Borotungstic Acid (BWA)-Polyacrylamide (PAM) Solid Polymer Electrolytes for Electrochemical Capacitors

by

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A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
Department of Materials Science and Engineering
University of Toronto

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Abstract

Solid polymer electrolytes (SPEs) are key enablers for thin and flexible electrochemical capacitors in wearable technologies. Polyacrylamide (PAM) is one such promising hygroscopic polymer host, but its performance had not been optimized. This thesis enhanced PAM with borotungstic acid (BWA) as the heteropolyacid conductors. The BWA-PAM electrolyte achieved a high initial conductivity of ca. 27 mS cm\(^{-1}\), but suffered from a short service life (\(< 40\%\) conductivity retention after 28 days) due to dehydration.

BWA-PAM modified with acidic (H\(_3\)PO\(_4\)) and neutral (glycerol) plasticizers showed improved conductivity of ca. 30 mS cm\(^{-1}\) and service life (\(\geq 70\%\) conductivity retention after 28 days). The high BWA and H\(_3\)PO\(_4\) content accelerated the hydrolysis of PAM to polyacrylic acid, resulting in the undesirable precipitation of NH\(_4\)\(^+\)-substituted BWA; whereas, glycerol was found to suppress this reaction. The solid CNT-graphite cells with the optimized electrolytes demonstrated a capacitance of ca. 19.5 mF cm\(^{-2}\); a high rate capability (\(\geq 75\%\) capacitance retention) at 1Vs\(^{-1}\); excellent cycle life (\(\geq 90\%\) retention of its initial capacitance); and maintained ca. -85\(^{\circ}\) phase angle over 10,000 charging-discharging cycles.
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<td>Alternating current</td>
</tr>
<tr>
<td>BWA</td>
<td>Borotungstic acid</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
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<tr>
<td>CV</td>
<td>Cyclic voltammetry / cyclic voltammogram</td>
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<td>EDLC</td>
<td>Electrochemical double-layer capacitor</td>
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<td>Resistor-capacitor</td>
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<td>R</td>
<td>Resistance (Ω) or gas constant (JK⁻¹mol⁻¹)</td>
</tr>
<tr>
<td>T</td>
<td>Temperature (K or °C)</td>
</tr>
<tr>
<td>t</td>
<td>Time (s)</td>
</tr>
<tr>
<td>U</td>
<td>Cell voltage (V)</td>
</tr>
<tr>
<td>W</td>
<td>Weight of electrolyte films (g)</td>
</tr>
<tr>
<td>Z(ω)</td>
<td>Complex impedance (Ω)</td>
</tr>
<tr>
<td>Z’</td>
<td>Real part of complex impedance (Ω)</td>
</tr>
<tr>
<td>Z”</td>
<td>Imaginary part of complex impedance (Ω)</td>
</tr>
<tr>
<td>ε₀</td>
<td>Permittivity of vacuum (Fm⁻¹)</td>
</tr>
<tr>
<td>εᵣ</td>
<td>Dielectric constant (-)</td>
</tr>
<tr>
<td>θ</td>
<td>Impedance phase shift (deg.)</td>
</tr>
<tr>
<td>π</td>
<td>Pi (-)</td>
</tr>
<tr>
<td>σ</td>
<td>Conductivity (Sm⁻¹)</td>
</tr>
<tr>
<td>ω</td>
<td>Angular frequency (rads⁻¹)</td>
</tr>
</tbody>
</table>
1.1 Demand for Energy Storage

Thin, flexible, and lightweight electronics have gained interests because of recent technological advancements [1-6]. This flexible form factor opens up a whole new dimension of design possibilities that cannot be achieved with conventional rigid electronic components. Some examples of flexible electronics are wearable devices, textile electronics, and flexible displays. These flexible and wearable electronics have potentially high market values when incorporating energy-harvesting and energy-storing capabilities.

Large scale commercialization of such devices remains challenging. One of the main limitations is the rigidity and bulkiness of the existing energy storage devices. The bulky packaging of the conventional energy storage devices not only adds to the deadweight of the electronic devices, but also precludes the flexible design aspect of wearable technologies.

Thin and flexible energy storage technologies become the key enabler for the future commercialization of most flexible electronics [7]. By replacing the conventional energy storage devices that contain liquid electrolytes, flexible energy storage devices can also eliminate potential electrolyte leakage, alleviate safety concerns, provide a thin and flexible form factor, and a higher energy density to power the wearable technologies.

1.2 Energy Storage Devices

Current commercial energy storage devices are dominated by fuel cells, batteries, flywheels, conventional capacitors, and electrochemical capacitors (ECs) [8, 9]. These devices can store different amounts of energy (energy density) and perform at different charging-discharging rates (power density) as represented in the Ragone chart in Figure 1 [10]. Their energy storage performance is summarized in Table 1 [11].

Batteries and fuel cells have high energy density and are frequently used in applications that require high energy storage capacity such as hybrid vehicles and grid energy storage [12-14]. However, they suffer from slow charging-discharging rates and a low specific power of $\leq 1 \text{ kW kg}^{-1}$ as demonstrated in Table 1. In contrast, the conventional capacitor displays a fast charging-
discharging rate, but has a limited energy density [15-17]. Therefore, conventional capacitors are often used in applications that require fast energy response such as smoothing power supplies and backup circuits for electronic devices. The goal of this thesis is to engineer an energy storage device that can achieve both a high energy density and high power density.

Figure 1: Ragone chart for various energy storage devices [10].

Table 1: Comparison of the energy storage performance for capacitor, electrochemical capacitor (EC), and battery [11].

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Capacitor</th>
<th>EC</th>
<th>Battery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific energy (W h kg⁻¹)</td>
<td>&lt; 0.1</td>
<td>1-10</td>
<td>10-100</td>
</tr>
<tr>
<td>Specific power (W kg⁻¹)</td>
<td>&gt;&gt; 10,000</td>
<td>500-10,000</td>
<td>&lt; 1,000</td>
</tr>
<tr>
<td>Discharge time</td>
<td>10⁻⁶ to 10⁻³</td>
<td>1 s to 2 min</td>
<td>0.3-3 h</td>
</tr>
<tr>
<td>Charge time</td>
<td>10⁻⁶ to 10⁻³</td>
<td>1 s to 2 min</td>
<td>1-5 h</td>
</tr>
<tr>
<td>Columbic efficiency (%)</td>
<td>ca. 100</td>
<td>85-98</td>
<td>70-85</td>
</tr>
<tr>
<td>Cycle life</td>
<td>Almost infinite</td>
<td>&gt;500,000</td>
<td>ca. 1,000</td>
</tr>
</tbody>
</table>
1.3 Electrochemical Capacitors (ECs)

Among all energy storage devices, only the electrochemical capacitor (EC) demonstrates hybrid properties by bridging the gap between batteries and conventional capacitors [18-21]. As shown in Figure 1, the EC exhibits 10-100 times higher specific energy than conventional capacitors [22, 23]. They also have longer cycle life (> 500,000 cycles) and fast charging-discharging capability (1-120s) compared to batteries [22, 24]. Due to their excellent properties, ECs can operate in either a stand-alone configuration, replace batteries, or form the battery-EC hybrid systems to provide peak assist and regenerative power in vehicles, as well as to reach high energy densities for fast-charging consumer electronics.

However, ECs have a lower energy density than batteries and require bulky packaging which adds to their deadweight. The energy density in an EC is defined by the voltage and capacitance in the following equation [25]:

$$E = \frac{1}{2}CU^2$$  \hspace{1cm} (1)

where $E = \text{energy density}$, $C = \text{capacitance}$, and $U = \text{voltage}$.

This equation is derived by integrating the voltage change in the discharge process. Therefore, to maximize energy, the capacitance and the operating voltage window are two key parameters. The power of an EC is given by:

$$P = I^2R$$  \hspace{1cm} (2)

where $P = \text{power}$, $I = \text{current}$, and $R = \text{resistance of the load}$.

The current can then be represented by the equation:

$$I = \frac{U}{r + R}$$  \hspace{1cm} (3)

where $U = \text{voltage}$, $r = \text{internal resistance of the EC}$, and $R = \text{resistance of the load}$. 
By substituting equation (3) into (2) yields:

\[ P = \frac{U^2R}{(r + R)^2} \]  

(4)

The maximum power from equation (4) can be found by taking the first differential with respect to R and setting it to zero:

\[ \frac{dP}{dR} = \frac{U^2(r + R)^2 - 2(r + R)U^2R}{(r + R)^4} = 0 \]  

(5)

Solving equation (5) yields:

\[ r = R \]  

(6)

Substituting the result in (6) back into equation (4) yields the maximum power of an EC defined by the voltage and resistance as given by equation (7) [25]:

\[ P_{\text{max}} = \frac{U^2}{4r} \]  

(7)

where \( P_{\text{max}} = \text{maximum power} \), \( U = \text{voltage} \), and \( r = \text{resistance} \).

The total resistance of the cell is a combination of resistances in the current collector, electrode material, and the electrolyte. Typically, the electrolyte is the most resistive component in a metallic cell. The power is also calculated by the energy released or restored during a charging-discharging period [25]:

\[ P = \frac{E}{t} \]  

(8)

where \( P = \text{power} \), \( E = \text{energy} \), and \( t = \text{charging or discharging period} \).
From the aforementioned equations, increasing the voltage improves the power density and energy density of the ECs, while reducing the resistance prevents losing the inherently high power density of ECs. Both the voltage and resistance are closely related to the ion movement in the electrolyte.

A conventional EC is constructed using an electrically insulating but ionically conducting separator film impregnated with a liquid electrolyte and sandwiched between two electrodes. The liquid electrolyte enables fast ion movement, thus the low resistance in liquid electrolyte helps to achieve high power density in EC devices. This thesis aims to engineer solid polymer electrolytes for ECs to replace the conventional liquid electrolytes and improve the energy density without losing the high power density of ECs.
Chapter 2
Literature Review

2.1 Solid Polymer Electrolytes (SPEs)

A typical solid polymer electrolyte (SPE) consists of a polymer host matrix, an ionic conductor, and additives. The polymer host functions as the structural support. Due to the low intrinsic conductivity of the polymer host, usually ionic conductors and additives are added to improve the electrolyte performance. SPEs not only act as an ionic conductor, but also function as the separator between the electrodes in cells or batteries. This enables SPEs to replace conventional liquid electrolytes to eliminate the occurrence of hazardous gas or corrosive solvent leakage, as well as remove the requirement for inert porous spacers to achieve thin, lightweight, and flexible designs [26-29].

SPEs also offer advantages such as high mechanical strength to withstand physical deformation to the cell. These advantages enable SPEs to have long service life and wide operating temperature range [30-33]. SPEs are easy to process and fabrication can be full automated, and configured into various geometries [33-35]. Various flexible solid ECs can be made using SPEs as shown in Figure 2. Figure 2 (a) depicts a multi-cell configuration assembled by sandwiching the polymer electrolyte between the bi-polar plates and terminal electrodes, which is favorable for compact energy storage designs. Interdigitated finger cells in Figure 2 (b) are optimal for 2D planar EC applications such as thin and flexible displays. Coaxial fiber ECs in Figure 2 (c) are highly flexible to be woven within textiles, cotton, or fabric for wearable electronics and medical monitoring devices [36].
Figure 2: Schematic of ECs based on SPEs in (a) flexible sandwiched cell configuration, (b) interdigitated finger cell configuration, and (c) coaxial fiber cell configuration [37].

The SPEs can be categorized into three types: organic-based, aqueous-based, and ionic liquid (IL)-based electrolytes as shown in Figure 3 [38]. Depending on the types of solvent, the electrochemical stability window can vary, leading to different energy densities for the ECs. Among the three categories, aqueous-based electrolytes have the narrowest electrochemical stability window limited by the water decomposition at 1.23 V [39-42]. Organic solvents have a wider decomposition potentials of 2.5 – 2.7 V [42-46], whereas the decomposition of the IL can exceed 3 V [47-51]. Using organic and IL-based electrolytes may lead to higher energy densities for ECs, but they are more expensive compared to aqueous-based electrolytes. The ionic conductivity of aqueous-based electrolytes is also the highest as compared to the organic and IL-based electrolytes.

Aqueous solvents are non-flammable, which is a valuable safety factor over organic solvents [52-54]. Aqueous solvents are also stable in air as compared to the volatile organic solvents and the ionic liquids which require inert atmosphere due to their sensitivity to moisture [55, 56]. Aqueous solvents are also relatively environmentally safe as compared to ionic liquids and organic solvents. These advantages favor aqueous-based SPEs compared to organic or IL-based SPEs for printable and flexible EC applications. Therefore, this thesis will focus only on engineering high-performing aqueous-based SPEs.
Figure 3: The different types of SPEs and the conducting species in aqueous-based SPEs.

Electrolytes with high ionic conductivities are required for high power applications. Polymers are generally non-conductive and require the addition of conducting species to increase their conductivity. The three different types of conducting species commonly added are hydroxyl ions (OH\(^-\)), proton (H\(^+\)), or a neutral salt as depicted in Figure 3.

Hydroxyl-conducting electrolyte utilizes the OH\(^-\) ion as the conducting species. OH\(^-\) ions (5.30 x 10\(^{-5}\) cm\(^2\) s\(^{-1}\)) have a lower diffusivity than H\(^+\) ions (9.31 x 10\(^{-5}\) cm\(^2\) s\(^{-1}\)) due to their larger ion size [57]. The most commonly studied OH\(^-\) conductor is potassium hydroxide (KOH) due to its wide applications in polyvinyl alcohol (PVA)-based electrolytes [58]. The KOH-PVA electrolytes can achieve high room temperature conductivities of 8-10 mS cm\(^{-1}\) as reported by Yang et al. [59] and Ma et al. [60].

Proton-conducting electrolytes are widely studied for EC applications due to their high ionic conductivity and compatibility to pseudocapacitive electrodes. Since protons or H\(^+\) ions are the smallest available ions, they demonstrate fast ion mobility for conduction. Aqueous proton-conducting electrolytes are usually polymers embedded with acids such as sulfuric acid (H\(_2\)SO\(_4\)), hydrochloric acid (HCl), or phosphoric acid (H\(_3\)PO\(_4\)). These aqueous acids can achieve high room temperature conductivity of 0.8 S cm\(^{-1}\) [61].
Neutral salts have the potential advantages of being less corrosive and a wider electrochemical stability window when compared with hydroxide and proton conducting electrolytes. This wider stability window is attributed to the local change in the pH of the neutral electrolyte near the electrode surfaces; thus achieving a higher potential window of 1.5 V as compared to the limited window of 1.2 V for proton and hydroxide conducting electrolytes [62]. However, the conductivity of neutral salts is lower than that of the proton-conducting electrolytes.

Before going forward with optimizing an SPE, it is crucial to understand the desired properties of an SPE. An ideal SPE should have the following properties:

- **Electrically insulating**: An SPE that is not electrically insulating will allow electrons to pass through the electrolyte, thus resulting in short-circuiting of the two electrode terminals, which would lead to the failure of the ECs.

- **High ionic conductivity**: An SPE with high electrolyte resistance will hinder the movement of ions for energy storage and thus impede the power performance of the ECs.

- **Large electrochemical stability window**: A small electrochemical stability window leads to limited cell voltage (U), resulting in lower energy storage (E) and maximum power ($P_{\text{max}}$) in the ECs according to equations (1) and (2). If the SPEs are pushed beyond its stability window, they may undergo O$_2$ or H$_2$ evolution. The electric charges will participate in these irreversible reactions, resulting in leakage current and degradation of the SPE after multiple charging-discharging cycles.

- **Good contact/compatibility with electrode surface**: A major disadvantage of switching from liquid to solid electrolytes was the lack of intimate contact at the electrode/electrolyte interface, resulting in high interfacial resistance. An SPE that is not compatible with the electrode can also lead to corrosion and degradation of the pseudocapacitive materials at the electrode surface.

The properties listed above are the fundamental characteristics of an ideal SPE electrolyte. For feasible commercial deployment of the SPEs, the cost, ease of fabrication, and stability should also be considered.
2.2 Charge Storage Mechanisms in ECs

To improve the performance of an EC, it is important to understand the charge storage mechanism. ECs store energy by the separation of charges in the electrolyte through electric double layer capacitance (EDLC) or pseudocapacitance.

2.2.1 Electric Double Layer Capacitance (EDLC)

Electric double layer capacitance (EDLC) utilizes reversible adsorption and desorption of solvated electrolytic ions onto the electrode surface electrostatically as shown in Figure 4 [63, 64]. The adsorbed ions will form a Helmholtz double layer at the electrode-electrolyte interface, resulting in non-faradaic energy storage.

\[ C = \frac{Q}{U} \]  (9)

where \( C \) = capacitance, \( Q \) = amount of charge stored, and \( U \) = voltage.

Figure 4: Charge separation in EDLC during a charging process.
The capacitance of an EC (unit: Farad, F) is described by the amount of charge (unit: Coulomb, C) at the surface of an electrode when a potential (unit: voltage, V) is applied across the electrodes. A typical smooth metallic electrode in a liquid electrolyte solution can achieve a double-layer capacitance of ca. 15-30 μF cm\(^{-2}\) [65]. The double layer capacitance can be calculated by:

\[
C = \frac{\varepsilon_r\varepsilon_0 A}{d}
\]

where \(C = \text{capacitance}, \varepsilon_r = \text{electrolyte dielectric constant}, \varepsilon_0 = \text{absolute permittivity of classical vacuum}, A = \text{electrode surface area}, \) and \(d = \text{effective thickness of the double layer}.

Since EDLCs rely only on electrostatic charge without charge transfer between the electrode and electrolyte, they can achieve high power performance with excellent conductivity and cycle life in the order of \(10^5\) to \(10^6\) cycles [66]. However, the transition from a conventional liquid electrolyte to SPEs results in a two to three orders of magnitude reduction in conductivity. This problem can be compensated by the ability of SPEs to form thin film configurations to reduce the effective electrolyte thickness.

### 2.2.2 Pseudocapacitance

Pseudocapacitance is another charge storage mechanism that relies on fast and reversible redox reactions on both of the electrodes as depicted in Figure 5. The faradaic redox reactions lead to charge separation of the ions in the electrode materials, resulting in multiple electron transfer process that is similar to the effect of an EDLC [67]. The overlapping redox potentials due to the electron transfer process can contribute to the pseudocapacitance, resulting in a capacitance 100 times larger than that of an EDLC.
Figure 5: Charge separation in a pseudocapacitive material through oxidation ($O_x$) and reduction ($R_{ed}$) reactions.

The mechanism of the pseudocapacitance depends on the potentials of the faradaic fast redox reaction of the 1-2 monolayers of surface materials on the electrodes. This implies that the redox properties of the electrode materials have large influence on the pseudocapacitive behavior of the EC. Ideally, the redox reactions of the electrode materials should have multiple overlapping oxidation states that have evenly distributed potentials to allow for a stable current flow during the charging and discharging of the EC. For instance, ruthenium dioxide ($RuO_2$) is a near ideal pseudocapacitive material which has evenly distributed redox potentials that results in an almost rectangular capacitance profile as shown in Figure 6 [68, 69].

Figure 6: Pseudocapacitive profile of ruthenium dioxide, depicting the evenly distributed redox potentials when subjected to incremental voltage scan [68].
Previous work demonstrated that this ideal rectangular profile can be also achieved by using conducting polymers such as polypyrrole (PPy) and polyaniline (Pani) which store charges in the bulk through redox reactions [70, 71]. Conducting polymers suffer from low power because of their slow bulk ionic diffusion [72]. Oxides, such as manganese oxide (MnO₂), are also widely used as pseudocapacitive materials because of its low cost and low toxicity [73, 74].

Adsorption of protons from the electrolyte is required for these pseudocapacitive reactions [75]. Proton-conducting SPEs are especially promising as they tend to have high ionic conductivity and contribute many protons during their self-dissociation to the faradaic redox reactions on the pseudocapacitive electrode surfaces [76-78]:

\[
\text{RuO}_2 + x\text{H}^+ + xe^- \leftrightarrow \text{RuO}_{2-x}(\text{OH})_x
\]

\[
H_x\text{MnO}_2 \leftrightarrow \text{MnO}_2 + x\text{H}^+ + xe^-
\]

\[
\text{Pani}_{\text{red}} + n\text{A}^- + n\text{H}^+ \leftrightarrow \text{Pani}_{\text{ox}} + ne^-
\]

where \( A = \text{anion from the electrolyte}. \)

Therefore, proton conducting SPEs are versatile materials that can be used in applications for both EDLC and pseudocapacitive ECs to store more energy. Other than energy density, another property of interest as mentioned in Chapter 1 is the power density of the ECs, which is heavily depended on the ion conduction in the SPEs.

### 2.3 Proton conduction mechanisms in SPEs

Ionic conductivity is a crucial characteristic for high-power applications. Therefore, it is important to understand the mechanism in which ion conduction occurs within an SPE system. The three distinct mechanisms for ion conduction in SPEs based on an aqueous system are displayed in Figure 7.
Figure 7: Ionic conduction mechanisms in polymer electrolytes: (a) ion hopping, (b) vehicular diffusion, and (c) segmental motion [37].

The specific description for each proton conduction mechanism is as follows:

**a) Ions hopping/Grotthuss mechanism**

The kinetics of hydrogen bond formation or bond breaking between a proton and a water molecule or other hydrogen-bonded liquids determine the ion mobility [79, 80]. Due to hydrogen-bonding, protons can exist at various states of H$_2$O$_2^+$, H$_7$O$_3^+$, or H$_6$O$_4^+$ which allows it to jump across different water molecules in the polymer matrix through the hydrolyzed ionic site as seen in Figure 7 (a) [81]. Site-to-site hopping requires local rearrangement and reorientation of molecules involving two potential wells separated by a barrier of only a few kJ mol$^{-1}$: the proton donor and the proton acceptor, respectively [82, 83]. Therefore, the Grotthuss mechanism is prominent in a system with many hydrogen bonding because of the low activation energy (typically under 15 kJ mol$^{-1}$) for conduction and the high proton mobility in this mechanism [84-86].
b) Vehicular diffusion mechanism

A proton can bond with the solvent molecules (e.g. water) to form a solvated complex that diffuses across the polymer matrix as in Figure 7 (b) [87, 88]. The diffusion process 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 (typically above 20 kJ mol⁻¹) and lower proton mobility [85, 86, 89].

c) Segmental motion mechanism

The ion moves together with the polymer side chains as shown in Figure 7 (c) [90, 91]. During the polymer chains movement, the polymer chain conformation changes and alters the bonding distance between the cation and the side chain. When a neighboring side chain becomes sufficiently close to the cation, it possesses sufficient attraction such that the cation can move from one side chain to the neighboring side chain. This mechanism is highly dependent on the flexibility for polymer matrix motion or vibration to reduce or eliminate the distance for proton conduction. Thus, this type of proton transportation is restricted to the amorphous phase of the solvating polymers, where the polymer molecules are free to move and as such become more prominent at temperature above the polymer glass transition temperature (T_g) of the polymer.

The understanding of the proton conduction mechanism enables researchers to better engineer different SPE systems. The previous work on different proton-conducting SPEs are discussed in the next section.
2.4 Polymer hosts

Proton conduction in SPEs relies heavily on the properties of the polymer hosts to remain amorphous, flexible, and have sufficient water retention capability to facilitate ion migration. Therefore, the selection of suitable polymer hosts for proton-conducting SPEs is essential for solid EC applications.

Wright et al. were the first group to attempt research in SPEs in 1975 [92, 93]. Armand et al. proposed the technological application of SPEs in batteries and electrochemical devices [92, 94]. The “dry solid” polymer electrolyte was later introduced as a solvent-free system without using the organic liquid [95]. This SPE demonstrated poor conductivity at room temperature. Thereafter, researches had been carried out to investigate various types of polymers for solid EC applications. The molecular structure, properties, and applications of previously studied polymer hosts are summarized in Table 2.

The benchmark materials for SPEs in energy storage application is perfluorosulfonic acid (PFSA) ionomers [96], which is often referred to as Nafion®. Due to the hydrophobic polytetrafluoroethylene (PTFE) backbone, PFSA exhibits high chemical resistance and compatibility with various pseudocapacitive electrode materials. The hydrophilic property of the terminal sulfonic acid (-SO₃H) group enables the dissociation of protons and facilitates hydrated proton mobility through Grotthuss and vehicle mechanism [97-99]. The -SO₃H groups can only bond to water molecules loosely, causing the film to lose water rapidly at low RH conditions [100]. Thus, proton conduction of Nafion relies heavily on the hydration state of the electrolyte.

Although PFSA solid electrolyte is highly conductive at high temperatures and RH conditions, its proton conductivity drops significantly at room temperature [101, 102]. Yongheng et al. has impregnated phosphoric acid organic framework into the Nafion and achieved higher conductivity (ca. 60 mS cm⁻¹ at 51% RH and 80°C) than the unmodified Nafion [103]. Similarly, Rafael et al. pretreated Nafion with hydrochloric acid and achieved 23.8% higher conductivity than untreated Nafion at 40% RH [99]. Other modifications to Nafion include hygroscopic materials such as inorganic oxides particles [104-107], clays [108-110], conductive polymers [111-113], and solid acids [114-116]. The preparation of Nafion® involves environmentally hazardous fluorine-based technologies [117-119]. Therefore, the commercial deployment of Nafion-based ECs is unfavorable due to environmental concerns.
Table 2: Summary of different polymer hosts for EC applications.

<table>
<thead>
<tr>
<th>Polymer type</th>
<th>Molecular structure</th>
<th>Monomer Mw (gmol⁻¹)</th>
<th>Tg (°C)</th>
<th>Properties</th>
<th>Advantages</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfluorosulfonic acid [PFSA]</td>
<td></td>
<td>544.14</td>
<td>100</td>
<td>Amorphous</td>
<td>• High chemical stability</td>
<td>• Polymer electrolyte for fuel cell</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• High thermal stability</td>
<td>• Ion-selective sensors</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Highly permeable to water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sulfonated poly(ether ether ketone) [SPEEK]</td>
<td></td>
<td>288.30</td>
<td>214</td>
<td>Amorphous</td>
<td>• High mechanical strength</td>
<td>• Fuel cell proton exchange membrane</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• High thermal stability</td>
<td>• High temperature shape memory</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Low cost</td>
<td>application</td>
<td></td>
</tr>
<tr>
<td>Poly(ethylene oxide)/Poly(ethylene glycol) [PEO/PEG]</td>
<td></td>
<td>44.05</td>
<td>-67</td>
<td>Semi-crystalline</td>
<td>• Structural integrity</td>
<td>• Drug delivery</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Biocompatible</td>
<td>• Biocompatible</td>
<td>• Solid electrolyte for electrochemical devices</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Low Glass transition</td>
<td>• Low Glass transition</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Structural integrity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly(vinyl pyrrolidone) [PVP]</td>
<td></td>
<td>111.14</td>
<td>180</td>
<td>Amorphous</td>
<td>• Water soluble</td>
<td>• Binder in pharmaceutical tablets</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Good adhesion</td>
<td>• Food additives</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Excellent film forming</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly(acrylic acid) [PAA]</td>
<td></td>
<td>72.06</td>
<td>106</td>
<td>Amorphous</td>
<td>• Water soluble</td>
<td>• Thickening agent for adhesives</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Hygroscopic</td>
<td>• Micellar drug delivery</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Excellent film forming</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyvinyl alcohol [PVA]</td>
<td></td>
<td>44.05</td>
<td>85</td>
<td>Semi-crystalline</td>
<td>• Water soluble</td>
<td>• Film for water transfer printing</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Excellent film forming</td>
<td>• Water-soluble film for packaging</td>
<td>process</td>
</tr>
<tr>
<td>Poly(acryl amide) [PAM]</td>
<td></td>
<td>71.08</td>
<td>165</td>
<td>Amorphous</td>
<td>• Water soluble</td>
<td>• Medium for electrophoresis</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Hygroscopic</td>
<td>• Absorbent in water treatment</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Excellent film forming</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly(acrylamide-co-acrylic acid) [P(AM-co-AA)]</td>
<td></td>
<td>143.14</td>
<td>177</td>
<td>Amorphous</td>
<td>• Water soluble</td>
<td>• Polymer electrolyte for insulin</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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Non-perfluorinated polymers were also good candidates for SPE applications. They have hydrocarbon backbones with various combinations of benzene rings or aromatic heterocyclic rings. These combinations enable different functionalization (i.e. introduction of polar sites) through doping, chemical grafting, or direct sulfonation to increase proton conductivity and water uptake [120]. Recently, sulfonation of non-perfluorinated polymers were widely investigated for energy storage applications, especially sulfonated poly(ether ether ketone) (SPEEK) [121-124].

Although sulfonation slightly decreases the chemical resistance of SPEEK, the SPEEK materials still exhibit excellent chemical resistance due to the higher C-H bond strength in the benzene ring compared with aliphatic C-H bond strengths [122, 125]. Other advantages of these materials include low cost, excellent chemical resistance, and good mechanical properties [122], but their overall performance is still inferior to Nafion. Application of the SPEEK family to ECs is still limited to proton exchange membrane in fuel cells or direct methanol fuel cells because of their higher temperature stability. Currently, only SPEEKK and SPEEK have been used for ECs applications due to their higher conductivity at low temperature.

Poly(ethylene oxide) (PEO) is a synthetic polyether commonly known as poly(ethylene glycol) (PEG) at a molecular weight less than 100,000 g mol⁻¹. The PEO polymers are amphiphilic and soluble in many solvents. They are also nontoxic for different pharmaceutical, food, and cosmetic formulations [126]. Due to these benefits, it is one of the earliest polymer matrix developed and most utilized for polymer electrolytes development and fundamental understanding of conductivity [94, 127]. In 1975, Wright et al. developed PEO-Na⁺ complex with conductivity of 10⁻⁷ S cm⁻¹ [93]. Thereafter, PEO has been mixed with various type of materials such as ionic liquids, salts, plasticizers, and fillers to enhance its conductivity close to 10⁻³ S cm⁻¹ [127]. These promising characteristics enabled PEO for high power ECs applications.

The linear nature of PEO also leads to semi-crystalline properties for PEO because the linear main chains can easily fold upon each other to create crystalline regions. The intrinsic crystallinity of PEO remains to be a challenge for PEO based polymer electrolytes. Therefore, the limitations of PEO due to its semi-crystalline properties were documented by Armand, which redirected the research attention into other amorphous polymer electrolyte systems [128].
Poly(vinyl pyrrolidone) (PVP) is an inexpensive amorphous polymer with a high glass transition temperature due to the pyrrolidone group [129, 130]. PVP is also non-toxic, biocompatible, and is readily soluble in polar solvents, which is ideal for fast printable SPEs fabrication methods such as ink jet printing. Due to the extremely low intrinsic conductivity of PVP at $10^{-8}$ mS cm$^{-1}$ at room temperature, sodium chlorite and sodium nitrite were added as the ionic conductors to enhance the conductivity to $10^{-4}$ mS cm$^{-1}$ [131, 132]. Vijaya et al. also developed PVP doped with ammonium iodide and achieved ca. $10^{-2}$ mS cm$^{-1}$ at ambient conditions [133].

Ravi et al. modified a PVP electrolyte with nano-TiO$_2$ fillers and successfully demonstrated conductivity of ca. 1 mS cm$^{-1}$ at room conditions [130]. However, PVP is very sensitive to the humidity because it was reported as the best candidate material for use in the application of a humidity sensor combined with iodine and cobalt [134]. This implies that the water retention capability of PVP is poor. Therefore, there is an interest to explore other hygroscopic polymer electrolytes for ECs applications.

Poly(acrylic acid) (PAA) is a polyelectrolyte that can readily absorb water as it was first used in diapers in 1982 [135-138]. Some other frequent applications of PAA include superabsorbent, coagulating agents, and hydrophilic adhesives [19]. Its bulky carboxylic acid functional group hinders the chains from packing, thus resulting in amorphous properties. The proton on the side chain also enables PAA to become hydrophilic and adhesive [139].

The weakly acidic PAA carboxylic groups can be hydrolyzed to release proton, thus, promoting proton conduction in polymer electrolytes. A gel electrolyte consisting of PAA and 1M H$_2$SO$_4$ exhibited high conductivity [37]. Complexation can occur upon mixing PAA with other ions that changes the physical properties of the PAA solution such as a reduction in viscosity [140]. Through polymer blending, PAA and poly(1-vinyl-imidazole) formed networks that showed high temperature resistance [141]. PVA/PAA blend also demonstrated that PAA can retain more water and increase the conductivity up to five times compared to PAA alone [142].

The research of PAA-based SPEs is still in its infancy. The PAA carboxylic groups can form radicals for crosslinking through UV radiation without a photo initiator [143]. This can enhance the mechanical stability [144], as well as improving its water retention and structural flexibility that PEO lacks. Many possibilities are yet to be discovered with uses of PAA as SPEs for EC applications.
2.4.1 Polyvinyl alcohol

Polyvinyl alcohol (PVA) is a very promising candidate for SPE applications. PVA is hygroscopic due to the hydroxyl functional group in its structure (see Figure 8). The small hydroxyl functional group also allows PVA to pack efficiently in zig-zag confirmation and form crystalline regions through hydrogen bonding between its hydroxyl groups; thus, exhibiting semi-crystalline properties [136].

![Figure 8: Structure of a PVA.](image)

PVA also has advantages such as high chemical resistance, non-toxic, water soluble, and biodegradable properties which enabled its frequent use in various applications, including adhesives, textiles, pharmaceutical, and biomedical industries [145]. PVA has also been widely studied for both Li-ion batteries and ECs owing to its good film formability and ease of forming gel or hydrogel for the electrolytes.

PVA was first investigated as a separator material for batteries in the field of electrochemical energy storage [146]. PVA were first developed as proton conductors with H₃PO₄ for hydrogen sensor applications by Polak et al. [147]. The PVA-H₃PO₄ polymer electrolyte was reported to have a conductivity of 3 x 10⁻² mS cm⁻¹ at room temperature [147]. The complexation between the acid and the polymer led to an increase in conducting species and the plasticizing effect of H₃PO₄ on PVA can enhance the conductivity to 1 mS cm⁻¹ [148]. Thus, PVA is suitable polymer with acids and form complexes that facilitate proton conduction.

Due to the demand for energy storage, PVA based polymer electrolytes were explored for EC applications and first patented by Lian et al. [149]. Kaempgen et al. demonstrated printable thin film EDLCs with single-wall carbon nanotubes (SWCNT) as electrodes [150] and El-Kady et al. used the same polymer electrolyte with graphene [151]. Both work demonstrated improved capacitance compared to an aqueous electrolyte.
Other than H₃PO₄, strong acid such as H₂SO₄ are also frequently used in PVA polymer electrolytes. It was demonstrated in a solid device with 3D graphene hydrogel electrolytes and exhibited comparable stability and lower leakage current compared to the 1M H₂SO₄ liquid device [85]. Fei et al. also demonstrated PVA-H₂SO₄ flexible devices with graphene-carbon black electrodes [152]. Recent efforts have involved the research into PVA-ionic liquid (IL) blends which show improved performance [153], as well as crosslinked PVA with sulfosuccinic acid to improve the conductivity to the range of 10⁻³ to 10⁻² S cm⁻¹ [154].

Since PVA is hydrophilic, the water content is highly influential in the mobility of ions. At the same time, this hydrophilic nature caused rapid changes in physical properties of PVA with RH because the absorbed water acts as a plasticizer for the polymer. This change in physical properties can be a potential issue in terms of the environmental stability of PVA electrolytes. These properties caused PVA solid electrolyte to suffer from poor mechanical properties and were susceptible to hydrolysis in water [155].

2.4.2 Polyacrylamide

In recent years, polyacrylamide (PAM) caught the attention of researchers for applications in ECs. This is due to the beneficial properties of PAM such as the higher water retention capability of PAM compared to PVA [156]. PAM has an amide functional group (see Figure 9) which helps in forming hydrogen bonding with water; thus, improving its water retention capability. Due to the bulky functional group, the chain alignment results in an amorphous structure. PAM also has an excellent film-forming capability. These features enabled its deployment in fuel cell electrolytes, absorbents for waste treatment, and moisture storage for soils [157-159].

![Figure 9: Structure of a PAM.](image-url)
In the field of energy storage, PAM-based electrolytes are widely used in fuel cell systems such as borohydride fuel cells and direct methanol fuel cell applications. Sumathi et al. demonstrated that hydrogel electrolytes consisting of PAM mixed with paratoluenesulfonic monohydrate acid and methane sulfonic acid showed a good conductivity around $10^{-2} \text{ S cm}^{-1}$ to $10^{-1} \text{ S cm}^{-1}$ at ambient conditions in batteries [160]. The increased conductivity was attributed to the higher amount of mobile $\text{H}^+$ ions from the acids.

Most of the reported work on proton-conducting SPEs consisted of PAM with either sulfuric acid ($\text{H}_2\text{SO}_4$) or phosphoric acid ($\text{H}_3\text{PO}_4$) additions for enhancing conductivity [161-165]. Wieczorek et al. compared the proton transport for PAM doped with $\text{H}_3\text{PO}_4$ and $\text{H}_2\text{SO}_4$. Doping PAM with these acids exhibit similar room temperature conductivity that increased to *ca.* 20 mS cm$^{-1}$ at 1.6:1 acid/acyr bil amide monomer ratio and reached a plateau at higher acid concentration as shown in Figure 10 [165].

![Figure 10: Room temperature conductivity as a function of acid/AM molar ratio for PAM gel electrolyte (40 vol% water) embedded with $\text{H}_3\text{PO}_4$ and $\text{H}_2\text{SO}_4$ [165].](image-url)
Tang et al. embedded H₃PO₄ into 3D crosslinked PAM network for proton exchange membrane [161]. The hydrophilic nature of PAM and the 3D framework enabled H₃PO₄ to be absorbed and retained in the membrane. At anhydrous state, the conductivity of H₃PO₄-PAM membrane increased with higher H₃PO₄ loading as shown in Figure 11 (a). A sudden increase in conductivity at ca. 60 wt% H₃PO₄ was attributed to the formation of percolation proton-conducting pathways. This H₃PO₄-PAM membrane can achieve 0.65 mS cm⁻¹ at 75.9 wt% H₃PO₄ loading in anhydrous state. Tang et al. also discovered that this conductivity can be further improved with H₂O absorption in the membrane, reaching a maximum of 73.3 mS cm⁻¹ in fully hydrated state (329% swelling volume ratio) as shown in Figure 11 (b). The conductivity of PAM membrane was highly dependent of the relative humidity of the electrolyte [161].

![Figure 11: Room temperature conductivity of 3D crosslinked PAM embedded with H₃PO₄ (a) as a function of H₃PO₄ loading in anhydrous state; and (b) as a function of swelling volume ratio from H₂O uptake [161].](image)

Rodriguez et al. also investigated the anhydrous PAM blended with H₃PO₄, focusing on the acid-PAM interaction and their compatibility [163]. H₃PO₄ is not strong enough to protonate PAM, but interact with the acrylamide functional groups via hydrogen bonding as follows [163]:

![Chemical structure](image)
This resulted in anhydrous H$_3$PO$_4$-PAM electrolyte to be relatively more stable from acid hydrolysis as compared to stronger acids such as HCl and H$_2$SO$_4$ [163]. Figure 12 (a) and (b) revealed the composition dependence of the conductivity for the H$_3$PO$_4$-PAM electrolyte. Rodriguez et al. reported in Figure 12 (a) that at low H$_3$PO$_4$ content, the active protons were isolated and cannot form connection. Further addition of H$_3$PO$_4$ result in percolation to form the conduction pathway, reaching a maximum of 260 mS cm$^{-1}$ at ca. 45 wt% H$_3$PO$_4$ due to extensive self-ionization in water. Figure 12 (b) showed that adding PAM resulted in reduction in the conductivity, but the slope of this variation was lower than any other polymer investigated [163]. This implies that acid-embedded PAM can be a good candidate for proton-conducting SPEs.

Figure 12: Room temperature conductivity of (a) H$_3$PO$_4$/H$_2$O system and (b) H$_3$PO$_4$/PAM system as a function of wt% H$_3$PO$_4$ [163].

Apart from the linear configuration of PAM, PAM copolymers with PAA (PAM-co-PAA) are also known for good water absorption due to the two hydrophilic COOH and NH$_2$ groups. The carboxylic group of PAA may link with the acryl amide group of PAM through hydrogen bonding [166, 167]. This property enables PAM-co-PAA to retain water efficiently for its applications in superabsorbent as well as drug delivery system [168, 169]. However, the applications of PAM-co-PAA in ECs have not been studied.

This thesis will focus on PAM as the polymer host for the SPE system. Since PAM is intrinsically not very conductive, proton conductors will be added into the polymer host to form an electrolyte matrix to improve its conductivity. The next section will discuss the selection of the proton conductors to be used with PAM to formulate the electrolyte system.
2.5 Keggin-type heteropolyacids

The utilization of liquid acids can achieve high conductivity, but the resulting electrolyte system may suffer from issues of leakage over time. Recently, the utilization of solid proton conductor was demonstrated to have high ionic conductivity. The most promising solid proton conductors are Keggin-type heteropolyacids (HPAs) [170-172]. These hydrous acids are metal-oxide clusters of early transition metals formulated as $H_2[MX_{12}O_{40}]$, where $z$ is the charge of the anion, $M$ is the heteroatom, and $X$ is the addenda atom as shown in Figure 13 (a) [173, 174].

The heteroatom $M$ forms an internal tetrahedron unit ($MO_4^-$) with four oxygen atoms ($O_a$) [175, 176]. This tetrahedron unit is surrounded by a cage of twelve $XO_6$ octahedral units. Three $XO_6$ octahedral units can link together to form $X_3O_{13}$ structural unit through sharing edges. Four of these $X_3O_{13}$ structural units will share corner oxygen to form the cage that encapsulates the internal tetrahedron unit through oxygen bonds to form the Keggin-type spherical structure. Figure 13 (b) indicates the four different types of oxygen atoms in the Keggin-type HPAs: tetrahedral oxygen ($MO_4$), edge-sharing oxygen ($O_b$), corner-sharing oxygen ($O_c$), and terminal oxygen ($O_d$) [86].

![Figure 13: (a) Ball-and-stick view of heteropolyacids with the Keggin-type structure, and (b) polyhedral representation of the Keggin structure showing the central tetrahedron ($MO_4$); the terminal oxygen atoms of each $X_3O_{13}$ group ($X-O_d$); the bridging bonds between edge-sharing oxygen atoms ($X-O_e-X$); and corner-sharing octahedra ($X-O_b-X$). [177, 178.](image)
The heteroatom can be P\(^{5+}\), Si\(^{4+}\), Ge\(^{4+}\), and B\(^{3+}\); while the most common addenda atoms include W\(^{6+}\), Mo\(^{6+}\), and V\(^{5+}\) [179, 180]. The two commonly used commercial Keggin-type HPAs are silicotungstic acid (SiWA, H\(_4\)SiW\(_{12}\)O\(_{40}\)) and phosphotungstic acid (PWA, H\(_3\)PW\(_{12}\)O\(_{40}\)).

The Keggin-type HPAs exhibit high proton conductivity at room temperature as inorganic solid proton conductors due to the large number of crystallized water molecules in the crystal hydrate. Its hygroscopic nature also allows high water absorption and leads to a “quasi-liquid” state [181-183]. 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 many crystallized water molecules in the crystal hydrate (e.g. SiWA•nH\(_2\)O), leading to “quasi-liquid” states that facilitate fast proton transport [184-186]. The protons (i.e. both intrinsic and dissociated protons), in the forms of H\(^+\)-nH\(_2\)O clusters (e.g. H\(_3\)O\(^+\) or H\(_5\)O\(_2\)\(^+\)), are transferred by hopping from H\(^+\)-nH\(_2\)O donor sites to nH\(_2\)O acceptors in the HPA, yielding a high proton conductivity in the solid-state (27 mS cm\(^{-1}\) for SiWA•28H\(_2\)O) [187].

HPAs are strong acids and all intrinsic protons of Keggin-type HPAs dissociate equally in aqueous solution. Their high ionic conductivity in aqueous solutions results 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 because of their un-solvated nature, in which its hydrodynamic radius is similar to its crystallographic radius.

The reduction potential of HPAs are dependent on the chemistry of molecule. These potentials are linearly related to the charge carried by the anions as shown in Figure 14 [179, 180]. When the heteroatom is replaced with another element, the reduction potential decreases with the valence of the central heteroatom, indicating their strong dependence on the Keggin structure.

The trend in Figure 14 is only an indication as there are other reactions (e.g. hydrogen evolution reaction) that can complicate the situation. Nevertheless, the redox reactions of W-based HPAs occur at more negative potentials compared to the Mo- or V-based HPAs; thus, the electrochemical inactive window is wider. The wider electrochemical inactive window ensures that no current leakage occurs within that range due to the reduction of the HPAs, which is an important characteristic of an ideal electrolyte.
Figure 14: The trend of reduction potential is shifted in a predictable manner with respect to the different anion charge for various heteroatom in HPAs [188].

2.6 Polymer-in-salt electrolytes

The polymer hosts are usually added with inorganic proton conductors to improve its conductivity for SPE applications. Depending on the proton-conducting species content in the polymer, this inorganic/polymer proton-conducting electrolytes can be further divided into two subgroups: (a) salt-in-polymer or (b) polymer-in-salt, as shown in Figure 15 [189].
Salt-in-polymer electrolytes are prepared by dispersing small amount of acids, bases, or salts in a polymer. Most salt-in-polymer electrolytes are aqueous-based polymers, such as poly(ethylene oxide) (PEO), poly(acrylonitrile) (PAN), or poly(methylmethacrylate) (PMMA), forming acid/polymer blends or acidic hydrogels with liquid acids (such as H$_2$SO$_4$ or H$_3$PO$_4$) because of their self-ionization and self-dehydration reactions in their pure states [190].

$$6\text{H}_2\text{SO}_4 \leftrightarrow \text{H}_3\text{SO}_4^+ + \text{H}_3\text{O}^+ + \text{HSO}_4^- + \text{HS}_2\text{O}_7^- + \text{H}_2\text{S}_2\text{O}_7^- + \text{H}_2\text{O} \quad (14)$$

$$5\text{H}_3\text{PO}_4 \leftrightarrow 2\text{H}_4\text{PO}_4^+ + \text{H}_3\text{O}^+ + \text{H}_2\text{PO}_4^+ + \text{H}_2\text{P}_2\text{O}_7^{2-} \quad (15)$$

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 formation. At high conductor concentration, the individual conductor clusters will interconnect to form a percolation pathway for ion conduction as shown in Figure 15. Most of the proton conductors have water molecules embedded in the structure (e.g. crystallized water in hydrous acids), which enable polymer-in-salt electrolytes to have much higher water retention capability compared to the loosely bound or free water in salt-in-polymer electrolytes. The crystallized water on the solid proton conductors can facilitate high conductivity for polymer-in-salt configurations.
2.6.1 Heteropolyacid-based membranes

The development of HPAs in SPEs for EC applications gained momentum in recent years. Li et al., Lei et al., Lian et al., and Xu et al. separately developed PVA-phosphotungstic acid (PWA) electrolytes which demonstrated high conductivity values [191-194]. PWA-based solid electrolytes for EC applications were patented by Li et al. [195, 196]. The PWA is reported to have high leakage current, thus research has focused on other HPA chemistries for EC applications [197]. Other HPA-based electrolytes have also been widely studied in PVA-based systems because of the high water retention ability of PVA which facilitates high ionic conductivity and better environmental stability.

Silicotungstic acid (H₄SiW₁₂O₄₀, SiWA) has been studied intensively by Gao et al. for both aqueous and polymer electrolytes [173, 198-200]. SiWA is one of many Keggin-type heteropolyacids, acid with huge cluster of metal oxides as its anions. The anion consists of one central heteroatom (Si) surrounded with 12 addenda atoms (W), the anion is illustrated in Figure 13. It has previously been demonstrated to be a highly promising electrolyte both as aqueous and polymer electrolytes. Performance optimization of SiWA-PVA polymer electrolytes by crosslinking and use of fillers has raised the conductivity up to the range of 10 mS cm⁻¹ to 20 mS cm⁻¹ with stable performance at different humidity conditions. The SiWA-PVA solid electrolytes were also demonstrated to be compatible with pseudocapacitive electrodes [201].

Recently, Gao et al. impregnated a crosslinked polyvinyl alcohol (XLPVA) polymer electrolyte with borotungstic acid (BWA, H₅BW₁₂O₄₀) to form BWA-XLPVA solid electrolyte [202]. In a three electrode setup, BWA demonstrated 0.2 V larger electrochemical stability window than SiWA as shown in Figure 16 (a) and (b), agreeing with the trend in Figure 14. The capacitor cell with BWA-XLPVA can achieve a larger maximum cell voltage of 1.3 V as shown in Figure 16 (c) than the 1.1 V of SiWA (Figure 16 (d)). Figure 16 (e) and (f) reveals that the BWA cell voltage is limited by oxygen evolution at the positive voltage of 0.7 V and tungsten reduction in BWA at the negative potential of -0.6 V. The larger cell voltage (U) allowed BWA-XLPVA capacitor cell to have higher energy and power performance according to equations (1) and (2).
The capacitor cells fabricated from BWA-XLPVA electrolyte also achieved a high conductivity of 13 mS cm\(^{-1}\) at 45% RH and 20 °C as shown in Figure 17 [202], similar to SiWA-XLPVA. The high conductivity values were attributed to the large number of crystallized water molecules in BWA and SiWA. The performance of these HPA-based capacitor cells still suffered from dehydration. Thus, it is necessary to leverage a highly hygroscopic polymer such as PAM combined with a suitable HPA to further improve these solid polymer electrolytes.
Even though Figure 14 shows that HPAs with cobalt (CoWA) and copper (CuWA) heteroatoms can theoretically achieve even wider voltage window than BWA for better energy storage performance, the copper and cobalt heteroatoms have their own redox potential Cu+/Cu²⁺ and Co+/Co²⁺ which limits the voltage window. Thus, this thesis will focus on BWA as the proton conductor in the SPEs.

2.7 Additives for polymer-in-salt electrolytes

Additives are sometimes used in polymer electrolytes to further enhance its electrochemical properties (e.g. improving ionic conduction) as well as improving the environment stability of the SPEs. Previous work on various plasticizers such as tetraglyme, ethylene glycol (EG), dimethyl formamide (DMF), and propylene carbonate (PC) demonstrated that plasticized
electrolytes such as urethane crosslinked polyethers, polymethylmethacrylate, and poly(2-hydroxyethylacrylate) can achieve 1-2 orders of magnitude higher conductivity while a decrease of Tg by 40 °C [203, 204].

A common additive in polymer electrolytes are plasticizers which are small molecules that increase polymer flexibility to ease segmental motion, as well as acting as the solvent that ease ion diffusion – both of which can improve conductivity of the electrolyte. The plasticizers can be categorized into acidic plasticizers and neutral plasticizers. The acidic plasticizers and neutral plasticizers will be discussed in the following section.

2.7.1 Acidic plasticizers

Acidic plasticizers are commonly used in proton-conducting polymer electrolytes because of their intrinsic conductivity. The proton dissociation from the plasticizers can help in providing more conducting species for higher conductivity in the electrolyte system. Some common examples of acidic plasticizers are strong acids such as phosphoric acid and sulfuric acid [205].

In the past, phosphoric acid (H₃PO₄) has been widely used as a plasticizer in proton-conducting SPEs [148, 206]. In these studies, the H₃PO₄-doped electrolyte system employed basic polymers such as PEO, polyvinyl acetate (PVAc), polyacrylamide (PAM), and polyethyleneimine (PEI) as the polymer hosts [207-210]. The extensive self-ionization of H₃PO₄ can result in 53 mS cm⁻¹ conductivity near room temperature.

The conductivity can be increased to a maximum of 0.27 S cm⁻¹ with 45 wt% acid due to the decrease in viscosity and water facilitation in the acid dissociation. Further increase in water will dilute the acid and decreases the number of charge carriers more rapidly [205]. High H₃PO₄ plasticizer concentrations will result in higher conductivity at the expense of sacrificing the mechanical stability of the polymer electrolytes due to the acid attack on some of the polymers, especially at high temperatures.

Sulfuric acid (H₂SO₄) modified PAM has comparable room conductivity (ca. 20 mS cm⁻¹) to H₃PO₄, except that H₂SO₄ is generally more acidic and has higher oxidizing properties which result in faster degradation of PAM polymer by H₂SO₄ [163, 165]. A better chemical stability can be achieved by utilizing highly thermostable polymers including polyimides, poly(ether ketones) (PEK) or poly(ether sulfones) (PES).
2.7.2 Neutral plasticizers

Neutral plasticizers are another alternative to avoid acid degradation of polymers. Similar to acidic plasticizers, neutral plasticizers can act as the solvent for the ionic conductors and soften the polymer chains. The neutral plasticizers also have functional groups that facilitate hydrogen bonding with water molecules; thus, enhancing the hygroscopic properties of the polymer electrolytes. Typical neutral plasticizers include glycerol and ethylene glycol.

Glycerol is a simple polyol compound that is non-toxic, which enabled its widespread deployment in food and pharmaceutical applications. It has three hydroxyl functional groups that help in its solubility in water and hygroscopic nature. Due to its hygroscopic nature, glycerol is often used both in sample preparation and gel formation for polyacrylamide gel electrophoresis.

Alves et al. demonstrated that glycerol promotes higher conductivity in chitosan-based polymer electrolytes because glycerol contributes to inefficient polymer chain packing and allow more chain flexibility that results in an improvement of the ionic transport [211]. Adding too much glycerol will result in adverse effects such that the solutions become too viscous to be handled properly due to the hydrophilic functional groups that bind with the water molecules [212]. Further addition of glycerol can lead to phase separation of the polymer and glycerol [211].

Similar to glycerol, ethylene glycol (EG) can also improve the polymer adhesion as well as the polymer water retention from its hydrophilic characteristics. EG is a smaller molecule than glycerol, which may require more EG quantity to achieve the same plasticizing effect as glycerol [213]. Therefore, this thesis will be focusing on using glycerol as the neutral plasticizers for the proton-conducting SPEs.
Chapter 3
Research Plan

3.1 Motivation

The literature review reported PAM as a promising candidate for SPEs due to its film-forming capability, as well as its hygroscopic nature and amorphous structure that enhance conductivity for fast-charging EC applications. The low intrinsic conductivity of PAM can be improved by adding proton conductors, especially Keggin-type HPAs such as BWA due to their high solid-state conductivity. To date, HPA-based SPEs are only demonstrated in PVA system, and the compatibility of HPAs in PAM have not been studied. Due to the lack in the research on the HPA-based PAM solid electrolyte, some gaps in previous research work were identified and listed below. This project aims to address those gaps and develop high-performing SPEs for flexible solid EC devices modified with plasticizers which exhibit the following properties:

a) **Wide electrochemical stability window for maximum cell voltage for higher energy;**

   This project will continue to use BWA as the ionic conductor due to their wide stability window. Focus will be placed on addressing the lack of characterization of the compatibility of PAM and BWA as SPEs.

b) **High ionic conductivity for high power;**

   The electrochemical performance of BWA-PAM electrolyte has not been studied. Focus will be placed on optimizing the BWA composition in PAM to achieve high ionic conductivity. The effects of acidic and neutral plasticizers on the conductivity of BWA-PAM electrolyte will be addressed.

c) **High environmental stability for long service life.**

   The stability of BWA-PAM + plasticizer electrolytes in EC applications have not been investigated. Focus will be placed on analyzing the cycle life of the capacitor cell fabricated with BWA-PAM + plasticizer electrolytes.
3.2 Experimental Design

The research objective can be achieved systematically by focusing on the aforementioned attributes to develop BWA-PAM based polymer electrolytes and to understand the mechanisms leading to their performance and properties. The experimental design developed was based on these attributes as shown in Figure 18. The following sub-sections describe the specific strategy in each phase of this research.

![Figure 18: Research Outline](image)

3.2.1 Phase 1: Optimization of BWA-PAM Binary System

Previous work reported that the cell voltage can be improved with wider stability window by using custom HPAs. Recent work demonstrated BWA in PVA system with 1.3 V cell voltage [202]. This phase of the research focused on developing the BWA-PAM SPE system. The chemical and electrochemical compatibility of BWA and PAM were analyzed along with the electrolyte conductivity and stability. The root cause of failure in this BWA-PAM electrolyte system was also investigated.
3.2.2 Phase 2: Enhancing of BWA-PAM with H$_3$PO$_4$ Plasticizer

Additives such as acidic plasticizers can enhance the film water retention for better environment stability. However, the nature of additive-polymer interactions are not well studied. This phase of the research focused on enhancing the ion conduction and environmental stability of BWA-PAM electrolyte system with acidic plasticizers. Chemical characterizations using Raman spectroscopy was performed to develop a fundamental understanding of the interactions between the BWA, PAM, and H$_3$PO$_4$. The nature of these interactions were then correlated with the electrolyte conductivity and performance. The plasticizer and electrolyte composition were then optimized and demonstrated in capacitor cells with CNT-graphite electrodes.

3.2.3 Phase 3: Enhancing BWA-PAM with Glycerol Plasticizer

The use of different plasticizers may result in different electrochemical performance in the BWA-PAM electrolyte system. This phase of the research focused on understanding the interactions between the BWA, PAM, and glycerol, as well as on comparing its properties with the H$_3$PO$_4$-modified BWA-PAM electrolytes. The plasticizer and electrolyte composition were then optimized and demonstrated in capacitor cells with CNT-graphite electrodes.

3.3 Thesis Outline

This thesis will describe a systematic approach to enhancing the performance of a solid ECs through engineering of proton-conducting solid polymer electrolytes (SPEs). The literature reviews and research plan have been described in Chapter 1-3. The rest of the thesis is organized as described below:

Chapter 4: This chapter describes the experimental design and techniques to engineer and characterize the proton-conducting SPEs. A detailed description is given for each characterization technique in order to establish how they provide a complementary characterization of the materials linked mechanistically to cell performance.
Chapters 5: This chapter describes the development of SPE with borotungstic acid (BWA) as the proton conductor and polyacrylamide (PAM) as the polymer host. The electrochemical and material characterizations on BWA-PAM electrolytes are analyzed to understand the compatibility of the materials and their performance. The compositions for the binary BWA-PAM electrolyte with highest conductivity and shelf life are chosen to proceed to the next stage of the research.

Chapter 6: This chapter describes the modification of BWA-PAM with both acidic plasticizer (H₃PO₄) and neutral plasticizer (glycerol). The effects of these plasticizers on the BWA-PAM material properties are discussed and correlated back to their electrochemical performance. The optimized electrolyte compositions with each plasticizer are chosen to proceed to the next stage.

Chapter 7: This chapter describes the SPE optimizations and solid cell demonstrations. The best electrolyte with acidic plasticizer and neutral plasticizer are demonstrated in solid cells with carbon electrodes and compared against the liquid cells.

Chapter 8: This chapter summarizes the highlights of this thesis and the findings from each stage of the research. Plans and experiments are suggested for the possible future continuation of this research.
Chapter 4
Experimental Method

4.1 Materials

This thesis analyzed the performance of BWA-PAM electrolyte system with electrochemical characterization and material characterization techniques. The experimental method from electrolyte preparation to SPE characterizations are described in this chapter.

The BWA-PAM SPE consists of polyacrylamide (PAM) as the polymer host and borotungstic acid (BWA) as the proton conductors. PAM, acidic plasticizers, and neutral plasticizers were commercially available, but BWA had to be synthesized as it is a novel HPA. The synthesis method of BWA is described below.

4.1.1 Heteropolyacids (BWA)

H$_5$BW$_{12}$O$_{40}$ ∙ xH$_2$O (BWA) was synthesized by a modified Copaux's method [202, 214]. Briefly, 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 6 N HCl and heated at 60 °C for 2 hours under stirring. Subsequently, the pH was further adjusted to 3.8 using 6 N HCl and the solution was heated at 80 °C for 6 hours. Finally, the solution was allowed to cool to room temperature for 6 hours. Solid precipitates (primarily tungsten oxides) were filtered out and the filtrate solution was extracted with diethyl ether. The extracted solid was washed with DI H$_2$O and dried, yielding ca. 2 g of a white crystalline product.

4.1.2 Polymer host (PAM)

The PAM was purchased from Scientific Polymer and was used as-received. The PAM has average molecular weight M$_w$ of 5,500,000 to 6,000,000 g/mol.
4.1.3 Additives

Phosphoric acid (H₃PO₄) was used as the acidic plasticizer, while glycerol (Gly) was used as the neutral plasticizer. The H₃PO₄ comes at 85 wt% concentration in H₂O, while Gly has above 99.5% purity. Both of these plasticizers were purchased from Sigma Aldrich and were used as-received.

4.2 Preparation of polymer electrolytes

This thesis explored three systems of the proton-conducting SPEs: BWA-PAM binary system, BWA-PAM + H₃PO₄ ternary system, and BWA-PAM + Gly ternary system. The preparation method and composition of each electrolyte system are listed below. The precursor solutions were cast in ambient conditions to form freestanding films. The film thickness was measured with a Mitutoyo Model 293-831 digital micrometer; the average film thickness was ca. 150 μm.

4.2.1 BWA-PAM

The BWA-PAM electrolyte was prepared by mixing a 3% PAM solution (Scientific Polymer, Mw: 5-6 000 000 g mol⁻¹) with BWA powder to form precursor solutions at 50 wt%, 75 wt%, and 85 wt% BWA composition.

Table 3: Compositions of BWA-PAM polymer electrolytes.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>BWA:PAM molar ratio</th>
<th>BWA wt%</th>
<th>PAM wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAM</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>50BWA-PAM</td>
<td>2,000</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>75BWA-PAM</td>
<td>5,000</td>
<td>75</td>
<td>25</td>
</tr>
<tr>
<td>85BWA-PAM</td>
<td>10,000</td>
<td>85</td>
<td>15</td>
</tr>
</tbody>
</table>

4.2.2 BWA-PAM + H₃PO₄

The BWA-PAM + H₃PO₄ electrolytes was prepared through adding phosphoric acid (H₃PO₄, Sigma Aldrich) as a plasticizer to the BWA-PAM electrolyte precursor solutions with the weight ratio controlled at ca. 5 wt% and ca. 10 wt%.
Table 4: Compositions of BWA-PAM + H$_3$PO$_4$ polymer electrolytes.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>H$_3$PO$_4$:PAM molar ratio</th>
<th>BWA wt%</th>
<th>PAM wt%</th>
<th>H$_3$PO$_4$ wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>75BWA-PAM + 0% H$_3$PO$_4$</td>
<td>0</td>
<td>75</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>75BWA-PAM + 5% H$_3$PO$_4$</td>
<td>10,000</td>
<td>70</td>
<td>25</td>
<td>5</td>
</tr>
<tr>
<td>75BWA-PAM + 10% H$_3$PO$_4$</td>
<td>20,000</td>
<td>67</td>
<td>24</td>
<td>9</td>
</tr>
<tr>
<td>85BWA-PAM + 0% H$_3$PO$_4$</td>
<td>0</td>
<td>85</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td>85BWA-PAM + 5% H$_3$PO$_4$</td>
<td>20,000</td>
<td>81</td>
<td>14</td>
<td>5</td>
</tr>
<tr>
<td>85BWA-PAM + 10% H$_3$PO$_4$</td>
<td>40,000</td>
<td>76</td>
<td>14</td>
<td>10</td>
</tr>
</tbody>
</table>

4.2.3 BWA-PAM + Glycerol

The BWA-PAM + Glycerol electrolytes was prepared through adding glycerol (Sigma Aldrich) as a plasticizer to the BWA-PAM electrolyte precursor solutions with the weight ratio controlled at ca. 5 wt% and ca. 10 wt%.

Table 5: Compositions of BWA-PAM + Glycerol polymer electrolytes.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Glycerol:PAM molar ratio</th>
<th>BWA wt%</th>
<th>PAM wt%</th>
<th>Gly wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>75BWA-PAM + 0% Gly</td>
<td>0</td>
<td>75</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>75BWA-PAM + 5% Gly</td>
<td>10,000</td>
<td>71</td>
<td>25</td>
<td>4</td>
</tr>
<tr>
<td>75BWA-PAM + 10% Gly</td>
<td>25,000</td>
<td>66</td>
<td>24</td>
<td>10</td>
</tr>
<tr>
<td>85BWA-PAM + 0% Gly</td>
<td>0</td>
<td>85</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td>85BWA-PAM + 5% Gly</td>
<td>20,000</td>
<td>81</td>
<td>14</td>
<td>5</td>
</tr>
<tr>
<td>85BWA-PAM + 10% Gly</td>
<td>40,000</td>
<td>76</td>
<td>14</td>
<td>9</td>
</tr>
</tbody>
</table>

4.3 Working Electrodes

All working electrodes have a geometric area of 1 cm$^2$ unless otherwise specified. Two types of working electrode materials (metallic electrodes and carbon electrodes) were used to characterize the properties of the electrolyte and demonstrate the performance in solid-state ECs.

4.3.1 Metallic Electrodes

The metallic electrodes were cut from Ti foil (127 μm thick, McMaster-Carr). The electrode surface was rinsed with isopropanol (IPA) and DI water before use. Electrodes were cut into two sizes, 3 x 1 and 3 x 1.2 cm. The slightly larger size of one electrode can prevent short-circuiting when the edge of two electrodes meet. A polyester tape (0.1 mm thick, ABI Tape, Series 9180) was used to limit the active area of the electrodes of 1 cm$^2$. 
4.3.2 Carbon Electrodes

The CNT-graphite electrodes were prepared using a modified method from a previous report [215]. The 75% CNT ink synthesis is as follows: 0.1050g (75 wt%) CNT and 0.0350g (25 wt%) graphite powders were mixed homogeneously. 0.7 g of 5 wt% PVA binder solution was diluted to 2 mL with DI water. The solution was stirred in a 20 mL disposable vial with a magnetic stirrer while slowly adding the carbon powders. The ink was stirred for 8-9 hours to ensure homogeneous mixing before adding 0.0035g glutaric acid as the crosslinker. The ink was stirred for another 5 days before coating onto the Ti current collector. The resultant 75% CNT ink has a composition of 20 wt% crosslinked PVA binder with 60 wt% CNT and 20 wt% graphite.

The procedure for doctor-blading the carbon ink is outlined in Figure 19. The Ti current collector was secured flatly on the bench with double sided tapes. Two strips of 60 μm thick tape were aligned along the ground area to control the thickness of the applied carbon ink. The smooth edge of a metallic plate was used as the doctor blade to coat the ink. The carbon coated electrode was dried for 1 hour in an oven pre-heated to 50 °C. The temperature was raised to 120 °C for the next hour to crosslink the PVA binder. The electrode was cooled in DI water overnight.

The electrode was cut with a paper trimmer into individual electrode with 1cm x 1cm carbon ink area. First, the two carbon ink electrodes were taped such that only the carbon ink area was exposed. The electrodes were then soaked in DI water for 1-2 hours to remove the loose carbon particles. The carbon electrodes had ca. 1.5-2 mg cm⁻² carbon loading with 60 wt% CNT, 20 wt% graphite, and 20 wt% crosslinked PVA binder. The geometric area of the electrode is 1 cm².

Figure 19: The steps for doctor-blading of carbon ink onto the titanium substrate.
4.4 Construction of liquid cells

4.4.1 Liquid 3-electrode cells

To understand the electrochemical behavior of the electrolyte, a three-electrode cell was employed. The setup consists of a working electrode (WE), counter electrode (CE), and reference electrode (RE) connected to the electrolytes. In three-electrode setup, the potential changes in the working electrode were measured against a saturated Ag/AgCl reference electrode. This isolation allows an accurate study of specific reaction that might occurs at the electrode-electrolyte interface, evaluates the performance of the individual ink electrodes, and matches the electrodes with similar capacitance for the symmetric cell construction. The carbon ink electrode served as the working electrode with the ink exposed in the 0.5 M BWA electrolyte, while a platinum (Pt) mesh as the counter electrode which has at least 10x the surface area of the working electrode. The setup was connected to the potentiostat for cyclic voltammetry test.

4.4.2 Liquid 2-electrode cells

The two-electrode liquid cells were fabricated to assess the electrochemical performance of the electrolyte. The setup consists of a Whatman glass microfiber (1 mm thick, 1.2 μm pore size, Sigma Aldrich) impregnated with 0.1 M BWA electrolyte solution sandwiched in between two electrodes. The electrodes were taped with polyester tape (0.1 mm thick, ABI Tape, Series 9180) to limit the 1 cm² geometric area exposed to the electrolyte. The cell was stabilized by clipping with two glass slides (see Figure 20). Ten test cells were fabricated and connected to the potentiostat for cyclic voltammetry test.

![Figure 20: A liquid 2-electrode cell.](image-url)
4.5 Construction of solid cells

4.5.1 Solid capacitor cells

The test cells were constructed with titanium foil (127 μm thick, McMaster-Carr) as electrode in the electrolyte performance study, while CNT-graphite electrodes coated on a titanium foil current collector were used for the solid EDLC cell. Ten test cells were fabricated for each electrolyte compositions. The CNT-graphite electrodes will be characterized with liquid 3-electrode setup prior to symmetric cell construction. The solid cells were assembled by:

1. **Electrode Fabrication:** Electrodes were cut into two sizes, 3 x 1 and 3 x 1.2 cm. The slightly larger size of one electrode prevent short-circuiting when the edge of two electrodes meet. A tape was used to limit the active area of the electrodes of 1 cm².

2. **Electrolyte Application:** 2-3 drops of precursor solution containing combinations of polymer, salt, and plasticizer were applied onto the electrode active surface cleaned with IPA and DI water. The electrolyte was left at ambient until it formed a film.

3. **Cell Construction:** Two electrodes/electrolyte assemblies were placed together as shown in Figure 21 and taped with polyester tape (0.1 mm thick, ABI Tape, Series 9180). Constant pressure was applied with 20-30 kPa pressure for 20 min on the cells to ensure good contact between electrode and electrolyte.

Figure 21 visualizes the assembly of the cells. After assembly, all cells were stored in a 45% humidity desiccator and were only taken out just before testing. The test cells’ thickness was measured with a Mitutoyo Model 293-831 digital micrometer; the average cell thickness was 0.6 mm with ca. 0.2 mm thick electrolyte. All solid cells were stored at room temperature in a 45% RH desiccator.

![Figure 21: The assembly of an electrochemical capacitor cell.](image)
4.6 Electrochemical characterization methods

Electrochemical characterization was intensively utilized in this thesis. There are 2 techniques to characterize the electrochemical performance of the cells: cyclic voltammetry (CV) and electrochemical impedance (EIS).

4.6.1 Cyclic voltammetry (CV)

Cyclic voltammetry (CV) was used to characterize the capacitance and voltage window by measuring the current response with respect to change in voltage. CV was performed on Potentiostat/Galvanostat Model 263A from the EG&G Princeton Applied Research at ambient condition. This potentiostat was operated with the CorrWare software and the data analysis is performed with the CView software version 3.3d.

This technique starts at a pre-set initial voltage and scans to a pre-set maximum voltage with a fixed linear sweep rate. Upon reaching the final voltage, it reverses the scan to the pre-set minimum voltage. The combinations of forward and reverse scan produce a cyclic voltammogram as shown in Figure 22. The ideal CV shape is represented by the blue line in Figure 22. The electrolyte should have a near rectangular CV shape (black line) when operated within its stable voltage window. As the electrolyte is pushed beyond its stability window, the irreversible peaks (grey line) indicate faradaic losses that can occur due to water breakdown. Figure 23 illustrates the rectangular voltammogram shape of an ideal capacitor versus the parallelogram voltammogram shape of a capacitor with resistivity.

![Figure 22: Rectangular CV shape of an ideal electrolyte material [216].](image-url)
There are two important parameters that can be obtained from CV:

1. **Charging/discharging capacitance**

   For areal capacitance analysis, dc capacitance (unit: Farad) can be calculated by the following equations: $C = Q / U$ where $Q$ is charge stored/discharged and $U$ is the voltage window in which the CV is performed; both $Q$ (unit: Coulomb) and $U$ (unit: Volt) can be extracted from the voltammogram data. In this project, CV on most cells was performed from 0 to 0.8 V with scan rate of 1 V s⁻¹. It should also be noted that the capacitance is directly proportional to the area under the voltammogram curve.

2. **Voltage window**

   Voltage window of an electrochemical cell can be measured using incremental CV where the voltage positive and negative limits are expanded incrementally until certain reactions (such as $O_2$ or $H_2$ evolutions and heteropolyacids reduction) occur on either cathode or anode. These reactions can be identified with slow scan rate of 50 mV s⁻¹ by the peaks in CV similar to the grey line in Figure 22. Potential window can be investigated through two-electrode test setup and/or three-electrode setup.
4.6.2 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is a common technique to extract frequency dependent responses from the cell. EIS subjected the tested cell to an alternating current (AC) perturbation with a range of frequencies as shown in Figure 24 (a). This allows the use of software to model the tested cell with an equivalent circuit as shown in Figure 24 (b) and calculate the relevant electrochemical parameters of the cell.

Figure 24: (a) AC perturbation input signal with various frequencies for EIS, and (b) an equivalent circuit for capacitor with resistance.

EIS was performed with 1255 HF Frequency Response Analyzer from Solartron Schlumberger. The EIS data was analyzed with ZView software version 2.9b. In this project, the initial potential in the EIS was set at 0V bias and the amplitude was set to be 0.005V with frequency ranging from 0.1 Hz to 100 kHz. From the EIS technique, a Nyquist plot or Bode plot can be generated as shown in Figure 25.

Figure 25: (a) Nyquist plot and (b) Bode plot obtained from EIS of an electrolyte test cell.
From the Nyquist plot in Figure 25 (a), the $Z_{\text{real}}$ intercept corresponds to the ionic resistance of the cell. This information can be extracted by using an equivalent circuit for a capacitor as shown in Figure 24 (b) to model the electrolyte test cell. Ionic conductivity of the cell was calculated by the following equations:

$$\sigma = \frac{d}{RA} \quad (16)$$

where $d$ is thickness of electrolyte, $R$ is the ionic resistance, and $A$ is the active area (in this project: $1 \text{ cm}^2$).

In the Bode plot of Figure 25 (b), the impedance angle and magnitude are plotted against the frequency. An ideal capacitor should have an impedance angle of -90° and therefore it is desirable for the impedance angle of EC to reach -90° as fast as possible in the Bode plot.

For ac capacitance, the real part of the capacitance ($C'$) and its corresponding imaginary part ($C''$) were separated [217]. In this method, the EC frequency behavior is considered. Then its impedance is

$$Z(\omega) = \frac{1}{j\omega \times C(\omega)} \quad (17)$$

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

$$Z(\omega) = Z'(\omega) + jZ''(\omega) \quad (18)$$

By rearranging equations (17) and (18),

$$C(\omega) = \frac{1}{\omega \times [jZ'(\omega) - Z''(\omega)]} = \frac{-[Z''(\omega) + jZ'(\omega)]}{\omega |Z(\omega)|^2} \quad (19)$$

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

$$C(\omega) = C'(\omega) - jC''(\omega) \quad (20)$$
Combination of equations (19) and (20) leads to \( C'(\omega) \) equation:

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

(21)

and the \( C''(\omega) \) equation:

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

(22)

These two values (\( C'(\omega) \) and \( C''(\omega) \)) can be plotted as a function of frequency. \( C'(\omega) \) represents the accessible capacitance of the cell at the corresponding frequency, which approaches the capacitance obtained from dc methods at low frequencies. \( C''(\omega) \) corresponds to energy dissipation by an irreversible process. The maximum of the \( C''(\omega) \) 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 ECs [218].

4.7 Material and structural characterizations

The electrochemical characterization discussed in the previous section should be coupled with material characterization so that the material properties can be correlated to the performance and establish deeper understanding of the underlying mechanisms governing the performance. The electrolytes were cast in ambient conditions and dried into thin free-standing films for materials characterizations.

4.7.1 Simulated cells

The simulated cells were assembled by casting the precursor solution onto each microglass slides followed by sandwiching the electrolyte between two microglass slides and stabilizing it with tape. The test cells’ thickness was measured with a Mitutoyo Model 293-831 digital micrometer; the average cell thickness was 0.6 mm with ca. 0.2 mm thick electrolyte. The simulated cells were used for optical microscopy and Raman spectroscopy.
4.7.2 Optical microscopy

The optical microscopy was performed with Jenaphot 2000 Reflected-light Photomicroscope. Images were collected with Camera Control Pro 2 software at various magnifications in bright field and dark field modes.

4.7.3 Raman spectroscopy

Raman spectroscopy measurements were recorded on a Horiba XploRATM PLUS Raman microscope system with a 532 nm laser and diffraction grating of 1800 g/mm. The spectra were recorded between 15 cm\(^{-1}\) and 4000 cm\(^{-1}\) wavenumbers. Raman film samples were cast and dried into films under ambient conditions and re-conditioned at 45% RH for 7 days before being characterized.

4.7.4 Fourier transform infrared (FTIR) spectroscopy

Fourier transformed infrared (FTIR) spectroscopy was performed with Bruker ALPHA FTIR Spectrometer and the data was collected with OPUS 7.2 software. The spectra were recorded at a resolution of 4 cm\(^{-1}\) within the range from 4000 cm\(^{-1}\) to 400 cm\(^{-1}\). FTIR film samples were cast and dried into films under ambient conditions and re-conditioned at 45% RH for 7 days before being characterized.

4.7.5 X-ray diffraction (XRD)

X-ray diffraction (XRD) measurements were carried out using a Philips XRD system, including a PW 1830 HT generator, a PW 1050 goniometer, and PW 3710 control electronics. The samples were analyzed with a Cu-K\(\alpha\) source of wavelength 1.5406 Å operating at 40 kV/30 mA. The diffraction patterns were recorded from 5\(^{\circ}\) to 50\(^{\circ}\) 2\(\theta\) with a step size of 0.02\(^{\circ}\) 2\(\theta\) and a scan step time of 2 seconds. All XRD film samples were cast and dried into films under ambient conditions and re-conditioned at 45% RH for 7 days before being characterized. The resulting pattern can be used to analyze the crystallinity of the electrolyte.
Chapter 5
Development of BWA-PAM binary system

5.1 BWA characterizations

This chapter discusses the development of a binary electrolyte system with borotungstic acid (H₅BW₁₂O₄₀, BWA) as the heteropolyacid (HPA) proton conductor and polyacrylamide (PAM) as the polymer host. Before incorporating the proton conductor with the polymer host, the synthesized BWA was characterized with cyclic voltammetry (CV), Raman spectroscopy, Fourier Transformed Infrared (FTIR), and x-ray diffraction (XRD). The characterization results were compared against the commercial Keggin HPA, silicotungstic acid (H₄SiW₁₂O₄₀, SiWA) that had a well-established database to examine the purity of the synthesized BWA.

5.1.1 Ionic conductivity of BWA (Two-electrode Beaker Cell)

The ionic conductivity of BWA solution was analyzed in a 2-electrode beaker cell. Figure 26 depicts the conductivity of SiWA and BWA solutions at various concentrations. The conductivity of both SiWA and BWA increased linearly with concentration due to the higher amount of protons available for conduction. This conductivity trend agreed with the work by Gao et al. [214]. As BWA had a more negative ionic charge than SiWA, BWA can provide a higher amount of protons for conduction. This led to the consistently higher conductivity of BWA compared to that of SiWA at all concentrations studied. This suggested that BWA is a better HPA candidate for ionic conduction than SiWA for SPEs.
5.1.2 Electrochemical window of BWA (Cyclic Voltammetry)

BWA solutions were also characterized with cyclic voltammetry to investigate the window of their electrochemical stability. Figure 27 shows the cyclic voltammograms (CVs) of 0.01 M SiWA and 0.01 M of the synthesized BWA at 50 mV s\(^{-1}\) in a 3-electrode cell with glassy carbon working electrode against a saturated Ag/AgCl reference electrode. Similar to SiWA, the CV of BWA reached an upper limit of oxygen evolution at 1.5 V. BWA demonstrated a wider electrochemical stability window at lower potential (-0.3V) than SiWA (-0.1 V). This lower limit was attributed to the redox activity of HPAs at negative potentials [214].

This 0.2 V increase in the electrochemical stability window from SiWA to BWA was in agreement with the trend reported by Song et al. [179, 180]. As the boron heteroatom had a larger anionic charge than silicon, the less electronegative boron had a lower tendency to attract electrons from the W\(_{12}\)O\(_{36}\) cage, leading to a higher electron density on the cage. Thus, a greater overpotential was required to reduce the W\(_{12}\)O\(_{36}\) cage, resulting in a linear negative shift of the redox potential [179, 219]. Due to the lower reduction potential, BWA can achieve a 1.8 V window as compared to the 1.6V for SiWA, in agreement with the reported values in literature [214]. This wider electrochemical window is one of the critical design concepts to achieve high energy and power ECs according to equations (1) and (2).
Figure 27: Third scan for the cyclic voltammograms in a 3-electrode cell with a glassy carbon working electrode and platinum mesh counter electrode, showing the electrochemical stability windows for 0.01 M SiWA and 0.01 M of the synthesized BWA at a scan rate of 50 mV s\(^{-1}\) against a saturated Ag/AgCl reference electrode.

5.1.3 Chemical bonding in BWA (Raman Spectroscopy)

The heteroatom and the chemical bonding of BWA were analyzed with Raman spectroscopy. Figure 28 depicts the Raman spectra of BWA in comparison with SiWA and the peak assignments are listed in Table 9 of Appendix A. The Raman peaks for SiWA were assigned according to the well-established literature reports [220-222]. Since the Raman analysis on BWA was not previously reported, the peaks were assigned from a cross comparison of known Keggin-type structures [220-222].

The Raman spectrum of SiWA can be divided into three major regions. The low Raman shift area revealed the W\(_{12}\)O\(_{36}\) cage vibration signals below 400 cm\(^{-1}\) [222]. The high-intensity peak at 1006.1 cm\(^{-1}\) was characteristic of the \(\nu(\text{Si-O})\) peak for the SiWA heteroatom [220-222]. The broad peak at \(ca.\) 3500 cm\(^{-1}\) belonged to the \(\delta(\text{O-H})\) peak of the crystallized water surrounding the SiWA [220-222]. Thus, the spectrum of SiWA is typical of the spectrum for Keggin-type HPAs.
The Raman spectrum of BWA powder had similar vibration signals to that of the SiWA powder below 400 cm\(^{-1}\) for the W\(_{12}O_{36}\) cage. This suggested that the synthesized BWA had the W-based Keggin cage structure. BWA also showed a high-intensity peak around 989.3 cm\(^{-1}\) which can be assigned to the \(\nu(B-O)\) signals. Figure 28 showed that BWA also had a broad \(\delta(O-H)\) peak at \textit{ca.} 3500 cm\(^{-1}\), suggesting that it also contained crystallized water.

As compared to SiWA, the peaks below 400 cm\(^{-1}\) in BWA were shifted to slightly lower frequencies (see Table 9 in Appendix A) likely due to the larger size of the BWA structure. The higher peak intensity of \(\delta(W-O-W)\) at 216.8 cm\(^{-1}\) in the BWA spectrum may indicate minor residual tungsten oxides from the synthesis process in the BWA powder. The shift of the \(\nu(B-O)\) peak (989.3 cm\(^{-1}\)) to a lower frequency than \(\nu(Si-O)\) peak (1006.1 cm\(^{-1}\)) in SiWA agrees with the trend reported by Bridgeman \textit{et al.} from density functional theory (DFT) calculations [222]. As BWA and SiWA had similar Keggin metal oxide cage sizes, the larger anionic charge and smaller ionic radius of boron led to a longer B-O than Si-O bond in the Keggin structure [219, 222]. The longer B-O bond caused the shift in the \(\nu(B-O)\) peak to a lower frequency. This Raman characterization confirmed that the BWA had a Keggin-type structure with a boron heteroatom. The BWA also showed a higher peak intensity at 3500 cm\(^{-1}\), suggesting that it retained more crystallized water as compared to SiWA.

FTIR analysis was also performed to characterize the BWA powder (refer to Appendix B). Both Raman and FTIR analyses confirmed that the BWA powder was successfully synthesized with a Keggin-type structure and a boron heteroatom. Since the Raman spectra was more sensitive and had sharper peaks than FTIR, it was used as the primary tool to characterize the chemical bonding for the rest of this thesis.
Figure 28: Raman spectra of (a) SiWA powder and (b) the synthesized BWA powder dried at 60°C for 24 hours prior to characterization. The Keggin-type structures of SiWA and BWA are shown as inset figures. The $\nu$(Si-O) and $\nu$(B-O) peaks were highlighted in blue color, while the $\delta$(W-O-W) peak was highlighted in red color.

5.1.4 Structure of BWA (XRD Analysis)

The structure of the synthesized BWA was also investigated using XRD analysis. Figure 29 shows the XRD patterns of BWA in comparison with SiWA, a commercial HPA with known Keggin-type structure. The XRD pattern of SiWA revealed the typical signature peaks for Keggin-type structure [214]. The three strongest Keggin signature peaks were at 10.0°, 25.2°, and 34.4°. In the XRD pattern, the peak at 10.0° and ca. 25.2° were associated with the dehydrated SiWA [223, 224].
The synthesized BWA powder had a similar XRD pattern as SiWA with the three strongest peaks at 10.2°, 25.3°, and 34.6°, confirming that BWA retained a Keggin structure. One additional peak was observed at \( ca. 7.7° \), which was the hydrated structure for Keggin-type HPAs [223, 224]. This implied that although both SiWA and BWA were dried under the same condition prior to the XRD characterization, BWA showed a slightly higher tendency to retain its hydrated state. Thus, the XRD analysis confirmed that the synthesized BWA retained the same Keggin-type structure with a slightly higher level of hydration than SiWA, which agrees with the Raman analysis in section 5.1.3. Thus, this custom synthesized BWA was further investigated for solid electrolytes in this project.

Figure 29: X-ray diffraction patterns of (a) SiWA powder and (b) the synthesized BWA powder dried at 80°C for 24 hours prior to the characterization. The structure of Keggin-type HPA was included as an inset. The hydrated HPA peak was highlighted in red color, while the dehydrated HPA peaks were highlighted in blue color.
5.2 PAM characterizations

5.2.1 Water retention in PAM (Raman and FTIR Analysis)

The PAM was characterized with Raman, FTIR, and XRD to investigate its water retention capability and structure. The chemical bonding within the PAM film was characterized with Raman spectroscopy as shown in Figure 30 (a). The signature peaks of PAM were also tabulated in Table 11 of Appendix A. The Raman spectrum for PAM agreed with the peaks reported by Gupta et al. [225]. This PAM spectrum was used as the baseline to compare against the polymer electrolytes developed in this thesis. The broad $\delta$(O-H) peak at 3355.3 cm$^{-1}$ corresponded to a large amount of water retention in the PAM film, suggesting the highly hygroscopic property of PAM which is desirable for polymer electrolyte applications.

The PAM had a strong peak with strong intensity at 1458.4 cm$^{-1}$, correspond to the $\delta$(CH$_2$) backbone in PAM. This signature peak was used as the baseline for peak intensity analysis in the characterization of the electrolytes because the CH$_2$ polymer backbone is usually inert to chemical reactions as compared to the functional group represented by $\nu$(C-N), $\delta$(NH$_2$), and $\nu$(C=O) peaks at 1426.9 cm$^{-1}$, 1610.0 cm$^{-1}$, and 1666.3 cm$^{-1}$, respectively.

Figure 30 (b) revealed the FTIR characterization of the PAM film. The FTIR peaks were assigned according to Lu et al. [226] and tabulated in Table 12 in Appendix A. Similar to the Raman analysis, a large broad peak was observed at 3324.3 cm$^{-1}$ that matched the $\delta$(O-H) of water, suggesting that the PAM film can retain water within its structure. This hygroscopic nature of PAM is desirable for SPE applications.
Figure 30: (a) Raman and (b) FTIR spectra of pure PAM film conditioned at 45% RH for 7 days. Inset shows the structure of PAM. The acrylamide functional group peaks were highlighted in blue, while the polymer backbone peak used as the reference in this thesis was highlighted in red.

5.2.2 Structure of PAM (XRD Analysis)

Figure 31 shows the XRD pattern for PAM film. The broad peaks in the XRD pattern suggest that the polymer film is amorphous. The peak at 11.9° was a silicone signature [227], which likely originated from the silicone gel used to attach the film samples during XRD characterization. The broad peak at ca. 15-25° was deduced to be the amorphous structure of PAM, according to Murthy et al. [228-230]. This amorphous structure is beneficial to enable the segmental motion of the polymer to enhance proton conductivity, as well as retain more water to facilitate ion migrations as mentioned in Chapter 2.
5.3 Proton conductivity

After characterizing the individual components, the BWA and PAM are mixed together to form the electrolyte precursor solutions. The BWA-PAM mixtures formed homogeneous precursor solutions that dried into translucent films when cast in ambient conditions. The tested electrolyte compositions were selected to be at least 50 wt% BWA to form the polymer-in-salt system as discussed in Chapter 2. The stability of PAM was compromised in highly acidic solution beyond a threshold of 85 wt% BWA as reported in Appendix C. Therefore, the precursor solutions of 50BWA-PAM, 75BWA-PAM, and 85BWA-PAM were selected to construct solid cells. Their conductivity were characterized to optimize the electrolyte compositions.

Figure 32 showed the room temperature conductivity of BWA-PAM binary electrolytes as a function of composition over 28 days while conditioned at 45% RH. The PAM electrolyte film had a low intrinsic conductivity of \(\text{ca. } 1 \text{ mS cm}^{-1}\). Adding BWA increased the conductivity of the as-fabricated solid electrolytes from \(\text{ca. } 7 \text{ mS cm}^{-1}\) for 50BWA-PAM, \(\text{ca. } 17 \text{ mS cm}^{-1}\) for 75BWA-PAM, to \(\text{ca. } 27 \text{ mS cm}^{-1}\) for 85BWA-PAM due to the extra protons available for conduction.
Figure 32: Room temperature conductivity versus time of electrolytes with PAM, 50BWA-PAM, 75BWA-PAM, and 85BWA-PAM conditioned at 45%RH over a period of 28 days.

The conductivity of H₃PO₄-PAM reported by Rodriguez et al. [163] was extracted from Figure 12 (b) and compared against BWA-PAM in Table 6. As expected, BWA-PAM exhibited significantly higher conductivity than the H₃PO₄-PAM because BWA can provide more protons per molecule than H₃PO₄ to enhance the conductivity.

Table 6: The comparison of conductivity as a function of acid content for BWA-PAM and H₃PO₄-PAM electrolyte systems [163].

<table>
<thead>
<tr>
<th>Acid content (wt %)</th>
<th>BWA-PAM (mS cm⁻¹)</th>
<th>H₃PO₄-PAM (mS cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>7.2</td>
<td>0.032</td>
</tr>
<tr>
<td>75</td>
<td>16.9</td>
<td>2.5</td>
</tr>
<tr>
<td>85</td>
<td>27.8</td>
<td>7.9</td>
</tr>
</tbody>
</table>

At the same condition of 45% RH under room temperature, the conductivity of as-fabricated 85BWA-PAM (ca. 27 mS cm⁻¹) was twice that of 90BWA-XLPVA developed by Gao et al. (ca. 13 mS cm⁻¹) [202] due to the more hygroscopic nature of PAM as compared to PVA [156]. This result is very promising as they demonstrated the potential to use BWA-PAM binary system as highly-conductive SPE for EC applications.
The conductivity of 50BWA-PAM was comparatively lower, thus only 75BWA-PAM and 85BWA-PAM were selected for further analysis. The conductivity of these two compositions decreased rapidly with time as shown in Figure 32, resulting in an average conductivity of ca. 7 mS cm\(^{-1}\) (≤ 40% conductivity retention) after 28 days of room temperature exposure to 45% RH.

The metallic cells were disassembled at this point to investigate the origin of the reduction in conductivity. The electrolytes were found to be dried, brittle, and delaminated from the electrode surface as shown in Figure 33 (a). Part of the electrolyte film turned an opaque white color because of the precipitation of BWA due to dehydration (see Figure 33 (b)). The size of the precipitation ranged from 10 µm to 40 µm. Thus, the reduction of conductivity was likely due to electrolyte dehydration, resulting in the short shelf life of the binary electrolytes.

![Figure 33: (a) Photo of electrolyte delamination from the electrode surface on day 28; and (b) optical micrograph of the delaminated area of the electrolyte, showing precipitation due to electrolyte dehydration.](image)

5.4 Material characterization

5.4.1 Chemical bonding in BWA-PAM binary electrolytes (Raman Analysis)

Since dehydration was identified as the cause of failure, the BWA-PAM binary electrolytes were analyzed with Raman spectroscopy and XRD to investigate the water bonding in the electrolyte. Figure 34 showed the Raman spectra for BWA-PAM electrolytes as a function of composition. The corresponding Raman peak assignments of the BWA and PAM in the binary electrolytes are given in Table 13 of Appendix A.
The Raman spectra for BWA and PAM were previously discussed in sections 5.1 and 5.2 respectively. After adding 50 wt% BWA to PAM, the Raman spectrum of 50BWA-PAM generally consisted of the signature peaks of both BWA and PAM components without any peak shifting (see Table 13). The characteristic strong peaks for BWA-PAM below 1000 cm\(^{-1}\) matched that of the BWA powder, suggesting that it retained the Keggin structure in PAM. The PAM peaks primarily in 1000-1800 cm\(^{-1}\) were overshadowed by the BWA signals, except the strong \(\nu(CH_2)\) peak at 2937.4 cm\(^{-1}\). The broad peak at \(ca\). 3500 cm\(^{-1}\) suggested that the 50BWA-PAM binary electrolyte can retain water in the film.

The 75BWA-PAM and 85BWA-PAM showed similar spectra to that of the 50BWA-PAM material without any peak shifting (see Table 13). The relative peak intensity ratio of BWA (represented by \(\nu(B-O)\) at 989.3 cm\(^{-1}\)) to PAM (represented by \(\nu(CH_2)\) at 1458.5 cm\(^{-1}\)) increased with increasing BWA content in the electrolytes. As more BWA was added into the electrolytes, the \(\delta(O-H)\) peak at \(ca\). 3300 cm\(^{-1}\) was reduced in intensity and shifted towards \(ca\). 3500 cm\(^{-1}\), suggesting that higher content of BWA led to a lower level of hydration in the film. This explains the more rapid reduction in conductivity of 85BWA-PAM due to dehydration over 28 days as compared to 75BWA-PAM and 50BWA-PAM as shown in Figure 32.

![Figure 34: Raman spectra for dried films of PAM, 50BWA-PAM, 75BWA-PAM, and 85BWA-PAM conditioned for 7 days at 45% RH. The \(\nu(B-O)\) peak was highlighted in red color, while the \(\delta(O-H)\) was highlighted in blue color.](image-url)
Since the PAM peaks were overshadowed by the high-intensity BWA signals, a focused analysis was performed over the range of 1000-1800 cm\(^{-1}\) in Figure 35. BWA powder did not have any peak in this region. The PAM backbone peaks at 1116.2 cm\(^{-1}\), 1329.8 cm\(^{-1}\), and 1458.5 cm\(^{-1}\) were identical for all binary electrolytes. They also showed similar acrylamide functional group peaks at 1426.9 cm\(^{-1}\), 1610.0 cm\(^{-1}\), and 1666.3 cm\(^{-1}\) without significant peak shifting, but the peak intensities at these three locations decreased with increased BWA content (see Table 7). Figure 35 also revealed that an additional peak appeared at 1712.8 cm\(^{-1}\) for all BWA-PAM electrolytes, which did not correspond to either PAM or BWA. This additional peak became more pronounced at higher BWA concentration (see Table 7), suggesting a possible reaction between BWA and PAM.

Figure 35: Raman spectra for dried films of PAM, 50BWA-PAM, 75BWA-PAM, and 85BWA-PAM conditioned for 7 days at 45% RH (focus on the range of 1000-1800 cm\(^{-1}\)). The acrylamide functional group peaks with changing intensity were highlighted in blue color, while the additional peak was highlighted in red color.
Table 7: Peak intensity ratios of the $\nu$(C-N), $\delta$(NH$_2$), $\nu$(C=O), and $\nu$(COO$^-$) peaks in PAM, 50BWA-PAM, 75BWA-PAM, and 85BWA-PAM normalized against the $\delta$(CH$_2$) at 1458.4 cm$^{-1}$ from the polymer backbone as the reference.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Peak intensity ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\nu$(C-N) at 1426.9 cm$^{-1}$</td>
</tr>
<tr>
<td>PAM</td>
<td>0.80</td>
</tr>
<tr>
<td>50BWA-PAM</td>
<td>0.67</td>
</tr>
<tr>
<td>75BWA-PAM</td>
<td>0.55</td>
</tr>
<tr>
<td>85BWA-PAM</td>
<td>0.49</td>
</tr>
</tbody>
</table>

A previous study on PAM by Pei et al. demonstrated that adding strong acids such as HCl to PAM can initiate chemical reactions to partially hydrolyze the acrylamide group in PAM to form PAM-co-polyacrylic acid (PAA) as shown below [231]:

$$\text{CH}_2\text{CH}^-\text{O}^-\text{H}_2\text{O} \rightarrow \text{CH}_2\text{CH}^-\text{O}^-\text{H}_2\text{O} \rightarrow \text{CH}_2\text{CH}^-\text{O}^-\text{H}_2\text{O}$$

This extra peak at 1712.8 cm$^{-1}$ matched the $\nu$(COO$^-$) signature peak of PAA [232] suggests that the highly acidic BWA may partially transform PAM to PAM-co-PAA. This was also supported by the change in relative peak intensities of the acrylamide functional groups and PAA peaks as a function of BWA content (see Table 7) because more BWA would initiate higher degree of PAM-co-PAA transformation. This transformation may be helpful for the electrolyte hydration capability because PAM-co-PAA is more hygroscopic than both PAM and PAA homopolymers [138, 233]. The improved hydration capability can facilitate ion conduction to achieve high initial conductivities for the binary electrolytes in Figure 32.

5.4.2 Structure of BWA-PAM binary electrolytes (XRD Analysis)

XRD analysis was performed to investigate the change in electrolyte structure due to the PAM to PAM-co-PAA transformation. Figure 36 is the XRD patterns for BWA-PAM films at various BWA concentrations conditioned at 45% RH for 7 days. The PAM film without BWA addition had been previously described in Section 5.2.

After adding 50 wt% BWA, the broad profile without any sharp peaks indicated that the 50BWA-PAM film was amorphous and well-hydrated with the same broad peak at ca. 15-25° as the PAM. The appearance of a peak at ca. 6° and a broad peak at ca. 30° can be associated with
the hydration level of the BWA [223, 224]. Similar to the trend observed in 50BWA-PAM, adding 75 wt% and 85 wt% BWA to PAM also yielded a similar XRD pattern as PAM, suggesting that all binary systems have an amorphous structure despite the high concentration of crystalline BWA.

The peak at ca. 6° systematically shifted with higher BWA content, from 7° for 75BWA-PAM to 8° for 85BWA-PAM due to the slightly lower hydration level of BWA. This was also supported by the increase in the relative peak intensity at ca. 30° that implied a lower hydration of BWA. This led to a higher crystallinity of the film with increased BWA content as indicated by the narrowing of the first peak at 8.0°.

Despite the slight difference in hydration level, all BWA-PAM electrolyte films were well-hydrated and retained an amorphous structure. This amorphous structure was desirable for ion conduction as discussed in Chapter 2. Thus, the amorphous structure of BWA-PAM binary electrolytes enabled them to achieve high initial conductivity values as shown in Figure 32. However, the dehydration at higher BWA contents led to the short shelf life of the electrolytes, thus plasticizers were investigated to enhance the conductivity and shelf life of the binary electrolytes.
5.5 Summary

A proton-conducting polymer electrolyte consisting of borotungstic acid (BWA) and polyacrylamide (PAM) was developed for electrochemical capacitor applications. The synthesized BWA powder was confirmed to have a Keggin structure. After mixing BWA with PAM, the precursor solution can form homogeneous electrolyte films. The strong acidity of BWA partially transformed PAM to PAM-co-PAA which also had a desirable water retention capability to facilitate ion conduction. When being cast into a film, the PAM had an intrinsic conductivity of only \(\text{ca. } 1\, \text{mS cm}^{-1}\), thus requiring the addition of BWA as a proton conductor to enhance its electrochemical performance. BWA-PAM electrolytes exhibited high conductivity of \(\text{ca. } 27\, \text{mS cm}^{-1}\) for as-fabricated 85BWA-PAM due to the high concentration of BWA. However, the binary electrolytes suffered from low service life due to dehydration, leading to electrolyte brittleness and delamination.

Figure 36: X-ray diffraction patterns for dried films of PAM, 50BWA-PAM, 75BWA-PAM, and 85BWA-PAM conditioned for 7 days at 45% RH.
Chapter 6
Effects of plasticizers in BWA-PAM

6.1 Acidic plasticizer

The water retention capability of binary BWA-PAM electrolytes can be improved by adding plasticizers to form a BWA-PAM + plasticizer ternary system. An acidic plasticizer was first investigated as previous work reported that acidic plasticizers not only help to retain water in the electrolyte system, but also provide extra protons for conduction [148, 205, 206].

In this work, phosphoric acid (H₃PO₄) was chosen to be the acidic plasticizer due to its higher stability with PAM as compared to HCl and H₂SO₄ [163, 165]. The composition was selected to be 5% and 10% H₃PO₄ because adding concentrations of H₃PO₄ beyond 10 wt% into the electrolyte system will result in electrolyte leakage issue in the cell.

6.1.1 Proton conductivity

The BWA-PAM + H₃PO₄ ternary electrolytes were sandwiched between two Ti electrodes to assemble the test cells and conditioned under room temperature at 45% RH. The ternary electrolytes were characterized with EIS for conductivity analysis. Figure 37 shows the conductivity of 75BWA-PAM and 85BWA-PAM with 5 wt% and 10 wt% H₃PO₄ additions over a period of 28 days.

The addition of H₃PO₄ improved the initial conductivity in both 75BWA-PAM and 85BWA-PAM, reaching an initial conductivity of ca. 25 mS cm⁻¹ for 5 wt% H₃PO₄ and ca. 30 mS cm⁻¹ for 10 wt% H₃PO₄. On the 28th day, all of the ternary electrolytes were found to have retained most of the initial conductivity as compared to the binary counterparts, indicating an improved shelf life with the addition of a plasticizer. No electrolyte delamination was observed for the ternary systems, suggesting that their water retention capability was better than that of their respective binary systems. Therefore, H₃PO₄ addition not only provided extra protons for conduction but also prolonged the electrolyte shelf life by reducing the rate of dehydration.
After adding the H$_3$PO$_4$ plasticizer, the initial conductivity of 75BWA-PAM (ca. 17 mS cm$^{-1}$) improved by 1.5x (ca. 25 mS cm$^{-1}$) with 5 wt% H$_3$PO$_4$ and the 75BWA-PAM + 10% H$_3$PO$_4$ achieved almost twice the conductivity (ca. 30 mS cm$^{-1}$) of its binary counterpart. In contrast, adding 5 wt% H$_3$PO$_4$ into 85BWA-PAM resulted in a similar conductivity as its binary counterpart (ca. 25 mS cm$^{-1}$), while 10 wt% H$_3$PO$_4$ only provided a minor enhancement in conductivity (ca. 30 mS cm$^{-1}$).

It was apparent that the H$_3$PO$_4$ affects the electrolyte differently in the 85BWA-PAM that resulted in less improvement in conductivity compared to the 75BWA-PAM system. Visual inspection of the electrolytes over time was performed to note any change in the electrolyte material that could lead to the discrepancy in the observed performance of the two compositions.

![Figure 37: Room temperature conductivity versus time of electrolytes with 75BWA-PAM and 85BWA-PAM, with 5 wt% and 10 wt% H$_3$PO$_4$, conditioned at 45%RH over 28 days.](image-url)
6.1.2 Crystallization at high content of BWA and H₃PO₄ (Visual inspection)

Visual inspection of the ternary electrolytes over 28-days period against a dark background was carried out by sandwiching the electrolyte films in between two microglass slides to create 1cm x 1cm simulated cells. The micrographs in Figure 38 (a) and (b) showed that both electrolytes modified with 5 wt% H₃PO₄ remained translucent. The addition of 10 wt% H₃PO₄ to 75BWA-PAM and 85BWA-PAM showed a significant difference in Figure 38 (c) and (d); where the 75BWA-PAM + 10% H₃PO₄ remained translucent, but the 85BWA-PAM + 10% H₃PO₄ exhibited phase separation. This suggested that the BWA-PAM electrolytes were compatible with 5 wt% H₃PO₄ and stayed well-hydrated in a homogeneous condition, whereas the addition of 10 wt% H₃PO₄ was compatible with 75BWA-PAM but initiated an undesirable reaction to deteriorate the stability of the 85BWA-PAM electrolyte.

In Figure 38 (e), a photo from the optical microscope over the white phase in 85BWA-PAM + 10% H₃PO₄ electrolyte revealed the formation of crystals with ca. 10 μm radius. The crystals agglomerated into a second phase different from that of the bulk electrolyte. The crystals were likely BWA precipitated from the polymer matrix, suggesting that the presence of 10 wt% H₃PO₄ may have accelerated the BWA to hydrolyze significantly more acrylamide groups and this drastic change in the polymer structure may lead to the BWA precipitation [231]. Raman spectroscopy was performed on the electrolytes with 10 wt% H₃PO₄ to test this hypothesis.
Figure 38: Day 1 and day 28 observations against a University of Toronto logo as the background of the electrolyte in 1cm x 1cm simulated cells for (a) 75BWA-PAM + 5% H₃PO₄, (b) 85BWA-PAM + 5% H₃PO₄, (c) 75BWA-PAM + 10% H₃PO₄ and (d) 85BWA-PAM + 10% H₃PO₄; and (e) optical micrographs of the 85BWA-PAM + 10% H₃PO₄ electrolyte.
6.1.3 Chemical bonding analyses of BWA-PAM + H$_3$PO$_4$ Ternary Electrolytes (Raman analysis)

As observed in Section 5.3, the most noticeable change in the Raman spectra due to the interactions between BWA and PAM were in the range of 1000-2000 cm$^{-1}$. Since the 10 wt% H$_3$PO$_4$ was hypothesized to accelerate this reaction, the Raman spectra in Figure 39 focused on 1000-2000 cm$^{-1}$ to reveal the chemical bonding present in each of the binary and ternary electrolytes with respect to PAM and PAA. The corresponding peak assignments according to the individual electrolyte component are listed in Table 14 of Appendix A.

Figure 39: Raman spectra of PAM, 75BWA-PAM, 75BWA-PAM + 10% H$_3$PO$_4$, 85BWA-PAM, 85BWA-PAM + 10% H$_3$PO$_4$, and PAA. The characteristic peaks for PAM were highlighted in blue color, while the PAA peak was highlighted in red color.
Figure 39 showed that both PAM and PAA had similar Raman spectra for the polymer backbones, represented by skeletal $\nu$(C-C), $\text{CH}_2$ wagging, and $\delta$(CH$_2$) at 1116.2, 1329.8, and 1458.4 cm$^{-1}$ respectively. The strong $\delta$(CH$_2$) peak at 1458.4 cm$^{-1}$ was used as the reference for peak intensity analysis. The PAM had signature peaks for $\nu$(C-N), $\delta$(NH$_2$), and $\nu$(C=O) at 1426.9, 1610.0, and 1666.3 cm$^{-1}$ respectively [225], whereas PAA had a signature peak for $\nu$(COO$^-$) at 1717.2 cm$^{-1}$ [232]. These signature peaks were used for the Raman spectra analyses.

Section 5.3 concluded that the binary electrolytes exhibited both characteristic peaks of PAM and PAA due to the formation of PAM-co-PAA. After adding 10 wt% H$_3$PO$_4$, all of the ternary electrolytes displayed similar peaks for their polymer backbones at 1116.2 cm$^{-1}$, 1329.8 cm$^{-1}$, and 1458.4 cm$^{-1}$. This observation was expected because the PAM-co-PAA formation primarily involved the functional groups.

The 75BWA-PAM + 10% H$_3$PO$_4$ spectrum in Figure 39 displayed slightly lower PAM and slightly higher PAA relative peak intensities than that of its binary counterpart as shown in Table 8. In contrast, the addition of 10 wt% H$_3$PO$_4$ into 85BWA-PAM resulted in the spectrum very different than that of the binary electrolytes due to the absence of PAM characteristic peaks at 1426.9 cm$^{-1}$ and 1666.3 cm$^{-1}$, as well as a significant reduction of the 1610.0 cm$^{-1}$ peak intensity. The 85BWA-PAM + 10% H$_3$PO$_4$ also displayed twice the intensity of the PAA peak at 1717.2 cm$^{-1}$ compared to its binary counterpart.

Table 8: Peak intensity ratios of the $\nu$(C-N), $\delta$(NH$_2$), $\nu$(C=O), and $\nu$(COO$^-$) peaks in PAM, 75BWA-PAM, 75BWA-PAM + 10% H$_3$PO$_4$, 85BWA-PAM, 85BWA-PAM + 10% H$_3$PO$_4$, and PAA normalized against the $\delta$(CH$_2$) at 1458.4 cm$^{-1}$ from the polymer backbone as the reference.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$\nu$(C-N) at 1426.9 cm$^{-1}$</th>
<th>$\delta$(NH$_2$) at 1610.0 cm$^{-1}$</th>
<th>$\nu$(C=O) at 1666.3 cm$^{-1}$</th>
<th>$\nu$(COO$^-$) at 1717.2 cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAM</td>
<td>0.80</td>
<td>0.85</td>
<td>0.61</td>
<td>-</td>
</tr>
<tr>
<td>75BWA-PAM</td>
<td>0.55</td>
<td>0.43</td>
<td>0.51</td>
<td>0.64</td>
</tr>
<tr>
<td>75BWA-PAM + 10% H$_3$PO$_4$</td>
<td>0.52</td>
<td>0.40</td>
<td>0.46</td>
<td>0.67</td>
</tr>
<tr>
<td>85BWA-PAM</td>
<td>0.49</td>
<td>0.41</td>
<td>0.47</td>
<td>0.80</td>
</tr>
<tr>
<td>85BWA-PAM + 10% H$_3$PO$_4$</td>
<td>0.00</td>
<td>0.28</td>
<td>0.00</td>
<td>1.64</td>
</tr>
<tr>
<td>PAA</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.00</td>
</tr>
</tbody>
</table>
At a constant level of H₃PO₄, 75BWA-PAM + 10% H₃PO₄ showed a slightly higher extent of PAM-co-PAA formation than its binary counterpart due to the acid addition; whereas 85BWA-PAM + 10% H₃PO₄ showed a spectrum very similar to PAA with almost no characteristics of PAM, implying a high degree of conversion from PAM to PAA. This affirmed that adding H₃PO₄ can accelerate the transformation of PAM to PAM-co-PAA and result in a greater extent of PAA conversion at very high BWA concentration due to the strong acidity in the electrolyte.

6.1.4 Structural and chemical analyses of the precipitates (XRD and Raman analysis)

The conversion process from PAM to PAA will release NH₄⁺ ions as a by-product [231], which can neutralize the BWA in the electrolyte system to form NH₄⁺-substituted BWA. The different solubility of salts and acids may be the reason behind the phase separation. X-ray diffraction (XRD) was performed to further characterize the crystallinity of these electrolyte films. Figure 40 shows the XRD patterns for 75BWA-PAM, 85BWA-PAM, 75BWA-PAM + 10% H₃PO₄, and 85BWA-PAM + 10% H₃PO₄. The XRD analysis of the binary electrolytes were previously discussed in section 5.4.2.

![Figure 40: X-ray diffraction patterns of dried films for (a) 75BWA-PAM; (b) 85BWA-PAM; (c) 75BWA-PAM + 10% H₃PO₄; and (d) 85BWA-PAM + 10% H₃PO₄.](image-url)
After adding 10 wt% H₃PO₄, the 75BWA-PAM + 10% H₃PO₄ film in Figure 40 (c) retained the same broad peak at ca. 15-25° as its binary counterpart (Figure 40 (a)). The significantly decreased intensity of the peak at 7.5° after the 10 wt% H₃PO₄ addition was due to a lower relative BWA content in the ternary electrolyte compared with that of the binary electrolytes (see Table 3 and Table 4). The XRD pattern of 75BWA-PAM + 10wt% H₃PO₄ showed a flat profile without any high-intensity peak, indicating a more amorphous structure to better facilitate ion conduction as compared to the binary counterparts [33]. Thus, this ternary electrolyte composition was preferable for high conductivity as shown in Figure 37.

A significant difference was observed in the ternary systems, where 75BWA-PAM + 10% H₃PO₄ film in Figure 40 (c) still showed an amorphous structure sufficiently hydrated to facilitate this ion conduction [33], while the 85BWA-PAM + 10% H₃PO₄ film in Figure 40 (d) showed crystalline peaks resulted from second phase precipitation in Figure 38 (b) and (c). These crystalline peaks in XRD pattern correspond to (NH₄)₅BW₁₂O₴₀ crystals in Figure 41 [234-236].

Figure 41 (a) shows the signature peaks for Keggin-type BWA powder dried at 80-90°C overnight prior to characterization. As discussed in Section 5.1, the BWA powder showed XRD peaks characteristic of a Keggin-type structure. (NH₄)₅BW₁₂O₴₀ powder was synthesized by drop-wise titration of ammonia carbonate, (NH₄)₂CO₃ into a solution of 0.3M BWA according to the stoichiometric ratio to substitute the proton with NH₄⁺ ions. The powder was dried at 80-90°C overnight and characterized with XRD as shown in Figure 41 (a).

Figure 41 (a) shows that the XRD pattern of (NH₄)₅BW₁₂O₄₀ powder was very similar to that of BWA powder, implying that it retained a Keggin-type structure. The appearance of a few extra peaks at 10°, 17.2°, and 20° were due to the different amounts and type of crystallized water in the (NH₄)₅BW₁₂O₄₀ powder. The (NH₄)₅BW₁₂O₄₀ powder had its peaks shifted to higher 2θ values compared to BWA powder due to the change in lattice spacing from NH₄⁺ substitution.

The crystalline peak from 85BWA-PAM + 10% H₃PO₄ electrolyte film exhibited similar pattern as the BWA powder XRD with the three strongest peaks at 10.7°, 26.0°, and 36.0°, implying that the BWA in the electrolyte remained in Keggin structure. All of the peaks in 85BWA-PAM + 10% H₃PO₄ electrolyte film were shifted to higher values as compared to BWA powder. The extent of crystalline peak shifting of the 85BWA-PAM + 10% H₃PO₄ electrolyte film to higher
angles matched the (NH₄)₅BW₁₂O₄₀ powder, thus confirming that the second phase precipitation on the 85BWA-PAM + 10% H₃PO₄ electrolyte film originated from the NH₄⁺-substituted BWA.

Raman spectroscopy was performed to differentiate the chemical bonding of the bulk electrolyte (top spectrum) and the crystals (bottom spectrum) in Figure 41 (b). Both the bulk electrolyte and crystal phase had the W₁₂O₃₆ cage peaks below 300 cm⁻¹ and strong υ(B-O) peak near 1000 cm⁻¹. The BWA peak locations in the bulk electrolyte matched the BWA powder characterized in Section 5.1. The precipitated crystal had shifted υ(W-Oc-W) peak from the original 539.9 cm⁻¹ to 564.3 cm⁻¹ and υ(B-O) from 989.3 cm⁻¹ to 1007.2 cm⁻¹, which implied a change in bond length within the BWA due to the NH₄⁺ substitution. This supported the notion in Figure 41 (a) that the phase separation is indeed the precipitation of NH₄⁺-substituted BWA from the bulk electrolyte.

Figure 41: (a) X-ray diffraction patterns of dried samples for BWA powder, 85BWA-PAM + 10% H₃PO₄ electrolyte, and NH₄⁺-substituted BWA powder; and (b) Raman spectra of non-crystal and crystal regions in 85BWA-PAM + 10% H₃PO₄ electrolyte. The shifted Raman peaks were highlighted in blue color.

Although BWA-PAM electrolytes would form PAM-co-PAA due to the reaction of acids with PAM, most of them remained amorphous and well-hydrated to maintain a high level of conductivity. The only exception was the 85BWA-PAM + 10% H₃PO₄ which showed phase separation due to an extensive conversion to PAA and formation of excess NH₄⁺-based crystalline side product. This explains the discrepancy in the optical, structural, and electrochemical analyses of the ternary electrolytes. Thus, an overly high BWA and H₃PO₄ content is undesirable for BWA-PAM electrolytes. Since 75BWA-PAM + 10% H₃PO₄ remained homogeneous and well-hydrated structure, it was selected for further investigation in Chapter 7.
6.2 Neutral plasticizer

Section 6.1 showed that a high concentration of BWA and H₃PO₄ can hydrolyze the PAM functional group and induce crystallization of the electrolyte system. Hence, a neutral plasticizer was investigated in the BWA-PAM system to evaluate the performance and compatibility of the electrolyte components.

In this work, glycerol (Gly) was selected as the neutral plasticizer because of its highly hygroscopic property. The BWA-PAM + Gly formed homogeneous precursor solutions. Higher concentrations of glycerol significantly increased the viscosity of the precursor solution. The precursor solutions with more than 10 wt% of glycerol were too viscous to be stirred well, resulting in non-homogeneous electrolytes. Thus, two compositions of glycerol were investigated, 5 wt% and 10 wt% Gly.

6.2.1 Proton conductivity

The BWA-PAM + Gly ternary electrolytes were sandwiched between two Ti electrodes to assemble the test cells. The test cells were conditioned under room temperature at 45% RH. The ternary electrolytes were characterized with EIS for conductivity analysis. Figure 42 shows the conductivity tracking for BWA-PAM and BWA-PAM with glycerol plasticizers conditioned at 45% RH over the period of 28 days.

The conductivity of as-fabricated 75BWA-PAM improved with increased glycerol content from an initial value of ca. 17 mS cm⁻¹, to ca. 24 mS cm⁻¹ with 5 wt% glycerol, and to ca. 27 mS cm⁻¹ with 10 wt% glycerol. As for the 85BWA-PAM system, although the addition of 5 wt% glycerol showed no improvement on the conductivity (ca. 27 mS cm⁻¹), a higher concentration of 10 wt% glycerol led to increased conductivity up to ca. 32 mS cm⁻¹. The improvement in conductivity was attributed to the hygroscopic property of glycerol that helped to retain water inside the solid electrolyte to facilitate ion conduction [211, 212].
When conditioned at 45% RH under room temperature, the conductivity of the glycerol-modified electrolytes decreased over time due to electrolyte dehydration, reaching \( \text{ca.} \) 19 mS cm\(^{-1} \) at day 28. They can retain \( \geq 70\% \) of the initial conductivity over 28 days compared to the binary system, suggesting an improved shelf life due to the glycerol addition. When the failed cells were dissembled, no delamination was observed because of their better water retention capability compared to their corresponding glycerol free binary systems.

Figure 42: Room temperature conductivity versus time of electrolytes with 75BWA-PAM, 85BWA-PAM, 75BWA-PAM + 10% Gly, and 85BWA-PAM + 10% Gly conditioned at 45%RH over a period of 28 days.
6.2.2 Chemical stability of BWA-PAM + Gly Ternary Electrolytes (Raman analysis)

The glycerol-modified BWA-PAM electrolytes were characterized with Raman, FTIR, and XRD to investigate their chemical bonding and structure. The chemical stability of glycerol in BWA-PAM electrolyte was analyzed with Raman spectroscopy. Figure 43 showed the Raman spectra for BWA-PAM modified with glycerol and the peak assignments are tabulated in Table 15.

The Raman analyses of PAM and BWA were previously discussed in sections 5.1 and 5.2. BWA was represented by its characteristic peak at 989.3 cm\(^{-1}\), while the PAM functional group was represented by the peaks at 1610.0 cm\(^{-1}\) and 1666.3 cm\(^{-1}\). Glycerol has strong peaks at three positions (859.1 cm\(^{-1}\), 1065.1 cm\(^{-1}\), and 1474.8 cm\(^{-1}\)), but most of these are overshadowed by the PAM peaks due to the relatively low concentration of glycerol in the BWA-PAM electrolytes. The only exception was the glycerol peak at 1065.1 cm\(^{-1}\) which did not overlap with any peaks from BWA and PAM, thus this peak was used to identify glycerol in the electrolytes.

When 5 wt% glycerol was added into PAM in the absence of BWA, the resultant spectrum in Figure 43 (a) showed both PAM and glycerol peaks. The intensity of glycerol peaks were lower due to the lower concentration of glycerol in the electrolyte. When 75 wt% BWA was added into the PAM modified with 5% glycerol, the resultant spectra showed all characteristic peaks for BWA, PAM, and glycerol. However, the glycerol peak was overshadowed by the relatively high-intensity BWA peaks. Adding 85 wt% BWA also resulted in the spectrum displaying all peaks from BWA, PAM and glycerol. The difference was the change in peak intensities, which were the simple addition of the BWA, PAM, and glycerol peaks according to their respective concentration.

Similar trend as the 5 wt% glycerol-modified electrolytes can be observed for the electrolytes modified with 10 wt% glycerol in Figure 43 (b). The ternary electrolytes showed all characteristic peaks from BWA, PAM, and glycerol. The only difference was the more prominent glycerol peak due to the higher glycerol content in the electrolytes. Thus, the BWA-PAM is compatible with glycerol because neither peak shifting nor additional peaks that did not belong to BWA, PAM, and glycerol were observed.
Figure 43: Raman spectra of PAM, BWA, and glycerol compared to Gly-PAM, 75BWA-PAM, 75BWA-PAM, and 85BWA-PAM modified with (a) 5 wt% Gly and (b) 10 wt% Gly. The characteristic peaks for BWA were highlighted in blue color, glycerol characteristic peak was highlighted in red color, and the PAM characteristic peaks were highlighted in green color.

Figure 44 shows a closer observation and comparison of the Raman spectra of 85BWA-PAM modified with glycerol in the range of 1000-2000 cm$^{-1}$ in comparison with its binary counterpart and 85BWA-PAM modified with 10 wt% H$_3$PO$_4$. As reported in Section 6.1, adding BWA into PAM will cause a partial transformation of PAM to PAM-co-PAA, which can be accelerated by H$_3$PO$_4$. This transformation was indicated by the decreased peak intensities for the PAM functional group of $\nu$(C-N), $\delta$(NH$_2$), and $\nu$(C=O) at 1426.9, 1610.0, and 1666.3 cm$^{-1}$ respectively, and an increased PAA peak intensity of $\nu$(COO$^-$) at 1717.2 cm$^{-1}$. 

The resultant spectrum of the 85BWA-PAM electrolyte modified with glycerol had a similar peak distribution as that of the pure PAM film, except for the δ(CH₂) peak at 1060 cm⁻¹ from the glycerol (see Table 15 in Appendix A). The slightly reduced υ(C-N) peak at 1426.9 cm⁻¹ for 85BWA-PAM + 10% Gly as compared to the PAM and the appearance of small PAA υ(COO⁻) peak at 1717.2 cm⁻¹ suggested a slight conversion of PAM to PAM-co-PAA.

When comparing 85BWA-PAM + 10% Gly with its binary counterpart, the PAM functional group peak intensities at 1426.9, 1610.0, and 1666.3 cm⁻¹ where higher and the PAA peak at 1717.2 cm⁻¹ had a smaller intensity. This suggested that the extent of PAM-co-PAA conversion in 85BWA-PAM + 10% Gly was much lower than its binary counterpart. The 85BWA-PAM + 10% H₃PO₄ showed a spectrum very similar to PAA, indicating that almost all PAM was converted to PAA. In contrast, glycerol as a neutral plasticizer showed a different interaction with BWA-PAM since the Raman spectrum still showed high intensities for the PAM peaks at 1426.9, 1610.0, and 1666.3 cm⁻¹ and just a minor PAA peak at 1717.2 cm⁻¹.

This suggested that the glycerol suppressed the conversion of PAM to PAA, thus preventing the crystallization and phase separation as observed in 85BWA-PAM + 10% H₃PO₄ as reported in Section 6.1. Therefore, glycerol is effective at enhancing the chemical stability of the BWA-PAM electrolytes.
Figure 44: Raman spectra of PAM, 85BWA-PAM, 85BWA-PAM + 10% H₃PO₄, 85BWA-PAM + 10% Gly, and PAA. The glycerol peak was highlighted in blue color, the PAM functional group peaks were highlighted in red color, and the PAA peak was highlighted in green color.
6.2.3 Water retention of BWA-PAM + Gly Ternary Electrolytes (XRD analysis)

Figure 45 is the XRD patterns of BWA-PAM electrolytes modified with glycerol. Figure 45 (a) shows that when PAM was modified with 5 wt% glycerol in the absence of BWA, the peaks at $ca. 11.9^\circ$ and $ca. 15-25^\circ$ merged into one as compared to that of PAM, suggesting a more amorphous characteristic of the films due to the water retention capability of glycerol.

When 75 wt% BWA was added into the PAM modified with 5 wt% glycerol, the XRD pattern in Figure 45 (a) showed a broad profile at $ca. 15-25^\circ$, indicating that the film retained an amorphous structure. The appearance of the strong peak at $ca. 7.0^\circ$ and a broad peak at $ca. 30^\circ$ was due to the BWA hydrates. At the higher concentration of 85 wt% BWA, the 85BWA-PAM + 5% Gly also showed the same broad peak at $ca. 15-25^\circ$, a strong peak at $ca. 7.7^\circ$, and a broad peak at $ca. 30^\circ$ as that of 75BWA-PAM + 5% Gly. The difference lies in the peak shifting from $ca. 7.0^\circ$ for 75BWA-PAM + 5% Gly to $ca. 7.7^\circ$ for 85BWA-PAM + 5% Gly and a slightly higher intensity of the peak at $ca. 30^\circ$. These observations suggested that the BWA became less hydrated at higher BWA concentration in the electrolyte.

Similar to the 5 wt% glycerol-modified electrolytes, the electrolytes modified with 10 wt% glycerol in Figure 45 (b) showed a similar trend where the 10% Gly-PAM showed a broad peak at $20^\circ$-$25^\circ$ and adding BWA resulted in an additional strong peak at $6.7-7.3^\circ$ and a broad peak at $ca. 30^\circ$. At higher BWA content, 85BWA-PAM + 10% Gly showed a shift of the peak from $ca. 6.7^\circ$ for 75BWA-PAM + 5% Gly to $ca. 7.3^\circ$ and an increase of peak intensity at $ca. 30^\circ$, again implying a lower level of hydration of BWA with increased BWA content.

When comparing Figure 45 (a) and (b), adding more glycerol shifted the strong peak at $7.0^\circ$-$7.7^\circ$ for 5 wt% glycerol down to $6.7^\circ$-$7.3^\circ$ range for 10 wt% glycerol, indicating a higher degree of film hydration with more glycerol. These observations were strong evidence that the hygroscopic glycerol helped to retain water in the films that resulted in a well-hydrated, amorphous structure. The high conductivity achieved with the addition of glycerol seen in Figure 42 was due to the enhanced water retention capability of the electrolytes to facilitate ion conduction. Since the 85BWA-PAM + 10% Gly showed both high conductivity and chemical stability, it was chosen for further investigation in Chapter 7.
6.3 Summary

The conductivity of BWA-PAM electrolyte can be improved by adding either an acidic plasticizer (H₃PO₄) or a neutral plasticizer (glycerol). Adding phosphoric acid (H₃PO₄) plasticizer can achieve higher conductivity of ca. 30 mS cm⁻¹ and longer service life by slowing the electrolyte dehydration. The combination of two acids (85 wt% BWA and 10 wt% H₃PO₄) at high concentration accelerated the hydrolysis reaction of PAM to PAM-co-polyacrylic acid (PAA) with NH₄⁺ as by-product. While partial conversion to PAA generally improves the hygroscopic behavior of the polymer, the NH₄⁺ by-product can react with BWA to form an undesirable phase separation. The neutral glycerol can lessen the conversion of PAM to PAM-co-PAA and mitigate this crystal precipitation issue. Thus, glycerol was proven to be better at maintaining the chemical stability and compatibility of the electrolyte system. Glycerol addition also demonstrated better water retention capability in the film to achieve a high conductivity of ca. 30 mS cm⁻¹ and longer service life than its binary counterpart.
Chapter 7
Device performance of the optimized ternary electrolytes

7.1 Acidic vs. Neutral Plasticizers

In Chapter 6, both 75BWA-PAM + 10% H₃PO₄ and 85BWA-PAM + 10% Gly solid polymer electrolytes were determined to be the optimal compositions because of their high conductivity and extended shelf life. Therefore, both electrolytes were tested in capacitor cells for further investigation. Figure 46 showed the room temperature conductivity of 75BWA-PAM + 10% H₃PO₄ and 85BWA-PAM + 10% Gly conditioned at 45% RH.

In general, both as-fabricated electrolytes modified with acidic and neutral plasticizers had comparable conductivity at \( \text{ca. } 30 \text{ mS cm}^{-1} \). After 28 days of tracking the cells, both electrolytes demonstrated a similar decrease in conductivity over time, resulting in \( \text{ca. } 70\% \) retention of their initial conductivity at day 28. The cells dehydrated over the tracking period due to the simple tape sealing of the cell setup (see Appendix D), which resulted in the reduction in the electrolyte thickness and self-shorting of the cells after day 28.

The high conductivity (\( \text{ca. } 30 \text{ mS cm}^{-1} \)) achieved by both 75BWA-PAM + 10% H₃PO₄ and 85BWA-PAM + 10% Gly outperformed the SiWA-PVA electrolyte with 10 wt% H₃PO₄ modification (\( \text{ca. } 20 \text{ mS cm}^{-1} \)) developed by Gao et al. [117, 224]. Both of the BWA-PAM + plasticizers were able to retain sufficient water to facilitate ion conduction at a high level comparable to the room temperature conductivity of SiWA-XLPVA + H₃PO₄ electrolyte (\( \text{ca. } 33 \text{ mS cm}^{-1} \)) at 45% RH condition [224]. Thus, both 75BWA-PAM + 10% H₃PO₄ and 85BWA-PAM + 10% Gly had comparable electrochemical performance with high conductivity and long shelf life suitable for EC applications. Both optimized ternary electrolytes were then tested with CNT-graphite electrodes in solid capacitor cells.
7.2 Solid Cells with 75BWA-PAM + 10% H$_3$PO$_4$ Electrolyte

A pair of CNT-graphite electrodes was first tested in liquid cells with 0.1 M BWA soaked in glass microfiber as the electrolyte. The same pair of electrodes was then used to assemble the 75BWA-PAM + 10% H$_3$PO$_4$ solid cells to evaluate the performance difference of replacing the liquid electrolyte with the solid polymer electrolytes.

7.2.1 Liquid Cells versus Solid Cells

Figure 47 shows the cyclic voltammograms (CVs) and the discharging capacitance as a function of scan rates for 75BWA-PAM + 10% H$_3$PO$_4$ solid cells against their BWA liquid cell counterparts. As shown in Figure 47 (a), the 0.1M BWA liquid cells demonstrated a near rectangular CV with a 1.2 V window at 50 mVs$^{-1}$. The 75BWA-PAM + 10% H$_3$PO$_4$ solid cells showed a different CV profile than their liquid cell counterparts likely due to the shift in open circuit potential.

At higher scan rate of 1 V s$^{-1}$, the liquid cells in Figure 47 (b) a near rectangular CV profile but slightly tilted as compared to that at 50 mVs$^{-1}$ (Figure 47 (a)). The 75BWA-PAM + 10% H$_3$PO$_4$ solid cells also showed a near rectangular CV at 1 V s$^{-1}$, but exhibited a slightly larger tilt than the cells with 0.1M BWA liquid electrolyte due to the increased resistance from the polymer as compared to the liquid. Nyquist and Bode plots for the solid cells are provided in Appendix E.
The rate capability of 75BWA-PAM + 10% H₃PO₄ solid cells was compared against the liquid counterparts in Figure 47 (c) using the same electrodes. The cells with 0.1M BWA liquid electrolyte exhibited a discharging capacitance of ca. 11.5 mF cm⁻² at 50 mV s⁻¹, and retained ≥ 75% of this capacitance (ca. 9.6 mF cm⁻²) at high scan rate of 1 V s⁻¹. The solid cells with 75BWA-PAM + 10% H₃PO₄ electrolyte showed ≥ 95% discharging capacitance (ca. 11.0 mF cm⁻²) as compared to that of the liquid electrolyte (ca. 11.5 mF cm⁻²), suggesting that replacing the liquid electrolyte with solid electrolyte did not significantly compromise the cell performance. The 75BWA-PAM + 10% H₃PO₄ solid cells also retained ≥ 75% of their discharging capacitance at 1 V s⁻¹ as compared to that at 50 mV s⁻¹ (see Figure 48 (c)), implying that the solid cells were capable of high rate performance.

These results suggested that the modification of BWA-PAM with 10 wt% H₃PO₄ plasticizers allowed the BWA-PAM-enabled capacitor cells to have high rate performance that is comparable to the liquid cells. Therefore, the solid cells with 75BWA-PAM + 10% H₃PO₄ electrolytes are very promising for solid ECs.

![Figure 47: Third scan of cyclic voltammograms (a) at 50 mV s⁻¹ and (b) at 1 V s⁻¹ for 75BWA-PAM + 10% H₃PO₄ on CNT-graphite solid cells against the liquid electrolyte cells; and (c) the discharging capacitance for 75BWA-PAM + 10% H₃PO₄ at various scan rates. Inset showed the solid capacitor cells.](image-url)
7.2.2 Cycle Life Analysis

A new set of CNT-graphite electrodes were used to assemble solid cells with 75BWA-PAM + 10% H₃PO₄ electrolyte for cycle life analysis in a galvanostatic cycling test over the voltage range of 0-1.2 V at 6 A g⁻¹. Figure 48 (a) depicts the charging-discharging cycle (CDC) curve for cycles 1-10 and 9,991-10,000 of the 75BWA-PAM + 10% H₃PO₄ solid cells. The capacitance of the solid cells dropped from ca. 9.88 mF cm⁻² in the first cycle to ca. 8.97 mF cm⁻² in the 10,000th cycle, an equivalent of ≥ 90 % capacitance retention that suggests a good cycle life.

Figure 48 (b) showed that the ESR of the 75BWA-PAM + 10% H₃PO₄ capacitor cells remained in a similar range of 1.0 Ω-1.2 Ω with a phase angle of ca. -85° before and after the CDC, suggesting that the electrolyte has a high stability under ambient condition to retain their highly capacitive behavior. The impedance response after the galvanostatic test showed a slightly larger hemispherical shape likely due to minor carbon ink delamination from the Ti substrate. The overlapping CVs in Figure 48 (c) for 75BWA-PAM + 10% H₃PO₄ cells suggests good cycle life to maintain their performance over the rigorous charging-discharging cycles.

Figure 48: (a) The capacitance retention rate of 75BWA-PAM + 10% H₃PO₄ solid cells throughout the 10,000 charging-discharging cycles (CDC) at 6 A g⁻¹ with the 1-10 cycles and 9,991-10,000 cycles shown in the inset; (b) Nyquist plots and (c) third scan of CVs at 50 mV s⁻¹ of 75BWA-PAM + 10% H₃PO₄ solid cells before and after the CDC.
7.3 Solid Cells with 85BWA-PAM + 10% Gly Electrolyte

A new pair of CNT-graphite electrodes was tested in 0.1 M BWA liquid cells and was used to assemble the 85BWA-PAM + 10% Gly solid cells to evaluate the performance difference of replacing the liquid electrolyte with the solid polymer electrolytes.

7.3.1 Liquid Cells versus Solid Cells

Figure 49 (a) revealed a near rectangular CV for the 85BWA-PAM + 10% Gly solid cells at 50 mVs\(^{-1}\), which is close to the liquid cell counterparts. Similar to the observation in 75BWA-PAM + 10% H\(_3\)PO\(_4\) solid cells, the 85BWA-PAM + 10% Gly solid cells showed a different CV profile than their liquid cell counterparts likely due to the shift in open circuit potential. The 85BWA-PAM + 10% Gly solid cells in Figure 49 demonstrated a slightly larger capacitance (\(ca. 15.6\) mF cm\(^{-2}\)) than that of 75BWA-PAM + 10% H\(_3\)PO\(_4\) solid cells in Figure 47 (\(ca. 11.5\) mF cm\(^{-2}\)) due to the difference in CNT-graphite loading on the electrodes.

Figure 49 (b) reveals that 85BWA-PAM + 10% Gly solid cells exhibited a near rectangular CV profile at 1 V s\(^{-1}\), but with a slightly more resistive response than its liquid cell counterpart as indicated by the tilting of the CV. Nyquist and Bode plots for the solid cells are provided in Appendix E. Figure 49 (c) shows that replacing the liquid electrolyte (\(ca. 16.2\) mF cm\(^{-2}\)) with 85BWA-PAM + 10% Gly solid cells (\(ca. 15.6\) mF cm\(^{-2}\)) also resulted in ≥ 95% discharging capacitance retention. The 85BWA-PAM + 10% Gly solid cells had high rate performance with ≥ 75% retention of their discharging capacitance at 1 V s\(^{-1}\) (\(ca. 10.8\) mF cm\(^{-2}\)) as compared to that of 50 mV s\(^{-1}\) (\(ca. 15.6\) mF cm\(^{-2}\)). Therefore, the solid cells with 85BWA-PAM + 10% Gly electrolyte are comparable to that of the liquid cells and are very promising for fast-charging solid ECs.
Figure 49: Third scan of cyclic voltammograms (a) at 50 mV s\(^{-1}\) and (b) at 1 V s\(^{-1}\) for 85BWA-PAM + 10% Gly on CNT-graphite solid cells against the liquid electrolyte cells; and (c) the discharging capacitance for 85BWA-PAM + 10% Gly at various scan rates. Inset showed the solid capacitor cells.

### 7.3.2 Cycle Life Analysis

A new set of CNT-graphite electrodes were used to assemble solid cells with 85BWA-PAM + 10% Gly electrolyte for cycle life analysis in a galvanostatic cycling test over the voltage range of 0-1.2 V at 6 A g\(^{-1}\). The 85BWA-PAM + 10% Gly cells exhibited a high initial capacitance of ca. 19.5 mF cm\(^{-2}\) and retained ≥ 90% of its initial capacitance (ca. 18.2 mF cm\(^{-2}\)) after 10,000 CDC as shown in Figure 50 (a). The symmetric triangular shape of the CDC curve after the galvanostatic cycling suggests that the cells have very good cycle life.

Figure 50 (b) compared the ESR of the 85BWA-PAM + 10% Gly cell before (0.83 Ω) and after (0.85 Ω) the 10,000 galvanostatic cycles which were very close to each other, implying that the glycerol-modified cells also have a high stability after the CDC. The impedance response after the CDC showed a slightly larger hemispherical shape likely due to minor carbon ink delamination from the Ti substrate.
The cyclic voltammograms of 85BWA-PAM + 10% Gly cells at slow scan rate of 50 mV s⁻¹ in Figure 50 (c) showed a near rectangular shape before and after the CDC. The ca. -85° phase angle and the near rectangular CV shapes for 85BWA-PAM + 10% Gly solid cells suggest a great cycle life and highly capacitive behavior.

In general, the performance of both 75BWA-PAM + 10% H3PO4 and 85BWA-PAM + 10% Gly solid capacitor cells were comparable to liquid cells and demonstrated long cycle life (≥ 90% capacitance retention and ca. -85° phase angle over 10,000 charging-discharging cycles). Therefore, the optimized ternary electrolytes have similar electrochemical performance suitable for high-rate and long-lasting EC applications.

Figure 50: (a) The capacitance retention rate of 85BWA-PAM + 10% Gly solid cells throughout the 10,000 charging-discharging cycles (CDC) at 6 A g⁻¹ with the 1-10 cycles and 9,991-10,000 cycles shown in the inset; (b) Nyquist plots and (c) third scan of CVs at 50 mV s⁻¹ of 85BWA-PAM + 10% Gly solid cells before and after the CDC.
7.4 Summary

The optimized ternary electrolytes with composition of 75BWA-PAM + 10% H₃PO₄ and 85BWA-PAM + 10% Gly were demonstrated to have similar conductivity despite the different plasticizers and BWA composition. These electrolytes can be made into solid capacitor cells that not only demonstrated a near rectangular CV window of 1.2 V up to 1 V s⁻¹ scan rate, but also displayed excellent cycle life of ≥ 90% capacitance retention and remained at ca. -85° phase angle over 10,000 charging-discharging cycles. The capacitance and rate performance of these solid cells were not significantly compromised when replacing the liquid electrolyte with solid polymer electrolytes. Therefore, both the 85BWA-PAM + 10% Gly and the 75BWA-PAM + 10% H₃PO₄ electrolytes are very promising candidates for SPE applications in fast-charging and long-lasting ECs.
Chapter 8
Summary and outlook

8.1 Conclusions

In this thesis, multiple electrochemical and material characterization techniques were performed to explore the structural and chemical bonding of the electrolyte system and the interactions between polymer, proton conductors, and additives. A thorough analysis of the experimental results helped to establish an understanding of the compatibility of the electrolyte materials; the effects of additives on the electrolytes; and the effects of material properties on conductivity.

The key attributes affecting the electrolyte properties and compatibility have been identified: water retention capability, concentration of ionic conductor, electrochemical stability window of HPAs, and types of plasticizers. The following understandings can be summarized.

- **BWA-PAM Binary Electrolytes:** The synthesized BWA had high purity. The BWA-PAM binary electrolyte system had been successfully developed. High concentration of BWA resulted in higher conductivity in PAM due to the availability of more ionic conductors. The strong acidity of BWA can hydrolyze acrylamide groups to partially transform PAM to PAM-co-PAA. This transformation may be beneficial as PAA is also hygroscopic. However, the BWA-PAM electrolyte system still suffers from water evaporation over time.

- **BWA-PAM + Plasticizers Ternary Electrolytes:** The dehydration of BWA-PAM can be improved by the addition of plasticizers. Two different plasticizers: acidic plasticizer (H₃PO₄) and neutral plasticizer (glycerol) were investigated. The hygroscopic H₃PO₄ not only helped to retain the water in the electrolyte, but also provide extra protons for conduction. The H₃PO₄ can increase the conversion of PAM to PAA. At high concentration of 85 wt% BWA, the by-product of this conversion reacted with BWA to form NH₄⁺-substituted BWA precipitation, which is undesirable for electrolyte performance. In contrast, glycerol assisted the polymer electrolytes to stay well-hydrated. The neutrality of glycerol helped to mitigate the conversion of PAM to PAA, thus eliminating the issue of phase separation as observed in the case of H₃PO₄ plasticizer.
- **Solid CNT-Graphite EC Cells:** The best compositions for acidic plasticizer- and neutral plasticizer-modified BWA-PAM electrolytes were used to assemble solid cells with CNT-graphite electrodes compared against the liquid cell counterparts. The electrolytes modified with both plasticizers had comparable conductivity and long-term performance. The solid cells demonstrated near rectangular CV profile of 1.2 V window and maintained $\geq 75\%$ discharging capacitance from 50 mV s$^{-1}$ to 1 V s$^{-1}$. Both cells with H$_3$PO$_4$-modified and glycerol-modified electrolytes demonstrated excellent cycle life and highly capacitive behavior by retaining $\geq 90\%$ capacitance and $ca. -85^\circ$ phase angle over the rigorous 10,000 charging-discharging cycles. Therefore, both the 85BWA-PAM + 10% Gly and the 75BWA-PAM + 10% H$_3$PO$_4$ ternary electrolytes are very promising candidates for SPE applications in ECs.
8.2 Future work

This thesis had developed solid polymer electrolytes based on BWA-PAM system and investigated the effects of different plasticizers on its performance. However, there are some properties that can be examined to further enhance this electrolyte system. This research can be carried forward by investigating the following aspects:

- The cell failure is attributed to the water loss due to poor sealing technique. Better sealing techniques such as hot press lamination can be explored to design ECs with longer service life.

- The characterizations presented in this thesis are limited to ambient temperature and 45% relative humidity (RH). The cell performance at lower RH and various temperature ranges can be investigated to analyze the versatility and feasibility of the cell under different environmental conditions.

- Other amorphous polymers can be explored to engineer a compatible electrolyte system with HPAs.

- Other structures and chemistries of HPAs can be investigated to further expand the electrochemical stability window for the electrolyte systems.

- Crosslinking of PAM or adding nanoparticles such as nano-silica (nano-SiO₂) or nano-titanium oxide (nano-TiO₂) as solid plasticizers to enhance the dimensional stability of the electrolyte.

- The compatibility of this electrolyte system with pseudocapacitive electrodes can be investigated.

- The conduction mechanism of the electrolyte systems can be characterized.
References


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Appendix A – Raman and FTIR Peak Assignments

This section presents the peak assignments for the Raman spectra for each of the samples discussed in this thesis. Table 9 and Table 10 were the Raman and FTIR peak assignments for SiWA and BWA. Table 11 and Table 12 were the Raman and FTIR peak assignments for PAM. Table 13, Table 14, and Table 15 were the Raman peak assignments for BWA-PAM binary electrolytes, BWA-PAM + H₃PO₄ ternary electrolytes, and BWA-PAM + Gly ternary electrolytes, respectively.

Table 9: Peak assignments for the Raman spectra of SiWA and BWA powders dried at 60ºC for 24 hours prior to the characterization [220-222].

<table>
<thead>
<tr>
<th>Raman Shift (cm⁻¹)</th>
<th>Band Assignments</th>
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<tbody>
<tr>
<td>SiWA</td>
<td>BWA</td>
</tr>
<tr>
<td>101.0</td>
<td>98.9</td>
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<tr>
<td>160.9</td>
<td>156.2</td>
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<td>980.5</td>
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<td>989.3</td>
</tr>
<tr>
<td>1006.1</td>
<td>-</td>
</tr>
<tr>
<td>3504.3</td>
<td>3504.3</td>
</tr>
</tbody>
</table>

Table 10: FTIR peak assignments for SiWA and BWA powders dried at 60ºC for 24 hours prior to the characterization [115, 173, 237-241].

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Band Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiWA</td>
<td>BWA</td>
</tr>
<tr>
<td>758.4</td>
<td>754.0</td>
</tr>
<tr>
<td>-</td>
<td>896.3</td>
</tr>
<tr>
<td>909.3</td>
<td>-</td>
</tr>
<tr>
<td>977.3</td>
<td>955.1</td>
</tr>
<tr>
<td>-</td>
<td>1001.4</td>
</tr>
<tr>
<td>1016.3</td>
<td>-</td>
</tr>
<tr>
<td>1618.0</td>
<td>1615.6</td>
</tr>
<tr>
<td>3500.2</td>
<td>3499.7</td>
</tr>
</tbody>
</table>
Table 11: Raman peak assignments for PAM film conditioned at 45% RH for 7 days [225].

<table>
<thead>
<tr>
<th>PAM Raman Shift (cm⁻¹)</th>
<th>Band Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>100.8</td>
<td>Lattice vibrations</td>
</tr>
<tr>
<td>485.7</td>
<td>skeletal δ(C-C)</td>
</tr>
<tr>
<td>638.6</td>
<td>ω(C=O)</td>
</tr>
<tr>
<td>776.2</td>
<td>(CH₂) rocking</td>
</tr>
<tr>
<td>846.4</td>
<td>υ(C-C) side-chain</td>
</tr>
<tr>
<td>1116.2</td>
<td>skeletal υ(C-C)</td>
</tr>
<tr>
<td>1217.0</td>
<td>(NH₂) wagging</td>
</tr>
<tr>
<td>1329.8</td>
<td>δ(C-H)</td>
</tr>
<tr>
<td>1426.9</td>
<td>υ(C-N)</td>
</tr>
<tr>
<td>1458.4</td>
<td>δ(CH₂)</td>
</tr>
<tr>
<td>1610.0</td>
<td>δ(NH₂)</td>
</tr>
<tr>
<td>1666.3</td>
<td>υ(C=O)</td>
</tr>
<tr>
<td>2877.9</td>
<td>υ(CH₂)</td>
</tr>
<tr>
<td>2937.4</td>
<td>υ(CH₂)</td>
</tr>
<tr>
<td>3199.9</td>
<td>υ(NH₂)</td>
</tr>
<tr>
<td>3355.3</td>
<td>δ(O-H)</td>
</tr>
</tbody>
</table>

Table 12: FTIR peak assignments for PAM film conditioned at 45% RH for 7 days [226].

<table>
<thead>
<tr>
<th>PAM Raman Shift (cm⁻¹)</th>
<th>Band Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1117.6</td>
<td>Skeletal (C-C) vibration</td>
</tr>
<tr>
<td>1178.8</td>
<td>(NH₂) wagging</td>
</tr>
<tr>
<td>1317.5</td>
<td>δ(C-H)</td>
</tr>
<tr>
<td>1344.0</td>
<td>(CH₂) wagging</td>
</tr>
<tr>
<td>1411.3</td>
<td>υ(C-N)</td>
</tr>
<tr>
<td>1446.0</td>
<td>δ(CH₂)</td>
</tr>
<tr>
<td>1596.9</td>
<td>δ(NH₂)</td>
</tr>
<tr>
<td>1645.8</td>
<td>υ(C=O)</td>
</tr>
<tr>
<td>2930.7</td>
<td>υ(C-H)</td>
</tr>
<tr>
<td>3175.4</td>
<td>υ(NH₂)</td>
</tr>
<tr>
<td>3324.3</td>
<td>δ(O-H)</td>
</tr>
</tbody>
</table>
Table 13: Peak assignments for the Raman spectra of BWA-PAM electrolyte systems [175, 176, 220-222, 225, 242].

<table>
<thead>
<tr>
<th>Raman Shift (cm(^{-1}))</th>
<th>Band Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BWA</strong></td>
<td><strong>PAM</strong></td>
</tr>
<tr>
<td>85.9</td>
<td>-</td>
</tr>
<tr>
<td>98.9</td>
<td>100.8</td>
</tr>
<tr>
<td>156.2</td>
<td>-</td>
</tr>
<tr>
<td>216.8</td>
<td>-</td>
</tr>
<tr>
<td>244.2</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>485.7</td>
</tr>
<tr>
<td>539.9</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>638.6</td>
</tr>
<tr>
<td>-</td>
<td>776.2</td>
</tr>
<tr>
<td>-</td>
<td>846.4</td>
</tr>
<tr>
<td>919.1</td>
<td>-</td>
</tr>
<tr>
<td>989.3</td>
<td>-</td>
</tr>
<tr>
<td>1116.2</td>
<td>-</td>
</tr>
<tr>
<td>1217.0</td>
<td>-</td>
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<tr>
<td>1329.8</td>
<td>1325.8</td>
</tr>
<tr>
<td>1426.9</td>
<td>1425.4</td>
</tr>
<tr>
<td>1458.4</td>
<td>1453.9</td>
</tr>
<tr>
<td>1610.0</td>
<td>1605.7</td>
</tr>
<tr>
<td>1666.3</td>
<td>1666.3</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2877.9</td>
<td>2873.5</td>
</tr>
<tr>
<td>2937.4</td>
<td>2928.5</td>
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<tr>
<td>-</td>
<td>3199.9</td>
</tr>
<tr>
<td>3355.3</td>
<td>3355.3</td>
</tr>
</tbody>
</table>

Table 14: Raman peak assignments for BWA-PAM + H\(_3\)PO\(_4\) electrolytes [175, 220-222, 225, 242-246].

<table>
<thead>
<tr>
<th>Raman Shift (cm(^{-1}))</th>
<th>Band Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BWA</strong></td>
<td><strong>PAM</strong></td>
</tr>
<tr>
<td>-</td>
<td>1116.2</td>
</tr>
<tr>
<td>-</td>
<td>1217.0</td>
</tr>
<tr>
<td>-</td>
<td>1329.8</td>
</tr>
<tr>
<td>-</td>
<td>1426.9</td>
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<td>-</td>
<td>1458.4</td>
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<td>-</td>
<td>1666.3</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 15: Raman peak assignments for BWA-PAM + glycerol electrolytes [175, 176, 220-
222, 225, 242, 245, 247, 248].

<table>
<thead>
<tr>
<th>Raman Shift (cm⁻¹)</th>
<th>Band Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>BWA</td>
<td>PAM</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>85.9</td>
<td>-</td>
</tr>
<tr>
<td>98.9</td>
<td>-</td>
</tr>
<tr>
<td>156.2</td>
<td>-</td>
</tr>
<tr>
<td>216.8</td>
<td>-</td>
</tr>
<tr>
<td>244.2</td>
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<td>-</td>
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<td>-</td>
<td>485.7</td>
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<td>539.9</td>
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<td>776.2</td>
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<td>846.4</td>
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<td>919.1</td>
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<td>-</td>
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<tr>
<td>989.3</td>
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<td>-</td>
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<td>-</td>
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<td>1426.9</td>
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<td>-</td>
<td>1666.3</td>
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<tr>
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<td>-</td>
</tr>
</tbody>
</table>
Appendix B – FTIR Analysis for SiWA and BWA

This section presents the FTIR for SiWA and BWA. Figure 51 showed the FTIR spectra of BWA in comparison with SiWA and the peak assignments were tabulated in Table 10 of Appendix A. The FTIR peaks for SiWA and BWA were assigned according to the well-established literature reports [115, 173, 237-241].

Both BWA and SiWA had δ(O-H) peaks near 1615 cm⁻¹ and 3500 cm⁻¹ which corresponded to the crystallized water in the HPAs. The FTIR spectrum for BWA was very similar to that of SiWA below 1100 cm⁻¹ region without any extra peak for the signature peaks of Keggin structure (see Table 10 in Appendix A). This suggested that BWA also had W-based Keggin structure. The slightly shift of BWA spectrum to a lower frequency as compared to that in SiWA was due to the larger size of BWA Keggin structure. Similar to observations in Raman spectroscopy, the BWA υ(B-O) peaks at 896.3 cm⁻¹ and 1001.4 cm⁻¹ were located at lower frequency than υ(Si-O) peaks (909.3 cm⁻¹ and 1016.3 cm⁻¹) due to the longer B-O than Si-O bond in the Keggin structure.

Thus, the FTIR results confirmed that the synthesized BWA had the required chemical bonding similar to SiWA to maintain the Keggin structure. The higher peak intensity of υ(W-O₆-W) at 754.0 cm⁻¹ as compared to SiWA agreed with the observation in Raman spectroscopy, suggesting that minor residual tungsten oxides may remain in BWA powder.

Figure 51: FTIR spectra of (a) SiWA powder and (b) the synthesized BWA powder dried at 60°C for 24 hours prior to the characterization.
Appendix C – Acid attack on PAM

Figure 52: The observations on the electrolytes for (a) 75BWA-PAM, (b) 85BWA-PAM, and (c) 90BWA-PAM after 6 months.

In this thesis, it was found out that the higher concentration of BWA can lead to higher conductivity of the electrolyte. Figure 52 shows the observation of the BWA-PAM electrolyte precursor after 6 months from their preparation. The 75BWA-PAM and 85BWA-PAM remained at similar viscosity to its pristine conditions. It was obvious from Figure 52 that 75BWA-PAM and 85BWA-PAM remained translucent after 6 months, suggesting the high stability of the electrolytes.

However, the 90BWA-PAM electrolyte became less viscous and turned into orange color with some solid precipitate at the bottom, which is an indication of the hydrolysis of PAM by the strong acids [231]. From this observation, it was deduced that 85BWA-PAM should be the upper limit for the electrolyte composition because the electrolyte is highly susceptible to chemical instability beyond this threshold. Therefore, this thesis will only investigate BWA concentration up to 85 wt% BWA.
Appendix D – Change in electrolyte thickness due to dehydration

Figure 53: The change in electrolyte thickness over a tracking period of 21 days conditioned at 45% RH.

The BWA-PAM electrolyte undergoes dehydration over time, which may result in the decrease in the electrolyte thickness from the water loss. Figure 53 shows the change in thickness of the electrolyte over a period of 21 days. Even though the device is stored in 45% RH for the entire tracking period, the electrolyte thickness still decreases over time for the cells packaged with tapes and packaged with photo laminates.

The taped cells have thickness decreased by roughly 30 μm per week. This indicates that the sealing of the cell with the polyester tape is not optimal for the flexible device. The electrolyte will still dry out over time. When the cell is packaged with photo laminates, the sealed cells have thickness decreased by roughly 20 μm per week. This indicates that a better sealing technique can help to improve the service life of the cell.
Appendix E – Electrochemical impedance spectroscopy (EIS) analyses for the liquid cells and the solid cells

Figure 54: The Nyquist (left) and Bode (right) plots for (a) 75BWA-PAM + 10% H₃PO₄ and (b) 85BWA-PAM + 10%Gly solid cells against their liquid cell counterparts.

The Nyquist plots for both 75BWA-PAM + 10% H₃PO₄ and 85BWA-PAM + 10% Gly solid cells showed reduced resistance as compared to their liquid cell counterparts. This reduction in resistance is attributed to the lower cell thickness enabled by solid polymer electrolytes. The Bode plots reveal that switching from liquid electrolytes to solid electrolytes in the cells also maintained the near -85° phase angle at low frequency, indicating a very capacitive behavior of the solid cells.