<tr>
<td>1877</td>
<td>Ice</td>
<td>&lt;0 °C</td>
<td>[20, 21]</td>
</tr>
<tr>
<td>1920s</td>
<td>Zeolites</td>
<td>&lt;100 °C</td>
<td>[23]</td>
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<tr>
<td>1930s</td>
<td>Hydrogen uranyl phosphate</td>
<td>100-400 °C</td>
<td>[24]</td>
</tr>
<tr>
<td>1960s</td>
<td>Nafion®</td>
<td>&lt;100 °C</td>
<td>[25, 26]</td>
</tr>
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<td>1970s</td>
<td>MHSO₄, where M=Cs, Rb</td>
<td>&gt;100 °C</td>
<td>[27]</td>
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<td>1970s</td>
<td>Zirconium hydrogenphosphate (Zr(HPO₄)₂)</td>
<td>200-350 °C</td>
<td>[28]</td>
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<td>1970s</td>
<td>β- and β”-alumina</td>
<td>100-300 °C</td>
<td>[29]</td>
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<tr>
<td>1980s</td>
<td>Perovskite type oxides</td>
<td>&gt;300 °C</td>
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<td>Acid/polymer blends (e.g. H₂SO₄/PVA)</td>
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<td>[30-32]</td>
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<td>1990s</td>
<td>Oxide gels</td>
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<td>[34]</td>
</tr>
<tr>
<td>1990s</td>
<td>Aromatic ionomers</td>
<td>&gt;100 °C</td>
<td>[35]</td>
</tr>
</tbody>
</table>

Proton conduction can be observed in many materials, from rigid inorganic oxides at high temperatures to flexible organic polymers at room temperature, leveraging different conduction mechanisms. Depending on the type of proton conductor, proton-conducting polymer electrolytes for low-to-room temperature applications can be classified into different groups, as shown in Figure 2-3. Polymeric proton-conducting electrolytes possess “intrinsic” proton conductivity from functional groups in polymer chains, whereas inorganic/polymer proton-conducting electrolytes blend inorganic proton conductors with a polymeric matrix to form gels or composites.

Most proton-conducting materials have been extensively studied for fuel cell applications. However due to the higher operating temperature of fuel cells compared to supercapacitors, development of low-to-room temperature proton-conducting polymer electrolytes has been limited. In order to design and optimize suitable proton-conducting polymer electrolytes for flexible solid supercapacitors, it is essential to understand proton migration mechanisms. Proton transport in polymer electrolytes can be described based on three main mechanisms, as shown in
Figure 2-4: (a) proton hopping or Grotthuss mechanism; (b) diffusion or vehicle mechanism; and (c) direct transport via polymer chain segmental motions [36-38].

Figure 2-3: Categories of low-to-room temperature proton-conducting polymer electrolytes depending on the type of proton conductor. Reproduced from Ref. [14] with permission from the Royal Society of Chemistry.

Figure 2-4: Schematic of low-to-room temperature proton conduction mechanisms: (a) hopping or Grotthuss mechanism; (b) diffusion or vehicle mechanism; and (c) direct transport via polymer chain motions. Reproduced from Ref. [14] with permission from the Royal Society of Chemistry.
Under Grotthuss mechanism, mobility of protons is determined by the formation or cleavage rate of the hydrogen bond between a hydronium ion (which itself can be hydrated in the form of H₃O₂⁺, H₅O₃⁺, H₇O₄⁺, etc.) and a water molecule (or other hydrogen-bonded liquids) [38, 39]. Protons “hop” from one hydrolyzed ionic site to another (Figure 2-4a). Site-to-site hopping between different sites with local rearrangement and reorientation is characterized by two potential wells, corresponding to the proton donor and the proton acceptor. In general, the potential wells are separated by a potential barrier of a few kJmol⁻¹. This low activation energy together with the high proton mobility of the proton hopping mechanism occurs primarily in a system with strong hydrogen bonding [37, 40].

In the diffusion or vehicle mechanism, a proton combines with solvent molecules (e.g. water), producing a complex and then diffuses [40]. As shown in Figure 2-4b, a proton can be transferred by the diffusion of hydrogen-water ions (H₃O⁺ in this example). The diffusion process is driven by a gradient in proton concentration and is commonly observed in a system with weak hydrogen bonding. Diffusion of the hydrogen-water ions may decrease because of hydrogen bonding with other solvent molecules. This diffusion process is much slower than proton hopping and is characterized by a higher activation energy and lower proton mobility.

Proton transfer can also result from segmental motions of polymer chains (Figure 2-4c). However, this type of proton transportation is restricted to the amorphous phase of the solvating polymers, where the polymer molecules are free to move. Therefore, proton conduction by segmental motions is only possible above the glass transition temperature of the polymer. In the amorphous phase, the polymer side chains can vibrate to a certain extent, thus reducing or eliminating the distance for proton conduction.

To reach high proton conductivity in polymer electrolytes for low-to-room applications, a high degree of hydration is essential, as proton conductivity increases with temperature and RH. At a constant temperature, protons are transported via Grotthuss mechanism with high mobility at high RH and via vehicle mechanism with lower mobility at low RH. In contrast, with increasing temperature, vehicle mechanism progressively dominates Grotthuss mechanism, as hydrogen bonds begin to elongate and break.

For flexible solid supercapacitor applications, polymer electrolytes should exhibit the properties listed in Section 1.2. Proton-conducting polymer electrolytes for low-to-room temperature
applications impose an additional requirement: to be capable of maintaining a high degree of hydration. The following sections will discuss current proton-conducting polymer electrolytes for supercapacitors.

2.3 Polymeric proton-conducting electrolytes

Polymeric proton-conducting electrolytes have been intensively studied for electrochemical energy storage devices. Of main interest are pure ionomers containing negatively charged functional sites (mainly -SO₃H, -PO₄H₂, -COOH), because of their higher proton conductivity below 100 °C. These polymer electrolytes typically have a multiphase structure containing both hydrophobic and hydrophilic regions. Charge from their fixed functional sites can be compensated for by mobile protons exchanged within the media. Polymer films soaked with phosphoric acid (e.g. polybenzimidazole (PBI)-H₃PO₄) and pure ionomers soaked with ionic liquids are also used in fuel cell applications, these electrolytes however have no application in room temperature supercapacitors.

2.3.1 Perfluorosulphonic acid electrolytes

Among polymeric proton-conducting electrolytes, perfluorosulphonic acid (PFSA) membranes have emerged as materials of choice for low temperature applications requiring high stability and chemical resistance. One of the most well-known PFSA is Nafion® [41-43]. By combining the extreme hydrophobicity of the polytetrafluorethylene (PTFE) backbone with perfluorinated side chains and terminated by sulfonic acid (-SO₃H) groups, strong hydration (solvation) can occur and lead to complete proton dissociation. Water not only dissociates the protons from acid groups, but also facilitates the mobility of hydrated protons via Grotthuss and vehicle mechanisms.

The water molecules are only loosely bonded to the hydrophilic -SO₃H groups and can be readily removed in low RH, causing a high energy barrier for proton transport and low proton conductivity. As a result, proton conduction mechanism of Nafion is highly dependent on the hydration state of the polymer electrolyte. Proton conductivity of different Nafion films has been characterized extensively as a function of temperature and RH [41, 42]. For example, Maréchal et al. have investigated the proton conductivity of Nafion-117 under different temperatures and RH and observed that the proton transport in Nafion-117 is highly sensitive to temperature and to
the level of hydration in the membrane [41]. In spite of the sensitivity to dehydration, the success and maturity of PFSA in fuel cells has made them a preferred choice for both EDLCs and pseudo-capacitors.

Staiti et al. constructed the first all solid EDLC using a Nafion ionomer solution and carbon electrodes [44, 45]. Both a commercial Nafion-115 membrane and a solution-casted Nafion-1100 film were investigated. The capacitor assembled with the cast Nafion membrane exhibited higher performance but its capacitance was lower than that of a liquid cell. To demonstrate the feasibility of scaling up Nafion polymer electrolyte-enabled solid EDLCs, a multi-cell prototype was constructed by stacking five single solid cells [46]. This device reached 1.5 F capacitance with 5 V working voltage and a 0.3 s RC time constant.

Since the use of pure Nafion is not economical due to its high cost, Subramaniam et al. investigated solid EDLCs based on composites of Nafion with PTFE or cellulose acetate [47]. Improvements in mechanical strength of the polymer electrolyte in the dry state and in dimensional stability in the hydrated state were observed. However, both Nafion/PTFE and Nafion/cellulose acetate composite films suffered from a substantial loss of proton conductivity.

To facilitate charge and ion transport at the electrode/electrolyte interface, Choi et al. prepared flexible solid EDLCs by slowly pouring a Nafion solution onto the thin film electrode [48]. This electrode/electrolyte integration promoted interconnected network structures at the interface, resulting in a two-fold increase in capacitance compared to the EDLC without Nafion integration. Similarly, Huang et al. assembled a flexible solid EDLC by spraying aqueous suspensions of multi-wall carbon nanotubes (MWNT) in a Nafion ionomer solution and an H$_2$SO$_4$ solution directly onto both sides of a Nafion membrane [49]. The Nafion and H$_2$SO$_4$ solutions ensured better proton penetration into the interior of the electrodes, promoting electrolyte wetting and ion adsorption, and consequentially higher cell capacitance and proton mobility.

One of the advantages of PFSA is its compatibility with many pseudo-capacitive electrodes that require protons for their redox reactions. The first Nafion-based solid pseudo-capacitor was developed in 1990 by Sarangapani using RuO$_2$-Nafion composite electrodes [50]. In these devices, the Nafion ionomer acts not only as an electrolyte but also coats the individual RuO$_2$ particles and provides continuous proton transport throughout the composite structure. Nafion-
enabled solid asymmetric supercapacitors exhibited a potential to further improve energy density when compared to EDLCs while maintaining high rate capability. A hybrid Nafion-enabled supercapacitor in an asymmetric cell configuration with RuO₂/carbon as the positive electrode and carbon as the negative electrode was studied by Staiti et al [51]. They showed that optimal performance is obtained by balancing the electrode capacitance in the solid device.

Although many PFSA-based solid supercapacitors have been constructed and characterized, few have been developed for commercial supercapacitors. Part of the problem lies in their high cost and sensitivity to dehydration. While PFSA film is highly conductive in a highly hydrated environment at higher temperatures, its proton conductivity drops significantly under ambient conditions. Modification to Nafion through dispersing nanoparticles is a popular approach to improve water retention capability or conductivity. Effect of different hygroscopic materials, such as inorganic oxides particles [52-56], clays [57-59], conductive polymers [60-62], and solid acids [56, 63] were investigated. However these modified Nafion materials have not been widely tested as polymer electrolytes for supercapacitors and require further study to understand the influence of these modifications on cell capacitance, cycle life, and power performance.

2.3.2 Sulfonated hydrocarbon electrolytes

Nafion is rather costly and preparation of Nafion involves environmentally unfriendly fluorine-based technologies [42, 43]. Non-perfluorinated alternatives based on hydrocarbon backbones have been developed. Most of them are composed of benzene rings or aromatic heterocyclic rings. The wide variability of their chemical structures permits different functionalization (i.e. introduction of polar sites) through doping, chemical grafting, or direct sulfonation to increase proton conductivity and water uptake. Some of these alternative sulfonated hydrocarbon-based proton conductors include poly(ether sulfones) (PES) and poly(ether ketones) (PEK) with varying numbers of ether and ketone functionalities (such as poly(ether ether ketone) (PEEK), poly(ether ether ketone ketone) (PEEKK), poly(arylene ethers), polyesters, or polyimides). These materials have excellent chemical resistance due to the higher C-H bond strength in the benzene ring compared with aliphatic C-H bond strengths. Other advantages of these materials include low cost, excellent chemical resistance, and good mechanical properties.

Although numerous acid-functionalized hydrocarbon proton conductors have been prepared, their overall performance is still inferior to Nafion. Currently, most efforts on sulfonated
hydrocarbon proton conductors are focused on fuel cell applications, especially for proton exchange membrane fuel cells or direct methanol fuel cells, because of their higher temperature stability and lower fuel cross-over. Application of this group of materials to supercapacitors is limited. An overview of the proton conductivity of sulfonated poly(ether ether ketone) (SPEEK) and sulfonated poly (ether ether ketone ketone) (SPEEKK) at different degrees of sulfonation as well as blends with PBI or PES and pure oligomers is shown in Figure 2-5. As a result of their higher proton conductivity at low temperatures, only SPEEKK and SPEEK (or other PEK with different ether and ketone functionalities) have been used for supercapacitor applications.

**Figure 2-5**: Temperature dependence of proton conductivity for various sulfonated polymer electrolytes at full hydration. Reproduced from Ref. [64] with permission from Elsevier.

The first solid EDLC based on SPEEK membranes was demonstrated by Kim et al. in 2006 [65]. The SPEEK film was obtained by sulfonation of commercial PEEK followed by solution casting and soaking in H₂SO₄. The free-standing film exhibited a conductivity of 4.3 mScm⁻¹ at room temperature. Further studies were conducted with differing degrees of sulfonation to improve cell performance [66]. The polymer electrolytes showed a maximum conductivity of 4.5 mScm⁻¹ at 78% sulfonation. Since a higher degree of sulfonation may further restrict mass transport caused by the interactions among the polar -SO₃H groups while a lower degree of sulfonation may impose higher resistance, an optimization of sulfonation is essential to achieve good EDLC cell performance.
SPEEK has also been used for solid pseudo-capacitors. For example, Sivaraman et al. constructed a solid supercapacitor with polyaniline (PANI) as electrode material [67]. A sandwiched 6-cell stack solid supercapacitor based on the cross-linked SPEEK polymer electrolyte and PANI electrodes achieved a specific capacitance of 480 Fg⁻¹ [68]. Other sulfonated hydrocarbon-based polymer electrolytes have been explored for solid pseudo-capacitors. For example, a pseudo-capacitor with composite PANI electrodes and a poly(vinyl sulfonic acid) proton-conducting polymer electrolyte optimized for fast ion transport and intimate electrode/electrolyte contact exhibited a good capacitance of 98 Fg⁻¹ [69]. However, the solid device exhibited an approximately 20% reduction in capacitance after 1500 cycles limited by the degradation of both the electrolyte and the PANI electrodes.

Sulfonated hydrocarbon polymers offer a more convenient and less expensive process than those used to fabricate PFSA membranes. As the backbones of these sulfonated polymers tend to be less hydrophobic and the acid groups are less polar, a high degree of hydration is required to maintain a sufficient level of proton conductivity at room temperature. For instance, water filled channels in SPEEK are narrower than those in Nafion, leading to a larger hydrophilic/hydrophobic interface and a larger separation of neighboring sulfonic acid functional groups [64]. In order to achieve better and stable supercapacitor device performance, enhancements in proton conductivity of PFSA films and sulfonated hydrocarbons at low RH conditions are required. Nevertheless, considering their higher temperature stability, sulfonated hydrocarbon proton conductors (especially those containing aromatic backbones) are attractive alternatives for high temperature supercapacitor applications [70-72].

### 2.4 Inorganic/polymer proton-conducting electrolytes

Inorganic/polymer proton-conducting electrolytes can be further divided into two subgroups: (a) salt-in-polymer and (b) polymer-in-salt. Salt-in-polymer electrolytes are prepared by dispersing acids, bases, or salts in a polymer such as poly(ethylene oxide) (PEO), poly(acrylonitrile) (PAN), or poly(methylmethacrylate) (PMMA). Most salt-in-polymer electrolytes are aqueous based and form acid/polymer blends or acidic hydrogels (i.e. aqueous gels). In contrast, polymer-in-salt electrolytes are prepared by using only a small amount of polymer material as a matrix to hold the solid proton conductors together during film forming. With increasing salt concentration, the discrete salt clusters are interconnected, forming a percolation pathway for ion conduction (see
Figure 2-6). Since many highly conductive proton-conductors rely on the water molecules embedded in the structure (e.g. crystallized water in hydrous acids) to conduct the protons rather than on the loosely bound or free water, polymer-in-salt electrolytes have much higher water retention capability compared to salt-in-polymer electrolytes.

![Diagram showing morphology model for a polymer electrolyte as a function of salt percentage.](image)

**Figure 2-6**: Morphology model for a polymer electrolyte as a function of salt percentage. Adapted from Ref. [73] with permission from Wiley.

### 2.4.1 Salt-in-polymer acid/polymer blend electrolytes

Acid/polymer blends resulted from mixing strong acids (e.g. H₂SO₄ or H₃PO₄) with polymers and are currently the most widely used polymer electrolytes for solid supercapacitors, especially for flexible and micro-devices. Unlike polymeric proton-conducting electrolytes (discussed in Section 2.3), which have been deployed primarily for rigid solid supercapacitors, acid/polymer blends have found a wide-range of applications in flexible solid devices on account of their ease of preparation, good conductivity, and high environmental stability. Polymers used in such systems include PEO, PVA, PAAM, poly(vinylpyrrolidone) (PVP), poly(2-vinylpyridine) (P₂VP), and poly(4-vinylpyridine) (P₄VP). Among these, PVA is widely used due to its good thin film forming capability, high water-solubility, and adhesive characteristics which ease processing. H₂SO₄ and H₃PO₄ are often chosen as proton donors because of their self-ionization and self-dehydration reactions [23] at pure states:

\[
6\text{H}_2\text{SO}_4 \leftrightarrow \text{H}_3\text{SO}_4^+ + \text{H}_3\text{O}^+ + \text{HSO}_4^- + \text{HS}_2\text{O}_7^- + \text{H}_2\text{S}_2\text{O}_7 + \text{H}_2\text{O}
\]

\[
5\text{H}_3\text{PO}_4 \leftrightarrow 2\text{H}_4\text{PO}_4^+ + \text{H}_3\text{O}^+ + \text{H}_2\text{PO}_4^+ + \text{H}_2\text{P}_2\text{O}_7^{2-}
\]

Even though polymers are less efficient than water in dissociating protons, the proton conductivity of acid/polymer blends falls between aqueous acidic solutions and pure acids.
Acid/polymer blend electrolytes are prepared by adding an acid solution to an aqueous polymer solution under stirring. This process can be applied only when mixing with aqueous acids does not result in chemical degradation of the polymer. They typically display a room temperature conductivity in the range from $10^{-6}$ to $10^{-4}$ Scm$^{-1}$ in the anhydrous state [23]. One of the first systems ($\text{H}_3\text{PO}_4$/PVA) for electrochemical applications has been described by Polak et al. in 1987 [74].

Acid/polymer blend electrolytes, in particular $\text{H}_2\text{SO}_4$/PVA, have been widely used for EDLCs with CNT or graphene electrodes, to achieve flexible and solid-state structures. For example, Wu et al. developed in-plane micro-supercapacitors using graphene electrodes in an $\text{H}_2\text{SO}_4$/PVA electrolyte, which showed an areal capacitance of 80.7 μFcm$^{-2}$ and were able to be charged/discharged at a 1000 Vs$^{-1}$ scan rate [75]. $\text{H}_2\text{SO}_4$/PVA polymer electrolytes have also been combined with other advanced electrode materials, such as cellulose nanofibers/multi-wall carbon nanotube (MWCNT) hybrid aerogel [76] or CNT coated cellulose paper [77], to fabricate solid-state flexible EDLCs.

$\text{H}_3\text{PO}_4$/PVA is another common acid/polymer blend system for flexible devices. Kaempgen et al. used $\text{H}_3\text{PO}_4$/PVA with single-wall carbon nanotube (SWCNT) electrodes to construct printable thin film EDLCs that showed lower internal resistance and higher capacitance than a liquid device [78]. An in-plane EDLC comprised of pristine graphene or multilayer reduced graphene oxide electrodes and a $\text{H}_3\text{PO}_4$/PVA polymer electrolyte was fabricated as a 2D solid device [79]. Limited by the high internal resistance, the device showed poor performance at high charge/discharge rates. Chen et al. demonstrated a coaxial fiber-type flexible EDLC with an $\text{H}_3\text{PO}_4$/PVA polymer electrolyte between aligned CNT fibers [80]. The highly aligned CNT showed high mechanical strength, and could be woven into a textile structure for flexible or wearable electronics. Nevertheless, the device showed high internal resistance.

PEO-modified poly(methacrylate) (PMA) dissolving anhydrous $\text{H}_3\text{PO}_4$ has been investigated as a polymer electrolyte for solid EDLCs [81]. A maximum conductivity of 0.2 mScm$^{-1}$ was achieved with optimized amounts of organic plasticizers at room temperature. Since good rate performance could only be achieved at a high temperature of 90 °C, further improvement in low-to-room temperature conductivity is necessary for practical supercapacitor applications.
Acid/polymer blend electrolytes are commonly used in pseudo-capacitive systems such as RuO$_2$, MnO$_2$, and conducting polymers. For example, nano-crystalline RuO$_2$ thin films were deposited on a stainless steel mesh [82]. The resultant RuO$_2$ thin films were solidified in and separated by the H$_2$SO$_4$/PVA polymer electrolyte. The rate performance of this solid device was limited by its high charge transfer resistance of 11 ohm. Si et al. developed an on-chip micro-supercapacitor, based on MnO$_x$/Au multilayers electrodes leveraging an H$_2$SO$_4$/PVA polymer electrolyte [83]. However, this device displayed a nearly 25% reduction in capacitance after 15000 cycles, probably caused by the electrochemical dissolution of active materials. Other H$_2$SO$_4$/PVA-enabled pseudo-capacitors, including nano-GeSe$_2$ [84] and nitrogen and boron co-doped graphene [85] have also been tested.

H$_2$SO$_4$/PVA polymer electrolytes have also been applied to PANI-based solid pseudo-capacitors. An on-chip flexible micro-supercapacitor was reported by Wang et al. using patterned PANI nanowire electrodes on Au/Cr and H$_2$SO$_4$/PVA polymer electrolytes [86]. Other H$_2$SO$_4$/PVA enabled pseudo-capacitors with PANI electrodes have been demonstrated, including PANI coated graphitic petals on carbon cloth [87] and PANI coated carbon paper [88].

H$_3$PO$_4$/PVA is also often selected as polymer electrolyte for solid pseudo-capacitors. The first H$_3$PO$_4$/PVA-based pseudo-capacitor was developed as a solid multi-cell RuO$_2$ device in single cell, 4-cell, and 9-cell configurations [89]. An interdigitated MnO$_2$-based pseudo-capacitor with an H$_3$PO$_4$-PVA semi-dried gel acting as both electrolyte and substrate was developed [90]. While the device had stable cycle life, it showed a distorted CV at a 100 mVs$^{-1}$ scan rate. H$_3$PO$_4$/PVA electrolytes have also been utilized for pseudo-capacitors with MnO$_2$ composite electrodes, such as MnO$_2$/carbon core-shell fiber [91], MnO$_2$/carbon nanoparticles [92], MnO$_2$/graphene nanosheets [93], and MnO$_2$/PPy [94]. In particular, the MnO$_2$/carbon core-shell fiber solid capacitor showed high rate capability with a scan rate of up to 20 Vs$^{-1}$ and a volumetric capacitance of 2.5 Fcm$^{-3}$.

The rate performance of current flexible EDLCs and pseudo-capacitors is mainly limited by the kinetics of ion adsorption/desorption at the electrode/electrolyte interface and/or the kinetics of pseudo-capacitive reactions (i.e. charge transfer reactions), rather than the movement of ionic species in the polymer electrolyte. Although both H$_3$PO$_4$/PVA and H$_2$SO$_4$/PVA have been shown as suitable polymer electrolytes with good stability, the low proton conductivity of these systems
limit the rate performance of the enabled solid devices. Polymers with intermediate basicity could be used, such as PAAM and PVP, to enhance the proton conductivity of the acid/polymer blend electrolytes. In such cases, the nitrogen or oxygen atoms in the polymer can be protonated by the acid, leading to additional proton exchange and conduction. For example, a proton conductivity of 6 mScm\(^{-1}\) was observed for an H\(_2\)SO\(_4\)/PAAM blend [30]. However very limited electrochemical studies investigating their compatibility with supercapacitor devices have been performed on such systems.

### 2.4.2 Salt-in-polymer acidic hydrogel electrolytes

To increase the proton conductivity of acid/polymer blend electrolytes, gel polymer electrolytes are developed by using low molecular-weight organic solvents, such as ethylene carbonate, propylene carbonate, dimethylformamide, or diethyl carbonate. When water is used as a solvent, the gel polymer electrolyte is referred to as hydrogel (or aqueous gel) polymer electrolyte.

**Figure 2-7:** Schematic of hydrogel polymer electrolyte preparation from chemically or physically cross-linked polymers with acidic solutions. Reproduced from Ref. [14] with permission from the Royal Society of Chemistry.

Hydrogel polymer electrolytes utilize superabsorbent or highly swollen polymers, such as PVA, poly(acrylic acid) (PAA), and poly(acrylamide) (PAAM), or physically or chemically cross-linked polymers as host materials. Due to interactions between the –OH and/or =O groups of the polymer and the acidic solutions, swelling of the polymer occurs throughout the structure by hydrogen bonding. To maintain the water-insolubility of the hydrogel, the polymer hosts are often chemically or physically cross-linked. As shown in Figure 2-7, chemically cross-linked polymer monomers are covalently bonded by a chemical cross-linker, whereas the physically cross-linked polymer hosts are non-covalently bonded but the polymer host is stabilized by small
polymer domains (typically crystalline domains), and thus exhibit less stability. The 3D networks in the polymer are able to trap acidic solutions in the polymer matrix.

The basic ion conduction principle of hydrogel polymer electrolytes is similar to aqueous electrolytes, in that ionic conduction relies on the excess water that the system contains. Acidic hydrogel electrolytes have been developed using PVA [95] and PAAM [96] with strong acids and can achieve a room temperature proton conductivity as high as 10 to 100 mScm⁻¹.

PVA is the most commonly used polymer matrix for acidic hydrogels. Wada et al. used glutaraldehyde to cross-link PVA in a H₂SO₄/PVA hydrogel electrolyte as a free-standing membrane for activated carbon EDLCs [95]. The device showed a capacitance and rate performance similar to a 1 M H₂SO₄ liquid cell. A more concentrated 4 M H₂SO₄ solution with cross-linked PVA was used to construct activated carbon EDLCs, and showed higher proton conductivity than a film containing 1M H₂SO₄ [97]. The capacitors exhibited higher capacitance but raise concerns over the chemical stability of hydrogels containing such high concentration of H₂SO₄.

Kalupson et al. demonstrated a flexible EDLC enabled by a cross-linked PVA hydrogel with an 1 M or 3 M H₂SO₄ electrolyte and binder-free single-wall carbon nanotube (SWCNT) electrodes [98]. Both pristine and oxidized (to introduce pseudo-capacitance) SWCNT were used to fabricate a flexible device. These ultra-thin EDLCs displayed a very high rate performance with a 15 ms time constant and almost no reduction in performance after 10000 cycles.

Acidic hydrogels have also been investigated as polymer electrolytes for pseudo-capacitors. A cross-linked PVA/PAA blend with 1.5 M HClO₄ was used as a hydrogel electrolyte.[99] Utilizing a RuO₅·nH₂O/carbon electrode, a solid pseudo-capacitor exhibited a capacitance of 1000 Fg⁻¹ at a 2 mVs⁻¹ scan rate. However this device suffered from a significant reduction in capacitance after 45 cycles. In a more recent study, different acrylic gel polymer electrolytes, including PAA and potassium polyacrylate were used for RuO₂ pseudo-capacitors [100].

Since acidic hydrogels exhibit low adhesion to the electrode surface, mechanical pressure is required to ensure good interfacial contact between the electrode and electrolyte in an assembled cell. This often adds extra volume, weight and other complexities to the devices, which needs to be addressed. In addition, the life time and shelf life of acidic hydrogel supercapacitors (both
EDLCs and pseudo-capacitors) have not been extensively studied and the long-term performance under operating conditions is unknown. Since the main content of these hydrogel polymer electrolytes is in a quasi-liquid state, preventing the cell from “drying” for long term storage is another major challenge. The loosely bonded and/or free water molecules in the hydrogels undergo fast dehydration, which significantly affects the conductivity of the electrolyte. For supercapacitors that operate in an ambient environment, water retention is critical. Alternatively, other inorganic hydrogels, such as sol-gels or fumed SiO₂ gels, have also been developed for supercapacitors [101-104] and shown promise of improved device performance.

2.5 Heteropolyacids for polymer-in-salt electrolytes

With the development of solid-state proton conductors, polymer-in-salt electrolytes have shown promising performance. The major content of a polymer-in-salt electrolyte is the solid ionic conductor, which is embedded in a polymer matrix (see Figure 2-6). Because of the small polymer percentage, the ionic conduction mechanism depends on its pure solid counterpart and often obeys an Arrhenius-type dependence. HPAs are hydrous salts having the highest proton conductivity at room temperature among inorganic solid-state proton conductors [15-19]. This section discusses the structure as well as the origin of the high solid-state proton conductivity of HPAs.

2.5.1 Primary structure

HPAs belong to a large family of metal-oxygen clusters of early transition metals formulated as \( \text{H}_2\text{[X}_n\text{M}_m\text{O}_y\text{]} \), where \( \text{M} \) is the addenda atom and \( \text{X} \) is the heteroatom [19, 105, 106]. The most common addenda atoms are \( \text{W}^{6+}, \text{Mo}^{6+} \) and \( \text{V}^{5+} \) while the heteroatoms can be \( \text{P}^{5+}, \text{Si}^{4+}, \text{Ge}^{4+} \) and \( \text{B}^{3+} \) [106, 107]. Their conjugated anions (i.e. heteropolyanions) are electrochemically active with multiple electron transfer redox processes. They have fast charge transfer kinetics with good stability in most of their oxidation states [105, 106]. In addition, their chemical properties, such as redox potentials and acidities, can be fine-tuned through varying constituent addenda and heteroatoms. Numerous types of heteropolyanions have been synthesized and investigated as electrode materials for electrocatalysts and supercapacitors [106, 108].

Keggin-type HPAs are the most stable HPAs and its heteropolyanion is represented by the formula \( [\text{X}^{n+}\text{M}_{12}\text{O}_{40}]^{(8-n)-} \). Two common Keggin-type HPAs are silicotungstic acid (SiWA,
H₄SiW₁₂O₄₀) and phosphotungstic acid (PWA, H₃PW₁₂O₄₀). The original Keggin structure (α-Keggin) is the most common isomer. Its central heteroatom X is bonded with four oxygen atoms, forming a tetrahedron internal unit (XO₄ⁿ⁻), that is surrounded by a cage of twelve MO₆ octahedral units linked to one another by the neighboring oxygen atoms as shown in Figure 2-8 [19]. Three MO₆ octahedra link together by sharing edges to form a M₃O₁₃ triplets (as known as the structural unit of HPAs). Four such M₃O₁₃ triplets encapsulates the central tetrahedron, forming a spherical polyanion. Oxygen atoms in the polyanion can be classified into 4 groups: tetrahedral oxygen (Oₐ), edge sharing oxygen (Oₐ), corner sharing oxygen (Oₙ), and terminal oxygen (Oₗ). The tetrahedral oxygen connects the central heteroatom X to one M atom in each of four M₃O₁₃ triplets. The two types of sharing oxygen atoms (Oₐ and Oₙ) bridge two M atoms in neighboring octahedral, whereas the terminal oxygen atom (Oₗ) is bonded to only one M atom. Besides the α-Keggin structure, there are 4 more isomers: β-, γ-, δ-, and ε-Keggin. These isomers involve different rotational orientations of the M₃O₁₃ triplets, as shown in Figure 2-9. Nevertheless, they can be considered chemically similar in general.

Figure 2-8: Polyhedral view of the α-Keggin anion structure (the external M₁₂O₃₆ encapsulates the internal unit).

Figure 2-9: Polyhedral representations of the five isomers of the Keggin polyanion (the rotated M₃O₁₃ units are highlighted). Reproduced from Ref. [109] with permission from the Royal Society of Chemistry.
HPAs are strong acids and all intrinsic protons of Keggin-type HPAs dissociate equally in aqueous solution and cannot be differentiated. Their high ionic conductivity in aqueous solutions are resulting from (a) the high ionic strength of the electrolyte solutions due to the complete dissociation of ions and (b) the high mobility of the Keggin anions as a result of their un-solvated nature, in which its hydrodynamic radius is similar to its crystallographic radius [110, 111]. It has been reported that the monovalent anion of SiWA $1/4$[SiW$_{12}$O$_{40}$]$^-$ demonstrates a high limiting molar conductivity of 23.7 mSm$^2$mol$^{-1}$, much higher than that of Cl$^-$ (7.6 mSm$^2$mol$^{-1}$), $1/2$[SO$_4$]$^-$ (8 mSm$^2$mol$^{-1}$), or NO$_3^-$ (7.1 mSm$^2$mol$^{-1}$) [112]. Because of their high ionic conductivity, Keggin-type HPA solutions have been reported as liquid electrolytes for fuel cells and supercapacitors [113-115]. The high acid strength of Keggin-type HPAs in solution has been reported and the general trends for the addenda atom are W$^{6+}$>Mo$^{6+}$>V$^{5+}$ [116].

The most common method for the preparation of HPAs is the acidification of aqueous solutions of oxyanions of addenda atoms and heteroatoms stoichiometrically, for example:

$$12\text{Na}_2\text{WO}_4 + \text{Na}_2\text{SiO}_3 + 26\text{HC}1 = \text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O} + 26\text{NaC}1 + 11\text{H}_2\text{O}$$

Acidification of the solutions is generally achieved by the addition of mineral acids (e.g. HCl and H$_2$SO$_4$). Since the rates of formation are large, the polyanions can be crystallized from acidified mixtures of the components at room temperature. Nevertheless, careful control of temperature and pH is important and in some cases, an excess heteroatom is necessary. HPA then can be separated and extracted with diethyl ether from the aqueous solutions.

<table>
<thead>
<tr>
<th>pH</th>
<th>Major products</th>
<th>Dimeric anions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1.5</td>
<td>[PW$<em>{12}$O$</em>{40}$]$^{3-}$</td>
<td></td>
</tr>
<tr>
<td>1.5-2.2</td>
<td>[PW$<em>{12}$O$</em>{40}$]$^{3-}$, [PW$<em>{11}$O$</em>{39}$]$^{2-}$</td>
<td>[P$<em>2$W$</em>{21}$O$_{71}$]$^{6-}$</td>
</tr>
<tr>
<td>2.2-3.5</td>
<td>[PW$<em>{12}$O$</em>{40}$]$^{3-}$, [PW$<em>{11}$O$</em>{39}$]$^{7-}$</td>
<td>[P$<em>2$W$</em>{21}$O$<em>{71}$]$^{6-}$, [P$<em>2$W$</em>{18}$O$</em>{62}$]$^{6-}$, [P$<em>2$W$</em>{19}$O$_{67}$]$^{10-}$</td>
</tr>
<tr>
<td>3.5-5.4</td>
<td>[PW$<em>{11}$O$</em>{39}$]$^{2-}$</td>
<td>[P$<em>2$W$</em>{21}$O$<em>{71}$]$^{6-}$, [P$<em>2$W$</em>{18}$O$</em>{62}$]$^{6-}$</td>
</tr>
<tr>
<td>5.4-7.3</td>
<td>[PW$<em>{6}$O$</em>{34}$]$^{9-}$</td>
<td></td>
</tr>
</tbody>
</table>

Table 2-2: Decomposition of H$_3$PW$_{12}$O$_{40}$ at pH < 8. Data reproduced from Ref. [117] with permission from the NRC Research Press.

The formation of Keggin species is observed in solution at low pH condition. At higher solution pH, other anion species are formed from decomposition of the Keggin species by removing one or more addenda atoms and their attendant oxide ions. This defective structure results in lacunary species as well as dimeric anions. For example, PWA (H$_3$PW$_{12}$O$_{40}$) decomposes partially with
removal of W=O units at pH>1.5 (Table 2-2). Nevertheless, even with the decomposition of the primary Keggin structure and the removal of W=O units at higher pH environments, the size of the resulting anions, such as [PW_{11}O_{39}]^{7-}, is relatively large and remains un-solvated. This can also lead to a higher ion mobility [118].

Most heteropolyanions are easily and reversibly reduced by one- and two-electron reductions to yield deeply colored mixed-valence heteropolyanions (called heteropoly blues) as a result of the presence of Mo^{6+}, W^{6+}, and V^{5+}. The electrons are accepted by the addenda atoms in the anion and delocalized over the anion framework by rapid electron hopping. For the heteropolytungstates (M=W) in acidic solution (e.g. 1M HCl or 1M H_{2}SO_{4}), electrons can be added without protonation until the charge of the reduced species is -6. Further reduction requires protonation keeping the overall ionic charge at -6. For example, in aqueous acidic conditions, [SiW_{12}O_{40}]^{4-} shows three reduction waves with 1:1:2 electron ratios while [H_{2}W_{12}O_{40}]^{6-} shows two reduction waves with 2:2 electron ratios [105]. These reduction waves can be described by the following reactions:

\[
[\text{SiW}_{12}\text{O}_{40}]^{4-} + e^{-} = [\text{SiW}_{12}\text{O}_{40}]^{5-}
\]
\[
[\text{SiW}_{12}\text{O}_{40}]^{5-} + e^{-} = [\text{SiW}_{12}\text{O}_{40}]^{6-}
\]
\[
[\text{SiW}_{12}\text{O}_{40}]^{6-} + 2e^{-} + 2H^{+} = [\text{H}_{2}\text{SiW}_{12}\text{O}_{40}]^{6-}
\]

and

\[
[\text{H}_{2}\text{W}_{12}\text{O}_{40}]^{6-} + 2e^{-} + 2H^{+} = [\text{H}_{2}\text{H}_{2}\text{W}_{12}\text{O}_{40}]^{6-}
\]
\[
[\text{H}_{2}\text{W}_{12}\text{O}_{40}]^{6-} + 2e^{-} + 2H^{+} = [\text{H}_{4}\text{H}_{2}\text{W}_{12}\text{O}_{40}]^{6-}
\]

Since the HPA polyanions with higher negative charges exhibit greater stability in solutions of higher pH, redox behavior of these species can be measured with increasing solution pH. For instance, at pH=4-6.3, the two-electron reduction waves of [H_{2}W_{12}O_{40}]^{6-} eventually split into one-electron waves each, which then remain pH-independent. Therefore the pH-independent 1st one-electron reduction potentials for Keggin anions can be used as a characteristic property. These potentials are linearly related to the charge carried by the anions, which is shown in Figure 2-10. In the figure, the reduction potential decreases with decrease in the valence of the central
heteroatom, indicating their strong dependence on the primary Keggin structure. However the trend in Figure 2-10 is only an indication as there are other reactions (e.g. hydrogen evolution reaction or two-electron reduction) that can complicate the situation. Nevertheless, the redox reactions of W-based HPAs do occur at more negative potentials compared to the Mo- or V-based HPAs, there is a wide window that is electrochemical inactive. Thus it is justified to utilize W-based HPAs for electrolyte applications.

![Figure 2-10](image)

**Figure 2-10**: Dependence of the pH-independent first one-electron reduction potentials on the negative charge for Keggin polyanions. Reproduced from Ref. [119] with permission from the American Chemical Society.

### 2.5.2 Secondary structure

HPAs are strong acids in both solution and in solid state. The solid acid strength reflects in general that in aqueous solution, that is \( W^{6+} > Mo^{6+} > V^{5+} \) for the addenda atom. With the arrangement of the polyanion, protons, and crystallized water molecules, HPAs form different secondary structures in the solid state. These secondary structures are crystalline with water molecules incorporated in the bulk hydrates. The water molecules are linked in a 3D network and all crystallized water are located in the interstice of Keggin anion.
These HPA crystalline hydrates have high solid-state proton conductivity at room temperature. Two major factors contribute to their proton conductivity: (a) highly hydrogen-bonded conduction pathways in the crystal lattice, and (b) the dynamic dissociation of crystallized water molecules in the crystal hydrate via interactions with oxygen atoms of the Keggin anion. The pathways result from a large number of crystallized water molecules in the crystal hydrate (e.g. SiWA•nH₂O), leading to “quasi-liquid” states, facilitate fast proton transportation [19, 120, 121]. The protons (i.e. both intrinsic and dissociated protons), in the forms of H⁺-nH₂O clusters (e.g. H₃O⁺ or H₅O₂⁺), are transferred by hopping from H⁺-nH₂O donor sites to nH₂O acceptors in the HPA, yielding high proton conductivity in the solid-state (e.g. 27 mScm⁻¹ for SiWA•28H₂O) [16]. In addition, the hygroscopic nature of HPAs may also adsorb water, contributing further to the quasi-liquid state.

HPA crystals tend to dehydrate when heated or when in low RH atmosphere, which results in a reduction in proton conductivity [17]. Studies have identified the temperature and humidity dependences of the number of crystalized water molecules in some HPAs [121, 122]. O. Nakamura et al. studied the number of crystallized water molecules in PWA at different temperatures and RH (Figure 2-11). Conductivity measurements at different temperatures showed an Arrhenius-type temperature dependence with an increasing activation energy as the number of water molecule decreases [15]. The loss of crystallized water also results in a structure change of HPA and a reduction in unit cell volume (Table 2-3). Nevertheless, HPA crystals can rehydrate when they are in a high RH environment after dehydration: thermal analysis showed that the rehydrated waters is crystallized water [122].

![Figure 2-11](image)

**Figure 2-11**: Temperature and RH ranges of solid H₃W₁₂PO₄₀•nH₂O under an atmosphere of hydrogen. Adapted from Ref. [121] with permission from Elsevier.
Protons of HPAs play important roles in conductivity and stability. There are two types of protons in solid HPAs: hydrated protons \((\text{H}^+(\text{H}_2\text{O})_n)\) having high mobility and non-hydrated protons localized at W-O oxygen as hydroxyl groups. The precise localization of such protons are still unknown [123]. Figure 2-12 shows the states of both types of protons in solid \(\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot6\text{H}_2\text{O}\). The non-hydrated proton is attached to oxygen of polyanion (position A) while hydrated protons, \(\text{H}_3\text{O}^+\) and \(\text{H}_5\text{O}_2^+\), are illustrated by B (or B’) and C, respectively.

**Table 2-3**: Crystal structure change of \(\text{H}_3\text{PW}_{12}\text{O}_{40}\) with dehydration at room temperature.

<table>
<thead>
<tr>
<th>Number of crystallized water molecules</th>
<th>Crystal structure</th>
<th>Unit cell volume ((\times10^6 \text{ pm}^3))</th>
<th>ICSD Reference code</th>
</tr>
</thead>
<tbody>
<tr>
<td>29</td>
<td>Cubic</td>
<td>12617</td>
<td>01-076-1815</td>
</tr>
<tr>
<td>20-21</td>
<td>Orthorhombic</td>
<td>5136</td>
<td>01-070-0705</td>
</tr>
<tr>
<td>13-14</td>
<td>Triclinic</td>
<td>2138</td>
<td>00-050-0656</td>
</tr>
<tr>
<td>6</td>
<td>Cubic</td>
<td>1800</td>
<td>01-070-9316</td>
</tr>
</tbody>
</table>

**Figure 2-12**: States of hydrated and non-hydrated protons in solid \(\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot6\text{H}_2\text{O}\). Adapted from Ref. [124] with permission from the American Chemical Society.

From another prospective, different water species can be classified in hydrated solid HPAs. Figure 2-13 summaries the different types of water molecules presented in solid HPAs. At higher hydrates \((i.e. \ n>6)\), water molecules can interact with terminal oxygen of the anion and/or hydrogen bonded to the hydroxyl group of the anion as well as forming protonated water clusters \((i.e. \ \text{H}_2\text{O}_2^+)\) [120]. For \(\text{H}_4\text{SiW}_{12}\text{O}_{40}\cdot\text{nH}_2\text{O}\), 3 out of 4 \(\text{H}^+\) can form \(\text{H}_3\text{O}_2^+\) [125-127] and thus
H₄SiW₁₂O₴₀•29H₂O can be reformulated as [H₅O₂⁺][HSiW₁₂O₴₀]•23H₂O, where H₅O₂⁺ are protonated water and H₂O are neutral water. These neutral water are loosely bonded water (also called “zeolite”-type water) but they can also link anions within the structure. At dehydration state (n=6), all water molecules are bonded to the protons, forming H₅O₂⁺. Each H₅O₂⁺ is linking four anions through hydrogen bonds involving terminal oxygen atoms (as shown in Figure 2-12, position C).

<table>
<thead>
<tr>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallized water</td>
</tr>
<tr>
<td>Protonated water</td>
</tr>
<tr>
<td>Neutral water</td>
</tr>
<tr>
<td>Surface adsorbed water</td>
</tr>
<tr>
<td>Free water</td>
</tr>
</tbody>
</table>

Figure 2-13: Overview of different types of water in solid HPAs.

Thermal stability of HPAs have been extensively studied by XRD and thermal analysis [120, 125, 127]. The departure of loosely bonded neutral water and adsorbed water accelerates at 50-60 °C, reaching max rate at 90-100 °C. Further dehydration leads to removal of water molecules held by multiple hydrogen bonds (i.e. protonated water). Fully dehydrated HPAs can be obtained by heating at ca. 250 °C. Dehydroxylation (or called deprotonation) occurs with remove of constitutional water (or acidic protons) between 400-500 °C. For example, H₄SiW₁₂O₴₀ → SiW₁₂O₃₈ + 2H₂O. This dehydroxylation of dehydrated HPAs is accompanied by the loss of lattice oxygen of polyanion without collapse of the primary Keggin structure. Decomposition of HPAs due to phase transformation is observed for temperature above 500 °C. This process is summarized in Figure 2-14. By taking the dihydroxylation as the limiting step, the thermal stability of HPAs has been characterized as W⁶⁺>Mo⁶⁺>V⁵⁺ for the addenda atom.

\[
\begin{align*}
H₃PW₁₂O₄₀•29H₂O \text{(cubic)} & \xrightarrow{298K} H₃PW₁₂O₄₀•13H₂O \text{(triclinic)} \\
& \xrightarrow{333–353K} H₃PW₁₂O₄₀•6H₂O \text{(cubic)} \xrightarrow{453–623K} \\
& H₃PW₁₂O₄₀•0 – 1H₂O \text{(cubic or tetragonal)} \xrightarrow{853K} WO₃, P₂O₅, etc.
\end{align*}
\]

Figure 2-14: Schematic representation of the thermal stability of solid H₃PW₁₂O₄₀. Adapted from Ref. [128] with permission from Elsevier.
2.5.3 Heteropolyacid-based membranes

Because of the high solid-state proton conductivity of HPAs, they have been investigated as solid electrolytes. However, pellet structures of pressed HPAs are not applicable to supercapacitors, as the electrodes and the solid electrolyte will not have the desired intimate contact, resulting in high interfacial resistance and low utilization of electrode surface area. More recently, HPAs have been used to modify PFSA membranes [129, 130]. This allows an enhancement in proton concentration with increasing number of active sites as well as number of water molecules. But the high solubility of HPAs in high RH conditions (as required by PFSA) as well as the low water retention have limited the performance of HPA-PFSA membranes. To overcome the high solubility, functionalized lacunary HPAs have been incorporated into a polymer backbone. \([\text{SiW}_{11}\text{O}_{39}]^{8-}\) or \([\text{SiW}_{10}\text{O}_{34}]^{8-}\), obtained from \([\text{SiW}_{12}\text{O}_{40}]^{4+}\), can be covalently bonded to an organic group through O-Si-C bond between the terminal oxygen of lacunary HPA and silicon of functionalized silanes to form a hybrid monomer. In addition, sol-gel based HPA membranes as well as other systems such as HPA-SPEEK/PEEK, HPA-PBI, HPA-poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP), HPA-PEO have also been demonstrated [131]. Nevertheless, all these membranes target high operating temperatures mainly for fuel cell applications [132-134]. The performance at room temperature ambient environments is yet to be studied.
3 Experimental method

3.1 Materials

The focus of this work was on polymer electrolytes using PVA as the polymer host and HPAs as the proton conductors with different additives.

3.1.1 Heteropolyacids

α-Keggin is the most common isomer for HPAs. To date, synthesis methods for α-H$_6$Co$_{12}$O$_{40}$ and α-H$_6$Cu$_{12}$O$_{40}$ are not available. Therefore these two HPAs were synthesized with unknown isomer structure in this study. Table 3-1 summarizes the HPAs used in this study. α-H$_4$SiW$_{12}$O$_{40}$·xH$_2$O (SiWA) was used as-received from Alfa Aesar. α-H$_5$BW$_{12}$O$_{40}$ (BWA) was synthesized by a modified Copaux’s method [135]. Na$_2$WO$_4$·2H$_2$O (5 g) was mixed with H$_3$BO$_3$ (4 g) in hot water (25 mL). The solution was adjusted to pH 5.5 using 6N HCl and heated at 60 °C for 2 hours with stirring. The pH was further adjusted to 3.8 using 6N HCl and heated at 80 °C for 6 hours. The solution was allowed to cool to room temperature and set for 6 hours. Solid precipitates were filtered out and the filtrate solution was extracted with diethyl ether. The isolated solid was washed with DI H$_2$O and dried, yielding a crystal product.

<table>
<thead>
<tr>
<th>HPA</th>
<th>Chemical formula</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiWA</td>
<td>α-H$<em>4$SiW$</em>{12}$O$_{40}$</td>
<td>Commercial</td>
</tr>
<tr>
<td>BWA</td>
<td>α-H$<em>5$BW$</em>{12}$O$_{40}$</td>
<td>Synthesized</td>
</tr>
<tr>
<td>CoWA</td>
<td>H$<em>6$Co$</em>{12}$O$_{40}$</td>
<td>Synthesized</td>
</tr>
<tr>
<td>CuWA</td>
<td>H$<em>6$Cu$</em>{12}$O$_{40}$</td>
<td>Synthesized</td>
</tr>
</tbody>
</table>

H$_6$Co$_{12}$O$_{40}$ (CoWA) was synthesized according to Baker’s method [136]. Na$_2$WO$_4$·2H$_2$O (9.9 g) was dissolved in DI H$_2$O and the solution pH was adjust to 6.5-7.5 by glacial acetic acid. A solution of Co(CH$_3$CO$_2$)$_2$·4H$_2$O was prepared (1.25 g in 6.5 mL DI H$_2$O). The Na$_2$WO$_4$ solution was heated to near boiling before adding the Co(CH$_3$CO$_2$)$_2$ solution with stirring. The mixture solution was heated for ca. 10 min and some insoluble matter was filtered out. Since the free acid of Co$_{12}$O$_{40}$ is not soluble in diethyl ether, a stainless steel mesh (McMaster-Carr) was used to collect the CoWA after ether extraction. The isolated solid was then washed and dried to obtain a crystal product. H$_6$Cu$_{12}$O$_{40}$ (CuWA) was synthesized by dissolving Na$_2$WO$_4$·2H$_2$O (9.4 g) in DI H$_2$O and the solution was converted into the para-salt by addition of HCl (final pH
A solution of CuCl₂ was prepared (1.3 g in 50 mL DI H₂O) and was added to the Na₂WO₄ solution dropwise at 60-70°C during 5 hours [137]. Solid precipitates were filtered out and the filtrate solution was diluted with DI H₂O and extracted with diethyl ether. The isolated solid was washed with DI H₂O and dried, yielding a crystal product.

### 3.1.2 Polymer host

The structure and properties of PVA are summarized in Table 3-2.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Repeating unit</th>
<th>Repeat unit molar weight (gmol⁻¹)</th>
<th>Mass average molar weight (Mₙ) (gmol⁻¹)</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA</td>
<td>-CH₂CH(OH)-</td>
<td>43.9</td>
<td>145000</td>
<td>Semi-crystalline</td>
</tr>
</tbody>
</table>

### 3.1.3 Additives

The properties and functions of the additives are listed in Table 3-3.

<table>
<thead>
<tr>
<th>Additives</th>
<th>Chemical formula</th>
<th>Molecular weight (gmol⁻¹)</th>
<th>Physical appearance</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphoric acid</td>
<td>H₃PO₄</td>
<td>98</td>
<td>Liquid</td>
<td>Acidic plasticizer</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>C₂H₆O₂</td>
<td>62.07</td>
<td>Liquid</td>
<td>Neutral plasticizer</td>
</tr>
<tr>
<td>Glycerol</td>
<td>C₃H₈O₃</td>
<td>92.09</td>
<td>Liquid</td>
<td>Neutral plasticizer</td>
</tr>
<tr>
<td>Glutaraldehyde</td>
<td>C₅H₈O₂</td>
<td>100.12</td>
<td>Liquid</td>
<td>Cross-linker</td>
</tr>
<tr>
<td>Silicon dioxide</td>
<td>SiO₂</td>
<td>60.8</td>
<td>10-20 nm particle</td>
<td>Nano-filler</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>TiO₂</td>
<td>79.87</td>
<td>15 nm particle</td>
<td>Nano-filler</td>
</tr>
</tbody>
</table>

### 3.2 Preparation of polymer electrolytes

The general procedure for preparing the electrolytes is depicted in Figure 3-1.

**Figure 3-1**: Preparation steps of HPA-PVA polymer electrolytes.
Various polymer electrolytes based on SiWA have been developed throughout the study as shown in Figure 3-2. Polymer electrolytes using BWA were also prepared (Section 3.2.6 and 3.2.7). The details are described in the following sections.

Figure 3-2: Summary of SiWA-based polymer electrolytes.

### 3.2.1 SiWA-PVA

SiWA-PVA electrolytes were prepared in the following procedures: (1) dissolved PVA in H₂O at 80 °C with stirring for 4-5 hr to obtain a 5 wt.% solution and; (2) added solid SiWA to the PVA solution, and mixed for 1 hr to obtain a homogeneous solution. The SiWA-PVA compositions in the electrolyte film is reported as a molar ratio (or weight ratio assuming all free water was removed during drying process).

Table 3-4: Compositions of SiWA-PVA polymer electrolytes.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>SiWA : PVA molar ratio</th>
<th>SiWA wt.%</th>
<th>PVA wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiWA(419)-PVA</td>
<td>419</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>SiWA(109)-PVA</td>
<td>109</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>SiWA(47)-PVA</td>
<td>47</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>SiWA(20)-PVA</td>
<td>20</td>
<td>30</td>
<td>70</td>
</tr>
</tbody>
</table>
3.2.2 SiWA-plasticizer-PVA

SiWA-PVA with three plasticizers (i.e. SiWA-H$_3$PO$_4$-PVA, SiWA-ethylene glycol-PVA, and SiWA-glycerol-PVA) were prepared by a procedure similar to that for SiWA-PVA. After mixing PVA solution and SiWA, liquid plasticizers were added to the precursor solution with stirring. SiWA to PVA molar ratio was kept as a constant of 419. The compositions of the plasticizer-added electrolytes are summarized in Table 3-7, Table 3-5, and Table 3-6.

**Table 3-5**: Compositions of SiWA-ethylene glycol-PVA polymer electrolytes.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Ethylene glycol : PVA molar ratio</th>
<th>SiWA wt.%</th>
<th>Ethylene glycol wt.%</th>
<th>PVA wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiWA-Egly(0)-PVA$^1$</td>
<td>N/A</td>
<td>90</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>SiWA-Egly(1000)-PVA</td>
<td>1000</td>
<td>86.3</td>
<td>4.1</td>
<td>9.6</td>
</tr>
<tr>
<td>SiWA-Egly(2000)-PVA</td>
<td>2000</td>
<td>82.9</td>
<td>7.9</td>
<td>9.2</td>
</tr>
<tr>
<td>SiWA-Egly(3333)-PVA</td>
<td>3333</td>
<td>78.8</td>
<td>12.4</td>
<td>8.8</td>
</tr>
<tr>
<td>SiWA-Egly(5000)-PVA</td>
<td>5000</td>
<td>74.1</td>
<td>17.7</td>
<td>8.2</td>
</tr>
</tbody>
</table>

**Table 3-6**: Compositions of SiWA-glycerol-PVA polymer electrolytes.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Glycerol : PVA molar ratio</th>
<th>SiWA wt.%</th>
<th>Glycerol wt.%</th>
<th>PVA wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiWA-Gly(0)-PVA$^1$</td>
<td>N/A</td>
<td>90</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>SiWA-Gly(1000)-PVA</td>
<td>1000</td>
<td>84.6</td>
<td>6.0</td>
<td>9.4</td>
</tr>
<tr>
<td>SiWA-Gly(2000)-PVA</td>
<td>2000</td>
<td>79.9</td>
<td>11.2</td>
<td>8.9</td>
</tr>
<tr>
<td>SiWA-Gly(3333)-PVA</td>
<td>3333</td>
<td>74.3</td>
<td>17.4</td>
<td>8.3</td>
</tr>
<tr>
<td>SiWA-Gly(5000)-PVA</td>
<td>5000</td>
<td>68.3</td>
<td>24.1</td>
<td>7.6</td>
</tr>
</tbody>
</table>

**Table 3-7**: Compositions of SiWA-H$_3$PO$_4$-PVA polymer electrolytes.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>H$_3$PO$_4$ : PVA molar ratio</th>
<th>SiWA wt.%</th>
<th>H$_3$PO$_4$ wt.%</th>
<th>PVA wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiWA-H$_3$PO$_4$(0)-PVA$^1$</td>
<td>N/A</td>
<td>90</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>SiWA-H$_3$PO$_4$(500)-PVA</td>
<td>500</td>
<td>85.9</td>
<td>3.6</td>
<td>10.5</td>
</tr>
<tr>
<td>SiWA-H$_3$PO$_4$(1500)-PVA</td>
<td>1500</td>
<td>80.2</td>
<td>10</td>
<td>9.8</td>
</tr>
<tr>
<td>SiWA-H$_3$PO$_4$(2500)-PVA</td>
<td>2500</td>
<td>75.2</td>
<td>15.6</td>
<td>9.2</td>
</tr>
</tbody>
</table>

$^1$ Same as SiWA(419)-PVA
3.2.3 SiWA-H$_3$PO$_4$-PVA/nano-fillers

SiWA-H$_3$PO$_4$-PVA electrolytes with nano-fillers were prepared in a similar way to those without fillers. SiWA-H$_3$PO$_4$-PVA precursor solution was first prepared and then mixed with the respective fillers. The fillers were added at 5 wt.% of the total film weight, assuming most of the water was removed in the process (Table 3-8). For comparison, a SiWA-H$_3$PO$_4$-PVA film with the same percentage of ionic conductive materials and 10 wt.% PVA (i.e. SiWA-H$_3$PO$_4$(1500)-PVA) was included. Before casting the filler-containing electrolytes, the solution was sonicated for 30 min for better dispersions of the nano-fillers.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>SiWA wt.%</th>
<th>H$_3$PO$_4$ wt.%</th>
<th>PVA wt.%</th>
<th>Filler wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiWA-H$_3$PO$_4$-PVA$^2$</td>
<td>80</td>
<td>10</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>SiWA-H$_3$PO$_4$-PVA/SiO$_2$</td>
<td>80</td>
<td>10</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>SiWA-H$_3$PO$_4$-PVA/TiO$_2$</td>
<td>80</td>
<td>10</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

3.2.4 SiWA-H$_3$PO$_4$-cross-linked PVA

SiWA-H$_3$PO$_4$-chemically cross-linked PVA (referred as XLPVA) electrolytes were prepared by first cross-linking the PVA host using Glutaraldehyde, then adding SiWA and H$_3$PO$_4$ drop-wise with stirring. Different amount of glutaraldehyde was added to achieve the respective degree of theoretical cross-link (Table 3-9). Both SiWA to PVA molar ratio (i.e. 419) and H$_3$PO$_4$ to PVA molar ratio (i.e. 1500) were kept constant. The resulting films have a composition of 80 wt.% SiWA, 10 wt.% H$_3$PO$_4$, and 10 wt.% XLPVA (same as the SiWA-H$_3$PO$_4$(1500)-PVA electrolyte except the PVA host was cross-linked instead of linear).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Glutaraldehyde : PVA repeating unit molar ratio</th>
<th>Theoretical % of cross-link</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiWA-H$_3$OP$_4$-XLPVA(0)$^2$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SiWA-H$_3$OP$_4$-XLPVA(2)</td>
<td>0.005</td>
<td>2</td>
</tr>
<tr>
<td>SiWA-H$_3$OP$_4$-XLPVA(4)</td>
<td>0.01</td>
<td>4</td>
</tr>
<tr>
<td>SiWA-H$_3$OP$_4$-XLPVA(5.2)</td>
<td>0.013</td>
<td>5.2</td>
</tr>
<tr>
<td>SiWA-H$_3$OP$_4$-XLPVA(6)</td>
<td>0.015</td>
<td>6</td>
</tr>
</tbody>
</table>

$^2$ Same as SiWA-H$_3$PO$_4$(1500)-PVA
3.2.5 SiWA-plasticizer-cross-linked PVA

Cross-linked electrolytes with optimized plasticizer contents were prepared by first cross-linking the PVA with glutaraldehyde before mixing with SiWA. Different amount of glycerol or H₃PO₄ was then added to the solutions (Table 3-10 and Table 3-11). In all samples, the SiWA to PVA molar ratio was 419 and the glutaraldehyde to PVA repeating unit molar ratio was controlled to be 0.013.

**Table 3-10:** Compositions of SiWA-cross-linked PVA with different glycerol contents.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Glycerol : PVA molar ratio</th>
<th>SiWA wt.%</th>
<th>Glycerol wt.%</th>
<th>PVA wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiWA-Gly(0)-XLPVA³</td>
<td>N/A</td>
<td>90</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>SiWA-Gly(250)-XLPVA</td>
<td>250</td>
<td>87.5</td>
<td>1.7</td>
<td>10.8</td>
</tr>
<tr>
<td>SiWA-Gly(500)-XLPVA</td>
<td>500</td>
<td>86.1</td>
<td>3.4</td>
<td>10.6</td>
</tr>
<tr>
<td>SiWA-Gly(1000)-XLPVA</td>
<td>1000</td>
<td>83.3</td>
<td>6.5</td>
<td>10.2</td>
</tr>
<tr>
<td>SiWA-Gly(1500)-XLPVA</td>
<td>1500</td>
<td>80.7</td>
<td>9.4</td>
<td>9.9</td>
</tr>
<tr>
<td>SiWA-Gly(2000)-XLPVA</td>
<td>2000</td>
<td>78.2</td>
<td>12.2</td>
<td>9.6</td>
</tr>
<tr>
<td>SiWA-Gly(2500)-XLPVA</td>
<td>2500</td>
<td>75.9</td>
<td>14.8</td>
<td>9.3</td>
</tr>
</tbody>
</table>

**Table 3-11:** Compositions of SiWA-cross-linked PVA with different H₃PO₄ contents.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>H₃PO₄ : PVA molar ratio</th>
<th>SiWA wt.%</th>
<th>H₃PO₄ wt.%</th>
<th>PVA wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiWA-H₃PO₄(0)-XLPVA³</td>
<td>N/A</td>
<td>90</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>SiWA-H₃PO₄(1500)-XLPVA⁴</td>
<td>1500</td>
<td>80</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>SiWA-H₃PO₄(2125)-XLPVA</td>
<td>2125</td>
<td>77.0</td>
<td>13.6</td>
<td>9.4</td>
</tr>
<tr>
<td>SiWA-H₃PO₄(2550)-XLPVA</td>
<td>2550</td>
<td>74.9</td>
<td>15.9</td>
<td>9.2</td>
</tr>
<tr>
<td>SiWA-H₃PO₄(2975)-XLPVA</td>
<td>2975</td>
<td>73.0</td>
<td>18.0</td>
<td>9.0</td>
</tr>
<tr>
<td>SiWA-H₃PO₄(3400)-XLPVA</td>
<td>3400</td>
<td>71.2</td>
<td>20.1</td>
<td>8.7</td>
</tr>
<tr>
<td>SiWA-H₃PO₄(4250)-XLPVA</td>
<td>4250</td>
<td>67.8</td>
<td>23.9</td>
<td>8.3</td>
</tr>
</tbody>
</table>

3.2.6 BWA-cross-linked PVA

BWA-XLPVA was prepared by first cross-linking the PVA with glutaraldehyde then mixing with BWA. For comparison, SiWA-XLPVA was also prepared by using the same HPA to PVA

³ Also can be referred as SiWA-XLPVA
⁴ Same as SiWA-H₃PO₄-XLPVA(5.2)
molar ratio of 419. The glutaraldehyde to PVA repeating unit molar ratio in both BWA-XLPVA and SiWA-XLPVA was controlled to be 0.013.

### 3.2.7 BWA-glycerol-cross-linked PVA

BWA-Gly(1500)-XLPVA was prepared in a similar way as the SiWA-Gly(1500)-XLPVA. The PVA was first cross-linked by glutaraldehyde with BWA. The BWA to PVA molar ratio was 419 and the glutaraldehyde to PVA repeating unit molar ratio was 0.013. The glycerol to PVA molar ratio was 1500.

### 3.3 Working electrodes

All working electrodes have a geometric area of 1 cm² unless otherwise specified. Three types of working electrode materials were used to characterize the properties of the electrolyte as well as to determine the performance of the supercapacitors:

a. metallic electrodes:
   - stainless steel foil (50 μm thick, Type 304, McMaster-Carr);
   - Ti foil (127 μm thick, McMaster-Carr).

b. carbon electrodes:
   - glassy carbon (3 mm diameter, CH Instruments);
   - graphite ink (Alfa Aesar) coated on stainless steel (5 mg/cm²);
   - mixture of MWCNT and graphite (refereed as CNT-graphite) coated on Ti foil (ca. 2-3 mg/cm²). To prepare CNT-graphite electrodes, chemically cross-linked PVA was used as binder and mixed with multi-wall carbon nanotubes and graphite powders in DI water [138]. The resultant CNT-graphite electrodes were composed of 22% CNT, 63% graphite, and 15% cross-linked PVA (all in wt. %).

c. pseudocapacitive electrodes:
   - RuO₂ on Ti foil. The process of making RuO₂ electrodes was described in [113].
3.4 Construction of liquid cells

3.4.1 Liquid 3-electrode cells

To characterize the electrochemical behavior of single electrodes or electrolyte solutions, a beaker cell was constructed using Ag/AgCl (1M KCl) as reference electrode and Pt mesh as counter electrode.

3.4.2 Liquid 2-electrode capacitors

To study the performance of liquid electrolytes on a device level, a filter paper (Whatman, Grade 1, 180 µm thick) was soaked with liquid H₂SO₄ electrolyte and then sandwiched between the electrodes. The filter paper impregnated with the liquid electrolyte and act as a separator.

3.4.3 Liquid 2-electrode capacitors with electrode potential tracking

Liquid capacitors were constructed as beaker cells with liquid electrolytes. The two electrodes were connected to a potentiostat. An Ag/AgCl reference electrode was added into the cell and connected externally to a dual-channel digital oscilloscope (DGS-122). In this configuration, the positive and negative electrodes were charged and discharged as a regular capacitor, while the potential variation for each electrode was simultaneously tracked and recorded (Figure 3-3).

![Figure 3-3: Schematic diagram of a liquid capacitor cell setup with in-situ electrode potential tracking. Reproduced from Ref. [139] with permission from the Electrochemical Society.](image)

3.5 Construction of solid cells

3.5.1 Solid capacitor cells

Both single and multi-cell solid capacitor devices were constructed:
1. For single-cell capacitor, the electrolyte precursor solution was coated on the electrode surface via brush painting and dried in ambient temperature. They were made by sandwiching the two electrolyte-coated electrodes under 20 to 30 kPa pressure for 20 min at ambient temperature (Figure 3-4a). The cells were protected with an insulating tape. Electrolyte thickness was calculated by subtracting the electrode and tape thickness from total cell thickness using an electronic micrometer (Mitutoyo). Single cells were also constructed by sandwiching a cast polymer electrolyte film between two electrodes under pressure. Ti or stainless steel spacers (100-250 μm thick) were used to obtain a consistent electrolyte thickness.

2. A multi-cell stacked supercapacitor was also constructed as shown in Figure 3-4b. For a 2-cell stacked device (i.e. 2-in-1 cell), one bipolar electrode was used in the center to act as anode for one cell and cathode for the other so that two capacitors were connected in series in a package. Similarly, a 3-cell stacked device would require two bi-polar electrodes. The fabrication process of electrolyte and cell assembly was as described above.

![Figure 3-4: Schematic assembly processes for (a) a solid single-cell supercapacitor; and (b) a solid 2-cell stacked supercapacitor. Adapted from Ref. [140] permission from Elsevier.](image)
3.5.2 Solid 3-electrode cells

Two types of solid 3-electrode cells were used to characterize polymer electrolytes and single electrodes, respectively:

1. For polymer electrolyte characterization, printed electrodes (graphite working/counter, Ag pseudo-reference) from Zensor R&D were used.

2. For electrode characterization, the solid electrochemical cells were assembled in the following steps: (i) A free-standing polymer electrolyte film (2×2 cm) was obtained. (ii) Ag pseudo-reference electrodes were cut from the commercially available printed electrodes and firmly attached to the polymer electrolyte film. (iii) Cells were assembled by sandwiching the free-standing electrolyte film with the reference electrode between the graphite working electrode and a counter electrode (Figure 3-5). The counter electrode had with the same graphite material but with much higher mass loading (i.e. ~20 mg/cm²).

![Figure 3-5: Schematic diagram of a solid 3-electrode cell for single electrode characterization in the solid state.]

3.5.3 Solid capacitor cells with electrode potential tracking

Solid capacitor cells with potential tracking was constructed by developing a “modified 2-electrode” cells (Figure 3-6). The configuration was similar to the solid 3-electrode cell shown in Figure 3-5. The difference between the “modified 2-electrode” and the 3-electrode was in the capacitance of the counter electrode. Electrodes with identical graphite loadings were used as positive and negative electrodes to mimic a “modified 2-electrode” cell for supercapacitor device characterizations. “Modified” here refers to that an external reference electrode was connected to the solid supercapacitor devices.
Stability and feasibility of Ag pseudo-reference electrodes were tested in 10 mM $K_3[Fe(CN)_6]$ (in 1 M KCl). Figure 3-7 shows the CVs of a glassy carbon electrode in the $K_3[Fe(CN)_6]$ solution using Ag/AgCl reference and Ag pseudo-reference electrodes. The Ag pseudo-reference electrode showed good stability to be used in the solid cells.

**Figure 3-7**: CVs of 10 mM $K_3[Fe(CN)_6]$ in 1 M KCl at 100 mVs$^{-1}$ using Ag/AgCl and Ag reference electrodes.
3.6 Electrochemical characterizations and methods

Polymer electrolytes and the enabled capacitors were characterized using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). CV and EIS were performed either on a CHI 760D bipotentiostat or an EG&G PAR 263A potentiostat/galvanostat. In the latter case, EIS was performed on a Solartron 1255 frequency response analyzer interfaced with the EG&G 263A. The EIS spectra were recorded from 100 kHz to as low as 0.01 Hz with 5 mV amplitude. Table 3-12 and Table 3-13 summarizes the parameters measured using each technique and the relationship between the electrolyte properties as well as solid capacitor performance. Unless otherwise specified, all electrochemical experiments were carried out at room temperature.

Table 3-12: Parameters of interest for properties of polymer electrolytes.

<table>
<thead>
<tr>
<th>Measured parameter</th>
<th>Cell setup</th>
<th>Polymer electrolyte properties</th>
<th>Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>ESR</td>
<td>Metallic 2-electrode</td>
<td>Proton conductivity</td>
<td>EIS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Activation energy</td>
<td></td>
</tr>
<tr>
<td>Dielectric properties</td>
<td>Metallic 2-electrode</td>
<td>Dielectric constant</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dielectric loss</td>
<td></td>
</tr>
<tr>
<td>Capacitance retention</td>
<td>Metallic 2-electrode</td>
<td>Cycle life</td>
<td>CV</td>
</tr>
<tr>
<td>Potential window</td>
<td>Glassy carbon 3-electrode and graphite 3-electrode</td>
<td>Electrochemical stability window</td>
<td></td>
</tr>
</tbody>
</table>

Table 3-13: Parameters of interest for evaluation of solid supercapacitor performance.

<table>
<thead>
<tr>
<th>Measured parameter</th>
<th>Cell setup</th>
<th>Capacitor performance</th>
<th>Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>ac response</td>
<td>2-electrode</td>
<td>ESR</td>
<td>EIS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ac capacitance</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Time constant</td>
<td></td>
</tr>
<tr>
<td>dc response</td>
<td>2-electrode</td>
<td>dc capacitance</td>
<td>CV</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ESR</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Voltage window</td>
<td></td>
</tr>
<tr>
<td>Potential of individual electrode</td>
<td>“modified” 2-electrode</td>
<td>Factors limiting the capacitor voltage window</td>
<td>CV+oscilloscope</td>
</tr>
</tbody>
</table>
### 3.6.1 Proton conductivity

Proton conductivity of polymer electrolytes was calculated using ESR values of the metallic cells. Figure 3-8 shows the equivalent circuit model used to obtain the ESR. L1 represents the inductance contributed by cables and instruments. Rs is total high frequency series resistance (i.e. ESR); constant phase element (CPE1) describes the capacitive behavior of the cell; the parallel resistance Rp represents a leakage resistance of the charge separation process.

![Figure 3-8: Equivalent circuit model of metallic cells for extraction of ESR.](image)

The assumption here is that metallic electrodes do not contribute to the measured ESR due to their intrinsically high electrical conductivity. Proton conductivity ($\sigma$) then can be calculated by

$$\sigma = \frac{d}{ESR \times A} = q\mu p_0$$

(7)

where $d$ is the electrolyte thickness, $A$ is the electrode area, $q$ is the elementary charge, $\mu$ is the proton mobility, and $p_0$ is the proton density. The reported conductivity was based on an average of at least five cells.

To investigate the proton conduction mechanism, proton conductivity ($\sigma$) was characterized as a function of temperature ($T$). In an Arrhenius plot, the logarithm of the proton conductivity was graphed against the inverse of the temperature. A straight line indicates an Arrhenius type temperature dependence, while a curved line can be empirically fitted using Vögel-Tamman-Fulcher (VTF) equations [141]. The activation energy can be evaluated from the slope of the $\ln(\sigma)$ vs. $(1000/T)$ plots.

### 3.6.2 Capacitance

For areal capacitance analysis, dc capacitance was obtained by dividing the total charge stored/delivered ($Q$) by electrode area ($A$) and voltage window ($U$). For ac capacitance, the real part of the capacitance ($C'$) and its corresponding imaginary part ($C''$) were separated [142]. In this method, the supercapacitor frequency behavior is considered as a whole. Then its impedance is
\[ Z(\omega) = \frac{1}{j\omega \times C(\omega)} \]  \hspace{1cm} (8)

Since the impedance, \( Z(\omega) \), can be represented in its complex form

\[ Z(\omega) = Z'(\omega) + jZ''(\omega) \]  \hspace{1cm} (9)

Therefore by rearranging eq. 8 and combing with eq. 9,

\[ C(\omega) = \frac{1}{\omega \times (jZ'(\omega) - Z''(\omega))} = \frac{-(Z''(\omega) + jZ'(\omega))}{\omega |Z(\omega)|^2} \]  \hspace{1cm} (10)

\( C(\omega) \) is also be represented in its complex form

\[ C(\omega) = C'(\omega) - jC''(\omega) \]  \hspace{1cm} (11)

Combination of eq. 10 and eq. 11 leads to

\[ C'(\omega) = \frac{-Z''(\omega)}{\omega |Z(\omega)|^2} \]  \hspace{1cm} (12)

\[ C''(\omega) = \frac{Z'(\omega)}{\omega |Z(\omega)|^2} \]  \hspace{1cm} (13)

These two values (\( C' \) and \( C'' \)) can be plotted as a function of frequency. \( C' \) represents the accessible capacitance of the device at the corresponding frequency, which approaches the capacitance obtained from dc methods at low frequencies. On the other hand, \( C'' \) corresponds to energy dissipation by an irreversible process. The maximum of the \( C'' \) vs. frequency curve represents a time constant, at which a transition from resistive-dominated to capacitive-dominated behavior occurs (i.e., capacitor phase angle reaches -45°). This time constant was used as a “factor of merit” to compare the rate capability of supercapacitors.

### 3.6.3 Dielectric analyses

Dielectric relaxation analysis is a useful tool for obtaining the characteristics of ionic and molecular motions and interactions. The frequency-dependent response of an electrolyte is measured in complex impedance (\( Z^* \)) and permittivity (\( \varepsilon^* \)), which reflect the motion of mobile particles.
ions and dipoles. A schematic diagram of the variation of dielectric constant ($\varepsilon_r'$) and dielectric loss ($\varepsilon_r''$) as a function of frequency for a polymer-in-salt electrolyte is shown in Figure 3-9. Because of the low polymer content and limited chain movements in a polymer-in-salt electrolyte, polarization caused by polymer main chain and/or side chain motions are small and negligible. Under such conditions, the two dominating types of polarization are dipole polarization at high frequencies and electrode polarization at low frequencies.

**Figure 3-9:** Schematic diagram of dielectric constant and dielectric loss response for a polymer-in-salt electrolyte exhibiting dipole polarization and electrode polarization as a function of frequency. Reproduced from Ref. [143] with permission from the American Chemical Society.

Dipole polarization derives mainly from the molecules of the ionic conductor and/or additives with permanent dipole moments, while electrode polarization is caused by the accumulation of ions at the blocking electrode surface (i.e. formation of the electrical double layer). In Figure 3-9, the corresponding dielectric constant at high frequencies (i.e. without electrode polarization) is denoted as static dielectric constant ($\varepsilon_{r,s}$) and the dielectric constant at low frequencies (i.e. with electrode polarization) is denoted as low frequency dielectric constant ($\varepsilon_{r,EP}$). In supercapacitors, a high $\varepsilon_{r,s}$ reflects a high intrinsic capacitance similar to the capacitance of an electrolytic capacitor, whereas a high $\varepsilon_{r,EP}$ reflects a greater amount of stored charge at the electrode/electrolyte interface (i.e. an EDLC). The capacitance from electrode polarization ($\varepsilon_{r,EP}$)
is generally much greater than the intrinsic capacitance and is the interest of supercapacitors. In the dielectric loss vs. frequency curve two dielectric loss peaks can be observed. These peaks correspond to (a) relaxation of dipole polarization and (b) relaxation of electrode polarization. Both loss peaks result from energy dissipation when the polarization lags behind the applied electric field. In addition, position of the $\varepsilon_r''$ peak represents the relaxation frequency. A loss peak with small magnitude and high relaxation frequency (i.e. small loss and fast response) is desirable for a capacitor. In general, a capacitor can be viewed as a macroscopic dipole with charge separation as a result of electrode polarization at low frequencies, and can be represented by a simple Debye relaxation in the Macdonald and Coelho model [144-147].

Dielectric measurements of the metallic cells were carried out from -30 to 50 °C. The key parameters of interest are: proton conductivity ($\sigma$), dielectric constant ($\varepsilon_r'$), dielectric loss ($\varepsilon_r''$), free proton density ($p_0$), and mobility ($\mu$). The solid sandwich cell can be considered as a capacitor such that the real part of the capacitance can be extracted using its impedance data. The dielectric constant ($\varepsilon_r'$) is extracted using

$$\varepsilon_r' = \frac{C'}{C_0} = \frac{-Z''}{2\pi f |Z|^2} \times \frac{d}{\varepsilon_0 A}$$  \hspace{1cm} (14)

where $Z$ is the complex impedance and $Z''$ is the imaginary part of the complex impedance. The dielectric loss ($\varepsilon_r''$) can be determined from

$$\varepsilon_r'' = (\varepsilon_r') \times \left(\frac{1}{\tan \theta}\right)$$  \hspace{1cm} (15)

where $\theta$ is the phase angle (or phase shift) of the metallic cell.

Macdonald and Coelho model (a single ion approach) was used to deconvolute the different contributions to proton conductivity under the presence of electrode polarization. The free ions in the polymer electrolyte were assumed to be protons due to the high HPA content and the immobile HPA anions. The proton transference number in HPAs is close to unity, which is also true for the polymer electrolytes. The free proton density, $p_0$, can then be obtained by

$$p_0 = \frac{4\pi^2 kT \sigma q^2 d^2 \tau_s}{e^2}$$  \hspace{1cm} (16)
where $K$ is Boltzmann's constant and $T$ is temperature. Here $\tau_{EP}$ is the dielectric time constant with electrode polarization at low frequencies while $\tau_s$ is the static dielectric time constant at high frequencies. $\tau$ is directly related to the dielectric constant and dc conductivity

$$\tau_s = \frac{\varepsilon_{r,s} \varepsilon_0}{\sigma}$$

(17)

$$\tau_s = \frac{\varepsilon_{r,EP} \varepsilon_0}{\sigma}$$

(18)

where $\varepsilon_{r,s}$ and $\varepsilon_{r,EP}$ are static dielectric constant and low frequency dielectric constant, respectively. Arrhenius relation was used to describe proton density and proton conductivity (and thus proton mobility) at different temperatures:

$$A_0 = A_\infty \exp\left(\frac{-E_a}{RT}\right)$$

(19)

where $A_\infty$ is a pre-exponential factor, $R$ is the gas constant, and $E_a$ is activation energy. Free proton density and mobility of the polymer electrolytes at low temperatures of -30 and -20 °C were directly calculated. At higher temperatures, the proton density was obtained by linear fitting using Arrhenius relation, and mobility was calculated based on dc conductivity and free proton density.

### 3.6.4 In-situ electrode potential tracking

In-situ electrode potential tracking was used to characterize individual electrode and electrolyte materials at the device level. A “third” electrode as reference is used to track both positive and negative electrodes during their charge and discharge in either a liquid [148-152] or a solid/semi-solid device [153-155]. The setup for the in-situ electrode potential tracking method for liquid and solid capacitors are shown in Figure 3-3 and Figure 3-6, respectively. Figure 3-10 shows a schematic diagram illustrating the electrode potential tracking for both symmetric (Figure 3-10b-d) and asymmetric (Figure 3-10e-g) cells during CV scans. The capacitors were charged and discharged to different voltages incrementally at a constant scan rate (Figure 3-10a).
Figure 3-10: Illustrations of (a) CV of a capacitor and the resultant electrode potential tracking curves as a function of cell voltage for (b-d) symmetric and (e-g) asymmetric cells.

For the symmetric cell, the results of electrode potential tracking is depicted in the potential ($E$) vs. time ($t$) plot (Figure 3-10b). $E_{\text{initial}}$ is the initial potential of both positive and negative electrodes before applying any voltage. They correspond to the open-circuit potential (OCP) of the respective electrodes. During the charging process, the potentials of both electrodes (i.e. $E_{+ve}$ and $E_{-ve}$) move away from $E_{\text{initial}}$ and reach their respective limits. The difference between the positive limit of $E_{+ve}$ and the negative limit of $E_{-ve}$ is the applied cell voltage ($U$). Upon discharging, the potential of both electrodes will reach $E_{\text{final}}$, which should be equal to $E_{\text{initial}}$ in the symmetric cell. At a constant discharge current, the smaller the absolute slope of the $E$ vs. $t$ curve is, the higher are charge capacity and capacitance.

Since the charge is balanced between the two electrodes in a symmetric cell, the change of potential for each electrode should be the same. For a better comparison of the two electrodes, the potential limits of each electrode ($E_{\text{limit}}$) are plotted as a function of cell voltage ($U$) (Figure 3-10c). This is particularly beneficial for analyzing cell voltage for supercapacitors. Curves in the $E_{\text{limit}}$ vs. $U$ plots should follow a linear relationship. Any deviation from linearity at a
particular applied voltage implied that one or both electrodes have exceeded the potential operation window and side reactions have started to occur. This results in an increase in the absolute slope of the $E_{\text{limit}}$ vs. $U$ curve for one electrode and a decrease for the other, such that the applied cell voltage is maintained. Also shown in Figure 3-10c is $\Delta E$, which is defined as the absolute difference between the potential limits and $E_{\text{initial}}$ (or $E_{\text{final}}$). Alternatively, the $\Delta E$ vs. $U$ relationship can be expressed as shown in Figure 3-10d. In this example the two curves are overlapping because the charge for both electrodes is balanced and their $E_{\text{initial}}$ values remain constant. Therefore, the potential change for each electrode at a given cell voltage is identical. Similar to Figure 3-10c, any deviation from linearity in the $\Delta E$ vs. $U$ plots indicates that the capacitor operation voltage window has been exceeded.

In an asymmetric cell, the OCP of the two electrodes are often different. In this example, the negative electrode has a higher charge capacity than that of the positive electrode shown by a smaller absolute slope in the $E$ vs. $t$ curve (Figure 3-10e). In addition, due to the higher charge in the negative electrode, both $E_{\text{initial}}$ and $E_{\text{final}}$ shift towards negative potentials with the applied voltage during CV cycles. As a result, the change in the negative limit of $E^{-ve}$ with cell voltage is less than the change in the positive limit of $E^{+ve}$ (Figure 3-10f), i.e., the absolute slope of $E_{\text{limit}}$ vs. $U$ of the negative electrode is smaller than that of the positive electrode. Therefore, the $\Delta E$ vs. $U$ plots for the positive and negative electrodes in Figure 3-10g are not identical. The smaller slope of the $\Delta E^{-ve}$ vs. $U$ plot confirmed the higher charge capacity of the negative electrode at the given cell voltages.

The principle behind these two scenarios is applicable to both liquid and solid cells. Since the two electrodes within a supercapacitor are operating against each other, it is important to track the state-of-charge and the actual potential of each electrode during charging and discharging. This can be used to understand the factors and the mechanisms that limit the cell voltage.

### 3.7 Material and structural characterizations

A summary of the material characterization techniques and test conditions are listed in Table 3-14. The water desorption of the films was determined by the following procedure:

1. Samples were first dried under ambient conditions and then in an oven at 80 °C for 1 hr.
2. Samples were then placed in an environmental chamber at 25 °C, 90% RH for 24 hours. The weight of the hydrated samples \( W_{\text{wet}} \) was recorded.

3. All hydrated samples were then exposed to an environment of 20% RH. The weight change of each sample was monitored over time as \( W_t \). The normalized weight at each point was calculated using equation: \( W_N = \frac{W_t}{W_{\text{wet}}} \times 100 \).

Table 3-14: Materials and conditions for physical and structural characterizations.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Material</th>
<th>Related electrolyte properties</th>
<th>Storage and test conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Water desorption</strong></td>
<td>Cast thin film on glass slide</td>
<td>Water retention</td>
<td>Pre-stored in an environmental chamber (90% RH) and tested at 20% RH (ambient).</td>
</tr>
<tr>
<td><strong>Water uptake</strong></td>
<td>Cast thin film on glass slide</td>
<td>Water absorption</td>
<td>Pre-dried in an oven and stored (tested) at 90% RH (in an environmental chamber)</td>
</tr>
<tr>
<td><strong>XRD</strong></td>
<td>Cast thin film on stainless steel or zero diffraction plate</td>
<td>Crystallinity and level of hydrations of HPAs</td>
<td>Pre-stored at the ambient or in desiccator (with controlled RH)</td>
</tr>
<tr>
<td><strong>FTIR</strong></td>
<td>Free-standing film or cast thin film on FTIR transparent window</td>
<td>Bond interactions and electrolyte components</td>
<td>Room temperature, varying RH</td>
</tr>
<tr>
<td><strong>DSC</strong></td>
<td>Free-standing thin film</td>
<td>Thermal stability and water content</td>
<td>Room temperature, varying RH</td>
</tr>
<tr>
<td><strong>NMR</strong></td>
<td>Free-standing thin film</td>
<td>Proton specie identification and local proton transport activation energy</td>
<td>Pre-dried at room temperature and tested at varying temperature</td>
</tr>
</tbody>
</table>

The water uptake of the films was determined by the following procedure:

1. Samples were dried under ambient conditions and then in an oven at 80 °C for 1 hour.
2. After recording the initial weight \( W_{\text{before}} \), the samples were placed in an environmental chamber at 25 °C, 90% RH for 3 days.
3. The weight of the samples after step 2 \( W_{\text{after}} \) was recorded. The water uptake of different samples was calculated by Water uptake (%) = \( 100 \times \frac{(W_{\text{after}} - W_{\text{before}})}{W_{\text{before}}} \).
X-ray diffraction (XRD) measurements were carried out using a Philips XRD system (PW-1830). The samples were analyzed with a Cu-Kα source operating at 40 kV, 40 mA and the diffraction patterns were recorded from 5° to 50° 2θ with a step scan of 0.02° 2θ and a scan step time of 2 seconds. Zero diffraction Si plates coated with a thin layer of vacuum grease were used to support electrolyte film samples that delaminated from their initial substrates.

Fourier transform infrared (FTIR) spectra were recorded on a Thermo Scientific Nicolet iS5 spectrometer with iD1 transmission module in the wavenumber range from 700 cm⁻¹ to 4000 cm⁻¹ at room temperature. A few drops of solutions were added on the central portion of an FTIR transparent silicon window. Water was allowed to evaporate under ambient conditions to form solid salts with uniform film thickness. This method minimizes the influence of the external matrix, such as KBr or nujol mull.

Differential scanning calorimetry (DSC) analyses were performed on either a DSC Q2000 or a DSC Q20 thermal analyzer, with a scan rate of 10 °Cmin⁻¹ in a nitrogen purged cell.

¹H solid-state nuclear magnetic resonance (NMR) spectra were recorded on an Agilent DD2-700 with the Larmor frequency 700 MHz and chemical shift has externally been referenced to tetramethylsilane (TMS). The ¹H NMR measurements have been taken as a function of temperature from -30 to 50 °C.

3.8 Shelf storage conditions for polymer electrolytes and capacitors

All polymer electrolytes as well as the enabled-solid cells were stored either under ambient conditions (ca. 25 °C, room RH) and/or in controlled conditions:

- For shelf life studies, performance tracking was performed at ambient conditions as a function of time with fluctuating RH values at room temperature.
- For controlled conditions, the equilibrated RH at 25 °C were controlled to simulate different environments (Table 3-15) [156]. The three RH levels were chosen to represent different conditions with stable and repeatable values at ambient room temperature. Before any measurements, cells were kept under the desired RH environment for at least
15 days to reach equilibrium. A temperature/humidity chamber (Espec SH-241) was used to conduct tests at desired humidity levels as a function of temperature.

**Table 3-15**: Shelf storage conditions at room temperature.

<table>
<thead>
<tr>
<th>RH</th>
<th>Controlled by</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>75 (±3)%</td>
<td>saturated NaCl solution</td>
<td>High humidity condition</td>
</tr>
<tr>
<td>45 (±3)%</td>
<td>saturated K$_2$CO$_3$ solution</td>
<td>Normal humidity condition</td>
</tr>
<tr>
<td>5 (±2)%</td>
<td>dried silica gel</td>
<td>Extremely low humidity condition</td>
</tr>
</tbody>
</table>

All solid 3-electrode cells and “modified 2-electrode” cells were stored at 75% RH overnight before any electrochemical tests to achieve a steady-state condition for ion conduction and to lower the electrode/electrolyte interfacial resistance. XRD samples were stored in the desired RH condition for a week before testing in order to investigate the structure change with respect to RH unless otherwise specified.
4 Development of SiWA-PVA binary system

This chapter discusses the development of a binary system using SiWA as a proton conductor and PVA as a polymer host. Although higher loading of SiWA in the polymer matrix could facilitate faster proton transport, proton conductivity and polymer electrolyte film integrity should be balanced for good electrode/electrolyte interface. Before developing a polymer electrolyte system, performance of SiWA as aqueous electrolytes for EDLCs and pseudo-capacitors were studied systematically [113, 157]. Table 3-4 shows the compositions of SiWA-PVA polymer electrolytes that have been included in this section.

4.1 Proton conductivity

Proton conductivity of the SiWA-PVA polymer electrolytes were measured with EIS and monitored over time and RH as shown in Figure 4-1. The polymer electrolytes were coated and “dried” between two stainless steel foils (stainless steel was used as electrodes to isolate the behavior of the polymer electrolytes). The proton conductivity of the electrolytes decreased with lower SiWA content. The highest average conductivity was ca. 10 mScm\(^{-1}\) of SiWA(419)-PVA while the lowest one was ca. 3 mScm\(^{-1}\) of SiWA(20)-PVA.

![Figure 4-1: Proton conductivity tracking of SiWA(419)-PVA, SiWA(109)-PVA, SiWA(47)-PVA, and SiWA(20)-PVA over time under uncontrolled ambient conditions.](image-url)
The ambient RH at each measurement was also tracked and plotted together with the proton conductivity and was shown in Figure 4-1. The conductivity dependence on the RH increased with SiWA content. For example, conductivity of SiWA(20)-PVA and SiWA(47)-PVA remained relatively independent on RH after the initial decay. In contrast, conductivity of SiWA(419)-PVA fluctuated much more with RH. Nevertheless, it still exhibited the highest proton conductivity. The results observed in Figure 4-1 is very promising, as they demonstrated the potential to use SiWA-PVA binary system in their “dry” state as polymer electrolytes for supercapacitors at the ambient.

Since proton conductivity of SiWA(419)-PVA is dependent on the RH and temperature, a comparative study of its conductivity was performed at three RH levels: 75%, 45%, and 5%, representing high humidity, normal humidity, and extremely low humidity conditions, respectively. Arrhenius plots of proton conductivity (σ) for SiWA(419)-PVA over a temperature range of -30 to 50 °C are illustrated in Figure 4-2 and the corresponding activation energies are summarized in Table 4-1. Proton conductivity values are listed in Appendix B, Table A1.

The plots of proton conductivity in Figure 4-2 can be divided into two regions, above and below 0 °C. The high linearity of the fitted lines in both regions supported the conduction of protons via Grotthuss (or hopping) mechanism, as opposed to the curved Arrhenius plots. The activation energies were obtained from the slopes of the fitted lines. At temperatures above 0 °C, the activation energies of SiWA(419)-PVA were 5.8, 12.2, and 41.8 kJmol⁻¹ at 75%, 45%, and 5% RH, respectively. The reduction in RH increased the activation barrier of proton transportation. At temperatures below 0 °C, activation energies for all three RH conditions increased to 21.5, 30.7, and 61.9 kJmol⁻¹, for the three RH levels, respectively. Since fast proton transportation is enabled by the rotation of water molecules within the SiWA structure, the motion of water molecules are limited at temperatures below the water freezing point. This would render a higher energy barrier against structural reorganization/reorientation of water molecules and H⁺-nH₂O clusters.

The Arrhenius plots also indicated that instead of low temperature, low humidity has a more negative effect limiting the electrolyte performance. For example, even at -30 °C, SiWA(419)-PVA still exhibited conductivity values of 4.3 and 1.0 mScm⁻¹ at 75% and 45% RH, respectively.
At a slightly higher temperature of 0 °C, it showed conductivity values of 14.0 mScm\(^{-1}\) at 75\% RH and 5.1 mScm\(^{-1}\) at 45\% RH.

**Figure 4-2**: Temperature dependence of proton conductivity for SiWA(419)-PVA at 5\%, 45\%, and 75\% RH from -30 to 50 °C.

**Table 4-1**: Proton conduction activation energies of SiWA(419)-PVA at 75\%, 45\%, and 5\% RH.

<table>
<thead>
<tr>
<th>RH</th>
<th>Activation energy (kJmol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T&gt;0 °C</td>
</tr>
<tr>
<td>75%</td>
<td>5.8</td>
</tr>
<tr>
<td>45%</td>
<td>12.2</td>
</tr>
<tr>
<td>5%</td>
<td>41.8</td>
</tr>
</tbody>
</table>

**4.2 Proton-conducting species**

To identify the presence of H\(^+\)-nH\(_2\)O clusters and to obtain structural, compositional, and bonding information concerning the polymer electrolyte, FTIR analyses were performed on SiWA(109)-PVA and SiWA(419)-PVA at ambient conditions. Pure SiWA was also included. Figure 4-3 shows the FTIR spectra of the two polymer electrolytes and SiWA. Table 4-2 summarizes the wavenumbers of the bands with their associated bonding interactions.
Both SiWA(109)-PVA and SiWA(419)-PVA had similar primary structures in the 700 to 1300 cm\(^{-1}\) region, representing the characteristics of the well characterized Keggin anion unit. The structure and interaction of SiWA are described as vibrational stretching modes of edge sharing oxygen (W\(-\text{Ob-W}\)), corner sharing oxygen (W\(-\text{Oc-W}\)), tetrahedral oxygen (Si\(-\text{Oa}\)), and terminal oxygen (W\(-\text{Od}\)) [128, 158-160]. This demonstrated that SiWA retained its Keggin anion structure after mixing with PVA. In addition, both electrolytes showed C-H stretching, C-H bending, C-O stretching peaks at \(\text{ca.}\ 2950, 1430,\) and 1087 cm\(^{-1}\) respectively, attributed to the presence of PVA. Due to the higher PVA content, these three peaks showed higher relative intensities (compared to the Keggin peaks) in SiWA(109)-PVA.

![Figure 4-3: FTIR spectra of SiWA(109)-PVA, SiWA(419)-PVA, and SiWA.](image)

Since the presence of water plays an important role, it is of interest to identify the water content and their bonding characteristics in the polymer electrolytes. The broad band at \(\text{ca.}\ 3400\) cm\(^{-1}\) was from O-H stretching in hydroxyl groups of PVA as well as the crystallized and/or free water molecules in the electrolytes. The O-H stretching peaks of free water occur at 3500 cm\(^{-1}\) [161]. For SiWA, this band was shifted negatively to 3400 cm\(^{-1}\), suggesting stronger hydrogen bonding [162, 163] due to the nature of crystallized water. Comparing both SiWA(109)-PVA and
SiWA(419)-PVA to SiWA, O-H stretching shifted to a higher frequency. The shifting of O-H stretching was caused by a decrease in hydrogen bonding in the polymer electrolytes. This could be explained by the presence of free water in the film. Although free water tends to be absorbed and desorbed more readily than crystallized water, they could still facilitate fast proton transport. More importantly, the O-H bending peaks at ca. 1700 and 1600 cm\(^{-1}\) in both the electrolytes and pure SiWA could be identified and assigned to protonated crystallized water (H\(_3\)O\(^+\) or H\(_5\)O\(_2\)\(^+\)) and neutral crystallized (or free) water (H\(_2\)O) [123, 164]. This strongly indicated the presence of protonated water in the SiWA-PVA electrolytes. The H\(_3\)O\(^+\) and H\(_5\)O\(_2\)\(^+\) species have a high mobility and thus result in high proton conductivity of SiWA(419)-PVA.

Table 4-2: FTIR band positions and associated bonding information for SiWA(109)-PVA, SiWA(419)-PVA, and SiWA.

<table>
<thead>
<tr>
<th>Wavenumber (\text{cm}^{-1})</th>
<th>Band assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td></td>
</tr>
<tr>
<td>O-H stretching in hydroxyl groups of PVA, crystallized water (both protonated and neutral) of SiWA, and free (neutral) water of film</td>
<td></td>
</tr>
<tr>
<td>3446  &amp; 3475  &amp; 3400</td>
<td></td>
</tr>
<tr>
<td>2948  &amp; 2951  &amp; -</td>
<td></td>
</tr>
<tr>
<td>1718  &amp; 1719  &amp; 1710</td>
<td></td>
</tr>
<tr>
<td>1647  &amp; 1629  &amp; 1602</td>
<td></td>
</tr>
<tr>
<td>1431  &amp; 1431  &amp; -</td>
<td></td>
</tr>
<tr>
<td>1087  &amp; 1087  &amp; -</td>
<td></td>
</tr>
<tr>
<td>1015  &amp; 1016  &amp; 1019</td>
<td></td>
</tr>
<tr>
<td>974   &amp; 975   &amp; 980</td>
<td></td>
</tr>
<tr>
<td>921   &amp; 921   &amp; 924</td>
<td></td>
</tr>
<tr>
<td>885   &amp; 884   &amp; 885</td>
<td></td>
</tr>
<tr>
<td>797   &amp; 793   &amp; 793</td>
<td></td>
</tr>
</tbody>
</table>

4.3 Structure characterizations

XRD was utilized to investigate the composition and structure of the polymer electrolytes. The XRD patterns of the SiWA-PVA mixture as well as pure PVA are shown in Figure 4-4. The PVA sample showed a broad peak at 19.7° due to its semi-crystalline nature. Two smaller peaks was found at ca. 43.6°, which were results of the diffraction from the stainless steel substrate. The diffraction peak at 19.7° is the (101) diffraction peak of PVA crystal from the intermolecular interference between PVA chains [165].
With the addition of SiWA, a new peak at 5.6° appeared in SiWA(47)-PVA together with a broad peak at 30°. With increasing high crystalline SiWA loading, one may expect that the overall structure of the polymer electrolytes became crystalline with very narrow peaks. However XRD patterns appeared to be semi-crystalline for both SiWA(109)-PVA and SiWA(419)-PVA with three notable features: (a) a shift and a narrowing of the peak at 5.6°; (b) a decrease in relative intensity of the peak at 19.7° (compared to the peak at 5.6°); and (c) an increase in relative intensity of the broad peak at 30° (compared to the peak at 5.6°). Although the reduction in relative intensity of the peak at 19.7° suggested a reduction in the crystallinity of PVA in the binary system, the shift and narrowing of the peak at 5.6° confirmed an increase in crystallinity of the polymer electrolyte with higher SiWA content.

**Figure 4-4**: XRD patterns of PVA, SiWA(47)-PVA, SiWA(109)-PVA, SiWA(419)-PVA after one-week storage at 45% RH (intensity in linear scale).

Since HPAs are highly crystalline materials with long-range ordered crystal structures, the increase in relative intensity of the broad peak at 30° could be related to the crystallization of
SiWA over time within the PVA matrix. The same SiWA(419)-PVA film was characterized via XRD after two- and three-week shelf storage and its patterns are shown in Figure 4-5. It can be observed that crystallization of SiWA definitely occurred. XRD patterns of week 2 and week 3 are indicative of the crystalline structure with very narrow peaks. Number of peaks increased with longer storage time. Peak intensity was also plotted in a logarithmic scale. Relative intensity of the broad peak at 30° decreased with time and SiWA crystalline peaks started to appear. Further discussions on the peak assignments of the SiWA-based polymer electrolytes will be presented in Chapter 4. Nevertheless, these three XRD patterns showed very similar amorphous baselines, which were contributed by the polymer matrix.

**Figure 4-5**: XRD patterns of SiWA(419)-PVA after one-, two-, and three-week storage at 45% RH (left: intensity in linear scale, right: intensity in logarithmic scale).

### 4.4 Summary

A SiWA-PVA binary polymer electrolyte system was successfully developed. SiWA(419)-PVA showed the highest proton conductivity. Proton hopping was the conduction mechanism in the
polymer electrolyte based on the activation energy analysis. Generally, it is desirable to have a high degree of hydration for high proton mobility, and thus high proton conductivity. Among the three types of water (see Figure 2-13), crystallized water species in polymer electrolyte are more desirable to form a stable proton-conducting network. The presence of crystallized water was indeed confirmed in SiWA-PVA polymer electrolytes via FTIR characterizations. The crystallized water is likely protonated with a structure of $\text{H}_3\text{O}_2^+$ and $\text{H}_3\text{O}^+$. Even though the freezing of water molecules caused a high activation energy barrier for proton condition at temperatures below 0 °C, such protonated water species form a stable network with SiWA molecules in the polymer electrolyte and exhibited high proton conductivity at room temperature. XRD analysis revealed that the addition of SiWA increased the crystallinity of the entire binary system due to SiWA crystallization over time. Nevertheless, SiWA(419)-PVA still showed amorphous baselines contributed by PVA.

Although SiWA(419)-PVA demonstrated promising performance in the solid state, its conductivity still fluctuated with RH. Limited by its low PVA content (ca. 10 wt.% in the solid state), the resulting polymer electrolyte film was also brittle and fragile, which is not ideal for flexible supercapacitor devices. Figure 4-6 displays the delamination of a SiWA(419)-PVA electrolyte film from electrode surface after opening a metallic cell. Therefore, overall properties of thin film SiWA(419)-PVA polymer electrolyte need to be improved.

![Figure 4-6: Photograph of a metallic cell enabled by SiWA(419)-PVA, showing the delamination of its electrolyte film from electrodes.](image)
5 Effects of plasticizers in SiWA-PVA

To improve the flexibility and tackiness of the polymer electrolyte films and to further minimize the interfacial resistance, plasticizers were incorporated into the SiWA-PVA system. There are two types of plasticizers: internal plasticizer through co-polymerization; and external plasticizer through addition of low MW compound. In both cases, secondary bonding between polymer chains will be reduced. An increase in plasticity and a decrease in polymer crystallinity can be achieved by increasing the segmental motions of polymer chains. This may promote a better electrode/electrolyte interface for maximum ion accessibility. In this study, effect of small MW external plasticizers were investigated on two types of plasticizers: neutral and acidic.

5.1 Neutral plasticizers

Ethylene glycol and glycerol are common neutral plasticizers for polymer electrolytes [141, 166, 167]. They were added to SiWA(419)-PVA and the resulting compositions are shown in Table 3-5 and Table 3-6. The purpose of this exercise is to choose an optimal neutral plasticizer (and composition). The adhesion and flexibility of the polymer electrolytes with plasticizers were much better than that of SiWA(419)-PVA, from a processing standpoint. The proton conductivity of the SiWA-Egly-PVA and SiWA-Gly-PVA electrolytes after one-week storage at 45% RH were shown in Figure 5-1.

The proton conductivity of SiWA-Egly(0)-PVA and SiWA-Gly(0)-PVA (i.e. SiWA(419)-PVA) was about 9 mScm⁻¹ at 45% RH, which agreed well with the previous results (see Section 4.1). In the ethylene glycol-added system (Figure 5-1a), the proton conductivity increased with ethylene glycol content, reaching a max conductivity of 18 mScm⁻¹. Further increase of ethylene glycol decreased the conductivity to 8 mScm⁻¹. The initial enhancement in conductivity was mainly a result of a solvation effect, in which ethylene glycol acted not only as a plasticizer but also a solvent to SiWA. This promoted higher proton mobility and thus higher conductivity. Further addition of ethylene glycol lowered the concentration of proton-containing species, leading to a reduction in conductivity. A similar trend was also observed in the glycerol-added system. Highest conductivity of ca. 13 mScm⁻¹ was obtained at a Glycerol to PVA molar ratio of 2000. However the conductivity of the glycerol-added electrolyte was slightly lower than its ethylene glycol counterpart. This could be explained by the smaller molecular size of ethylene glycol, such that protons can be transferred via proton/ethylene glycol complex with a higher mobility.
(i.e. a stronger solvation effect). In addition, it is also easier for ethylene glycol to penetrate into PVA chain, reducing the ordered chain structure and increasing amorphous region, and further promote conductivity (i.e. a greater plasticizer effect).

Figure 5-1: Proton conductivity of (a) SiWA-Egly-PVA and (b) SiWA-Gly-PVA polymer electrolytes at 45% RH.

To further characterize the effect of these two plasticizers on the long-term performance of the polymer electrolytes, proton conductivity of SiWA-Egly(2000)-PVA and SiWA-Gly(2000)-PVA were monitored and compared to SiWA(419)-PVA under uncontrolled ambient conditions with tracked RH as shown in Figure 5-2. Initially SiWA-Egly(2000)-PVA was more conductive than both SiWA-Gly(2000)-PVA and SiWA(419)-PVA at ca. 50% RH. After exposure to ambient RH, the conductivity values of all three electrolytes decreased rapidly caused by the film dehydration. However SiWA-Gly(2000)-PVA demonstrated somewhat higher proton conductivity than the other two electrolytes. This was attributed to the positive effect of higher water retention capability of glycerol (by its more available hydroxyl groups) outweighed the negative effect of the reduction in the SiWA content.

Although the addition of glycerol enhanced the proton conductivity, the loss of crystallized water molecules in the SiWA structure at low RH still limited the electrolyte performance at the extremely dry condition. Since the increase in charge carrier concentration (i.e. higher proton
density) can lead to a higher proton conductivity. It is of interest to investigate the effect of acidic plasticizers on the proton density, and thus proton conductivity.

Figure 5-2: Proton conductivity tracking of SiWA(419)-PVA, SiWA-Egly(2000)-PVA, and SiWA-Gly(2000)-PVA over time under uncontrolled ambient conditions.

5.2 Acidic plasticizers

As discussed in Section 2.4, H₃PO₄ incorporated in the PVA matrix can be used as a polymer electrolyte but its performance is strongly influenced by temperature and RH. In this study, H₃PO₄ was added to SiWA(419)-PVA as an acidic plasticizer. In this section, the focus is on the impact of H₃PO₄ on the conductivity, structure, and thermal stability of the SiWA-PVA polymer electrolyte system. The performance of solid supercapacitors enabled by SiWA-H₃PO₄-PVA is also discussed.

5.2.1 Proton conductivity

The study was performed on a binary SiWA(419)-PVA (i.e. SiWA-H₃PO₄(0)-PVA as baseline) and a ternary SiWA-H₃PO₄-PVA electrolytes so that the effect of H₃PO₄ could be derived. Table 3-7 lists the compositions of the SiWA-H₃PO₄-PVA electrolyte system. Conductivity of SiWA(419)-PVA and SiWA-H₃PO₄-PVA electrolytes at 45% RH were first measured and the results are shown in Figure 5-3. All three electrolytes with H₃PO₄ showed higher proton conductivity than its binary counterpart. Among the three, SiWA-H₃PO₄(1500)-PVA showed the
highest value of *ca.* 18 mScm\(^{-1}\) even though SiWA-H\(_3\)PO\(_4\)(2500)-PVA contained more H\(_3\)PO\(_4\). The lower conductivity of SiWA-H\(_3\)PO\(_4\)(2500)-PVA was caused by a liquid H\(_3\)PO\(_4\) leakage in the film. This also caused a higher standard deviation in conductivity. Further discussion in this section focus on the comparison between SiWA-H\(_3\)PO\(_4\)(1500)-PVA and SiWA-H\(_3\)PO\(_4\)(0)-PVA.

![Figure 5-3](image)

**Figure 5-3**: Proton conductivity of SiWA-H\(_3\)PO\(_4\)(0)-PVA, SiWA-H\(_3\)PO\(_4\)(500)-PVA, SiWA-H\(_3\)PO\(_4\)(1500)-PVA, and SiWA-H\(_3\)PO\(_4\)(2500)-PVA at 45% RH.

Arrhenius plots of proton conductivity for both SiWA-H\(_3\)PO\(_4\)(1500)-PVA and SiWA-H\(_3\)PO\(_4\)(0)-PVA were obtained to see the effect of H\(_3\)PO\(_4\) on proton conductivity of the electrolyte at different RH levels (Figure 5-5). Their activation energies are summarized in Table 5-1 and their conductivity values are listed in Appendix B, Table A1 and Table A2.

Both SiWA-H\(_3\)PO\(_4\)(1500)-PVA and SiWA-H\(_3\)PO\(_4\)(0)-PVA shared a similar trend of conductivity increasing with temperature and RH. Two regions with different activation energies were observed for both electrolytes. The high linearity of the ln \(\sigma\) vs. 1000/\(T\) plots was consistent with proton hopping. When the activation energies were comparable for the two polymer electrolytes, the addition of H\(_3\)PO\(_4\) enhanced the proton conductivity especially at the extremely dry condition and at low temperatures with normal RH condition. This enhancement was due to the higher proton density provided by the H\(_3\)PO\(_4\) addition. In contrast, at high temperatures with normal RH
condition and all temperatures with high humidity condition, proton mobility dominated the proton conductivity, leading to a similar conductivity of samples with and without H₃PO₄ addition.

Figure 5-4: Temperature dependence of proton conductivity for SiWA-H₃PO₄(1500)-PVA and SiWA-H₃PO₄(0)-PVA at 75%, 45%, and 5% RH from -30 to 50 °C.

Table 5-1: Proton conduction activation energies of SiWA-H₃PO₄(0)-PVA and SiWA-H₃PO₄(1500)-PVA at 75%, 45%, and 5% RH.

<table>
<thead>
<tr>
<th>RH</th>
<th>SiWA-H₃PO₄(0)-PVA (kJmol⁻¹)</th>
<th>SiWA-H₃PO₄(1500)-PVA (kJmol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T&gt;0 °C</td>
<td>T&lt;0 °C</td>
</tr>
<tr>
<td>75%</td>
<td>5.8</td>
<td>21.5</td>
</tr>
<tr>
<td>45%</td>
<td>12.2</td>
<td>30.7</td>
</tr>
<tr>
<td>5%</td>
<td>41.8</td>
<td>61.9</td>
</tr>
</tbody>
</table>

To further understand the impact of charge carrier concentration from H₃PO₄ addition, ac capacitance of the metallic cells at 5% RH were extracted from EIS measurements (Figure 5-5). Both solid cells showed increased capacitance with temperature. SiWA-H₃PO₄(1500)-PVA cell had higher capacitance cell over the entire range of temperatures tested, likely attributable to the
higher number of protons available for charge separation in the film and a more intimate electrode/electrolyte contact. Although the brittle nature of the SiWA-H₃PO₄(0)-PVA at this ultra-low RH condition could also negatively affect the accessible electrode surface area, leading to a low capacitance value, Figure 5-4 and Figure 5-5 still clearly demonstrate the enhanced proton conductivity through the addition of H₃PO₄.

**Figure 5-5**: Capacitance (at 1 Hz) of stainless steel cells enabled by SiWA-H₃PO₄(1500)-PVA and SiWA-H₃PO₄(0)-PVA at 5% RH from -30 to 50 °C.

### 5.2.2 Structural characterizations

FTIR was used to obtain the effect of H₃PO₄ on bonding information of the polymer electrolytes. Figure 5-6 shows FTIR spectra of SiWA-H₃PO₄(1500)-PVA and SiWA-H₃PO₄(0)-PVA. For both electrolytes, all bands can be associated with its individual components and interactions. Most primary structures appeared in the region between 700 and 1200 cm⁻¹, suggesting the Keggin structure/composition was retained in SiWA-H₃PO₄-(1500)-PVA. Detailed peak assignments in this region can be referred to Table 4-2 (Section 4.2).

At higher wave numbers ranging from 1200 to 4000 cm⁻¹, the spectra of both SiWA-H₃PO₄(1500)-PVA and SiWA-H₃PO₄(0)-PVA exhibited several similar peaks. The only difference between the two polymer electrolytes was a broad peak appearing between 2100 and
2500 cm\(^{-1}\) in SiWA-H\(_3\)PO\(_4\)(1500)-PVA related to stretching vibration of the P-OH groups of H\(_3\)PO\(_4\) [168]. Similar to the SiWA-H\(_3\)PO\(_4\)(0)-PVA spectrum, peaks from Keggin unit of SiWA could be identified in SiWA-H\(_3\)PO\(_4\)(1500)-PVA, confirming that the anion structure was retained in SiWA-H\(_3\)PO\(_4\)(1500)-PVA. Protonated water in the form of hydrated protons (\textit{i.e.} H\(_5\)O\(_2^+\) and/or H\(_3\)O\(^+\)) were also identified in SiWA-H\(_3\)PO\(_4\)(1500)-PVA. These protonated water species are responsible for the proton conduction in the electrolytes. The addition of H\(_3\)PO\(_4\) did not alter the structure of the polymer electrolyte but instead provided additional protons resulting in higher ionic conductivity of SiWA-H\(_3\)PO\(_4\)(1500)-PVA.

![FTIR spectra of SiWA-H\(_3\)PO\(_4\)(1500)-PVA and SiWA-H\(_3\)PO\(_4\)(0)-PVA.](image)

**Figure 5-6:** FTIR spectra of SiWA-H\(_3\)PO\(_4\)(1500)-PVA and SiWA-H\(_3\)PO\(_4\)(0)-PVA.

The effect of H\(_3\)PO\(_4\) on the crystallization of SiWA within SiWA-H\(_3\)PO\(_4\)(1500)-PVA was investigated using XRD as a function of RH level. Figure 5-7 shows the XRD patterns of SiWA-H\(_3\)PO\(_4\)(1500)-PVA at different RH conditions. Higher degrees of SiWA crystallization were observed in SiWA-H\(_3\)PO\(_4\)(1500)-PVA than in SiWA(419)-PVA binary system (see Figure 4-4) and further investigations are needed to understand this phenomenon.
The structure of HPAs are highly dependent on the amount of crystallized water in the crystal lattice, such that their XRD patterns vary significantly with the levels of hydration [17, 121, 169, 170]. It was reported that HPAs with overall asymmetrical XRD patterns (from 5° to 50° 2θ) tend to be more hydrated than those with symmetrical patterns [169-171]. A series of XRD patterns for pure SiWA powder and comparisons to literature data can be found in Appendix C. For fully hydrated HPAs (e.g. SiWA·28H2O), the most intense fingerprint peaks occurs at ca. 6.5° and 26.5°. Dehydration are closely associated with the disappearance of the two strong peaks at 6.5° and 26.5°, followed by the appearance of new peaks at ca. 10.5° and 25.3°. These features correspond to a consecutive changes in the structure of SiWA along the dehydration process (i.e. cubic → orthorhombic → triclinic → cubic, see Appendix C).

![XRD patterns of SiWA-H3PO4(1500)-PVA after one-week storage at 50%, 40%, 30%, and 5% RH](image)

**Figure 5-7**: XRD patterns of SiWA-H3PO4(1500)-PVA after one-week storage at 50%, 40%, 30%, and 5% RH (left: intensity in linear scale, right: intensity in logarithmic scale).

Examining the XRD pattern at 75% RH, no SiWA peaks were observed, the pattern was very similar to the one of SiWA(419)-PVA (as shown in Figure 4-5). This indicated that SiWA did
not crystalize at this high RH condition. At 50% RH, sharp peaks observed at 6.5°, 26.5°, and 33.4° confirmed SiWA in SiWA-H₃PO₄(1500)-PVA was fully hydrated. The diffraction patterns obtained at 40% RH was very similar to the one obtained at 50% RH. This implied no major structure change of SiWA occurred. However the salt crystallized more at this condition since a number of smaller peaks could be identified, including those at 7.8°, 8.5°, 10.6°, 17.2°, and 34.4°. In addition, a decrease in intensity of the peak at 6.5° and/or an increase in intensity of the peak at 26.5° (i.e. a lower peak intensity ratio between 6.5° and 26.5°) were observed. Indeed this suggested the relative intensity ratio between these two peaks can serve as an indicator, as the ratio is expected to decrease with the decrease in hydration within this mid-RH range.

Further dehydration caused a structure change of SiWA within the polymer electrolyte, such that fewer peaks were observed. A significant peak growth at 8.5° was noted and both peaks at 26.5° and 33.4° still presented. At dehydrated condition (i.e. 5% RH), the pattern became more symmetrical. The three most intense peak were at 25.3°, 10.2°, and 34.6°, agreeing the cubic crystal structure of SiWA with six crystallized water molecules. Since the peaks at 6.5° and 10.5° are two signature peaks for hydrated and dehydrated conditions, respectively, the relative intensity ratio between these two peaks is expected to increase with the level of hydration and can serve as an indicator. Again, the relative intensity ratio between the peaks at 10.5° and 25.3° (or 26.5°) increased with the decrease of hydration, which can also serve as an indicator for the level of dehydration. Although the XRD patterns of SiWA-H₃PO₄(1500)-PVA changed significantly during dehydration, the polymer electrolyte remained its amorphous baseline.

5.2.3 Thermal stability

Thermal stability of SiWA-H₃PO₄(1500)-PVA and SiWA-H₃PO₄(0)-PVA polymer electrolytes were analyzed by DSC; the obtained thermograms are shown in Figure 5-8. Both samples were dried at 5% RH before testing to eliminate the influence of free water content. In Figure 5-8, both electrolytes exhibited one endothermic peak above 100 °C. In addition, the glass transition temperature was found to be ca. 58 °C for SiWA-H₃PO₄(1500)-PVA. There was also an exothermic peak at 133 °C, attributable to the partial dehydration of H₃PO₄ (2H₃PO₄ ↔ H₄P₂O₇ + H₂O). Furthermore, while both SiWA-H₃PO₄(1500)-PVA and SiWA-H₃PO₄(0)-PVA showed a
continued decrease of water content in the low temperature region, the extent of reduction in SiWA-H₃PO₄(1500)-PVA was less than that in SiWA-H₃PO₄(0)-PVA.

Since the removal of water molecules requires the system to absorb energy, the endothermic peaks in Figure 5-8 are likely associated with the loss of certain forms of water. Since at this low RH condition, SiWA in the polymer electrolytes was in the hexahydrate form (see Figure 5-7) and all crystallized water molecules were protonated as discussed in Section 2.5.2. In the case of SiWA-H₃PO₄(0)-PVA, the complete release of the crystallized protonated water occurred at 140 °C. This endothermic peak appeared at 152 °C for SiWA-H₃PO₄(1500)-PVA. Addition of H₃PO₄ had a positive effect of providing additional stability to crystallized water content, resulting in a 12 °C increase in its dehydration temperature.

Figure 5-8: DSC thermograms of SiWA-H₃PO₄(1500)-PVA and SiWA-H₃PO₄(0)-PVA stored at 5% RH.
5.2.4 Capacitor performance

In this section, a comparative study of SiWA-H$_3$PO$_4$(1500)-PVA and Nafion D-521 (PFSA dispersion) was performed, focusing on ultra-high rate capability of SiWA-H$_3$PO$_4$(1500)-PVA in ambient conditions and its shelf life. In addition, a solid 2-cell capacitor stack enabled by SiWA-H$_3$PO$_4$(1500)-PVA was demonstrated.

The conductivity of SiWA-H$_3$PO$_4$(1500)-PVA, SiWA(419)-PVA, and Nafion at 40-60% RH is shown as a function of time in Figure 5-9. Initially, the conductivity of both SiWA-H$_3$PO$_4$(1500)-PVA and Nafion was in the same order of magnitude, ranging between 15-20 mScm$^{-1}$, while SiWA(419)-PVA was ca. 12 mScm$^{-1}$. Both SiWA-based electrolytes showed stable performance. The addition of H$_3$PO$_4$ indeed increased proton conductivity. Nafion, however, exhibited a continuous decrease in conductivity over time, eventually dropping to 2 mScm$^{-1}$, in agreement with Maréchal et al. under similar conditions [41]. The hydrogen-bond network enabled by crystallized water in SiWA-H$_3$PO$_4$(1500)-PVA and SiWA(419)-PVA facilitated fast and stable proton hopping in the polymer electrolyte. In contrast, the water molecules in Nafion are loosely bonded to the hydrophilic acid groups and can be readily removed in the ambient condition, causing a high activation energy barrier for proton transport and low conductivity.

![Figure 5-9](image_url)

**Figure 5-9:** Proton conductivity of SiWA-H$_3$PO$_4$(1500)-PVA, SiWA(419)-PVA, and Nafion over time at uncontrolled ambient conditions.
CV profiles of metallic cells enabled by SiWA-H₃PO₄(1500)-PVA and Nafion at a pristine condition were shown in Figure 5-10a. Both CVs exhibit near rectangular profiles indicating good capacitive behavior at a scan rate of 5000 Vs⁻¹. Double-layer capacitance is expected to range from 15 to 30 µFcm⁻² for a smooth metallic electrode in a liquid electrolyte [1]. At this high scan rate, both solid cells were still able to deliver 10 µFcm⁻². Both polymer electrolytes can transfer ions at very high rates in the beginning. Figure 5-10b shows the CVs of the same solid cells at the same rate, but after 14 days of storage at 40-50% RH. The solid SiWA-H₃PO₄(1500)-PVA capacitor retained its capacitance and capacitive behavior as well as its rate capability. In contrast, the Nafion capacitor showed a significant decrease in capacitance, which can be related to the decreased proton conductivity of Nafion. The increased ESR of the Nafion device limited ultra-high rate performance, resulting in a greater ohmic loss.

![Figure 5-10](image)

**Figure 5-10:** CVs solid metallic capacitors enabled by SiWA-H₃PO₄(1500)-PVA and Nafion at (a) day 1, and (b) day 14 (scan rate = 5000 Vs⁻¹)

To derive full advantage from SiWA-H₃PO₄(1500)-PVA and to reach higher cell voltage, a 2-in-1 stacked device was developed using graphite electrodes. Although, the specific capacitance is small, graphite was selected to allow focusing on the impact of the polymer electrolyte on the high rate performance of EDLCs by minimizing the influence of pores. Figure 5-11 shows two CV profiles of a single cell and a 2-in-1 cell, at a voltage scan rate of 1 Vs⁻¹. Both CVs were near-rectangular in shape. The 2-in-1 cell had a voltage window of 1.8 V, twice that of the single cell. At 1 Vs⁻¹, the area specific capacitance was 4 mFcm⁻² for the single cell and 1.8 mFcm⁻² for
the 2-in-1 cell. This was expected for a two cell in series connection. Although the capacitance of
the 2-in-1 device is half that of the single-cell capacitor, the higher cell voltage is desirable for
higher energy storage. Further addition of cells to increase the cell voltage is possible.

Figure 5-11: CVs of solid graphite capacitors enabled by SiWA-H₃PO₄(1500)-PVA at a scan
rate of 1 Vs⁻¹: (a) single cell and (b) 2-in-1 package.

The 2-in-1 solid cell were subjected to various high rate CV scans to determine the impact of
these polymer electrolytes on the high rate performance of solid multi-cell EDLCs. Figure 5-12
shows a series of CVs of an EDLC at scan rates of 5, 10, 25, and 50 Vs⁻¹. Most CVs (up to 25
Vs⁻¹) showed near rectangular shape indicating good capacitive behavior. At 50 Vs⁻¹, the cell
could still deliver a specific capacitance of 0.6 mFcm⁻². At such high rates, the capacitance
obtained was most likely contributed from the surface rather than the bulk of the graphite layer.

EIS analyses were performed on both single- and 2-in-1 solid supercapacitor cells. C’ was
separated from C” and plotted both as a function of frequency (Figure 5-13). Examining the
curves in Figure 5-13, C’ was approaching 3.7 mFcm⁻² for single-cell and 1.8 mFcm⁻² for 2-in-1
cell at low frequency (1 Hz). The capacitance decreased gradually over 3 decades of frequency.
The C” vs. frequency curve exhibited its maximum at ca. 30 Hz. This maximum translates to a
time constant of 33 ms for the solid EDLC, providing additional evidence that the SiWA-
H₃PO₄(1500)-PVA polymer electrolyte is capable of transporting protons at very high speed.
Figure 5-12: CVs of a solid 2-in-1 graphite capacitor enabled by SiWA-H₃PO₄(1500)-PVA at scan rates of (a) 5 Vs⁻¹, (b) 10 Vs⁻¹, (c) 25 Vs⁻¹, and (d) 50 Vs⁻¹.

Figure 5-13: Real part $C'$ (a) and imaginary part $C''$ (b) of capacitance vs. frequency for single and 2-in-1 graphite capacitors enabled by SiWA-H₃PO₄(1500)-PVA.
5.3 Summary

Effects of both neutral (i.e. glycerol or ethylene glycol) and acidic (i.e. H$_3$PO$_4$) plasticizers on SiWA(419)-PVA were characterized at different plasticizer contents first at a normal RH condition (i.e. 45%). The electrolyte with ethylene glycol showed higher conductivity than the electrolytes either with glycerol or without any additive due to its stronger plasticizer and solvation effects. This situation was reversed at low RH conditions. The electrolyte with glycerol showed a better water retention capability and higher conductivity over the other two electrolytes. However they all experienced a significant reduction in performance caused by the loss of crystalized water.

In contrast, the electrolyte with H$_3$PO$_4$ addition exhibited similar conductivity as the ethylene glycol-containing sample at 45% RH. More importantly, the addition of H$_3$PO$_4$ enhanced the proton density of the electrolyte, which improved its conductivity at the extremely dried conditions over the binary counterpart. Although the addition of H$_3$PO$_4$ did not alter the bonding structure of the original SiWA(419)-PVA polymer electrolyte, it promoted the retention of crystallized water (i.e. higher thermal stability). In addition, XRD analysis revealed that the relative intensity ratios between characteristic diffraction peaks of SiWA could be used as indicators to identify the level of hydration of SiWA in the polymer electrolytes.

To demonstrate SiWA-H$_3$PO$_4$(1500)-PVA as a polymer electrolyte for high rate supercapacitors. A solid 2-in-1 package EDLC was constructed using graphite electrodes. The solid 2-in-1 device was able to be charged and discharged at very high rate with a time constant of 33 ms. However, the conductivity of SiWA-H$_3$PO$_4$(1500)-PVA still fluctuated in the mid-RH ambient conductions (see Figure 5-9). A strengthening in the hydrogen bond interactions between water molecules and components in the polymer electrolytes could be a promising strategy to improve the environmental stability of the polymer electrolyte.
6  Effect of nano-fillers in SiWA-H₃PO₄-PVA

As a sustainable high performance polymer electrolyte should possess both high ionic conductivity and high environmental stability, nano-SiO₂ and nano-TiO₂ were selected as a water retention agent to improve the environmental stability of SiWA-H₃PO₄(1500)-PVA. SiO₂ has been extensively studied in polymer electrolytes and membranes. Their multiple functions have been reported [56, 172-177]. As a plasticizer, SiO₂ can reduce glass transition temperature of the polymer phase and increase the amorphous region to achieve higher ionic conductivity at lower temperatures [172]. As a cross-linker, SiO₂ can form inter-connected networks with the polymer phase to enhance mechanical and thermal properties [172-174]. As a water retention agent [56, 175-177], hydroxyl groups present on the SiO₂ surface could promote the formation of hydrogen bonds to stabilize water molecules [178]. However, these nano-filler-containing electrolytes displayed low ionic conductivity at ambient conditions. The limiting factor proved to be the high percentage of non-conductive material because of their salt-in-polymer configuration.

Although many studies have focused on the effect of these nano-fillers on salt-in-polymer electrolytes, the impact of SiO₂ or TiO₂ in polymer-in-salt, especially with large amount of filler (as compared to the polymer phase), has yet to be understood. In this section, effect of high SiO₂ and TiO₂ content on SiWA-H₃PO₄(1500)-PVA was first investigated under ambient conditions and then in controlled temperature environments. The compositions of the nano-SiO₂ and nano-TiO₂ containing polymer electrolytes are listed in Table 3-8.

6.1 Proton conductivity

Proton conductivity of the polymer electrolytes with and without fillers was tracked over a period of two months under ambient conditions as shown in Figure 6-1. The average conductivity of SiWA-H₃PO₄-PVA was 11 mScm⁻¹. SiWA-H₃PO₄-PVA/TiO₂ and SiWA-H₃PO₄-PVA/SiO₂ had similar average conductivity (11 and 10 mScm⁻¹, respectively). However, the filler-free electrolyte showed a stronger fluctuation in conductivity with RH compared to the electrolytes with fillers. Although the SiO₂-containing electrolyte has the lowest average conductivity among the three electrolytes, it demonstrated the best stability with the least fluctuation. This can be explained by a higher concentration of surface hydroxyl groups available on SiO₂ leading to a stronger water retention effect than that of TiO₂. Therefore, the first part of
this chapter (Section 6.2) focuses on the effect of SiO$_2$ on the water retention capability of the polymer electrolytes.

Fillers may not only impact the environmental stability of the electrolytes but also affect the ion transportation and charge separation in the film. The difference between the intrinsic dielectric constant of TiO$_2$ (80) and SiO$_2$ (3.9) [179] could also influence the static dielectric constant ($\varepsilon_{\text{r,s}}$) of the electrolyte film and the intrinsic capacitance of a polymer electrolyte-enabled cell at high frequencies. This is also of interest because of the possibility to enhance supercapacitor performance at ultra-high rates. The second part of this chapter (Section 6.3) focus on a comparative study of SiO$_2$ and TiO$_2$ fillers on proton conduction properties and dielectric response of SiWA-H$_3$PO$_4$-PVA with and without fillers.

![Figure 6-1: Proton conductivity tracking of SiWA-H$_3$PO$_4$-PVA/TiO$_2$, SiWA-H$_3$PO$_4$-PVA/SiO$_2$, and SiWA-H$_3$PO$_4$-PVA over time under uncontrolled ambient conditions.](image-url)
6.2 Effect of SiO₂*

The effect of SiO₂ on SiWA-H₃PO₄-PVA was investigated along the following aspects: a) environmental stability *via* water retention of the electrolytes with and without SiO₂ as well as *via* cell performance at different RH conditions; and (b) crystal and bonding structures with XRD and FTIR to identify key indicators of their change and to relate them to proton conductivity and environmental stability.

6.2.1 Water retention of SiWA-H₃PO₄-PVA/SiO₂

Water retention characteristics of the polymer electrolytes were compared at a low RH level of 20%. The water desorption curves at 20% RH of hydrated SiWA-H₃PO₄-PVA/SiO₂ and hydrated SiWA-H₃PO₄-PVA are shown in Figure 6-2. The weight of each electrolyte film was normalized to focus on the rate of weight change rather than on the absolute weight values. In Figure 6-2, both electrolytes showed a decrease in weight over time but at a different rate. SiWA-H₃PO₄-PVA/SiO₂ showed a slower water desorption as compared to the electrolyte without SiO₂. This may be attributed to the high water retention capability of SiO₂.

![Figure 6-2: Water desorption of hydrated SiWA-H₃PO₄-PVA/SiO₂ and SiWA-H₃PO₄-PVA films over time at 20% RH.](image)

6.2.2 XRD characterization

Since the XRD patterns of the polymer electrolyte can be used to identify the level of hydration of SiWA as discussed in Section 5.2.2, the stability of SiWA in the two polymer electrolytes was compared at room temperature but with different RH levels (i.e. 55% and 40%).

![XRD patterns of SiWA-H₃PO₄-PVA/SiO₂ and SiWA-H₃PO₄-PVA at 55% RH](image1)

![XRD patterns of SiWA-H₃PO₄-PVA/SiO₂ and SiWA-H₃PO₄-PVA at 40% RH](image2)

**Figure 6-3**: XRD patterns of SiWA-H₃PO₄-PVA/SiO₂ and SiWA-H₃PO₄-PVA at (a, b) 55% RH and (c, d) 40% RH.

The XRD patterns of SiWA-H₃PO₄-PVA/SiO₂ and SiWA-H₃PO₄-PVA at 55% RH are depicted in Figure 6-3a&b. Addition of SiO₂ promoted more SiWA crystallization within the film. For example, peaks at 7.8° and 8.5° could be identified. This implied that the fillers acted as
nucleation sites in the film. However when comparing the baselines of the two electrolytes, the addition of SiO₂ increased the amorphous baseline even with a reduction of PVA in SiWA-H₃PO₄-PVA/SiO₂. This was due to the amorphous nature of the SiO₂ phase. More importantly, the higher peak intensity ratio between 6.5° and 26.5° observed in SiWA-H₃PO₄-PVA/SiO₂ showed that SiWA in SiWA-H₃PO₄-PVA/SiO₂ was more hydrated than in SiWA-H₃PO₄-PVA.

The same electrolyte samples were analyzed in a lower RH environment (i.e. 40% RH) to test the stability of hydrated SiWA in the polymer electrolytes. The resulted XRD patterns are shown in Figure 6-3c&d. Both SiWA-H₃PO₄-PVA/SiO₂ and SiWA-H₃PO₄-PVA showed a certain extent of dehydration based on the lower peak intensity ratio between 6.5° and 26.5° when compared to Figure 6-3a&b. This pointed out a loss of some crystallized water at low RH. However, again comparing SiWA-H₃PO₄-PVA/SiO₂ to SiWA-H₃PO₄-PVA, the higher peak intensity ratio between 6.5° and 26.5° of the SiO₂-containing electrolyte implied that SiWA in SiWA-H₃PO₄-PVA/SiO₂ remained in a more hydrated state than that in SiWA-H₃PO₄-PVA.

6.2.3 FTIR analyses

FTIR analyses were performed on both SiWA-H₃PO₄-PVA/SiO₂ and SiWA-H₃PO₄-PVA polymer electrolytes to obtain structural, compositional, and bonding information. Pure PVA films with and without SiO₂ were first characterized. Figure 6-4 presents the FTIR spectra of pure PVA and PVA/SiO₂. The bands and related bonding information are summarized in Table 6-1.

In Figure 6-4, both PVA/SiO₂ and PVA showed similar spectra, indicating no alternation of the original PVA structure with SiO₂. SiO₂ was reported to be able to cross-link PVA to form a network [180-182]. This interaction should be observed at 836 cm⁻¹ as a characteristic Si-O-C band [183], resulting from the condensation reaction between the silanol group of SiO₂ and the hydroxyl group of PVA. Indeed, this was the case in Figure 6-4. In order to characterize the water retention effect of SiO₂, further analysis was focused on the O-H stretching band at 3300 to 3400 cm⁻¹ region. There were fewer hydroxyl groups in PVA/SiO₂ than in PVA because of the reduction in PVA content by 50% and the cross-linking effect of SiO₂. Nevertheless, a shifting of the O-H stretching band to a lower wavenumber was observed. This shifting implied a strengthening of the hydrogen bonding in PVA/SiO₂, likely as a result of the presence of excess free SiO₂ (non-cross-linked) with silanol groups in PVA/SiO₂. Accordingly, this might lead to
additional hydrogen bonds between hydroxyl groups on the free SiO₂ and either water molecules or the hydroxyl groups of PVA.

![FTIR spectra of PVA/SiO₂ and PVA](image)

**Figure 6-4**: FTIR spectra of PVA/SiO₂ and PVA.

**Table 6-1**: FTIR band positions and associated bonding information for PVA and PVA/SiO₂.

<table>
<thead>
<tr>
<th>PVA/SiO₂</th>
<th>Wavenumber (cm⁻¹) PVA</th>
<th>Band assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3315</td>
<td>3332</td>
<td>O-H stretching</td>
</tr>
<tr>
<td>2939</td>
<td>2942</td>
<td>C-H asymmetric stretching</td>
</tr>
<tr>
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<td>2910</td>
<td>C-H symmetric stretching</td>
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<tr>
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<tr>
<td>N/A</td>
<td>1238</td>
<td>C-C stretching</td>
</tr>
<tr>
<td>N/A</td>
<td>1093</td>
<td>C-O stretching</td>
</tr>
<tr>
<td>1091, 1183 (shoulder)</td>
<td>-</td>
<td>Si-O-Si asymmetric stretching</td>
</tr>
<tr>
<td>960</td>
<td>N/A</td>
<td>Si-OH stretching</td>
</tr>
<tr>
<td>-</td>
<td>919</td>
<td>Characteristic of syndiotactic structure</td>
</tr>
</tbody>
</table>
FTIR spectra of SiWA-H₃PO₄-PVA/SiO₂ and SiWA-H₃PO₄-PVA are shown in Figure 6-5, wavenumbers of the bands with their associated bonding interactions are depicted in Table 6-2. In Figure 6-5, both SiWA-H₃PO₄-PVA/SiO₂ and SiWA-H₃PO₄-PVA have similar primary structures in the 700 to 1300 cm⁻¹ region, representing the characteristics of the Keggin unit. To determine the interaction between SiO₂ and SiWA, the vibrations involving different oxygen atoms were investigated. Caused by the unique geometry of the SiWA Keggin unit, stretching vibration of both W-Ob-W and W-Oc-W involves a combination of bending and stretching characteristics. Therefore, edge sharing W-Ob-W and corner sharing W-Oc-W were expected to show different directions in band shift depending on the dominating oscillation. The edge sharing W-Ob-W at 885 cm⁻¹ (in SiWA-H₃PO₄-PVA) shifted to a slightly higher wavenumber of 888 cm⁻¹.

<table>
<thead>
<tr>
<th>Wavenumber</th>
<th>Bonding Interaction</th>
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<tr>
<td>853</td>
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</tr>
<tr>
<td>836</td>
<td>N/A Si-O-C stretching</td>
</tr>
<tr>
<td>810</td>
<td>N/A Si-O-Si symmetric stretching</td>
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</tbody>
</table>
(in SiWA-H$_3$PO$_4$-PVA/SiO$_2$) because of an increase in stretching frequency. The corner sharing oxygen W-O$_c$-W, on the other hand, decreased from 797 cm$^{-1}$ (in SiWA-H$_3$PO$_4$-PVA) to 791 cm$^{-1}$ (in SiWA-H$_3$PO$_4$-PVA/SiO$_2$) due to an increase in bending frequency. In addition, the terminal oxygen W=O$_d$ band at 977 cm$^{-1}$ did not show any significant shift. The small frequency shifts involving the O$_b$ and O$_c$ oxygen atoms as well as the stable O$_d$ oxygen atoms confirmed only a limited interaction between SiWA and SiO$_2$.

Table 6-2: FTIR band positions and associated bonding information for SiWA-H$_3$PO$_4$-PVA, and SiWA-H$_3$PO$_4$-PVA/SiO$_2$.

<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Band assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiWA-H$_3$PO$_4$-PVA/SiO$_2$</td>
<td>SiWA-H$_3$PO$_4$-PVA</td>
</tr>
<tr>
<td>3478</td>
<td>3483</td>
</tr>
<tr>
<td>2956</td>
<td>2955</td>
</tr>
<tr>
<td>2350</td>
<td>2348</td>
</tr>
<tr>
<td>1711</td>
<td>1702</td>
</tr>
<tr>
<td>1627</td>
<td>1630</td>
</tr>
<tr>
<td>1404</td>
<td>1402</td>
</tr>
<tr>
<td>1097 and 1185 (shoulder)</td>
<td>-</td>
</tr>
<tr>
<td>1017</td>
<td>1017</td>
</tr>
<tr>
<td>978</td>
<td>977</td>
</tr>
<tr>
<td>923</td>
<td>924</td>
</tr>
<tr>
<td>888</td>
<td>885</td>
</tr>
<tr>
<td>791</td>
<td>797</td>
</tr>
</tbody>
</table>

Characteristic bands of C-H bending and C-H stretching were observed in both SiWA-H$_3$PO$_4$-PVA/SiO$_2$ and SiWA-H$_3$PO$_4$-PVA. The characteristic bands of SiO$_2$ confirmed the incorporation of SiO$_2$ in SiWA-H$_3$PO$_4$-PVA/SiO$_2$. For both electrolytes, O-H bending band at 1700 cm$^{-1}$ and O-H stretching band at 3500 cm$^{-1}$ were observed. Similar to PVA/SiO$_2$ films (Figure 6-4), the most significant O-H stretching band in SiWA-H$_3$PO$_4$-PVA/SiO$_2$ shifted to a lower frequency as well (Figure 6-5). This shifting indicated an increase in hydrogen bonding interaction between (a) SiO$_2$ and absorbed water molecules in the polymer electrolyte; (b) SiO$_2$ and crystallized water molecules in SiWA; and (c) SiO$_2$ and PVA. In summary, the function of high SiO$_2$ in SiWA-H$_3$PO$_4$-PVA/SiO$_2$ is to enhance the water retention through hydration bond interaction; the secondary function of SiO$_2$ is a cross-linking agent for PVA. There is little interaction between SiO$_2$ and SiWA.
6.3 Effect of TiO2 vs. SiO2*

The effects of TiO2 and SiO2 on SiWA-H3PO4-PVA polymer electrolytes were first investigated in ambient conditions and then in controlled temperature environments. At room temperature, CVs of all solid metallic cells were compared to differentiate any observed reduction in capacitance. In controlled temperature environments, capacitance of solid metallic cells was evaluated under a high scan rate to investigate the effect of the intrinsic dielectric constant of the fillers. Dielectric properties were used to extract the free proton density and the mobility of the electrolytes from dc conductivity at different temperatures. Table 6-3 lists the relationship between parameters of solid capacitor and the polymer electrolyte properties of interest. Since all solid cells share the same electrodes, cell geometry and configuration, comparisons of cell performance can be directly related to the properties of the electrolytes.

Table 6-3: Parameters of capacitor performance and related polymer electrolyte properties.

<table>
<thead>
<tr>
<th>Capacitor performance</th>
<th>Related electrolyte material properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>High frequency cell capacitance</td>
<td>Static dielectric constant ($\varepsilon_{rs}$)</td>
</tr>
<tr>
<td>Low frequency cell capacitance</td>
<td>Low frequency dielectric constant ($\varepsilon_{r,EP}$)</td>
</tr>
<tr>
<td>ESR</td>
<td>Proton conductivity ($\sigma$)</td>
</tr>
<tr>
<td>RC time constant</td>
<td>Relaxation time of electrode polarization</td>
</tr>
</tbody>
</table>

6.3.1 Cell capacitance at room temperature

To determine the effect of TiO2 and SiO2 fillers on cell capacitance, CVs of three solid cells were overlaid in Figure 6-6a together with CV of a liquid H2SO4 cell (1M concentration). All four cells showed a highly capacitive response with near rectangular shape in an ambient environment. The liquid H2SO4 cell demonstrated the highest capacitance of 29 µFcm^{-2} at 1 Vs^{-1}. Among the three polymer electrolyte-based cells, the SiWA-H3PO4-PVA cell had the highest cell capacitance (27 µFcm^{-2}), comparable to the liquid H2SO4 cell. The TiO2 and SiO2-containing cells showed lower capacitance, 25 and 21 µFcm^{-2}, respectively.

The capacitance of each solid cell was measured and compared as a function of frequency in Figure 6-6b. All cells showed increased capacitance towards low frequencies. At low frequencies, both TiO2 and SiO2-containing cells showed lower capacitance than that of the

* Part of this section published as ACS Appl. Mater. Interfaces, 6, 464-472 (2014)
SiWA-H₃PO₄-PVA-based cell, similar to the CV results in Figure 6-6a. This may be a result of the physical blocking of the electrode surface by the presence of non-conductive fillers (referred to as barrier effect). SiO₂ showed a stronger barrier effect when compared to TiO₂, resulting in a greater reduction in cell capacitance at a low scan rate of 1 Vs⁻¹.

**Figure 6-6:** (a) CVs of metallic capacitors enabled by SiWA-H₃PO₄-PVA/TiO₂, SiWA-H₃PO₄-PVA/SiO₂, SiWA-H₃PO₄-PVA, and liquid H₂SO₄ (scan rate=1 Vs⁻¹); and (b) real part $C'$ of the solid metallic cells.

### 6.3.2 Temperature dependence of cell capacitance

In order to investigate the influence of TiO₂ and SiO₂ fillers on cell performance at different temperatures, the cells were tested at an ultra-high rate of 5000 Vs⁻¹ from -30 to 50 °C, as depicted in Figure 6-7a-c.

At higher temperatures (*i.e.*, $T>0$ °C), all cells showed rectangular CV profiles, exhibiting rapid charge/discharge characteristics. A reduction in cell capacitance with decreasing temperature was observed in all cells. Tilted CVs were observed at low temperatures, resultant from a significant increase in cell ESR. Nevertheless, the SiWA-H₃PO₄-PVA/TiO₂-based cell exhibited less distortion relative to the other two cells at lower temperatures. For a better comparison of the three polymer electrolytes, the discharge capacitance of each cell at different temperatures was extracted and is shown in Figure 6-7d. The SiO₂-containing cell had the lowest capacitance, similar to what was observed at a 1 Vs⁻¹ scan rate (see Figure 6-6a). Although the SiWA-H₃PO₄-
PVA-based cell showed a higher capacitance than that of the cell with TiO\textsubscript{2} at 1 Vs\textsuperscript{-1}, this situation was reversed at 5000 Vs\textsuperscript{-1}. At a high scan rate, SiWA-H\textsubscript{3}PO\textsubscript{4}-PVA/TiO\textsubscript{2} had consistently higher cell capacitance compared to both SiWA-H\textsubscript{3}PO\textsubscript{4}-PVA and SiWA-H\textsubscript{3}PO\textsubscript{4}-PVA/SiO\textsubscript{2}, across the entire temperature range.

**Figure 6-7:** CV overlays of metallic capacitors enabled by (a) SiWA-H\textsubscript{3}PO\textsubscript{4}-PVA/TiO\textsubscript{2}, (b) SiWA-H\textsubscript{3}PO\textsubscript{4}-PVA/SiO\textsubscript{2}, (c) SiWA-H\textsubscript{3}PO\textsubscript{4}-PVA, at 50 °C (outer most) to -30 °C (inner most), and (d) discharge capacitance of the metallic cells at a scan rate of 5000 Vs\textsuperscript{-1}.

### 6.3.3 Dielectric analyses

As discussed in Section 3.6.3, dielectric analysis can be used to derive the macroscopic charge transportation properties in the polymer electrolytes. To identify the origin of the variations in
capacitance of the solid cells between Figure 6-6 and Figure 6-7, dielectric analyses were performed based on ac impedance measurements for the polymer electrolytes with and without fillers. The dielectric constant of each polymer electrolyte is plotted from -30 to 50 °C and is shown in Figure 6-8a-c. The dielectric loss spectra were plotted against frequency for these electrolytes in Figure 6-9a-c.

All three polymer electrolytes showed high apparent dielectric constants at low frequencies (Figure 6-8a-c) related to the electrode polarization. As frequency increased, the dielectric constant generally decreased, similar to the trend in $C'$ vs. frequency (Figure 6-6b). All three
solid cells showed resonance behavior at the high frequency end from the influence of residual inductance. Moreover, the dielectric constants decreased with the decrease of temperature throughout the frequency range. At any given temperature, the low frequency dielectric constants of SiWA-H$_3$PO$_4$-PVA were higher than those of SiWA-H$_3$PO$_4$-PVA with fillers, in agreement with the dc capacitance measured at 1 Vs$^{-1}$ (Figure 6-6a).

To minimize the influence of self-resonance on the dielectric response of the polymer electrolytes, the dielectric constants at a low temperature were first analyzed, so that the effects of fillers could be more clearly isolated. Plots of the dielectric constants of SiWA-H$_3$PO$_4$-PVA, SiWA-H$_3$PO$_4$-PVA/TiO$_2$, and SiWA-H$_3$PO$_4$-PVA/SiO$_2$ vs. frequency at -30 °C were overlaid in Figure 6-8d. At this low temperature, both $\varepsilon_{r,EP}$ and $\varepsilon_{r,s}$ could be obtained from Figure 6-8d, where $\varepsilon_{r,EP}$ was the dielectric constant at 1 Hz and $\varepsilon_{r,s}$ was extrapolated from the steady-state dielectric constant between 70 kHz and 90 kHz. At the low frequency region, $\varepsilon_{r,EP}$ decreased in the order of SiWA-H$_3$PO$_4$-PVA > SiWA-H$_3$PO$_4$-PVA/TiO$_2$ > SiWA-H$_3$PO$_4$-PVA/SiO$_2$, showing the same trend as observed in Figure 6-6. At high frequencies, the dielectric constants of the three polymer electrolytes showed a different trend, with SiWA-H$_3$PO$_4$-PVA/TiO$_2$ the highest, followed by SiWA-H$_3$PO$_4$-PVA/SiO$_2$ and SiWA-H$_3$PO$_4$-PVA, as expected from the intrinsic dielectric constant of TiO$_2$ (80) and SiO$_2$ (3.9) [179]. At high frequencies, the dielectric constant is dominated by the molecular dipole polarization of inorganic solids such as SiWA or filler. The incorporation of fillers with high molecular polarizability increased the static dielectric constant of the polymer electrolytes. This also explained the observation in Figure 6-8d that a SiWA-H$_3$PO$_4$-PVA/TiO$_2$-based cell could store and deliver more charge at a high voltage scan rate.

Even at high frequencies, the dielectric constants were still in the order of $10^2$ to $10^3$. This was due to the heterogeneous nature of the polymer composite, where interfacial polarization among SiWA, PVA, fillers, and even water molecules all contributed to the dielectric constants of the electrolytes [184].

In the dielectric loss vs. frequency plots (Figure 6-9a-c), in most spectra two loss peaks were observed. The loss peak at higher frequencies corresponded to the relaxation of electrode polarization. The peak at lower frequencies represented conduction loss by the flow of charge through the electrolyte [184]. This conduction loss may be linked to the self-discharge phenomena of the solid capacitors. The frequency of the peaks decreased with the decrease of temperature. SiWA-H$_3$PO$_4$-PVA exhibited the highest conduction loss at all temperatures.
SiWA-H$_3$PO$_4$-PVA/TiO$_2$ showed a similar trend as SiWA-H$_3$PO$_4$-PVA while SiWA-H$_3$PO$_4$-PVA/SiO$_2$ electrolyte showed almost no conduction loss. The low conduction loss of SiWA-H$_3$PO$_4$-PVA/SiO$_2$ may be related to its smaller capacitance (see Figure 6-6 and Figure 6-7) and a lower number of free protons (discussed below).

![Figure 6-9: Dielectric loss of (a) SiWA-H$_3$PO$_4$-PVA/TiO$_2$, (b) SiWA-H$_3$PO$_4$-PVA/SiO$_2$, (c) SiWA-H$_3$PO$_4$-PVA, from 50 to -30 °C, and (d) relaxation time of electrode polarization for the three electrolytes as a function of temperature.](image)

Since the dielectric loss at high frequencies resulted from the energy dissipation from the lag between the charge separation in the polymer electrolytes and the ac electric field, a shorter relaxation time suggests a faster response of the cell. This characteristic relaxation time can be used to evaluate rate performance of a cell, in close analogy to the RC time constant of a
supercapacitor. For example, among capacitors with similar capacitance, the one with the lowest ESR will have a faster transition from a resistive-dominated state to a capacitive-dominated state, demonstrating the smallest RC time constant [142]. Figure 6-9d shows the relaxation time of electrode polarization for all three polymer electrolytes with respect to temperature, which all increased with a decrease in temperature. At high temperatures, there was little difference among the three polymer electrolytes in their response times. At low temperatures (i.e. T<0 °C), the TiO2-containing electrolyte exhibited a faster response over both SiWA-H3PO4-PVA and SiWA-H3PO4-PVA/SiO2, implying a better rate capability of the SiWA-H3PO4-PVA/TiO2-based devices. From Figure 6-7d and Figure 6-8d, it is clear that SiWA-H3PO4-PVA/TiO2 demonstrated the fastest response and had the highest dielectric constants and capacitance at low temperatures. Therefore, based on the RC model, SiWA-H3PO4-PVA/TiO2 should possess the highest proton conductivity at low temperatures.

6.3.4 Temperature dependence of proton conductivity

The relaxation frequencies of electrode polarization in Figure 6-9 are closely related to the cell ESR and, thus, the proton conductivity of the electrolytes at the respective temperature. Proton conductivity (\(\sigma\)) at different temperatures for all three electrolytes was further studied via Arrhenius plots in Figure 6-10. Activation energies are summarized in Table 6-4 and their conductivity values are listed in Appendix B, Table A3.

The plots of proton conductivity in Figure 6-10 can be divided into two regions as well, above and below 0 °C. The high linearity in both regions confirmed the conduction of protons via Grotthuss (or hopping) mechanism. At temperatures above 0 °C, the activation energy of SiWA-H3PO4-PVA was 8.5 kJmol\(^{-1}\). The addition of TiO2 or SiO2 slightly increased the activation energy within this temperature range caused by the barrier effect.

At temperatures below 0 °C, all three polymer electrolytes showed higher activation energies. The activation energy increased to 30.2 , 34.3 , and 32.1 kJmol\(^{-1}\), for SiWA-H3PO4-PVA, SiWA-H3PO4-PVA/SiO2, SiWA-H3PO4-PVA/TiO2, respectively. This was due to the water freezing effect similar to the other SiWA-based polymer electrolytes. Under such conditions, an enhancement in proton conductivity is mainly attributed to the increase in proton density rather than proton mobility. Utilizing the Arrhenius plot, proton density and proton mobility could be
extracted from each electrolyte to study the influence and the contributions of SiO₂ and TiO₂ fillers.

**Figure 6-10**: Temperature dependence of proton conductivity for SiWA-H₃PO₄-PVA/TiO₂, SiWA-H₃PO₄-PVA/SiO₂, and SiWA-H₃PO₄-PVA at 45% RH from -30 to 50 °C.

**Table 6-4**: Proton conduction activation energies of SiWA-H₃PO₄-PVA/TiO₂, SiWA-H₃PO₄-PVA/SiO₂, and SiWA-H₃PO₄-PVA.

<table>
<thead>
<tr>
<th>Polymer electrolyte</th>
<th>Activation energy (kJmol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T&gt;0 °C</td>
</tr>
<tr>
<td>SiWA-H₃PO₄-PVA/TiO₂</td>
<td>9.8</td>
</tr>
<tr>
<td>SiWA-H₃PO₄-PVA/SiO₂</td>
<td>11.8</td>
</tr>
<tr>
<td>SiWA-H₃PO₄-PVA</td>
<td>8.5</td>
</tr>
</tbody>
</table>

6.3.5 Free proton density and mobility

The proton density of each electrolyte was first calculated from the respective dielectric time constants (τₛ and τₑₑ). Values at low temperatures of -30 and -20 °C were first extracted to obtain τₛ more accurately, with minimum influence of self-resonance at high frequencies. The calculated proton density and mobility at -30 and -20 °C are listed in Table 6-5. Proton density was lower for SiWA-H₃PO₄-PVA with fillers than for the electrolytes without fillers. This may be caused
by a reduction of water molecule dissociation in the presence of fillers. In general, the equilibrium between protonated water and free protons in HPAs was assumed as:

\[ \ce{H5O2+ ↔ H3O+ + H2O ↔ H+ + 2H2O↑} \] [19]

Dehydration in SiWA will shift the equilibrium towards the right to generate more free protons. However, this dehydration process may reduce the pathway for protons and thus limit proton transportation and decrease proton mobility.

With the addition of TiO₂ or SiO₂, this equilibrium becomes more difficult to proceed to the right, so that there are fewer free protons in SiWA-H₃PO₄-PVA/TiO₂ and SiWA-H₃PO₄-PVA/SiO₂ than in their filler-free counterparts. As a consequence of the lower water retention effect, the filler-free SiWA-H₃PO₄-PVA had the largest proton density value among the three electrolytes. Also shown in Table 6-5 is the mobility for the three polymer electrolytes. The dissociation of \( \ce{H5O2^+} \) ions, in spite of generating more free protons, might have reduced the proton transport pathway. Among the three polymer electrolytes, SiWA-H₃PO₄-PVA showed the lowest ion mobility, whereas both SiWA-H₃PO₄-PVA/TiO₂ and SiWA-H₃PO₄-PVA/SiO₂ demonstrated higher proton mobility. This trend was also observed for proton density and mobility of the three electrolytes at -20 °C (Table 6-5).

Table 6-5: Proton density, mobility, and conductivity of SiWA-H₃PO₄-PVA, SiWA-H₃PO₄-PVA/TiO₂, and SiWA-H₃PO₄-PVA/SiO₂ at -30 and -20 °C.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Polymer electrolyte</th>
<th>Proton density (m⁻³)</th>
<th>Proton mobility (m²V⁻¹s⁻¹)</th>
<th>Proton conductivity (Scm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-30</td>
<td>SiWA-H₃PO₄-PVA</td>
<td>1.14 \times 10²⁵</td>
<td>5.96 \times 10⁻¹⁰</td>
<td>1.09 \times 10⁻³</td>
</tr>
<tr>
<td></td>
<td>SiWA-H₃PO₄-PVA/TiO₂</td>
<td>3.02 \times 10²⁴</td>
<td>2.49 \times 10⁻⁹</td>
<td>1.21 \times 10⁻³</td>
</tr>
<tr>
<td></td>
<td>SiWA-H₃PO₄-PVA/SiO₂</td>
<td>2.66 \times 10²⁴</td>
<td>2.17 \times 10⁻⁹</td>
<td>9.22 \times 10⁻⁴</td>
</tr>
<tr>
<td>-20</td>
<td>SiWA-H₃PO₄-PVA</td>
<td>1.22 \times 10²⁵</td>
<td>1.28 \times 10⁻⁹</td>
<td>2.50 \times 10⁻³</td>
</tr>
<tr>
<td></td>
<td>SiWA-H₃PO₄-PVA/TiO₂</td>
<td>3.22 \times 10²⁴</td>
<td>4.82 \times 10⁻⁹</td>
<td>2.51 \times 10⁻³</td>
</tr>
<tr>
<td></td>
<td>SiWA-H₃PO₄-PVA/SiO₂</td>
<td>2.83 \times 10²⁴</td>
<td>4.68 \times 10⁻⁹</td>
<td>2.12 \times 10⁻³</td>
</tr>
</tbody>
</table>

Since \( \varepsilon_r \) is difficult to extract from Figure 6-8a-c at temperatures above -20 °C due to the lack of a clear plateau at the high frequency region, an indirect approach was chosen for calculating proton density. The proton density at -30 and -20 °C (Table 6-5) and the Arrhenius relationship (Figure 6-10) were used to obtain the proton density at temperatures from -10 to 50 °C, and then calculated proton mobility using dc conductivity at respective temperatures. Figure 6-11 shows
the mobility of all three polymer electrolytes as a function of temperature. Both SiWA-H₃PO₄-PVA/SiO₂ and SiWA-H₃PO₄-PVA/TiO₂ possess higher proton mobility than SiWA-H₃PO₄-PVA over the entire temperature range. Although the effect of water retention below 0 °C is much less significant than at higher temperatures, both SiO₂- and TiO₂-containing electrolytes still showed much higher proton mobility than their filler-free counterpart. This suggested the addition of SiO₂ and TiO₂ could facilitate proton transportation not only by the retention of water molecules but also through their hydroxyl-rich nanoparticle surfaces in filler-containing electrolytes.

![Graph](image)

**Figure 6-11:** Temperature dependence of proton mobility in SiWA-H₃PO₄-PVA/TiO₂, SiWA-H₃PO₄-PVA/SiO₂, and SiWA-H₃PO₄-PVA at 45% RH from -30 to 50 °C.

While the proton mobility of the SiO₂ and TiO₂-containing electrolytes is identical below 0 °C, above freezing temperature the proton mobility of SiWA-H₃PO₄-PVA/SiO₂ exceeded that of SiWA-H₃PO₄-PVA/TiO₂. At 50 °C, the proton mobility of the SiO₂-containing electrolyte was more than 20% higher than the mobility of the TiO₂-containing electrolyte. This might be the result of stronger water retention in the form of H₃O⁺ or H₅O₂⁺ in the presence of SiO₂, leading to a more stable proton transport network in the nano-SiO₂-containing electrolyte at higher temperatures.
While proton density and mobility are both important contributors to proton conduction, they do not exhibit a clear relationship in the HPA-based polymer electrolyte systems, especially in the presence of fillers. The dissociation of H$_5$O$_2^+$ ions will increase the proton density, but lower the proton mobility and conductivity. For example, the proton conductivity of H$_3$PW$_{12}$O$_{40}\cdot21$ H$_2$O (another common HPA) was found to be two orders of magnitude higher than that of H$_3$PW$_{12}$O$_{40}\cdot6$ H$_2$O.[15, 19] This was attributed to higher proton mobility in the higher hydrates despite that more free protons were available in the hexahydrate. An opposite example shows that the proton conductivity of anhydrous H$_3$PW$_{12}$O$_{40}$ was five orders of magnitude higher than for its hexahydrate form, caused by a release of a large number of protons after calcination [185]. Therefore, a high performance proton conducting electrolyte for supercapacitors will require a balance between H$_5$O$_2^+$ and H$^+$ for optimum proton density and mobility without sacrificing cell capacitance. The addition of SiO$_2$ or TiO$_2$ promotes such optimization with respect to water retention and intrinsic capacitance, as discussed in this section.

6.4 Summary

In this chapter, the effects of SiO$_2$ and TiO$_2$ fillers on SiWA-H$_3$PO$_4$-PVA polymer electrolytes were characterized. Three major effects have been identified:

a) The barrier effect of the filler is a direct result of the reduction in extent of electrode polarization, leading to lower double layer capacitance in a supercapacitor. Among the two fillers, SiO$_2$ showed a stronger barrier effect than TiO$_2$.

b) The intrinsic dielectric constant effect is related to the static dielectric constants of polymer electrolytes. The higher intrinsic dielectric constant of TiO$_2$ resulted in a higher capacitance of SiWA-H$_3$PO$_4$-PVA/TiO$_2$-based cells over that of SiWA-H$_3$PO$_4$-PVA/SiO$_2$- and SiWA-H$_3$PO$_4$-PVA-based cells at high frequencies.

c) The water retention effect influences the environmental stability of the electrolyte as well as the dynamic dissociation of water molecules in the SiWA structure, impacting both proton density and proton mobility. Both SiO$_2$ and TiO$_2$ fillers improved environmental stability of the electrolyte, and SiWA-H$_3$PO$_4$-PVA/SiO$_2$ demonstrated a higher water retention effect and the least fluctuation of proton conductivity with RH. A stronger water retention effect of SiO$_2$ at
higher temperatures ensured a more stable proton transport network in the electrolyte and maintained high proton mobility.

While the functions of SiO$_2$ and TiO$_2$ nano-fillers in solid SiWA-H$_3$PO$_4$-PVA are complex, dielectric analysis provides a powerful method to differentiate these functions at different operating conditions. Using a single-ion approach, the temperature dependent proton conduction properties were derived. These data could be used to answer key questions regarding the design of highly conductive polymer electrolytes. The developed SiWA-based systems (with or without fillers) have shown excellent performance and shelf life. However they suffer from performance degradation and low dimensional stability at high RH conditions due to the linear nature of the PVA polymer (see Appendix D). Therefore to reach optimum proton conductivity as well as better dimensional and environmental stability, further improvement is necessary.
7 From linear to cross-linked polymer host*

Cross-linking of PVA provides a feasible route to improve the dimensional and environmental stability of the polymer films particularly under high RH conditions. In addition, it may help to increase the water storage capability in the electrolyte by forming network structures. Several cross-linking methods are suitable for PVA, including irradiation, and thermal, physical, or chemical treatment [186-188]. Chemical cross-linking is an easy and feasible method for PVA chains that have a high density of hydroxyl groups [188]. In the presence of protons, hydroxyl groups of PVA react with aldehydes to form acetal linkages as shown in Figure 7-1. In addition, viscosity of the resulting electrolyte precursor solution can be easily controlled by altering the amount of liquid water (see Appendix E).

![Figure 7-1](image)

**Figure 7-1**: Schematic illustration of the cross-linking reaction of polyvinyl alcohol (PVA) by glutaraldehyde under acidic conditions.

Nevertheless, a high degree of cross-link may cause a decrease in water uptake as well as a reduction on film adhesion properties as a result of the reduction of hydroxyl groups in PVA. This in turn will lead to loss of water storage capability and intimate contact at the electrode/electrolyte interface, resulting in low proton conductivity. Therefore, in this study low degree chemical cross-linking of PVA was investigated to achieve optimal proton conduction. The aims of this section are: a) to develop and optimize a high performance proton conducting polymer electrolyte with good conductivity and stability under ambient conditions; and (b) to develop an understanding of the relationship between structure (*i.e.*, the degree of cross-linking), water content, and proton conductivity of the polymer electrolyte. Performance of the optimized electrolyte was evaluated using a simple metallic EDLCs. In addition, a solid graphite EDLC

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* Part of this section published as J. Mater. Chem., 22, 21272-21278 (2012)
was constructed to demonstrate the feasibility of the developed electrolyte for ultra-high rate and high power devices. Table 3-9 lists the composition of SiWA-H$_3$PO$_4$-XLPVA prepared by chemically cross-linking the PVA polymer host. Figure 7-2 shows the photographs of a typical SiWA-H$_3$PO$_4$-XLPVA electrolyte film at dried and humidified conditions.

![Figure 7-2](image)

**Figure 7-2**: Photographs of a SiWA-H$_3$PO$_4$-XLPVA film at (a, b) dried condition, and (c) humidified condition

### 7.1 Electrolyte film hydration

At the ambient, the cross-linked films were much more flexible than linear films. In addition, supported by cross-linking, the dimensional stability of the SiWA-based polymer electrolyte increased. Unlike the linear films that tend to dissolve at high RH and lose film integrity, the cross-linked films “locked” the solution in the 3D polymer framework.

![Figure 7-3](image)

**Figure 7-3**: Percentage of water uptake of cross-linked and linear polymer electrolytes after three-day storage in an environmental chamber at 90% RH.
Since the hydration of the electrolyte films is closely related to their conductivity, it is desirable to store as much water as possible without losing dimensional stability. The variations of the water uptake of the polymer electrolyte films after a 3-day humidification are shown in Figure 7-3. All films showed a significant water uptake including the linear SiWA-H_3PO_4-PVA film, which had a 140% increase, owing to the hydrophilic nature of the film. Water uptake increased with the extent of cross-linking. For example, when comparing SiWA-H_3PO_4-XLPVA(0) to SiWA-H_3PO_4-XLPVA(6), a 45% increase in water uptake was observed. This may be a result of the formation of an internal 3D polymer network, such that more volume was available to store water compared to linear polymers.

### 7.2 Proton conductivity

Proton conductivity of the polymer electrolytes was first characterized at 45% RH as a function of temperature. Arrhenius plots of proton conductivity (σ) for the five electrolytes are shown in Figure 7-4 and their activation energies are listed in Table 7-1.

![Figure 7-4](image-url)

**Figure 7-4:** Temperature dependence of proton conductivity for SiWA-H_3PO_4-XLPVA(0), SiWA-H_3PO_4-XLPVA(2), SiWA-H_3PO_4-XLPVA(4), SiWA-H_3PO_4-XLPVA(5.2), and SiWA-H_3PO_4-XLPVA(6) at 45% RH from 0 to 50 °C.
Table 7-1: Proton conduction activation energies of cross-linked and linear polymer electrolytes at 45% RH.

<table>
<thead>
<tr>
<th>Polymer electrolyte</th>
<th>Activation energy (kJmol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiWA-H₃PO₄-XLPVA(0)</td>
<td>8.3</td>
</tr>
<tr>
<td>SiWA-H₃PO₄-XLPVA(2)</td>
<td>9.9</td>
</tr>
<tr>
<td>SiWA-H₃PO₄-XLPVA(4)</td>
<td>11.7</td>
</tr>
<tr>
<td>SiWA-H₃PO₄-XLPVA(5.2)</td>
<td>16.1</td>
</tr>
<tr>
<td>SiWA-H₃PO₄-XLPVA(6)</td>
<td>13.8</td>
</tr>
</tbody>
</table>

Proton conductivity of all electrolytes increased with temperature. Conductivity of cross-linked samples were consistently higher than that of SiWA-H₃PO₄-XLPVA(0). Interestingly, SiWA-H₃PO₄-XLPVA(6) showed a lower proton conductivity than that of SiWA-H₃PO₄-XLPVA(5.2). This was attributed to the decrease of adhesion (from the reduction of hydroxyl groups) at the electrode/electrolyte interface, which increased cell ESR.

The Arrhenius plots in Figure 7-4 were consistent with proton hopping deduced in the previous SiWA-based electrolytes. At 45% RH, the activation energies of the SiWA-H₃PO₄-PVA, SiWA-H₃PO₄-XLPVA(5.2), and SiWA-H₃PO₄-XLPVA(6) electrolytes was 8.3, 16.1, and 13.8 kJmol⁻¹, respectively. The increase in activation energy was related to the reduction of polymer chain motion from cross-linking. The lower activation energy of SiWA-H₃PO₄-XLPVA(6) was because of the decreased film adhesion, leading to an underestimation of its activation energy. Nevertheless, since SiWA-H₃PO₄-XLPVA(5.2) exhibited the highest proton conductivity among the samples, the following sections will focus on the comparison between SiWA-H₃PO₄-XLPVA(5.2) and its linear counterpart. Detailed analysis on the proton conductivity of SiWA-H₃PO₄-XLPVA(5.2) at different RH conditions will be discussed in Chapter 8.

7.3 Structural characterizations

7.3.1 Water content

In order to investigate and confirm the water content in the polymer electrolytes, thermal analyses were performed using DSC. The obtained thermograms are shown in Figure 7-5. The DSC peaks are summarized Table 7-2.

Both samples exhibited two major endothermic peaks. It is known that water molecules can exist in HPA-based polymer electrolytes as absorbed free water and crystallized water (protonated and non-protonated). Table 7-2 lists the major peaks and the possible causes of these peaks for cross-
linked and linear samples. As seen from Figure 7-5, the cross-linked samples have more endothermic heat flow, indicating more water content was released compared to the linear electrolyte film. The trend obtained from thermal analyses agrees with the water uptake shown in Figure 7-3. Both Figure 7-3 and Figure 7-5 confirm that SiWA in the cross-linked polymer electrolytes retained more water molecules under ambient conditions.

Figure 7-5: DSC thermograms of SiWA-H₃PO₄-XLPVA(5.2) and SiWA-H₃PO₄-XLPVA(0) polymer electrolytes stored at 45% RH.

Table 7-2: DSC peak assignments for SiWA-H₃PO₄-XLPVA(5.2) and SiWA-H₃PO₄-XLPVA(0).

<table>
<thead>
<tr>
<th>Electrolyte film identification</th>
<th>Glass transition temperature</th>
<th>Absorbed free water loss</th>
<th>Crystallized water loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiWA-H₃PO₄-XLPVA(5.2)</td>
<td>55.2 °C</td>
<td>88 °C</td>
<td>148 °C</td>
</tr>
<tr>
<td>SiWA-H₃PO₄-XLPVA(0)</td>
<td>55 °C</td>
<td>84 °C</td>
<td>145 °C</td>
</tr>
</tbody>
</table>

7.3.2 XRD characterization

To identify the level of hydration of SiWA in the polymer electrolytes, the XRD patterns of SiWA-H₃PO₄-XLPVA(5.2) and SiWA-H₃PO₄-XLPVA(0) are compared in Figure 7-6 (i.e. cross-linked vs. linear polymer electrolytes). Both diffraction patterns showed similar peak positions but with different peak intensities. For example, both electrolytes had intensive peaks at 6.5° and 26.5°. Although the signature peak of dehydration (i.e. at 10.5°) appeared in both patterns,
SiWA-H₃PO₄-XLPVA(5.2) was more hydrated than SiWA-H₃PO₄-XLPVA(0). This notion is supported by the higher relative intensity ratio between the peaks at 6.5° and 10.5° as well as a smaller relative intensity ratio between peak at 10.5° and 26.5°. Although the change in peak intensity at 31° and the relation to the exact number of crystallized water in SiWA is still unclear, both XRD and DSC analyses confirmed SiWA in SiWA-H₃PO₄-XLPVA(5.2) was in a higher level of hydration than its linear counterpart.

Figure 7-6: XRD patterns of SiWA-H₃PO₄-XLPVA(5.2) and SiWA-H₃PO₄-XLPVA(0) at ambient conditions.

Further investigations focused on the change of SiWA-H₃PO₄-XLPVA(5.2) structure with RH under controlled environments as shown in Figure 7-7. Its overall XRD patterns were similar to the electrolyte based on linear PVA host (i.e. SiWA-H₃PO₄(1500)-PVA) (see Section 5.2.2). In Figure 7-7, all three XRD patterns shared the same amorphous baseline from PVA. At 75% RH, only one sharp diffraction peak observed at 26.5° with a broad peak at 6.8°, suggesting a very limited crystallization of SiWA in the cross-linked polymer host. However compared this pattern with the SiWA-H₃PO₄(1500)-PVA (i.e. linear polymer host) at 75% RH (Figure 5-7), the PVA
cross-linking promoted more SiWA crystallization at this RH condition. This may be caused by the interconnected structures of the polymer in a chemically cross-linked PVA, which entrapped SiWA and provided initiation sites for crystallization. When dehydrated, more peaks were observed at 45% RH, including ones at 6.5°, 10.5°, 19.7°, 29.4°, 33.4°, and 36.2°. The most intense peak was at 6.5° with the appearance of the 10.5° peak indicated a certain degree of dehydration. At 5% RH, more crystallization of SiWA in its hexahydrate form occurred.

![Figure 7-7](image-url): XRD patterns of SiWA-H₃PO₄-XLPVA(5.2) at 75%, 45% and 5% RH (left: intensity in linear scale, right: intensity in logarithmic scale).

### 7.3.3 FTIR analyses

FTIR analyses were performed on cross-linked and linear samples to obtain structural, compositional, and bonding information of the polymer electrolytes. Figure 7-8 shows the FTIR spectra of SiWA-H₃PO₄-XLPVA(5.2) and SiWA-H₃PO₄-XLPVA(0). Table 7-3 summarizes the wavenumbers of the bands with their associated bonding interactions for the two spectra.

In Figure 7-8, both spectra have similar primary structures in the 700 to 1300 cm⁻¹ region, representing the characteristics of the Keggin structure. Both SiWA-H₃PO₄-XLPVA(5.2) and
SiWA-H_3PO_4-XLPVA(0) showed C-H stretching and C-H bending peaks at *ca.* 2955 and 1400 cm\(^{-1}\), respectively, attributed to the presence of PVA. The broad peak at 2350 cm\(^{-1}\) was determined as stretching vibration of the P-OH groups in H_3PO_4.

Since O-H stretching is the most significant band, the following analysis was focusing on the features at *ca.* 3450 cm\(^{-1}\). For cross-linked SiWA-H_3PO_4-XLPVA(5.2), O-H stretching shifted to a lower frequency relative to the linear counterpart, indicating a stronger hydrogen bonding after cross-linking. This indicated that, in spite of the elimination of a small amount of hydroxyl groups in PVA for cross-linking, a stronger hydrogen bond interaction still occurred. This might be a result of the extra absorbed water molecules within SiWA-H_3PO_4-XLPVA(5.2) that were transformed into crystallized water bonded with SiWA.

![FTIR spectra of SiWA-H_3PO_4-XLPVA(5.2) and SiWA-H_3PO_4-XLPVA(0) at ambient conditions.](image)

**Figure 7-8**: FTIR spectra of SiWA-H_3PO_4-XLPVA(5.2) and SiWA-H_3PO_4-XLPVA(0) at ambient conditions.
Table 7-3: FTIR band positions and associated bonding information for SiWA-H₃PO₄-XLPVA(5.2) and SiWA-H₃PO₄-XLPVA(0).

<table>
<thead>
<tr>
<th>Wavenumber</th>
<th>SiWA-H₃PO₄-XLPVA(5.2)</th>
<th>SiWA-H₃PO₄-XLPVA(0)</th>
<th>Band assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3444</td>
<td>3484</td>
<td></td>
<td>O-H stretching</td>
</tr>
<tr>
<td>2955</td>
<td>2955</td>
<td></td>
<td>C-H stretching</td>
</tr>
<tr>
<td>2350</td>
<td>2359</td>
<td></td>
<td>P-OH stretching</td>
</tr>
<tr>
<td>1712</td>
<td>1724</td>
<td></td>
<td>O-H bending (protonated water)</td>
</tr>
<tr>
<td>1621</td>
<td>1631</td>
<td></td>
<td>O-H bending (neutral water)</td>
</tr>
<tr>
<td>1408</td>
<td>1402</td>
<td></td>
<td>C-H bending</td>
</tr>
<tr>
<td>1017</td>
<td>1016</td>
<td></td>
<td>N/A</td>
</tr>
<tr>
<td>981</td>
<td>976</td>
<td></td>
<td>W=O₄ stretching</td>
</tr>
<tr>
<td>925</td>
<td>923</td>
<td></td>
<td>Si-O₈ stretching</td>
</tr>
<tr>
<td>885</td>
<td>885</td>
<td></td>
<td>W-O₀-W stretching</td>
</tr>
<tr>
<td>786</td>
<td>797</td>
<td></td>
<td>W-O₂-W stretching</td>
</tr>
</tbody>
</table>

The results from FTIR analyses were in agreement with the DSC and XRD analyses. From thermal analysis, an increase of water content was observed in the cross-linked SiWA-H₃PO₄-XLPVA(5.2). XRD showed that SiWA in SiWA-H₃PO₄-XLPVA(5.2) was more hydrated than SiWA in SiWA-H₃PO₄-XLPVA(0). SiWA in SiWA-H₃PO₄-XLPVA(5.2) was rehydrated by the extra water content held by the internal cross-linked 3D PVA network. The increase in crystallized water in SiWA formed a network with stronger hydrogen bond interaction and facilitated proton hopping, thus leading to high conductivity.

Further analyses were performed to investigate the O-H bands in the cross-linked electrolyte. Figure 7-9 shows the FTIR spectra of SiWA-H₃PO₄-XLPVA(5.2) from liquid solution form to “dried” film dehydrated at ambient conditions (ca. 15% RH, 10 min interval between each measurement). In Figure 7-9a, the overall spectra reminded the same along dehydration. The narrowing of the O-H stretching peak at ca. 3400 cm⁻¹ was caused by a reduction in free water content. This leads to less hydrogen bond interactions. Therefore, it can be assumed that at the “dried” condition, O-H stretching from the hydroxyl groups of PVA dominated. Another important FTIR band is the O-H bending peak at ca. 1600 cm⁻¹. The reduction in its relative peak intensity (compared to the Keggin peaks) confirmed the loss of free water over dehydration. More importantly, the presence of protonated H₂O (i.e. H₃O⁺ and H₅O₂⁺) could be identified as well, even at the “dried” film condition. This further support the higher stability of the protonated H₂O of the crystallized water molecules in the polymer electrolyte. At the same time, it can be observed that the structure of anion was very stable along dehydration (Figure 7-9b).
Figure 7-9: FTIR spectra of (a) SiWA-H$_3$PO$_4$-XLPVA(5.2) from liquid solution to “dried” film; and (b) the enlarged low wavenumber region.

7.4 Capacitor performance

Since the intended application of the polymer electrolytes is for supercapacitors, solid symmetric devices were constructed using stainless steels and graphite electrodes. Based on the results shown in Figure 7-4, SiWA-H$_3$PO$_4$-XLPVA(5.2) was selected as the electrolyte of choice. To derive the optimum behaviour from the SiWA-H$_3$PO$_4$-XLPVA polymer electrolyte and demonstrate its stability at high RH, all capacitors were stored in a chamber at 90% RH before testing. Figure 7-10 shows a comparison of two metallic capacitors, H$_2$SO$_4$ (liquid cell) and SiWA-H$_3$PO$_4$-XLPVA(5.2) (solid cell), with planar stainless steel electrodes. Both cells were able to charge and discharge at a super high rate of 5000 Vs$^{-1}$. At the ultra-high rate, both capacitors were still able to deliver 10 μFcm$^{-2}$, 50% of the capacitance obtained at 1 Vs$^{-1}$. This suggested that both polymer electrolytes can transfer ions at very high speeds, which is desirable for high rate devices. Furthermore, the solid SiWA-H$_3$PO$_4$-XLPVA(5.2) based device appeared to have less resistance and higher capacitance than the H$_2$SO$_4$ cell.
Figure 7-10: CVs of metallic capacitors enabled by SiWA-H₃PO₄-XLPVA(5.2) and liquid H₂SO₄ (scan rate = 5000 Vs⁻¹).

Figure 7-11: CVs of a graphite capacitor enabled by SiWA-H₃PO₄-XLPVA(5.2) at scan rates of (a) 1 Vs⁻¹, (b) 10 Vs⁻¹, (c) 25 Vs⁻¹, and (d) 50 Vs⁻¹.
Similar to the EDLCs enabled by the linear SiWA-H₃PO₄(1500)-PVA (Section 5.2.4), graphite was selected as electrode to minimize the influence of pores in order to focus on the impact of the electrolyte on the ultra-high rate performance of the cells. The EDLC were scanned incrementally from 1 Vs⁻¹ to 50 Vs⁻¹. Figure 7-11 shows CVs of a device at scan rates of 1, 10, 25, and 50 Vs⁻¹. All CVs showed near rectangular shape indicating capacitive behavior. In addition, the average current density in Figure 7-11 increased linearly with the scan rate, further suggesting the high charge/discharge rate capability of the polymer electrolytes. The capacitance at 1 Vs⁻¹ was about 2.5 mFcm⁻², higher than either onion-like nanocarbon-based liquid supercapacitors [189] or graphene-based liquid and solid supercapacitors [9, 190-192]. Further increase in scan rates resulted a slight decrease of the capacitance to 2 mFcm⁻² at 50 Vs⁻¹.

EIS analyses were performed on the polymer electrolyte-based capacitor (Figure 7-12). $C'$ was approaching 2.5 mFcm⁻² at low frequency (0.1 Hz), agreeing with the capacitance obtained from CV analyses in Figure 7-11. The capacitance decreased gradually over 4 decades of frequency. The $C''$ vs. frequency curve exhibited its maximum at \( ca. 100 \text{ Hz} \). This maximum translates to a time constant of 10 ms for the solid EDLC.

![Figure 7-12: Real part $C'$ (left axis) and imaginary part $C''$ (right axis) of capacitance vs. frequency for a solid graphite capacitor enabled by SiWA-H₃PO₄-XLPVA(5.2).](image)
7.5 Voltage window of SiWA-based solid capacitors

Besides proton conductivity, another important parameter of polymer electrolyte is the voltage operating window. It is necessary to understand the redox reactions of SiWA that interact with the electrodes to reveal the factors that affect the capacitor cell voltage.

The CV of a single graphite electrode in SiWA-H$_3$PO$_4$-XLPVA(5.2) was first acquired using a solid 3-electrode cell (Figure 7-13). The positive potential limit is about 0.65 V (vs. Ag), while the negative potential limit of SiWA-H$_3$PO$_4$-XLPVA(5.2) was -0.4 V (vs. Ag). A pair of redox peaks from the carbon functional groups were observed at ca. 0 V (vs. Ag). The double-layer capacitance of the electrode was about 7 mFcm$^{-2}$ at 100 mVs$^{-1}$ which agrees well with other systems employing similar graphite electrodes [113, 193]. The OCP of the graphite electrode with SiWA-H$_3$PO$_4$-XLPVA(5.2) electrolyte was also about 0 V (vs. Ag).

![Figure 7-13: CV of a graphite electrode with SiWA-H$_3$PO$_4$-XLPVA(5.2) in a solid 3-electrode cell (scan rate = 100 mVs$^{-1}$).](image)

A solid symmetric EDLC was constructed using graphite electrodes and the CV profiles with incremental cell voltages are shown in Figure 7-14a. In Figure 7-14a, the CVs if the solid cell depicts a near-rectangular-shaped profile at a cell voltage below 1 V. The increased current density limited the maximum cell voltage to ca. 1.1 V for this system.
Figure 7-14: (a) CVs of a solid graphite capacitor enabled by SiWA-H₃PO₄-XLPVA(5.2) at cell voltages from 0.5 V to 1.3 V (10th cycle, scan rate = 100 mVs⁻¹); (b) change in potential at the positive and negative electrodes during CV scans (10th cycle) as a function of time; (c) electrode potential limits of both positive and negative electrodes as a function of cell voltage; (d) change of potential for both positive and negative electrodes as a function of cell voltage.

As discussed in Section 3.6.4, in-situ electrode potential tracking is a useful method to characterize individual electrode and electrolyte materials at the device level. A “third” electrode as reference is used to track both electrodes during their charge and discharge. In this study, a solid double-layer capacitor with a SiWA-H₃PO₄-XLPVA(5.2) electrolyte was constructed using graphite electrodes and linked to an external reference electrode. Figure 7-14b shows the change
in the respective electrode potential against a Ag reference during the CV incremental scans in Figure 7-14a. The smaller slope of the E vs. t curve of the negative electrode implied a higher charge capacity of the negative electrode (Figure 7-14b).

Figure 7-14c shows electrode potential limit of both positive and negative electrodes while the changes of potential for the electrodes are shown in Figure 7-14d. Also marked in Figure 7-14c are the onsets of SiWA anion redox reaction (-0.4 V vs. Ag) and oxygen evolution (0.65 V vs. Ag) obtained from the CV of the single graphite electrode in Figure 7-13. At a cell voltage of 0.9 V, the negative limit of $E_{-ve}$ reached the redox reaction of the SiWA anion and at a cell voltage of 1.1 V, the positive limit of $E_{+ve}$ reached the oxygen evolution potential.

The reduction of the SiWA anion led to an increase in net charge at the negative electrode. The unbalanced charge in the electrode causes $E_{initial}$ to shift towards negative potentials with cell voltage as shown in Figure 7-14c. Therefore, $\Delta E_{+ve}$ was greater than $\Delta E_{-ve}$ even at a cell voltage of 0.5 V in Figure 7-14d, due to the higher slope of the $\Delta E_{+ve}$ vs. U curve (and thus lower capacity) than its counterpart, as shown in Figure 7-14b. In addition, both $\Delta E$ vs. U curves deviated from linearity at cell voltage of 0.9 V. In this case, one may expect the slope of the positive electrode curve would decrease when reaching the oxygen evolution potential at 1.1 V (Figure 7-14c). However because of the greater charge from dominating anion redox reaction of SiWA, the $\Delta E_{+ve}$ vs. U curve still showed an increase in slope while its negative counterpart showed a decrease in slope. As a result, the maximum cell voltage was limited by the positive electrode reaching the oxygen evolution potential.

### 7.6 Summary

In this chapter, a cross-linked SiWA-H$_3$PO$_4$-XLPVA polymer electrolyte was developed. Free-standing polymer electrolyte films were obtained after the chemical cross-linking. The degree of cross-linking was optimized to achieve a high proton conductivity and high water uptake compared to its linear counterpart. Thermal analysis revealed an increase of water content with increasing degree of cross-linking. XRD showed that SiWA in the cross-linked polymer electrolyte had a higher level of hydration than SiWA in its linear counterpart. FTIR analysis supported the stronger hydrogen bonding interaction as well as hydrated SiWA in the cross-linked polymer electrolyte. In addition, the cross-linked sample from liquid solution to “dried” film was characterized by FTIR. Although a reduction in free water content was observed, the
presence of protonated water was identified even at the “dried” film condition. The anion structure also showed high stability against dehydration.

The all-solid EDLC enabled by the cross-linked polymer electrolyte with graphite electrodes has shown exceptionally high rate capability with a 10 ms time constant. This confirmed that the SiWA-H$_3$PO$_4$-XLPVA(5.2) electrolyte could transfer ions at an ultra-high speed. The results showed that SiWA supported by a cross-linked PVA network is an effective way to enhance its performance. In addition, the reactions and factors limiting the solid capacitor cell voltage were identified and deconvoluted through a potential tracking method. Further analysis revealed that the cell voltage was limited by the negative electrode reaching the potential of SiWA anion reduction and the positive electrode reaching the potential of oxygen evolution.
8 Optimization of plasticizer in cross-linked electrolytes

As demonstrated in Chapter 5, the addition of plasticizers significantly improve the flexibility and conductivity of the polymer electrolytes. Since the effects of plasticizer were only investigated in the linear PVA-based electrolytes, it is of interest to study and optimize the plasticizers in the cross-linked samples developed in Chapter 7. Therefore the objective of this chapter is to further enhance the electrolyte properties via optimizing the plasticizer content. Since both glycerol and H₃PO₄ are suitable plasticizers, the following sections will discuss the cross-linked electrolytes with these two additives.

8.1 SiWA-Gly-XLPVA

The effect of glycerol was characterized in linear PVA-SiWA electrolyte (Section 5.1). This section will focus on the effect of glycerol on cross-linked PVA-SiWA electrolyte. The compositions of SiWA-Gly-XLPVA electrolytes are listed in Table 3-10.

8.1.1 Proton conductivity at room temperature

Room temperature proton conductivity of SiWA-Gly-XLPVA with different glycerol to PVA molar ratios were measured at 75%, 45%, and 5% RH. Figure 8-1 shows the proton conductivity of SiWA-Gly-XLPVA as a function of glycerol to PVA. For all samples, proton conductivity increased with RH as expected. The addition of glycerol initially increased the proton conductivity. Further increase however led to a loss in conductivity, which was caused by the non-conductive glycerol and a reduction in concentration of proton conductor. Because of the limited conductivity at 5% RH, this trend was not as clear as these at higher RH conditions. Nevertheless, the optimal glycerol to PVA molar ratio was 1500 among the tested samples. The conductivity of SiWA-Gly(1500)-XLPVA was ca. 2-3 times higher than the electrolyte without plasticizers (i.e. SiWA-Gly(0)-XLPVA) at all three RH conditions. For example, at 45% RH, the conductivity values for SiWA- Gly(1500)-XLPVA and SiWA- Gly(0)-XLPVA were 23.6 and 9.5 mScm⁻¹, respectively. The significant improvement in conductivity was mainly contributed by: (a) the plasticizer effect with lowered contact resistance at the electrode/electrolyte interface for low RH conditions; and (b) solvation effect with higher proton mobility for mid-to-high RH conditions (see Section 5.1).
Figure 8-1: Proton conductivity of SiWA-Gly-XLPVA as a function of glycerol to PVA molar ratio at 75%, 45%, and 5% RH.

With the addition of glycerol, the polymer electrolyte film became more flexible. Its ability to undergo elastic and/or plastic deformation was significantly improved. Figure 8-2 shows a photograph of a SiWA-Gly(1500)-XLPVA electrolyte film pasted on a glass slide being stretched vertically. It should also be noted that the adhesion property was also improved. Further studies on the mechanical properties of the electrolyte films are required.

Figure 8-2: Photograph of a SiWA-Gly(1500)-XLPVA film showing its high flexibility at ambient conditions.
Since the H$_3$PO$_4$ to PVA molar ratio was also 1500 in the cross-linked polymer electrolyte (see Section 5.2 and Chapter 7), it is of interest to compare the effect of glycerol and H$_3$PO$_4$. Figure 8-3 compares the conductivity of SiWA-Gly(1500)-XLPVA, SiWA-H$_3$PO$_4$(1500)-XLPVA, and SiWA-XLPVA (*i.e.* the electrolyte with no plasticizers) at room temperature.

The addition of either H$_3$PO$_4$ or glycerol enhanced the proton conductivity of the polymer electrolyte. At 75% RH, the conductivity of SiWA-Gly(1500)-XLPVA and SiWA-H$_3$PO$_4$(1500)-XLPVA were similar. Even though SiWA-H$_3$PO$_4$(1500)-XLPVA had more proton-containing species in the film, the proton conductivity was more dominated by proton mobility at this high RH condition. The difference in proton-containing species concentration did not vary the conductivity significantly. SiWA-Gly(1500)-XLPVA at 45% and 5% RH, on the other hand, showed higher conductivity than SiWA-H$_3$PO$_4$(1500)-XLPVA. This may be attributed to the plasticizer effect, which promoted a more intimate contact at the electrode/electrolyte interface and reduced cell ESR.

![Proton conductivity of SiWA-Gly(1500)-XLPVA, SiWA-H$_3$PO$_4$(1500)-XLPVA, and SiWA-XLPVA at 75%, 45% and 5% RH.](image)

**Figure 8-3:** Proton conductivity of SiWA-Gly(1500)-XLPVA, SiWA-H$_3$PO$_4$(1500)-XLPVA, and SiWA-XLPVA at 75%, 45% and 5% RH.
8.1.2 Proton conductivity at controlled temperatures

To investigate the effect of glycerol on the activation energy of proton conduction and compare it to the H$_3$PO$_4$-containing counterpart, the proton conductivity of SiWA-Gly(1500)-XLPVA and SiWA-H$_3$PO$_4$(1500)-XLPVA (i.e. SiWA-H$_3$PO$_4$-XLPVA(5.2)) were characterized as a function of temperature at the three RH conditions and shown in Arrhenius plots (Figure 8-4). Their activation energies are summarized in Table 8-1 while their conductivity values for the two polymer electrolytes are listed in Appendix B, Table A4 and Table A5.

![Figure 8-4](image)

**Figure 8-4**: Temperature dependence of proton conductivity for SiWA-Gly(1500)-XLPVA and SiWA-H$_3$PO$_4$(1500)-XLPVA at 75%, 45%, and 5% RH from -30 to 50 °C.

**Table 8-1**: Proton conduction activation energies of SiWA-Gly(1500)-XLPVA and SiWA-H$_3$PO$_4$(1500)-XLPVA at 75%, 45%, and 5% RH.

<table>
<thead>
<tr>
<th>RH</th>
<th>SiWA-H$_3$PO$_4$(1500)-XLPVA</th>
<th>Activation energy (kJmol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T&gt;0 °C</td>
<td>T&lt;0 °C</td>
</tr>
<tr>
<td>75%</td>
<td>8.8</td>
<td>23.8</td>
</tr>
<tr>
<td>45%</td>
<td>16.4</td>
<td>33.2</td>
</tr>
<tr>
<td>5%</td>
<td>42.5</td>
<td>57.0</td>
</tr>
</tbody>
</table>
In Figure 8-4, both samples showed higher conductivity with increasing temperature and RH. The high linearity of the fitted line confirmed the proton hopping mechanism. The same transition at 0 °C was observed, similar to other SiWA-based electrolytes. At 75% RH, both electrolytes exhibited similar conductivity, because of the dominating contribution from proton mobility. Therefore, neither the effect of lower proton density from replacing H3PO4 with glycerol nor the enhanced interfacial contact from glycerol was significant. Instead, the glycerol-containing sample showed a lower conductivity at low temperature regions. The activation energy of SiWA-Gly(1500)-XLPVA was also higher.

At 45% and 5% RH, as a result of the enhanced interfacial properties, SiWA-Gly(1500)-XLPVA demonstrate higher proton conductivity than its H3PO4 counterpart at higher temperatures. But due to the non-conductive nature of glycerol, conductivity of SiWA-Gly(1500)-XLPVA at lower temperatures were lower than that of SiWA-H3PO4(1500)-XLPVA. At low temperatures and low two RH conditions, the contribution from proton density to conductivity is dominating. The lowered proton density from SiWA-Gly(1500)-XLPVA caused the reduction in proton conductivity and a higher activation energy.

8.1.3 Structural characterization

The effect of glycerol within SiWA-Gly(1500)-XLPVA as well as the structural change of polymer electrolytes with RH were investigated using XRD and the patterns are shown in Figure 8-5. Replacing H3PO4 with glycerol significantly reduced the amount of SiWA crystallization in SiWA-Gly(1500)-XLPVA (see Figure 7-7). At all three RH conditions, the baseline from PVA was more amorphous compared to their H3PO4-containing counterparts. The addition of glycerol reduce the secondary bonding between cross-linked PVA chains. The diffraction pattern of SiWA-Gly(1500)-XLPVA at 75% RH was very similar to the ones of SiWA(109)-PVA and SiWA(419)-PVA (see Figure 4-4): no sharp diffraction peaks were observed except the one at 7.2°. This implied no long-range ordered structure within the polymer electrolyte film.

When dehydrating to 45% RH, three notable features were observed: (a) shift of the 7.2° peak to a higher 2θ value of 7.9°; (b) reduction in full width at half maximum (FWHM) of the peak at 7.2° (now 7.9°); and (c) appearance of new peaks at 9.1° (a shoulder), 10.7°, 15.7°, 21.6°, and 22.9°. These peaks were very different compared to the original SiWA diffraction peaks at 45% RH, implying a different structure was formed within the electrolyte film.
Similar to the 45% RH case, the diffraction pattern at 5% RH showed further reduction in FWHM of the peak at 7.2° as well as an increase in relative intensity of the peaks at 9.1°, 10.7°, 15.7°, 21.6°, and 22.9° (compared to the peak at 7.2°). In addition, new peaks at 26.6°, 36.3°, and 39.6° were observed. Comparing this XRD pattern to the one of SiWA-H$_3$PO$_4$(1500)-XLPVA at 5% RH (Figure 7-7), the peaks at 10.7°, 15.7°, 21.6°, 26.6°, 36.6°, and 39.6° could be assigned to the hexahydrate form of SiWA in the film. However, the presence of peaks at 7.9°, 9.1°, and 22.9° were very similar to the XRD pattern of SiWA(419)-PVA after 3-week storage (see Figure 4-5). This implied that some SiWA in SiWA-Gly(1500)-XLPVA at 5% RH was still in their initial crystallization stage although the rest SiWA was already in the hexahydrate form. The addition of glycerol greatly slowed down or reduced the crystallization of SiWA.

8.2 SiWA-H$_3$PO$_4$-XLPVA

Although SiWA-Gly(1500)-XLPVA showed higher proton conductivity over SiWA-H$_3$PO$_4$(1500)-XLPVA at T>0 °C for the three RH conditions (see Figure 8-4), the addition of
non-conductive glycerol and the reduction of the concentration of proton-containing species in the film resulted in a loss of conductivity at low temperatures. As discussed in Section 5.2, the maximum amount of \( \text{H}_3\text{PO}_4 \) was limited by the liquid leakage in the film. In order to improve the low temperature conductivity, the amount of acidic plasticizers (i.e. \( \text{H}_3\text{PO}_4 \)) should be further optimized in the cross-linked polymer electrolyte. This section will focus on the optimization of \( \text{H}_3\text{PO}_4 \) content in cross-linked PVA-based electrolyte. The compositions of SiWA-\( \text{H}_3\text{PO}_4 \)-XLPVA electrolytes with different \( \text{H}_3\text{PO}_4 \) to PVA molar ratios are listed in Table 3-11.

### 8.2.1 Proton conductivity at room temperature

Proton conductivity of SiWA-\( \text{H}_3\text{PO}_4 \)-XLPVA electrolytes with different \( \text{H}_3\text{PO}_4 \) to PVA molar ratios were first tracked at 45% RH over time (Figure 8-6a). The conductivity increased with \( \text{H}_3\text{PO}_4 \) content as well as storage time. This was because the cells were made in a low RH ambient condition and the equilibrium of the polymer electrolytes with the 45% RH storage environment required certain time.

At 45% RH, both SiWA-\( \text{H}_3\text{PO}_4(2125) \)-XLPVA and SiWA-\( \text{H}_3\text{PO}_4(2550) \)-XLPVA retained their dimensional stability with no liquid leakage. Since the maximum amount of \( \text{H}_3\text{PO}_4 \) in the linear electrolyte (i.e. SiWA-\( \text{H}_3\text{PO}_4 \)-PVA) was at a \( \text{H}_3\text{PO}_4 \) to PVA molar ratio of 1500, the higher \( \text{H}_3\text{PO}_4 \) content that can be incorporated in the new electrolyte further confirmed the effect of polymer cross-linking. Nevertheless, liquid leakage was observed for electrolytes with a \( \text{H}_3\text{PO}_4 \) to PVA molar ratio higher than 2550. SiWA-\( \text{H}_3\text{PO}_4(8500) \)-XLPVA leaked at day 2; SiWA-\( \text{H}_3\text{PO}_4(4250) \)-XLPVA, SiWA-\( \text{H}_3\text{PO}_4(3825) \)-XLPVA, and SiWA-\( \text{H}_3\text{PO}_4(3400) \)-XLPVA leaked at day 3; SiWA-\( \text{H}_3\text{PO}_4(2975) \)-XLPVA leaked at day 6 (indicated by the red circles in Figure 8-6a). An example of the liquid leakage from the electrolyte film is shown in Figure 8-6b. Since SiWA-\( \text{H}_3\text{PO}_4(2125) \)-XLPVA had less \( \text{H}_3\text{PO}_4 \) content but showed comparable conductivity, the following sections will focus on SiWA-\( \text{H}_3\text{PO}_4(2125) \)-XLPVA.
8.2.2 Proton conductivity at controlled temperatures

The proton conductivity of SiWA-H₃PO₄(2125)-XLPVA and SiWA-H₃PO₄(1500)-XLPVA were characterized as a function of temperature to investigate the effect of additional H₃PO₄. The results are shown in Arrhenius plots (Figure 8-7). Their activation energies are summarized in Table 8-2 while their conductivity values are listed in Appendix B, Table A4 and Table A6.

Similar to all other SiWA-based polymer electrolytes, conductivity of SiWA-H₃PO₄(2125)-XLPVA increased with temperature and RH. Proton hopping dominated the conduction mechanism with a transition of activation energy at the water freezing temperature. At 75% RH, the effect of H₃PO₄ content was more significant at low temperatures than at high temperatures. For example, the conductivity increased from 8.3 to 13.6 mScm⁻¹ at -30 °C (ca. 64% increase) while at 50 °C, the conductivity only increased from 60 to 67 mScm⁻¹ (ca. 12% increase). This is because at the high temperature high humidity condition, contribution from high proton mobility dominated the conductivity. The increase in proton density (from additional H₃PO₄) did not have a significant impact.

**Figure 8-6:** (a) Proton conductivity tracking of SiWA-H₃PO₄-XLPVA over time at 45% RH (red circles indicate liquid leakage); and (b) photograph of a SiWA-H₃PO₄(8500)-XLPVA film after two-day storage at 45% RH, showing the liquid leakage issue.
Figure 8-7: Temperature dependence of proton conductivity for SiWA-H₃PO₄(2125)-XLPVA and SiWA-H₃PO₄(1500)-XLPVA at 75%, 45% and 5% RH from -30 to 50 °C.

Table 8-2: Proton conduction activation energies of SiWA-H₃PO₄(2125)-XLPVA and SiWA-H₃PO₄(1500)-XLPVA at 75%, 45%, and 5% RH.

<table>
<thead>
<tr>
<th>RH</th>
<th>Activation energy (kJmol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiWA-H₃PO₄(2125)-XLPVA</td>
</tr>
<tr>
<td></td>
<td>T&gt;0 °C</td>
</tr>
<tr>
<td>75%</td>
<td>8.8</td>
</tr>
<tr>
<td>45%</td>
<td>14.7</td>
</tr>
<tr>
<td>5%</td>
<td>34.9</td>
</tr>
</tbody>
</table>

At 45% RH, the increasing H₃PO₄ content enhanced the conductivity at entire temperature region. The conductivity increased from 1.1 to 2.8 mScm⁻¹ (ca. 150% increase) and from 22 to 51 mScm⁻¹ (ca. 130% increase) at -30 and 50 °C, respectively. The percentage of increase was much higher than the 75% RH case, implying an increasing effect of proton density at this condition. The same observation was also noted at 5% RH. In this case, a substantial enhancement in proton conductivity was observed for both high temperature and low temperature regions. In particular, SiWA-H₃PO₄(2125)-XLPVA exhibited conductivity values of
0.042 and 8.5 mScm⁻¹ at -30 and 50 °C. Comparing these values to the conductivity of SiWA-H₃PO₄(1500)-XLPVA at the same temperatures (0.008 and 3.4 mScm⁻¹), the additional H₃PO₄ led to an over 400% and 150% increase over the SiWA-H₃PO₄(1500)-XLPVA electrolyte. Besides the proton conductivity, additional H₃PO₄ also reduced the activation energies for proton hopping in the film (Table 8-2). Similar to the observations in Figure 8-7, the positive effect of additional H₃PO₄ were more pronounced at low temperatures and low RH conditions.

### 8.3 Summary

In this chapter, the amount of plasticizers (*i.e.* glycerol or H₃PO₄) was adjusted in the cross-linked polymer electrolytes. The conductivity of the optimized SiWA-Gly(1500)-XLPVA was similar to that of SiWA-H₃PO₄(1500)-XLPVA at 75% RH as the proton conductivity was more dominated by proton mobility at this condition. At lower RH, SiWA-Gly(1500)-XLPVA demonstrated higher proton conductivity than SiWA-H₃PO₄(1500)-XLPVA at room-to-high temperatures due to the enhanced interfacial properties. But because of the non-conductive nature of glycerol, the conductivity of SiWA-Gly(1500)-XLPVA at lower temperatures was lower than that of SiWA-H₃PO₄(1500)-XLPVA. On the other hand, the increased H₃PO₄ content in SiWA-H₃PO₄(2125)-XLPVA further enhance the proton conductivity of the polymer electrolytes over the entire tested temperature and RH conditions and exhibited lower activation energies. A summary of preferred electrolyte between the two optimized samples at different conditions is shown in Figure 8-8.

![Figure 8-8](image)

**Figure 8-8:** Schematic of application conditions for SiWA-Gly(1500)-XLPVA and SiWA-H₃PO₄(2125)-XLPVA with no packaging.
It is confirmed that instead of low temperature, low humidity has a more negative effect on the electrolyte performance. For example, even at -30 °C, SiWA-H$_3$PO$_4$(2125)-XLPVA still exhibited a high conductivity of 13.6 mScm$^{-1}$ at 75% RH and a moderate conductivity of 2.8 mScm$^{-1}$ at 45% RH. At a slightly higher temperature of 0 °C, it exhibited high conductivity of 35.2 mScm$^{-1}$ at 75% RH and 12.6 mScm$^{-1}$ at 45% RH. It should be emphasized that SiWA-H$_3$PO$_4$(2125)-XLPVA demonstrated even higher proton conductivity than pure SiWA (27 mScm$^{-1}$ at its fully hydration) at room temperature.

Although the room temperature conductivity of SiWA-H$_3$PO$_4$(2125)-XLPVA at the extremely dry condition was moderate (2.7 mScm$^{-1}$ at 20 °C), its low temperature conductivity was still fairly low (e.g. 0.04 mScm$^{-1}$ at -30 °C and 0.8 mScm$^{-1}$ at 0 °C), albeit higher than those of SiWA-Gly(1500)-XLPVA. Therefore to overcome the low conductivity at the low temperature low humidity conditions, a hermetically sealed design can be used to maintain the humidity level inside the cell.
9 Alternative heteropolyacids as proton conductors

As demonstrated in Section 7.5, a limitation of SiWA-based polymer electrolyte system is its somewhat narrow electrochemical stability window by the reduction of the SiWA anion. To mitigate this limitation, alternative HPAs as proton conductors to replace SiWA are necessary. The following sections will discuss the development of alternative Keggin-type HPAs.

9.1 Development of alternative heteropolyacids

According to Figure 2-10, the charge of central heteroatom affect the potential of the 1st one-electron reduction of the Keggin anions. In this work, alternative Keggin-type HPAs with $\text{B}^{3+}$, $\text{Co}^{2+}$, $\text{Cu}^{2+}$ as the central heteroatoms were investigated and compared to SiWA. Before developing a solid HPA polymer electrolyte, a systematic study of these HPAs as aqueous electrolytes was performed. The feasibility and mechanism of these Keggin-type HPAs was studied. Their ionic conductivity and electrochemical stability window were determined. A standard $\text{H}_2\text{SO}_4$ solution was used as baseline for comparison at different concentrations. CNT-graphite and RuO$_2$ electrodes were employed for double layer and pseudo-capacitive electrodes, respectively. This could be used to explore the feasibility of alternative HPAs as electrolyte for supercapacitors and to expand the voltage operation window for proton conducting electrolytes.

9.1.1 Confirmation of Keggin structure

Since the FTIR spectra of HPAs share similarly vibrational features in the 400-1100 cm$^{-1}$ region as the characteristic structures of the primary Keggin unit, the structure of synthesized BWA, CoWA, and CuWA in this frequency region are compared to SiWA in Figure 9-1. Table 9-1 summarizes the wavenumbers of the bands with their associated bonding interactions for the three spectra.

In Figure 9-1, all four FTIR spectra have similar structures. The spectra of crystallized solid HPAs on the silicon FTIR window resembled typical Keggin structures. In the 400 to 1100 cm$^{-1}$ region, the structure and interaction of HPAs are well established as vibrational stretching modes of four types of oxygen. In Figure 9-1, no impurity peaks were observed for all four HPAs. This confirmed the successful synthesis of the HPA anion structure.
Figure 9-1: FTIR spectra of SiWA, BWA, CoWA, and CuWA.

Table 9-1: FTIR band positions and associated bonding information for SiWA, BWA, CoWA, and CuWA.

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Band assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1019(^a)</td>
<td>N/A</td>
</tr>
<tr>
<td>1018(^b)</td>
<td></td>
</tr>
<tr>
<td>1018(^c)</td>
<td></td>
</tr>
<tr>
<td>1002(^a)</td>
<td></td>
</tr>
<tr>
<td>1006(^c)</td>
<td></td>
</tr>
<tr>
<td>1010(^d)</td>
<td></td>
</tr>
<tr>
<td>961(^a) (960(^c))</td>
<td>W=O(_d) stretching</td>
</tr>
<tr>
<td>960(^c) (960(^d))</td>
<td></td>
</tr>
<tr>
<td>944(^a) (943 (or 941)(^e))</td>
<td></td>
</tr>
<tr>
<td>925(^a) (912(^a))</td>
<td>X-O(_a) stretching (X=Si, B)</td>
</tr>
<tr>
<td>930(^b) (914(^c))</td>
<td></td>
</tr>
<tr>
<td>926(^c) (920(^d))</td>
<td></td>
</tr>
<tr>
<td>880(^a) (902(^d))</td>
<td>W-O(_b)-W stretching</td>
</tr>
<tr>
<td>885(^b) (895(^c))</td>
<td></td>
</tr>
<tr>
<td>878(^c) (900(^d))</td>
<td></td>
</tr>
<tr>
<td>778(^a) (814(^a))</td>
<td>W-O(_c)-W stretching</td>
</tr>
<tr>
<td>792(^b) (810(^c))</td>
<td></td>
</tr>
<tr>
<td>779(^c) (820(^d))</td>
<td></td>
</tr>
<tr>
<td>443(^a) (443(^d))</td>
<td>Co-O(_a) stretching</td>
</tr>
</tbody>
</table>
XRD was utilized to investigate the composition and structure of the bulk HPA crystals. XRD patterns of BWA, CoWA, and CuWA were compared to the standard SiWA at the same level of hydration. All HPA samples were heated at 90 °C for two days before XRD analyses. The XRD patterns of heated BWA, CoWA, and CuWA are depicted in Figure 9-2 and compared to the heated SiWA. The narrow peaks in the XRD patterns of the three samples showed long-range ordered crystal structure. Further investigations are required to understand the slight difference in their patterns below 10° 2θ and above 40° 2θ. Nevertheless, the four HPA patterns are very close and indicative of the same characteristic Keggin structure.

Figure 9-2: XRD patterns of SiWA, BWA, CoWA, and CuWA after a 2-day heating at 90 °C.
9.1.2 Ionic conductivity

A test vehicle using two stainless steel electrodes was employed to measure the ionic conductivity of aqueous solutions of BWA, CoWA, and CuWA at room temperature. As a baseline, H$_2$SO$_4$ and SiWA were also included for this study. Figure 9-3a shows the ionic conductivity of the electrolytes as a function of concentrations. As expected, the ionic conductivity increased with concentration. CoWA and CuWA showed the highest conductivity while H$_2$SO$_4$ had the lowest.

![Figure 9-3: Comparison of SiWA, BWA, CoWA, CuWA, and H$_2$SO$_4$ in terms of (a) ionic conductivity; and (b) molar ionic conductivity as a function of concentration.](image)

Table 9-2: Limiting molar conductivity of SiWA, BWA, CoWA, CuWA, and H$_2$SO$_4$.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Estimated limiting molar conductivity (S cm$^{-2}$ mol$^{-1}$)</th>
<th>Cation limiting molar conductivity (S cm$^{-2}$ mol$^{-1}$)</th>
<th>Anion limiting molar conductivity (S cm$^{-2}$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$SO$_4$</td>
<td>835</td>
<td>700</td>
<td>80$^a$</td>
</tr>
<tr>
<td>H$<em>4$SiW$</em>{12}$O$_{40}$ (SiWA)</td>
<td>1533</td>
<td>1400</td>
<td>237$^b$</td>
</tr>
<tr>
<td>H$<em>5$BW$</em>{12}$O$_{40}$ (BWA)</td>
<td>1938</td>
<td>1750</td>
<td></td>
</tr>
<tr>
<td>H$<em>6$Co$^{III}$W$</em>{12}$O$_{40}$ (CoWA)</td>
<td>2357</td>
<td>2100</td>
<td></td>
</tr>
<tr>
<td>H$<em>6$Cu$^{II}$W$</em>{12}$O$_{40}$ (CuWA)</td>
<td>2358</td>
<td>2100</td>
<td></td>
</tr>
</tbody>
</table>

$^a$reference [112], $^b$reference [110]

To understand the origin of the difference in ionic conductivity, the molar ionic conductivity of the five electrolytes were plotted in Figure 9-3b. Since all five solutions are strong electrolytes, Kohlrausch's law was used to estimate the limiting ionic conductivity. All four HPAs exhibited
higher molar ionic conductivity than $\text{H}_2\text{SO}_4$, resulted from: (a) higher ionic strength of HPAs solutions owing to a higher number of protons in HPAs; and (b) higher anion limiting molar conductivity (Table 9-2). Considering the similar anion mobility in BWA, CoWA, and CuWA, their differences in the limiting molar conductivity were mainly from additional protons ($350 \text{ Scm}^2\text{mol}^{-1}$) [112].

9.1.3 Electrochemical stability window

To determine the electrochemical stability window of the electrolytes, CVs of a glassy carbon electrode in the four HPAs solutions are shown in Figure 9-4. Table 9-3 summaries the electrochemical stability windows of the HPAs.

![Figure 9-4: CVs of 1mM SiWA, BWA, CoWA, and CuWA in 1 M HCl at (a) 100 mVs$^{-1}$; (b) 10 mVs$^{-1}$.](image)

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Lower potential limit (V vs. Ag/AgCl)</th>
<th>Upper potential limit (V vs. Ag/AgCl)</th>
<th>Potential window (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiWA</td>
<td>-0.2</td>
<td>1.25</td>
<td>1.45</td>
</tr>
<tr>
<td>BWA</td>
<td>-0.4</td>
<td>1.25</td>
<td>1.65</td>
</tr>
<tr>
<td>CoWA</td>
<td>-0.2</td>
<td>0.9</td>
<td>1.1</td>
</tr>
<tr>
<td>CuWA</td>
<td>-0.3</td>
<td>1.25</td>
<td>1.55</td>
</tr>
</tbody>
</table>

Table 9-3: Electrochemical stability window of SiWA, BWA, CoWA and CuWA.
It is clear from the CVs that all four HPAs are redox active at negative potentials. SiWA showed three pairs of district peaks, corresponding to reversible redox reactions [199, 200]. The onset of anion reduction occurred at -0.2 V. The CV of BWA differed from that of SiWA, in which the onset reduction was observed at ca. -0.4 V. The oxidation peaks were ill-defined except a broad peak at 0.5 V. This broad peak may be the result of hydrogen produced at negative potentials. The CV of CoWA was similar to that of SiWA, with the onset reduction at ca. -0.2 V. A pair of redox peaks at 0.9 V was ascribed to a Co$^{3+}$/Co$^{2+}$ quasi-reversible redox couple [201]. The CV of CuWA showed a pair of redox peaks at -0.3 V attributable to Cu$^{1+}$/Cu$^{2+}$ couple [202] and anion reduction at -0.4 V. To better compare the electrochemical stability windows of the HPAs, the CVs of the electrochemically inert region of SiWA, BWA, CoWA, and CuWA were extracted from Figure 9-4a and are shown in Figure 9-4 at a lower scan rate of 10 mVs$^{-1}$. The electrochemical stability window increased in an order of CoWA<SiWA<CuWA<BWA.

9.1.4 Electrochemical characterizations of a carbon EDLC

Although CoWA showed high ionic conductivity, it was excluded from the capacitor cell study because of its limited potential window. Figure 9-5 shows the CVs of a CNT-graphite electrode in 0.05 M SiWA, BWA, CuWA, and H$_2$SO$_4$ in 3-electrode cells.

Small oxidation and reduction peaks at ca. 0.4 V were observed on the carbon electrode for all four electrolytes. This could be attributed to the pseudo-capacitance from the oxidation and reduction of surface functional groups such as quinone and its derivatives. For the HPAs, the broad anodic peak and its corresponding cathodic peak observed at negative potentials is either related to the redox reaction of the Keggin anion (for SiWA and BWA) or the Cu$^{1+}$/Cu$^{2+}$ couple (for CuWA). All three HPAs electrolytes reached their negative potential limits at between -0.2 to -0.5 V and their positive potential limits at 1.2-1.3 V. These are in a good agreement with Figure 9-4. Among the HPAs, the CNT-graphite electrode in BWA showed the widest potential window while the one in CuWA was similar to the one in SiWA. Although the CNT-graphite electrode demonstrated the widest potential window in H$_2$SO$_4$, its double-layer capacitance was smaller than that in BWA (12 vs. 17 mFcm$^{-2}$). The higher capacitance of the HPA electrolytes may be attributed from their highly dissociated protons.
To understand the behavior of these HPA electrolytes on capacitor cells, EDLC cells were constructed using two identical CNT-graphite electrodes. The CVs of the cells in 0.05 M SiWA, BWA, CuWA, and H$_2$SO$_4$ are shown in Figure 9-6a. The cells in HPA electrolytes had a capacitance of about 8 mFcm$^{-2}$ while the H$_2$SO$_4$-enabled one showed a smaller capacitance of 6 mFcm$^{-2}$. These values are approximately 50% of the values of a single electrode (Figure 9-5), in agreement with the interpretation of the two-cell system as two electrodes in series. Similar to the CVs of 3-electrode cells, the EDLCs have different maximum cell voltage limited by an increase in current density at high voltage regions. The trend of maximum cell voltage agrees well with the results in the 3-electrode cell (Figure 9-5), pointing to the higher voltage window
of the EDLC cells with BWA and H₂SO₄ electrolytes. In-situ electrode potential tracking of the liquid BWA and liquid SiWA EDLCs were also performed and the results are included in Appendix G.

The areal capacitance of the capacitors at different scan rates is shown in Figure 9-6b. The capacitance decreased with the increase of scan rates for all electrolytes. Due to the higher ionic conductivity of HPA solutions, the EDLCs with HPA electrolytes showed better capacitance retention at all the scan rates. Similar to the trend in conductivity, the capacitance increased from H₂SO₄<SiWA<BWA<CuWA. Since the electrodes and the cell setup are all identical, the charge separation process in the EDLCs were more dominated by ionic diffusion in the electrolyte at high scan rates. Therefore, CuWA showed the highest capacitance at high scan rates.

Figure 9-6: (a) CVs of CNT-graphite capacitors enabled by 0.05 M SiWA, BWA, CuWA, and H₂SO₄; (b) capacitance of the CNT-graphite capacitors as a function of scan rate; (c) real part $C'$ and (d) imaginary part $C''$ of capacitance vs. frequency for the capacitors.
EIS analysis was performed to complement the dc characterization and to confirm the trend in Figure 9-3a and Figure 9-6b. In Figure 9-6c, at low frequency, $C'$ of the H$_2$SO$_4$ cell approached 6 mFcm$^{-2}$ while the HPA cells approached 9 mFcm$^{-2}$, similar to the capacitance obtained from CV profiles (Figure 9-6a). The HPA-enabled ELDC showed higher capacitance than the H$_2$SO$_4$ cell over the entire frequency range. The $C''$ of the H$_2$SO$_4$ cell and the HPA-enabled ELDC exhibited maxima at ca. 2 and 8-10 Hz, respectively (Figure 9-6d). It should be noted that even though the HPA-enabled cells showed higher capacitance, it still exhibited a faster response (i.e. higher relaxation frequency), further demonstrated the higher ionic conductivity of HPAs.

Although HPAs are electrochemically active materials, they can function as electrolytes in both EDLCs and pseudo-capacitors at the proper voltage window. Their high ionic conductivity and good electrode compatibility make certain HPAs, especially BWA, attractive alternatives to other standard acidic electrolytes. Study on the compatibility of BWA with pseudo-capacitive electrodes is included in Appendix H.

9.2 Characterizations of BWA-based polymer electrolyte

9.2.1 Voltage window analysis

BWA exhibited a wider electrochemical stability window than SiWA in aqueous solutions and is worth further investigation. Purity of the synthesized BWA was confirmed via DSC characterizations (see Appendix F) before making it into polymer electrolytes. The study was first focusing on the BWA-XLPVA and SiWA-XLPVA polymer electrolytes without any plasticizers. The electrochemical stability windows of SiWA-XLPVA and BWA-XLPVA were characterized on screen-printed electrodes and are shown in Figure 9-7.

The onset SiWA anion reduction in SiWA-XLPVA occurred at -0.4 V (vs. Ag) while its upper potential limit was at ca. 1.25 V (vs. Ag), resulting in a 1.65 V potential window. The BWA-based sample exhibited a wider potential window, in good agreement with Figure 9-4. Considering the onset of its anion reduction at -0.6 V (vs. Ag) and the onset oxygen evolution at 1.25 V (vs. Ag), BWA-XLPVA has a stability window of ca. 1.85 V. Although both polymer electrolytes showed wider potential windows compared to their liquid counterparts (with glassy carbon), the difference in potential window between SiWA and BWA (i.e. 0.2 V) are identical regardless of solid or liquid.
Figure 9-7: CVs of BWA-XLPVA and SiWA-XLPVA on screen printed electrode (scan rate = 100 mVs⁻¹).

Figure 9-8: CV of a graphite electrode with BWA-XLPVA polymer electrolyte in a solid 3-electrode cell (scan rate = 100 mVs⁻¹).
A similar approach was used to analyze the voltage window of a BWA-based graphite EDLC as shown in the SiWA case (Section 7.5). The same electrode material for the SiWA-based graphite EDLC was used for comparison. Before constructing a BWA-based solid supercapacitor, a solid 3-electrode cell with BWA-based polymer electrolyte was first studied. A CV of a single graphite electrode in such solid 3-electrode cell is depicted in Figure 9-8.

The OCP of the working electrode was ca. 0.2 V (vs. Ag). From the CV a pair of redox peaks from the carbon functional groups were observed. The positive potential limit of the cell is about 0.7 V (vs. Ag) while the negative potential limit is -0.6 V (vs. Ag). This extended negative potential limit agrees well with the difference between the onsets of 1st electron reduction between BWA and SiWA in aqueous solutions (Figure 9-4). Consequently, a broad peak related to the hydrogen evolution was identified. Although this hydrogen peak shifted to a much lower potential in the solid-state cell, it did not affect the overall capacitor performance (at that the negative electrode potential > -0.6 V (vs. Ag)).

![Figure 9-9: (a) CVs of a solid graphite capacitor enabled by BWA-XLPVA at cell voltages from 0.5 V to 1.4 V (10th cycle, scan rate = 100 mVs⁻¹); and (b) electrode potential limits of both positive and negative electrodes as a function of cell voltage.](image)

A solid double-layer capacitor with a BWA-based electrolyte was assembled with the external reference electrode. CVs of the cell with an incremental voltages increase are shown in Figure 9-9a. The cell yields a near-rectangular-shaped CV profile at voltages up to 1.3 V, suggesting highly capacitive behavior. An increase in current density at the positive end of the cell voltage
was observed. Although these distortions limited the maximum cell voltage of this double-layer capacitor to 1.3 V, it is still 200 mV wider than its SiWA counterpart. Figure 9-9b shows $E_{\text{limit}}$ of the two electrodes as a function of cell voltage. Also marked in Figure 9-9b are the onsets of BWA anion redox reaction (-0.6 V vs. Ag) and oxygen evolution (0.7 V vs. Ag) obtained from the CV of the single graphite electrode in Figure 9-8. At a cell voltage of 1.3 V, the lower limit of $E_{\text{ve}}$ and the upper limit of $E_{+\text{ve}}$ reached these two reactions.

9.2.2 Proton conductivity

The proton conductivity of both BWA-XLPVA and SiWA-XLPVA polymer electrolytes was characterized from -30 to 50 °C at three RH levels: 75%, 45%, and 5%. Figure 9-10 shows their proton conductivity as a function of temperature at different RH conditions via Arrhenius plots. Proton conductivity of SiWA-XLPVA and BWA-XLPVA are listed in Appendix B, Table A7 and Table A8, respectively.

![Figure 9-10: Temperature dependence of proton conductivity for BWA-XLPVA and SiWA-XLPVA at 75%, 45%, and 5% RH from -30 to 50 °C.](image-url)
The proton conductivity trend of BWA-XLPVA in Figure 9-10 were very similar to the SiWA-based system, and both increased with temperature and RH. The high linearity of the fitted lines in both regions (above and below 0 °C) confirmed the conduction of protons via Grotthuss mechanism in the BWA system. An increase in activation energy of BWA-XLPVA at temperatures below 0 °C was also observed at all three RH conditions due to the freezing of water. However this limitation in proton mobility became less significant at high RH levels. Significant reductions in activation energy barriers in both high temperature and low temperature regions for the two electrolytes were observed with increasing RH. Both BWA- and SiWA-based polymer electrolytes exhibited similar proton conductivity at 75% and 45% RH while the sample with BWA showed higher conductivity at 5% RH.

![Figure 9-11: Dielectric constant of (a) BWA-XLPVA, (b) SiWA-XLPVA, and dielectric loss of (c) BWA-XLPVA, (d) SiWA-XLPVA, from -30 to 50 °C.](image-url)
Since a clear differentiation between BWA-XLPVA and SiWA-XLPVA can only be observed at 5% RH, further investigations based on ac impedance measurements was carried out at this condition. As demonstrated in Section 6.3.3, dielectric analysis can be used to derive the macroscopic charge transportation properties in the polymer electrolytes as a function of temperature. Figure 9-11 shows the dielectric constant and dielectric loss of SiWA-XLPVA and BWA-XLPVA.

Similar to the higher RH condition in Section 6.3.3, both polymer electrolytes showed high apparent dielectric constants at low frequencies related to the electrode polarization (Figure 9-11a&b). As frequency increased, the dielectric constant generally decreased. The dielectric constant at high frequencies is dominated by the molecular dipole polarization of SiWA and PVA as well as interfacial polarization among SiWA, PVA, and water molecules. The dielectric constants decreased with the decrease of temperature throughout the frequency range. At any given temperature, the low frequency dielectric constants of BWA-XLPVA were higher than those of SiWA-XLPVA. At high temperatures, both cells showed resonance behavior at the high frequency from the influence of residual inductance. At low temperatures, both $\varepsilon_{EP}$ and $\varepsilon_{s}$ were obtained.

In the dielectric loss vs. frequency plots (Figure 9-11c&d), peaks from both relaxation of electrode polarization (at high frequencies) and conduction loss (at low frequencies) were observed similar to the electrolytes at a higher RH condition (see Figure 6-9). However at this extremely dry condition, the shifting of the electrode polarization peak with temperature was much more significant and the conduction loss peak only partially appeared. The former is due to a higher sensitivity of proton conductivity with temperature variation at this extremely dry condition while the latter is a result of limited ion mobility.

In both BWA-XLPVA and SiWA-XLPVA, the frequency of the dielectric loss peak decreased with the decrease of temperature (Figure 9-11c&d). Although BWA-XLPVA exhibited higher magnitude of loss peak than SiWA-XLPVA owning to its higher dielectric constant values, BWA-XLPVA still exhibited faster response with shorter relaxation (i.e. peaks at higher frequency) compared to SiWA-XLPVA at all temperatures. In addition, due to the more conductive nature of BWA-XLPVA, the tail in the loss spectra occurred at a much lower temperature than that of SiWA-XLPVA.
Using a single-ion approach as described in Section 3.6.3, proton densities were calculated similarly as the study on filler-containing electrolytes (Section 6.3.3). Figure 9-12 shows the free proton density of BWA-and SiWA-based electrolytes as a function of temperature. At a low RH of 5%, the proton conductivity of both electrolytes were based on proton density rather than proton mobility, especially at low temperatures. Since BWA (H$_5$BW$_{12}$O$_{40}$) has more protons than SiWA (H$_4$SiW$_{12}$O$_{40}$), the BWA-based electrolyte showed consistently higher proton density than that of SiWA-based sample throughout the temperatures. The ratio of proton density shown in Figure 9-12 also agreed well with the theoretical value of $5/4$.

![Figure 9-12: Proton density of BWA-XLVA and SiWA-XLPVA at 5% RH from -30 to 50 °C.](image)

To further examine the effect of high proton density, the Debye length of BWA-XLPVA and SiWA-XLPVA were calculated based on Macdonald and Coelho model [145-147]. In this case, the Debye length represents the minimum distance required for charge separation (i.e. scale of double layer). A schematic diagram of the ideal charge separation process for BWA-XLPVA and SiWA-XLPVA is shown in Figure 9-13. At initial state, the protons are uniformly distributed across the electrolyte film. Under an applied electric field, charge separation occurs, in which protons accumulate on one end. This leads to an unbalanced macroscopic charge across the electrolyte film. Depending on the density or concentration of free protons, double layer with different thicknesses will form.
Figure 9-13: Schematic representations of charge separation in BWA-XLPVA and SiWA-XLPVA under an electric field.

Figure 9-14: Debye length of BWA-XLVA and SiWA-XLVA at 5% RH from -30 to 20 °C.

Figure 9-14 shows the Debye length of the two electrolytes as a function of temperature. The Debye length increased with temperature for both samples as protons and water molecules became more mobile. It is easier for protons to return to their initial state (i.e. to minimize the concentration difference across the film) by hopping through H⁺-nH₂O clusters. BWA-based sample consistently showed smaller Debye length compared to its SiWA counterpart, indicating a smaller minimum distance required for charge separation. This further confirmed the higher proton density of BWA-XLPVA over SiWA-XLPVA.
9.2.3 Proton mobility

Proton mobility at 5% RH for BWA-XLPVA and SiWA-XLPVA was calculated using proton conductivity (Figure 9-10) and proton density (Figure 9-12). Figure 9-15 shows the mobility of both polymer electrolytes as a function of temperature.

![Proton mobility of BWA-XLPVA and SiWA-XLPVA at 5% RH from -30 to 50 °C](image)

**Figure 9-15**: Proton mobility of BWA-XLPVA and SiWA-XLPVA at 5% RH from -30 to 50 °C

Both BWA-XLPVA and SiWA-XLPVA possessed higher proton mobility with increasing temperature similar to the electrolytes with fillers (see Figure 6-11). At low temperatures, while both electrolytes had very low proton mobility due to the freezing of water, BWA-XLPVA showed higher proton mobility than its SiWA counterpart. One assumption was that BWA contained more water at this condition, facilitating faster proton transportation. Since at this low RH condition (*i.e.* 5% RH), all free water were likely to be eliminated, the water in the electrolyte films were purely from crystallized water molecules. It is well known that SiWA forms hexahydrate at low RH, in which three of its four protons are hydrated forming a protonated dimer \( \text{H}_2\text{O} \cdots \text{H}^+ \cdots \text{OH}_2 \) (*i.e.* \( \text{H}_5\text{O}_2^+ \)). This results in a single isolated proton (*i.e.* non-hydrated proton) in SiWA. Therefore it is necessary to investigate the condition of protons in BWA and compare them to the ones in SiWA to gain insights on the level of hydration of BWA at low RH condition.
Solid-state \(^1\)H NMR analysis was used to investigate the nature of protons in BWA-XLPVA samples stored at 5% RH as well as the local environments of proton in the polymer electrolyte. Figure 9-16 shows the \(^1\)H NMR spectra of BWA-XLPVA from -30 to 50 °C. The extracted line width and line position are shown in Figure 9-17.

**Figure 9-16:** Solid-state \(^1\)H NMR spectra of BWA-XLPVA from -30 to 50 °C (stored at 5% RH).

In Figure 9-16, a relatively broad peak (e.g. a few kHz wide) was observed at all temperatures. The broad nature of the peak was primarily due to the strong \(^1\)H-\(^1\)H dipolar interactions in the electrolyte film. This peak broadening can be used as an indicator for proton mobility. At low temperatures, the line width (defined as FWHM) was broader (Figure 9-17a), implying that the proton were essentially immobile because of the strong dipole-dipole interaction. With increasing temperature, the line width decreased as a result of increased proton mobility. The proton mobility at higher temperatures increased enough to balance dipolar interactions, producing this line narrowing effect (Figure 9-17a). The NMR results also supported the trend in proton mobility obtained from the result in conductivity vs. temperature study. Further investigations focused on the line position to identify the origin of these peaks (Figure 9-17b).
Typically the resonance \(i.e.\) line position moved to lower frequency with the increase in temperature. This was a result of the reduction in hydrogen bonding within the polymer electrolyte. With the increasing of temperature, the hydrogen bonds begin to elongate and break. At room temperature \(i.e.\) 20-30 °C, the proton chemical shift was \(ca.\) 12 ppm. It has been reported that the chemical shift of isolated protons in HPAs is 9 ppm [124] while the predicted chemical shifts of hydrated protons in the form of \(\text{H}_3\text{O}_2^+\) and \(\text{H}_5\text{O}^+\) were 10.6 and 13.4 ppm, respectively [203]. Therefore, the observed peak in Figure 9-17b could be regarded as a coalesced peak of the \(\text{H}_3\text{O}^+\) and \(\text{H}_5\text{O}_2^+\). These indeed indicated that all protons in BWA-XLPVA were hydrated with no isolated protons. Since BWA (\(\text{H}_5\text{BW}_{12}\text{O}_{40}\)) has more protons associated with its anion than SiWA (\(\text{H}_4\text{SiW}_{12}\text{O}_{40}\)), BWA must contained more crystallized water molecules as well.

**Figure 9-17:** (a) Solid-state \(^1\text{H} \) NMR line width of BWA-XLPVA and (b) line position of BWA-XLPVA extracted from Figure 9-16.

Different from the impedance and dielectric analyses, which focus on the dynamics of proton transportation in long range diffusion, NMR analysis provides a microscopic view on the short range localized motion of protons. With emphasizing the nature of protons in BWA-XLPVA, useful information on the proton dynamics and the microscopic environment was obtained from the study of temperature dependent line width in Figure 9-17a. An estimation of the activation energy for the line narrowing process could be obtained by a Bloembergen-Purcell-Pound model:
\[
\tau_c = \left(\frac{1}{FWHM}\right)\tan\left(\left(\frac{\pi}{2}\right)\left(\frac{FWHM}{\Delta RL}\right)^2\right)
\]

(20)

where \(\tau_c\) is the correlation time, FWHM is the line width at a given temperature, \(\Delta RL\) is the rigid lattice line width. Unlike traditional polymer electrolytes, there was no sharp turning point with increasing temperature for line narrowing in BWA-XLPVA. Therefore \(\Delta RL\) could not be directly extracted from Figure 9-17a and it was estimated using Boltzmann function. Figure 9-18 displays the relationship between temperature and correlation time of BWA-XLPVA.

![Graph](image)

**Figure 9-18:** Temperature dependence of correlation time of BWA-XLPVA obtained from \(^1H\) NMR line narrowing from -30 to 50 °C.

A thermally activated correlation time is often assumed to follow an Arrhenius function. The fitting of the line narrowing data using Arrhenius equation yielded an activation energy of 6.5 kJmol\(^{-1}\) below the freezing temperature of water and 3.1 kJmol\(^{-1}\) above. These activation energies corresponded to the localized motion of \(\text{H}_3\text{O}^+\) and \(\text{H}_5\text{O}_2^+\) cluster rotation within the polymer electrolyte. Indeed this trend agreed with the conductivity measurements obtained from impedance (see Figure 9-10) and confirmed the positive effect of temperature on proton mobility, and thus proton conductivity in the polymer electrolytes.
9.2.4 Optimized BWA-based polymer electrolyte

Both glycerol and H$_3$PO$_4$ has been identified as suitable plasticizers to enhance the proton conductivity of the SiWA-based electrolytes (see Chapter 5 and Chapter 8). In this section, glycerol was incorporated into the BWA-XLPVA electrolyte to further enhance its performance. BWA-Gly(1500)-XLPVA was prepared in a similar way as the SiWA-Gly(1500)-XLPVA since the SiWA-based electrolytes demonstrated the best performance at the glycerol to PVA molar ratio of 1500.

The proton conductivity of BWA-Gly(1500)-XLPVA and BWA-XLPVA were characterized as a function of temperature at the three RH conditions and shown in Arrhenius plots (Figure 9-19). Their activation energies are summarized in Table 9-4 while their conductivity values for the two electrolytes are listed in Appendix B, Table A8 and Table A9.

![Figure 9-19: Temperature dependence of proton conductivity for BWA-Gly(1500)-XLPVA and BWA-XLPVA at 75%, 45%, and 5% RH from -30 to 50 °C.](image)

At 75% and 45% RH, the addition of glycerol enhanced the proton conductivity of the polymer electrolyte above the freezing temperature of water while this improvement in conductivity was
not as significant at temperatures below 0 °C. The enhanced proton conductivity was due to the plasticizer and solvation effects (see Section 5.1 and Section 8.1). At 5% RH, the glycerol slightly improve the proton conductivity of the electrolyte above the freezing point of water but significantly reduced the conductivity below similar to the SiWA-based electrolytes (see Figure 8-4). This was because the negative effect of non-conductive glycerol was most significant at this dehydrated and freezing condition as discussed in Section 8.1.2.

Although the activation energies of BWA-Gly(1500)-XLPVA were all higher than those of BWA-XLPVA, BWA-Gly(1500)-XLPVA still showed much higher proton conductivity at room temperature. In addition, comparing the conductivity of BWA-Gly(1500)-XLPVA (Figure 9-19) with SiWA-Gly(1500)-XLPVA (Figure 8-4), BWA-Gly(1500)-XLPVA exhibited higher proton conductivity for all three RH conditions, especially at low temperatures. This further supported the positive effect of additional protons in the electrolyte by using BWA as the proton conductor.

**Table 9-4:** Proton conduction activation energies of BWA-Gly(1500)-XLPVA and BWA-XLPVA at 75%, 45%, and 5% RH.

<table>
<thead>
<tr>
<th>RH</th>
<th>BWA-Gly(1500)-XLPVA</th>
<th>BWA-XLPVA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T&gt;0 °C</td>
<td>T&lt;0 °C</td>
</tr>
<tr>
<td>75%</td>
<td>11.3</td>
<td>24.0</td>
</tr>
<tr>
<td>45%</td>
<td>20.1</td>
<td>38.8</td>
</tr>
<tr>
<td>5%</td>
<td>51.3</td>
<td>80.2</td>
</tr>
</tbody>
</table>

The structure of BWA-Gly(1500)-XLPVA was investigated via XRD. Figure 9-20 shows the XRD patterns of BWA-Gly(1500)-XLPVA at 75%, 45%, and 5% RH. All three samples showed highly amorphous nature with no sharp diffraction peaks. The amorphous baselines were very similar to those of the SiWA-based system. After dehydration, the peak at 5.0° shifted to ca. 5.8° 2θ. Other than that, no significant difference were observed for the three samples. This suggested that BWA in the BWA-Gly(1500)-XLPVA had no long-range order structure. Comparing the XRD patterns of BWA-Gly(1500)-XLPVA to those of SiWA-Gly(1500)-XLPVA (see Figure 8-5), the latter showed SiWA crystallization at 45% and 5% RH. This implied that the effect of glycerol was more significant in the BWA-based system. More importantly, even at the extremely low RH, BWA-Gly(1500)-XLPVA still retained its highly amorphous structure. These results indirectly demonstrated the solvent effect of glycerol. This amorphous structure is highly desirable as it could facilitate higher proton mobility with less interactions with the crystalline
regions and promote intimate electrode/electrolyte interface for maximum ion accessibility. Ragone plots of solid supercapacitor devices enabled by BWA-Gly(1500)-XLPVA is shown in Appendix I.

![XRD patterns of BWA-Gly(1500)-XLPVA at 75%, 45% and 5% RH.](image)

**Figure 9-20**: XRD patterns of BWA-Gly(1500)-XLPVA at 75%, 45% and 5% RH.

### 9.3 Summary

In this chapter, H₅BW₁₂O₄₀ (BWA), H₆Co⁺W₁₂O₄₀ (CoWA), and H₆Cu⁺W₁₂O₄₀ (CuWA) were synthesized. These HPAs were characterized as aqueous electrolytes first. Their performance was compared to the existing H₄SiW₁₂O₄₀ (SiWA) electrolyte and H₂SO₄ benchmark. Among them, BWA can achieve a comparable potential window to H₂SO₄, which is much wider than that of SiWA, CoWA, and CuWA. The CNT-graphite-based EDLC utilizing BWA were able to achieve a cell voltage of 1.6 V and showed good capacitance retention at high rates.

A BWA-based polymer electrolyte was developed and it exhibited a wider potential window than its SiWA counterpart in the solid state. Solid graphite capacitors enabled by the BWA-based electrolyte demonstrated higher cell voltage than their SiWA-based counterpart. Detailed characterization of BWA-XLPVA was performed to investigate the effect of replacing SiWA
with BWA on the conductivity of the polymer electrolytes. BWA-XLPVA demonstrated higher proton density and mobility than its SiWA-XLPVA in conductivity, dielectric, and NMR analyses. BWA-Gly(1500)-XLPVA (i.e. with plasticizers) was also characterized and showed further improvement in performance. The addition of glycerol significantly reduce the crystallinity of the polymer electrolyte from high to low RH conditions. Even at the extremely dry condition, BWA-Gly(1500)-XLPVA still retained its amorphous structure, which is very promising and desirable. Further improvement in its proton conductivity is necessary to make it a high performance polymer electrolyte for solid and flexible supercapacitors.
10 Summary and outlook

With the current advances in printed electronics, wearable electronics, and e-textiles, solid energy storage systems that are light-weight, thin, and flexible are facing tremendous opportunities. Utilizing polymer electrolytes will be particularly beneficial in these next-generation energy storage devices. Polymer electrolytes can prevent leakage, minimize sealing or packaging processes, and provide more flexibility for device fabrication. Although the conductivity of polymer electrolytes is typically a few orders of magnitude lower than that of their liquid counterparts, deploying them in the form of very thin films helps to mitigate the problems with their inherently low intrinsic proton conductivity. Short and consistent proton-conducting paths within a thin electrolyte film can enable good conductivity.

In this thesis, a high performance proton-conducting polymer-in-salt electrolyte system using HPA and PVA has been developed. Three RH levels were chosen to simulate: (a) a high humidity (75%); (b) normal humidity (45%), and (c) extremely low humidity (5%). The HPA-based polymer electrolyte system has been optimized for fast proton transportation, good stability and cyclability at ambient conditions. Several modifications to the PVA polymer host as well as additives have been investigated to enhance the electrolyte environmental stability in extreme environments (e.g. low RH and/or low temperature). The resulting optimized polymer electrolyte even showed higher proton conductivity than its pure HPA counterpart. In addition, the non-hazardous chemicals (e.g. water soluble PVA, environmental friendly HPA) used in the developed polymer electrolytes ensures a minimum environmental impact.

A thorough understanding of the structural and chemical bonding of the electrolyte system and the interactions between polymer, proton conductors, and additives has been established using various electrochemical and material characterization techniques. Mechanism of proton conduction in the polymer electrolytes as well as its effect on conductivity has been studied as a function of temperature at different RH conditions. Accordingly, key attributes affecting the electrolyte properties and ion conduction mechanisms have been identified, including proton density, proton mobility, hydrogen bond interactions, additives, plasticizers, and type of polymer host. The following observations and conclusions have been drawn from the studies.
In Chapter 4, a SiWA-PVA binary polymer electrolyte system was successfully developed. Proton hopping was the proton conduction mechanism in SiWA-PVA. Crystallized water formed a stable proton-conducting network, which was confirmed via FTIR characterizations. These crystallized water was protonated with a structure of \( \text{H}_3\text{O}^+ \) and \( \text{H}_2\text{O}^+ \), forming a network with SiWA molecules in the polymer electrolyte for high conductivity at room temperature. Freezing of water molecules was identified as the cause of the high activation energy barrier for proton conduction at temperatures below 0 °C. Although the degree of amorphousness of PVA was enhanced by the addition of SiWA, the crystallinity of the entire binary system was increased due to the crystallization of SiWA. The resulting polymer electrolyte film was brittle and fragile.

In Chapter 5, the effects of both neutral (i.e. glycerol or ethylene glycol) and acidic (i.e. \( \text{H}_3\text{PO}_4 \)) plasticizers on SiWA-PVA were studied. Ethylene glycol showed stronger plasticizer and solvation effects than glycerol while glycerol exhibited better water retention effect. Nevertheless, both neutral plasticizers suffered a significant reduction in proton conductivity at low RH conditions limited by their non-conductive nature. In contrast, proton conductivity (especially at low RH levels) could be enhanced by the addition of \( \text{H}_3\text{PO}_4 \). Although the addition of \( \text{H}_3\text{PO}_4 \) did not alter the bonding structure and proton conduction mechanism of the original SiWA-PVA, it increased proton density of the polymer electrolytes and promoted the retention of crystallized water with higher thermal stability. In addition, relative intensity between the characteristic XRD diffraction peaks of SiWA could be used as indicators to identify the level of hydration in the polymer electrolytes.

In Chapter 6, the effects of nano-SiO\(_2\) and nano-TiO\(_2\) fillers were investigated. The proton conduction properties were derived as a function of temperature using dielectric analysis and a single-ion approach. Three major effects have been identified:

a) The barrier effect leading to lower double layer capacitance in a supercapacitor. Among the two fillers, SiO\(_2\) showed a stronger barrier effect than TiO\(_2\).

b) The intrinsic dielectric constant effect is related to the static dielectric constants of polymer electrolytes. The higher intrinsic dielectric constant of TiO\(_2\) resulted in a higher capacitance of SiWA-H\(_3\)PO\(_4\)-PVA/TiO\(_2\)-based cells over that the one with SiO\(_2\) at high frequencies.
c) The water retention effect influences the environmental stability of the electrolyte as well as the dynamic dissociation of water molecules in the SiWA structure, impacting both proton density and proton mobility. Both SiO$_2$ and TiO$_2$ fillers improved environmental stability of the electrolyte, and SiWA-H$_3$PO$_4$-PVA/SiO$_2$ demonstrated a higher water retention capability. This stronger water retention effect of SiO$_2$ at higher temperatures ensured a more stable proton transport network in the electrolyte and maintained high proton mobility.

- In Chapter 7, cross-linked SiWA-H$_3$PO$_4$-XLPVA electrolytes were developed. Water uptake and the level of hydration of SiWA increased with higher degree of cross-link. However due to the decreased of electrolyte film adhesion, proton conductivity first increased then decreased with the degree of cross-link. Therefore, the level of cross-link was optimized to achieve high proton conductivity and high water uptake. Similar to the linear (non-cross-linked) polymer electrolyte, protonated H$_2$O and the structure of SiWA anion showed high stability even at “dried” conditions. In addition, the factors limiting the solid capacitor cell voltage were identified and deconvoluted through a potential tracking method. The potential of the positive electrode changed much more than that of the negative electrode once the negative electrode reached the SiWA anion reduction potential. This was the dominating factor that limited the cell voltage.

- In Chapter 8, the amount of glycerol and H$_3$PO$_4$ was optimized in the respective cross-linked polymer electrolytes to further improve their performance. The addition of glycerol significantly enhanced the flexibility and adhesion property of the electrolyte film as well as its conductivity at high RH and high temperature conditions. The addition of H$_3$PO$_4$, on the other hand, improved electrolyte conductivity at all tested conditions. One important insight is that, instead of low temperature, low humidity affects the electrolyte performance more negatively. Both optimized electrolytes exhibited similar conductivity values at high RH and high temperature, as they were more dominated by proton mobility at this condition. At the other conditions, electrolyte with the optimized H$_3$PO$_4$ content showed higher proton conductivity attributed to its enhanced proton density.

- In Chapter 9, the electrochemical stability window of the polymer electrolyte system has been increased via synthesizing alternative HPAs. In particular, H$_3$BW$_{12}$O$_{40}$ (BWA) could achieve a comparable potential window to H$_2$SO$_4$, which was much wider than that
of SiWA, $\text{H}_6\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}$ (CoWA), and $\text{H}_6\text{Cu}^{\text{III}}\text{W}_{12}\text{O}_{40}$ (CuWA). A BWA-based electrolyte was investigated and characterized. It was revealed that the BWA-based polymer electrolyte not only exhibited a wider electrochemical stability window (resulted in a higher cell voltage in the enabled solid capacitor) but also a higher proton conductivity. By utilizing dielectric and NMR analyses, proton density and mobility of BWA-based electrolytes were extracted, which were all higher than its SiWA-based counterpart. An optimized BWA-Gly(1500)-XLPVA showed enhanced proton conductivity and limited salt crystallization even at the extremely dry condition attributed to the plasticizer and solvent effects of glycerol.

With the development of flexible energy storage devices, polymer electrolytes have become the key components. Although it is very challenging to develop an electrolyte system that can possess excellent properties in all aspects, including electrochemical stability window, ionic conductivity, contacts/interfaces, thermal stability, safety, and etc., balance among these properties for specific applications is always the key for a high performance material system. Therefore, it is essential to develop a solid understanding of the mechanism and interactions among these properties in a polymer electrolyte system. The finding of this thesis can be used to answer these key questions not only for supercapacitors, but also for other electrochemical devices such as sensors, batteries, electrochromic displays, and fuel cells. Nevertheless, there are still much fundamental properties need to be explored in future work:

- to develop an understanding on the local ionic dynamics at the interfaces by investigating different plasticizers and/or nano-particles fillers on the energy barrier for the ion transfer between the polymer electrolyte and electrodes. Dielectric and NMR measurements at extreme conditions (e.g. low temperature and low RH) may provide useful information on ion dissociation and ion transportation properties within the film.
- to develop numerical models of charge separation within the film under different environmental conditions and to explore the mechanism of the double-layer formation in the case of the developed single-ion (e.g. proton) conducting polymer electrolytes. Surface characterization techniques can be used to identify the accommodated species on the electrode surface.
- to confirm the transference numbers for all the ionic species in the developed polymer electrolytes. Electrochemical techniques such as galvanostatic polarization method,
potentiostatic polarization method, electromotive force method can be applied. Pulsed field gradient NMR can also be used to supplement the electrochemical measurements.

- to study the microstructure and morphology of the polymer electrolyte films through surface characterization techniques including scanning electron microscope and atomic force microscope. For example, the smooth morphology can verify the complete amorphous nature of the polymer electrolyte and complete dissolution of the salt, which can be related to XRD analysis. Three dimensional topography images of the electrolyte film can be used to measure the pore size of the sample as well as the roughness factor of the film.

- to characterize the thermal stability of the polymer electrolytes with different plasticizers and fillers as a function of different RH levels. The amount of heat release (or weight loss) can be used as a figure of merit to evaluate the water retention property of the films. These results can also be correlated with the XRD analysis to quantify the exact number of crystallized water molecules in the structure as well as to understand the kinetic of polymer electrolyte dehydration at different environment.

- to understand the reasons behind the HPA crystallization within the polymer electrolyte. For example, the degree of SiWA crystallization was higher in the linear PVA-based polymer electrolyte when incorporating H₃PO₄ in the film, as shown in Section 5.2. The effects of such HPA crystallization on the electrode/electrolyte interfacial properties as well as proton transportation should also be investigated.

- to develop a solid understanding on the origin of improved performance of the glycerol-containing electrolyte. Although solvation effect and the enhanced electrolyte/electrolyte interfacial properties are assumed to be the dominating factors, a more detailed sturdy should be performed to quantify these possible explanations.

- to investigate the mechanical properties of the polymer electrolyte films, such as stress-strain relations at different RH conditions for flexible and/or stretchable applications. Properties such as yield strength and tensile strength can be measured.

- to characterize and optimize the polymer electrolyte precursor solution properties (e.g. viscosity and curing/drying time) for applications in inkjet printing, screen printing, spray painting, and/or roll-to-roll fabrication of printed devices.
Following directions should also be addressed in the further to push for the polymer electrolyte material performance excellence:

- to improve the proton conductivity of the polymer electrolyte and to reduce the sensitivity to the environment by identifying the effects of hygroscopic materials on the ion conduction mechanisms in the polymer electrolytes. Nano-fillers with different density of surface hydroxyl groups and different particle sizes can be used to enhance the electrolyte performance.
- to achieve wider electrochemical stability windows by synthesizing other Keggin-type HPAs (e.g. H₆H₂W₁₂O₄₀) as well as other types of HPAs (e.g. Dawson-type). Non-aqueous organic- or ionic liquid-based solvents can also be incorporated. Such gel polymer electrolytes with multi-functional components and structures may also be beneficial for high temperature applications.
- to explore other techniques to cross-link PVA in the polymer electrolyte, eliminating the use of glutaraldehyde. In addition, other water soluble polymers or polymer blends can be investigated as the polymer host to improve the film water retention, potential candidates include PAAM, PAA, PVP, and etc.
- to enhance the performance of BWA-based polymer electrolytes by incorporating acidic plasticizers and or fillers. Since both cross-linking of the PVA framework and the incorporation of hydroscopic nano-filler are effective to improve the environmental stability of the polymer electrolytes, it is of interest to combine the cross-linked polymer host and nano-fillers together for enhanced performance.
References

[1] B.E. Conway, Electrochemical supercapacitors: scientific fundamentals and technological
589-593.
[22] M.L. Di Vona, P. Knauth, Introduction and Overview: Protons, the Nonconformist Ions, in:


Appendix A – Applications of flexible solid supercapacitors

AC line filtering

To convert ac current to dc power for modern electronics, the removal of voltage fluctuations (i.e. ripples) after rectification is necessary to create pure dc voltage (Figure A1). This requires a capacitor that releases its stored energy when the AC source changes its phase (i.e. not supplying any power). In this case, the load can still be powered without any interruption (Figure A1).

Electrolytic capacitors are the current solution for 120 Hz power filtering. However they suffer from bulky cell configuration, restricting the volume minimization of the power electronics. Supercapacitors, such as planar interdigitated EDLCs, can enable light-weight and small-volume electronics with much more energy density (Figure A2). Polymer electrolytes are preferred since it can cover the planar cell without flowing away.

Figure A1: (a) ac input, (b) rectifier output without a smoothing capacitor, and (c) dc output with a smoothing capacitor.

Figure A2: A planar EDLC prototype enabled by a polymer electrolyte showing (a) interdigitated electrode pattern and (b) photograph of the prototype [192].
**High peak load leveling**

Supercapacitors can support batteries to reach higher power performance for continuous load function when they are connected in parallel. Since battery life time is often reduced by power cycling and peak power loads, the supercapacitor in the hybrid system can provide voltage leveling in the case of high peak load and reduce both peak power and average power load on batteries (Figure A3). This significantly improves the performance and life time of batteries. More flexibility in application design can be also achieved. Normally when adding high power function, re-design of the power supply (*e.g.* additional battery units) is needed. However, the additional power requirement can be assisted by using a supercapacitor hybrid system.

In the case of thin and flexible solid supercapacitors, they can have various form factor and can be readily combined with the batteries. Applications include high brightness optical flash, GPS tracking meter, portable medical devices, audio devices, and etc.

![Figure A3: Loading pattern of a battery; peak load leveling (a) without and, (c) with a supercapacitor.](image)

**Figure A3:** (a) Loading pattern of a battery; peak load leveling (b) without and, (c) with a supercapacitor.

![Figure A4: Supercapacitor-battery hybrid system by wrapping the flexible solid supercapacitor around a battery cell.](image)

**Figure A4:** Supercapacitor-battery hybrid system by wrapping the flexible solid supercapacitor around a battery cell.
Storage for energy harvest

Supercapacitors can be used for energy harvest systems that have unstable power generation. They can be connected between the harvester and load, getting charged from the harvester and discharged to the load (Figure A5). For example, supercapacitors can buffer solar energy to achieve longer life time, lower maintenance, and higher operational robustness. This results in a self-sustainable (or self-powered) power supply system without expensive wires or batteries that need repeated replacement.

With the development of polymer electrolytes, flexible solid supercapacitors can be constructed for smart and electronic textiles. For example, wearable supercapacitors can be knitted into full textiles and garments and can be paired with solar panels or textile-piezoelectrics to harvest energy from sunlight or body movements (Figure A6). Such wearable electronics offer the combined advantages of both electronics and fabrics. Applications include sensors, location tracking devices, RFID and other on-body antennas.

Figure A5: Supercapacitors for energy storage from non-constant power supply.

Figure A6: Example of wearable supercapacitors providing power for antennas from different energy harvesting components [204].
Appendix B – Proton conductivity of polymer electrolytes

**Table A1**: Proton conductivity of SiWA(419)-PVA.

<table>
<thead>
<tr>
<th>T (°C)</th>
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<th>45% RH</th>
<th>5% RH</th>
</tr>
</thead>
<tbody>
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<td>-30</td>
<td>4.311</td>
<td>0.966</td>
<td>0.001</td>
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<td>-20</td>
<td>7.522</td>
<td>1.888</td>
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**Table A2**: Proton conductivity of SiWA-H$_3$PO$_4$(1500)-PVA.

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<th>5% RH</th>
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**Table A3**: Proton conductivity of SiWA-H$_3$PO$_4$-PVA/TiO$_2$, SiWA-H$_3$PO$_4$-PVA/SiO$_2$, and SiWA-H$_3$PO$_4$-PVA at 45% RH.

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<th>SiWA-H$_3$PO$_4$-PVA/SiO$_2$</th>
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### Table A4: Proton conductivity of SiWA-H₃PO₄(1500)-XLPVA(5.2).

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<th>5% RH</th>
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### Table A5: Proton conductivity of SiWA-Gly(1500)-XLPVA(5.2).

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### Table A6: Proton conductivity of SiWA-H₃PO₄(2125)-XLPVA(5.2).

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**Table A7: Proton conductivity of SiWA-XLPVA(5.2).**

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**Table A8: Proton conductivity of BWA-XLPVA(5.2).**

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<th>5% RH</th>
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**Table A9: Proton conductivity of BWA-Gly(1500)-XLPVA(5.2).**

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Appendix C – Structures of SiWA at different RH conditions

70% RH

55% RH
43% RH

37% RH
The above XRD patterns were obtained from powder samples stored at ambient conditions (i.e. with no humidity control) over time except the ones at 70% RH and “dried” condition. The 70% RH sample were humidified in an environmental chamber for 2 days and the “dried” sample were stored in a 5% desiccator for a month before being characterized. For the other samples, the RH values only indicate the humidity level of the particular test date. Since small fluctuations in RH is very common at the ambient conditions, the obtained XRD patterns for those ambient samples might not represent their actual structure at that particular RH. Nevertheless, the trend of structure change of SiWA can still be observed. From the above XRD patterns, there are at least three stable phases of SiWA hydrates: higher hydrates at 70-43% RH, intermediate hydrates at 37-26% RH, and lower hydrates < 26% RH).

Since PWA (H$_3$PW$_{12}$O$_{40}$) is the most widely characterized HPA, the XRD patterns of SiWA and PWA at “dried” conditions (i.e. RH < 26%) are compared in Figure A7. Both patterns are very similar in terms of the peak positions and relative intensities. The obtained XRD pattern for PWA was identical to that from X-ray and neutron diffractions of a single crystal of H$_3$PW$_{12}$O$_{40}$$\cdot$6H$_2$O with a cubic unit cell [123]. Therefore it is reasonable to assume SiWA at this condition also adopts a cubic unit cell in the hexahydrate form. This finding agrees with an early study on SiWA by Scroggie and Clark [205]. Their peak list and stick patterns are shown in Table A10 and Figure A8.

![Figure A7: XRD patterns of SiWA and PWA dehydrated at a RH level below 26%](image)
Table A10: XRD peak list of SiWA•6H₂O. Data reproduced from the Inorganic Crystal Structure Database (00-001-0559) (see Ref. [205] for the original work).

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<th>Intensity (%)</th>
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<td>80</td>
</tr>
<tr>
<td>21</td>
<td>640</td>
<td>1.68</td>
<td>54.582</td>
<td>10</td>
</tr>
<tr>
<td>22</td>
<td>732</td>
<td>1.53</td>
<td>60.459</td>
<td>80</td>
</tr>
</tbody>
</table>

Figure A8: XRD stick pattern of SiWA•6H₂O. Reproduced from the Inorganic Crystal Structure Database (00-001-0559) (see Ref. [205] for the original work).
Although there was no structure analysis of SiWA at its intermediate and higher hydrates reported in the literature. The XRD diffraction patterns of SiWA at intermediate hydrates are similar to the diffraction patterns of single crystal H$_3$PMo$_{12}$O$_{40}$$\cdot$14H$_2$O [206] and H$_3$PW$_{12}$O$_{40}$$\cdot$14H$_2$O [170], which both have triclinic structure. Their XRD stick patterns are shown in Figure A9 and Figure A10. Single crystal X-ray and neutron diffraction studies of H$_3$PW$_{12}$O$_{40}$$\cdot$21H$_2$O [15, 170, 207] and H$_3$PW$_{12}$O$_{40}$$\cdot$29H$_2$O [170, 208] have revealed that these hydrates adopt orthorhombic and cubic unit cells, respectively. Similar observations have been made for H$_3$PMo$_{12}$O$_{40}$$\cdot$21H$_2$O [15] and H$_3$PMo$_{12}$O$_{40}$$\cdot$30H$_2$O [209], having orthorhombic and cubic unit cells, respectively. Therefore, it is reasonable to consider SiWA at its intermediate and higher hydrates also adopts orthorhombic and cubic unit cells.

**Figure A9:** XRD stick pattern of H$_3$PMo$_{12}$O$_{40}$$\cdot$14H$_2$O. Reproduced from the Inorganic Crystal Structure Database (01-075-1588) (see Ref. [206] for the original work).
Figure A10: XRD stick pattern of H$_3$PW$_{12}$O$_{40}$$\cdot$14H$_2$O. Reproduced from the Inorganic Crystal Structure Database (01-075-1588) (see Ref. [170] for the orginal work).
Appendix D – Humidification test of linear and cross-linked polymer electrolytes

Stainless steel metallic cells enabled by SiWA-H₃PO₄(1500)-PVA has been stored and tested in 90% RH. EIS measurements were performed after 1-, 3-, and 24-hour storage. The ESR of the device increased from 0.82 to 2.84 ohm, which was due to the dissolution of SiWA at this high RH condition, causing liquid solution leakage.

Conversely, metallic cells enabled by SiWA-H₃PO₄(1500)-XLPVA(5.2) showed excellent stability at 90% RH. EIS measurements were performed after 1-, 2-, 3-, and 70-hour storage. ESR decreased continuously, confirming the excellent stability of the cross-linked electrolyte at this high RH.

Figure A11: Nyquist plot of a metallic capacitor enabled by SiWA-H₃PO₄(1500)-PVA after 1-, 3-, and 24-hour humidification (left) and a metallic cell enabled by SiWA-H₃PO₄(1500)-XLPVA(5.2) after 1-, 2-, 3-, and 70-hour humidification (right).
Appendix E – Effect of water content on the viscosity of cross-linked precursor solutions

At higher degrees of cross-link (e.g. 0.03:1 glutaraldehyde to PVA repeating unit molar ratio), more H₂O contents are required to obtain suitable solution viscosity for electrolyte casting.

<table>
<thead>
<tr>
<th>H₂O wt.%</th>
<th>Effect of water content on solution viscosity of SiWA-H₃PO₄-XLPVA(12)</th>
</tr>
</thead>
<tbody>
<tr>
<td>53%</td>
<td><img src="image1.png" alt="Image" /></td>
</tr>
<tr>
<td>61%</td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>66%</td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>80%</td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
</tbody>
</table>
Appendix F – DSC thermograms of SiWA and BWA

The DSC thermograms of SiWA and BWA are shown in Figure A12 and Figure A13, respectively. Due to the different number of crystallized water molecules presented in the HPAs, different endothermic peaks were observed for both HPAs because of the loss of water. For example, SiWA showed two small endothermic peaks (at 90 °C and 150 °C) and one large endothermic peak (at 170-180 °C) while BWA exhibited very similar behavior with the exception of lacking the very first small endothermic peak. This indicated the BWA had less crystallized water content than the SiWA for these two particular samples. Nevertheless, this still confirmed the high purity of our synthesized BWA.

Figure A12: DSC thermogram of SiWA.

Figure A13: DSC thermogram of BWA.
Appendix G – In-situ electrode potential tracking for SIWA- and BWA-based liquid EDLCs

Since the intended application of BWA is to serve as an electrolyte for supercapacitors, CVs of a single CNT-graphite electrode in 0.05 M SiWA and 0.05 M BWA at a scan rate of 100 mVs\(^{-1}\) are shown in Figure A14. The positive potential limit for SiWA was about 1.2 V due to oxygen evolution while the negative potential limit was ca. -0.25 V. This resulted in a 1.45 V potential window for SiWA with CNT-graphite electrode. The OCP of the electrodes were ca. 0.2 V. The CV of BWA using the same electrode material differed from the CV of SiWA. The OCP of the electrodes in BWA were ca. 0.3 V. The positive potential limit for BWA was about 1.2 V while the negative potential limit was shifted to ca. -0.45 V. This led to a 1.65 V potential window for BWA, which was 200 mV wider than that of SiWA.

**Figure A14**: CVs of a CNT-graphite electrode in 0.05 M (a) SiWA and (b) BWA (scan rate = 100 mVs\(^{-1}\)).

EDLCs were constructed using two identical CNT-graphite electrodes linked to an external reference electrode. Figure A15 shows the CV profiles of the SiWA-based EDLC with incremental cell voltages. The cell depicts a near-rectangular-shaped profile at a cell voltage below 1.5 V. The increased current density limited the maximum cell voltage to ca. 1.4 V in this system. It is revealed that BWA exhibited a wider electrochemical stability window than SiWA. A double-layer capacitor with 0.05 M BWA electrolyte also was constructed and CVs of the EDLC at different cell voltages are shown in Figure A15b. The capacitor cell yields a near-rectangular-shaped profile at cell voltages up to 1.6 V, exhibiting in a 200 mV wider maximum...
cell voltage than its SiWA-based counterpart. This agrees well with results obtained from the 3-electrode cell.

Figure A15: CVs of a CNT-graphite capacitor enabled by 0.05 M (a) SiWA at cell voltages from 0.5 V to 1.5 V and (b) BWA at cell voltages from 0.5 V to 1.7 V (10th cycle, scan rate = 100 mVs\(^{-1}\)); and electrode potential limits of positive and negative electrodes as a function of cell voltage for (c) the SiWA-based cell and (d) the BWA-based cell.

To investigate the interactions between the HPA and the electrodes, Figure A15c&d show \(E_{lim}\) of the two electrodes (i.e. \(E_{lim}\) of positive electrode and \(E_{lim}\) of negative electrode) as a function of cell voltage. Also marked in Figure A15c&d are the potential limits of the two HPA obtained from the CVs of the single graphite electrode. They are -0.25 V and 1.2 V for SiWA as well as -0.45 V and 1.2 V for BWA. In both Figure A15c&d, the \(E_{lim}\) of positive electrode exhibited a faster increase with cell voltage (i.e. a higher slope) compared to \(E_{lim}\) of the negative electrode.
This was because of the higher electrode capacity in the negative region (of the open-circuit potential) for both cells. As a result, the change in the $E_{\text{limit}}$ of the negative electrode with cell voltage is much less than the change in the $E_{\text{limit}}$ of the positive electrode, i.e., the absolute slope of $E_{\text{limit}}$ vs. cell voltage of the negative electrode is smaller than that of the positive electrode.

In Figure A15c, the $E_{\text{limit}}$ of the positive electrode reached the oxygen evolution at a cell voltage of 1.4 V for the SiWA-based cell while the $E_{\text{limit}}$ of the positive electrode reached the same gas reaction at a higher cell voltage of 1.6 V for the BWA-based cell. These results were in consistent with the CV results (Figure A15a&b). In the SiWA-based cell, it was easier for the negative electrode to reach the anion reduction reaction since it had limited potential window at negative regions. Consequently, the reduction of the SiWA anion led to an increase in the net charge at the negative electrode. This provides much more charge capacity compared to the positive electrode and caused a significant increase in the $E_{\text{limit}}$ of the positive electrode. As a result, the positive electrode exceeded the oxygen evolution only at a cell voltage of 1.4 V. In contrast, owing to a wider potential window of BWA at negative regions, the negative electrode could only reach the anion redox reaction at a more negative potential (i.e. -0.45 V). Therefore, the slope of the $E_{\text{limit}}$ vs. cell voltage of the positive electrode was smaller compared to its SiWA-based counterpart. As a result, its positive electrode hit the oxygen evolution limit at a higher cell voltage of 1.6 V. Although the unbalanced charge in the electrodes causes the change in slope of $E_{\text{limit}}$ vs. cell voltage in both ELDCs, BWA-based EDLC still demonstrated a wider cell voltage.
Appendix H – Electrochemical characterizations of RuO₂ pseudo-capacitors

To demonstrate the compatibility of BWA with pseudo-capacitive electrodes, RuO₂ was used although it may not be practical as electrode material for commercial use due to cost concerns. Nevertheless, it can serve as proof of concept as it represents a typical pseudo-capacitive material. Similar to the approach with EDLC, CV profiles for the RuO₂ electrode in H₂SO₄ and BWA solutions in a 3-electrode cell (Figure A16a&b) were first obtained. CVs of the 2-electrode devices to imitate a supercapacitor cell are shown in Figure A16c.

![CV profiles for RuO₂ electrode in H₂SO₄ and BWA solutions in a 3-electrode cell](image)

**Figure A16**: CVs of a RuO₂ electrode in 0.05 M (a) H₂SO₄ and (b) BWA (scan rate = 100 mVs⁻¹); (c) CVs of RuO₂ pseudo-capacitor in 0.05 M BWA and H₂SO₄ (scan rate = 100 mVs⁻¹); (d) capacitance of the RuO₂ pseudo-capacitors as a function of scan rate.
Figure A16a&b show the CV profiles of a single RuO$_2$ electrode in 0.05 M H$_2$SO$_4$ and BWA electrolytes. Electrode capacitance was in the range of 50–70 mFcm$^{-2}$ measured at 100 mVs$^{-1}$ and clearly exhibited the pseudo-capacitive effect. It should be noted that although RuO$_2$ in H$_2$SO$_4$ showed a wider potential window, it exhibited less capacitance when compared to the one in BWA. Figure A16c show the CVs of the RuO$_2$ cell in 0.05 M H$_2$SO$_4$ and BWA. Both CV profiles were quite rectangular, indicating highly capacitive response of the cells. Moreover, the two CVs in Figure A16c showed the same maximum working voltage of 1.4 V. The capacitance of the 2-electrode RuO$_2$ device was again half that of an individual electrode. Further analysis were performed by varying the scan rates (Figure A16b). Similar to the EDLCs, the capacitance decreased with the increase of scan rates for both cells enabled by H$_2$SO$_4$ and BWA electrolytes. At low scan rates, the use of RuO$_2$ electrodes yielded about a 5-fold increase in capacitance when compared to the CNT-graphite cells. Due to the higher number of dissociated protons in BWA as well as its higher ionic conductivity, the BWA-enabled device consistently showed higher cell capacitance than the H$_2$SO$_4$ cell over the tested scan rates. For example, it could still deliver a capacitance of 9 mFcm$^{-2}$ at 5 Vs$^{-1}$. 
Appendix I – Ragone plots of the developed solid supercapacitors

A comparison of the different energy storage devices designed for microelectronics applications (a 500 mAh thin-film lithium battery, a 25 mF supercapacitor and a 220 μF electrolytic capacitor) with the solid supercapacitors enabled by SiWA-Gly(1500)-XLPVA and BWA-Gly(1500)-XLPVA with CNT-graphite electrodes is presented in Figure A17. The volumetric energy densities and power densities of the solid devices were calculated based on the volume of the electrodes (60 μm in thickness) and the polymer electrolyte (100 μm in thickness) for each individual cell.

![Figure A17](image)

Figure A17: Comparison, in a Ragone plot, of the specific energy and power density of typical electrolytic capacitors, supercapacitors and batteries with the solid supercapacitors enabled by SiWA-Gly(1500)-XLPVA and BWA-Gly(1500)-XLPVA and CNT-graphite electrodes. Data for the commercial cells are reproduced from Ref. [189] with permission from Nature Publishing Group.