Nanocarbon/Polyoxometalate Composite Electrodes for Electrochemical Capacitors

by

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

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Abstract

Carbon materials are commonly studied as the electrode material for electrochemical double layer capacitance (EDLC) due to their high surface area. The present work aimed to leverage both EDLC and pseudocapacitance through chemical modification of multi-wall carbon nanotubes (MWCNTs) and onion-like carbon (OLC) with polyoxometalates (POMs) to further enhance the performance of these electrodes. Layer-by-layer (LbL) deposition of two commercially available POMs (PMo$_{12}$O$_{40}^{3-}$ and SiMo$_{12}$O$_{40}^{4-}$) and three synthesized POMs (PMo$_{11}$VO$_{40}^{4+}$, PMo$_{10}$V$_2$O$_{40}^{5-}$ and PMo$_9$V$_3$O$_{40}^{6-}$) has been investigated. A single-layer of POMs increased the area specific capacitance by approximately three-times, while superimposing of these POMs into two-layer coatings increased the capacitance by approximately five-times. The morphology and composition of these composite materials were investigated using Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS).
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List of Abbreviations

CD – Charge/Discharge

CNT – Carbon nanotubes

CV – Cyclic Voltammetry

E – Energy

EC – Electrochemical capacitor

ECs – Electrochemical capacitors

EDLC – Electrochemical double layer capacitance

EDLCs – Electrochemical double layer capacitors

EDX – Energy-dispersive X-ray Spectroscopy

ESR – Equivalent series resistance

GC – Glassy carbon

LbL – Layer-by-Layer

ML – Multi-layer

MWCNTs – Multi-wall carbon nanotubes

ND – Nanodiamond

OLC – Onion-Like Carbon

P – Power

PDDA – Poly (diallyldimethylammonium chloride)

PM\textsubscript{(12-x)}V\textsubscript{x} – Vanadium substituted phosphomolybdic acid
PMo$_{10}$V$_2$ – 10-Molybdo-2-vanadophosphoric acid or PMo$_{10}$V$_2$O$_{40}$$^{5-}$

PMo$_{11}$V – 11-Molybdo-1-vanadophosphoric acid or PMo$_{11}$VO$_{40}$$^{4-}$

PMo$_{12}$ – Phosphomolybdic acid or PMo$_{12}$O$_{40}$$^{3-}$

PMo$_9$V$_3$ – 9-Molybdo-3-vanadophosphoric acid or PMo$_9$V$_3$O$_{40}$$^{6-}$

POM – Polyoxometalate

POMs – Polyoxometalates

SEM – Scanning Electron Microscopy

SiMo$_{12}$ – Silicomolybdic acid or SiMo$_{12}$O$_{40}$$^{4-}$

SL – Single-layer

SWCNTs – Single-wall carbon nanotubes

TEM – Transmission Electron Microscopy

TNT – Trinitrotoluene

XPS – X-ray Photoelectron Spectroscopy

XRD – X-ray Diffraction
1 Introduction

As the world’s population increases, energy consumption has become a global concern. The decreasing availability of fossil fuels and climate change require society to shift towards sustainable and renewable energy resources. Renewable power generation systems such as solar cells and wind turbines are currently preferred for clean energy. However, due to the intermittent and unpredictable nature of these power generation systems, the use of electrical energy storage systems is equally important. The development of new electrical energy storage systems with higher energy densities, higher power densities, faster charging/discharging cycles, longer cycle life and lower cost is critical to move towards a society that completely relies on sustainable and renewable energy resources [1-3].

Electrochemical devices such as batteries and electrochemical capacitors (ECs) are among the leading electrical energy storage technologies. The focus of this work was on the latter, ECs. Figure 1-1 is a Ragone plot of specific power against specific energy for various electrochemical energy storage devices. Batteries have high specific energy but suffer from low specific power. ECs have high specific power but their energy density is lower than that of batteries. However, the energy density of ECs is 20 to 200 times higher than conventional electrostatic capacitors. ECs can be rapidly charged and discharged, have long cycle life, are highly reliable with low maintenance and operate within a wide temperature range [1,4-6]. A comparison of the properties of electrostatic capacitors, ECs and batteries is shown in table 1-1.

The distinctive properties of ECs have led to their use in numerous applications, including electric vehicles, digital communication devices, digital cameras, mobile phones, and storage of energy generated by solar cells [7-10]. A recent application is the use of ECs in emergency doors (16 per plane) on an Airbus A380 [1]. This warrants that in terms of safety, performance and reliability ECs are ready for large-scale applications. However, the use of ECs is still limited in many potential applications. These limitations are mainly due to two disadvantages, high cost and low specific energy. The cost of ECs is highly dependent on the material cost, and will
continue to decrease as the demand for ECs increases [1]. Subsequently, methods to increasing the specific energy of ECs have been highly researched [1,3-5,11-14] and were also the focus of this work.

*Figure 1-1: Ragone plot of specific power versus specific energy for various electrochemical energy storage devices, extrapolated from ref. [4].*

Specific energy and other proprieties of ECs are dependent on the different components of these devices. A schematic representation of ECs is shown in figure 1-2. Similar to a battery, ECs consist of two electrodes (anode and cathode), an electrolyte, current collectors and the separator. The electrodes are important components of ECs and were investigated in this project. To enhance the performance of ECs, particularly the specific energy density while retaining its intrinsic high specific power, researchers have focused on improving the properties of the electrode material [1,3,5,11,12,14-18].
Table 1-1: Comparison of the properties of electrostatic capacitors, electrochemical capacitors and batteries [5].

<table>
<thead>
<tr>
<th></th>
<th>Electrostatic Capacitor</th>
<th>Electrochemical Capacitor</th>
<th>Battery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discharge time</td>
<td>$10^{-3}$ to $10^{-6}$ seconds</td>
<td>0.3-30 seconds</td>
<td>0.3-3 hours</td>
</tr>
<tr>
<td>Charge time</td>
<td>$10^{-3}$ to $10^{-6}$ seconds</td>
<td>0.3-30 seconds</td>
<td>1-5 hours</td>
</tr>
<tr>
<td>Energy density (Wh/kg)</td>
<td>&lt;0.1</td>
<td>1-10</td>
<td>10-100</td>
</tr>
<tr>
<td>Specific power (W/kg)</td>
<td>&gt;10,000</td>
<td>≈1000</td>
<td>50-200</td>
</tr>
<tr>
<td>Charge-discharge efficiency</td>
<td>≈1</td>
<td>0.85-0.98</td>
<td>≈1</td>
</tr>
<tr>
<td>Cycle life</td>
<td>&gt;500,000</td>
<td>&gt;100,000</td>
<td>500-2000</td>
</tr>
</tbody>
</table>

Figure 1-2: Schematic representation of an electrochemical capacitor and its essential components, extrapolated from ref. [1].
The energy (E) and power (P) of ECs can be calculated using equations (1) and (2), respectively. Here, C is the overall capacitance of the cell in Farads, V is the cell voltage, and R is the equivalent series resistance (ESR) in ohms [4]. Energy may be increased by increasing either capacitance or cell voltage, while power may be increased by either increasing cell voltage or decreasing ESR. These properties are related to the primary components of ECs, where capacitance is dependent on the electrode, cell voltage is dependent on the electrolyte and ESR is dependent on both the electrode and electrolyte.

\[
E = \frac{1}{2} CV^2 \tag{1}
\]

\[
P_{\text{max}} = \frac{V^2}{4R} \tag{2}
\]

The operating voltage of ECs is dependent on electrolyte stability [4,19,20]. There are two types of electrolytes, aqueous electrolytes and non-aqueous electrolytes. Aqueous electrolytes (acids and alkaline) have the advantage of high ionic conductivity (up to \(\sim 1\) S/cm), high dielectric constant, low cost and wide acceptance [4]. However, they have a restricted voltage window of approximately 1.23 V [21], beyond which they are unstable and will start to decompose. Non-aqueous electrolytes allow much higher operating voltages, as high as 2.5 V [4,21]. However, the electrical resistivity of non-aqueous electrolytes is at least an order of magnitude higher than that of aqueous electrolytes [4], which leads to a high internal resistance and thus ESR. Although the high operating voltage increases the energy, the high internal resistance will limit the power capability of the capacitor. Therefore, a vast amount of research has been focused on developing electrode material with a high specific capacitance in order to improve the energy storage performance of ECs. The focus of this work was also on the electrode material, where the specific energy may be increased by increasing the capacitance and power may be maintained by minimizing the increase in electrode resistance.

There are two types of capacitance in ECs, electrochemical double layer capacitance (EDLC) and pseudocapacitance. EDLC arises from charge generated by the electrostatic and reversible adsorption/desorption of ions of the electrolyte onto the surface of the electrode. Pseudocapacitance arises from reversible oxidation/reduction Faradaic reactions on the surface
of the electrode. High specific surface area carbon materials are ideal for EDLC [1,4,5], while transition metal oxides such as ruthenium dioxide (RuO₂) exhibit ideal pseudocapacitance properties[22]. The specific capacitance of pure pseudocapacitance materials can be 10 to 100 times greater than EDLC [20]. Carbon electrodes may be modified with RuO₂ in order to increase the energy storage of ECs [23,24]. However, the high capacitance of RuO₂ comes at a very high cost. Therefore, polyoxometalates (POMs) were investigated as low cost alternatives to RuO₂. The following work investigated the fabrication of carbon/polyoxometalate composites using the layer-by-layer (LbL) chemical modification process.

Previous work has demonstrated the feasibility and application of the LbL technique for the fabrication of carbon/polyoxometalate composites [11,12,14,15,25,26] and has opened the door for further investigations into this topic. A detailed understanding of each layer in the LbL technique and their impact on the proceeding layers must be developed in order to further improve this deposition process. As well, only the application of commercially available POMs has been investigated. There are hundreds of POMs with unique electrochemical properties that still remain to be investigated for this particular application. Also, there is still no notable work that demonstrated the use of these carbon/polyoxometalate composites in actual devices. Therefore, the aim of the following project was to investigate these approaches in order to further enhance the performance of carbon/polyoxometalate composites for application as the electrode material in ECs.
Chapter 2
Objectives

2 Objectives

In this work, two different double-layer carbon materials, multi-wall carbon nanotubes (MWCNTs) and onion like carbon (OLC) were modified using several different polyoxometalate (POM) chemistries via the LbL technique. The objective of this work is to add pseudocapacitive material to the double layer electrode to increase the specific energy (by increasing capacitance) of ECs, while maintaining high specific power (maintaining low ESR). These composite electrodes must also have the following properties:

1. Fast Charging/Discharging
2. Ideal Capacitive Behaviour
3. Long Cycle Life
4. Low Cost
5. Easy Fabrication

With the purpose of accomplishing the above objectives, the following approaches were explored:

1. Developing a robust methodology to design and engineer the electrode surface via chemical modification.
2. Developing an understanding of the effects of each layer in the LbL technique on the subsequent layers and the final properties of the composite material, including carbon substrate, along with positive and negative layers in the configuration.
3. Synthesizing non-commercial POMs to compliment the current commercial POMs and investigate their properties.
4. Applying the developed carbon/polyoxometalate electrode materials for EC devices.
3 Literature Review

3.1 Charge Storage Mechanism of Electrochemical Capacitors

The capacitance of ECs originates from two different charge storage mechanisms, electrochemical double layer capacitance (EDLC) and pseudocapacitance. EDLC arises from the reversible adsorption/desorption of ions from the electrolyte onto the surface of the electrode, which results in double-layer charging/discharging [1,5]. Pseudocapacitance occurs from fast and reversible redox reactions at the electrode surface [1,5]. A comparison between the different properties of EDLC and pseudocapacitance is shown in table 3-1.

Table 3-1: Comparison between EDLC and pseudocapacitance [5].

<table>
<thead>
<tr>
<th></th>
<th>EDLC</th>
<th>Pseudocapacitance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Non- Faradaic</td>
<td>Involves Faradaic reactions</td>
</tr>
<tr>
<td>2.</td>
<td>20–50 µF/cm²</td>
<td>200-2000 µF/cm²</td>
</tr>
<tr>
<td>3.</td>
<td>Current is independent of potential</td>
<td>Current is highly dependent on potential, except for RuO₂, which exhibits multiple overlapping Faradaic reactions</td>
</tr>
<tr>
<td>4.</td>
<td>Highly reversible charging/discharging</td>
<td>Highly reversible charging/discharging as long as the scan rate is low in comparison to kinetics of Faradaic reactions</td>
</tr>
<tr>
<td>5.</td>
<td>Has restricted voltage range</td>
<td>Has restricted voltage range</td>
</tr>
<tr>
<td>6.</td>
<td>Exhibits mirror-image cyclic voltammograms</td>
<td>Exhibits mirror-image cyclic voltammograms</td>
</tr>
</tbody>
</table>
3.2 Electrochemical double layer capacitance

3.2.1 Charge Storage Mechanism of EDLC

Electrochemical double layer capacitors (EDLCs) store charge electrostatically, using reversible adsorption/desorption of ions of the electrolyte onto the surface of the electrode \[1,5\]. The charged and discharged states of EDLCs are schematically represented in figure 3-1a and 3-1b, respectively. Carbon materials are most commonly used for EDLCs due to their high specific surface area and low cost \[1,5\]. Due to the low cost associated with these capacitors, the commercial market of ECs is dominated by EDLCs. The structure of EDLCs consists of two electrodes immersed in an electrolyte, with an ion permeable separator in between the two electrodes. In this device, the two electrodes are completely isolated electrically such that each electrode-electrolyte interface represents a capacitor (figure 3-1c). Therefore, the complete cell is considered to be two capacitors in series and the cell capacitance \((C_{cell})\) is represented by:

\[
\frac{1}{C_{cell}} = \frac{1}{C_a} + \frac{1}{C_c}
\]  

(3)

where \(C_a\) and \(C_b\) correspond to the capacitance of the anode and the cathode, respectively \[4\]. Literature often shows specific capacitance values of a single electrode, which are derived from a three-electrode cell consisting of a reference electrode and a counter electrode \[1,4,11,14,25\]. For a symmetrical capacitor (identical anode and cathode) the overall cell capacitance is half the capacitance value of each individual electrode. On the other hand, an asymmetrical capacitor (different anode and cathode) will have an overall capacitance that is dominated by the electrode with the lower capacitance value \[27\]. The double layer capacitance \((C_{dl})\), at each electrode interface can be represented by:

\[
C_{dl} = \frac{\varepsilon_r\varepsilon_o A}{t}
\]  

(4)

where \(\varepsilon_r\) is the dielectric constant of the electrolyte, \(\varepsilon_o\) is the dielectric constant of a vacuum, \(A\) is the surface area of the electrode and \(t\) is the effective thickness of the electrical double layer. As discussed earlier, the energy \((E)\) and power \((P)\) of ECs is represented by equation 1 and 2, respectively.
The amount of energy stored in ECs is proportional to the capacitance as well as the square of cell voltage. Thus the energy of ECs can be increased by either increasing the specific capacitance, or the cell voltage. The focus of this work was on increasing the capacitance, which is dependent on the electrode component and proportional to the amount of charge stored. It should be noted that increasing the energy density of ECs usually comes at the cost of losses in power and cycle life, which are unique advantages of ECs [28]. Blindly increasing energy without considering power will lead to ECs becoming mediocre batteries. Therefore, the approach in this project was not only increasing the capacitance, but also limiting the increase in electrode resistance so that the high power capability of ECs is preserved.

Figure 3-1: Schematic representation of an EDLC a) discharged state b) charged state and c) charged equivalent circuit model, extrapolated from ref. [4].
3.2.2 Electrode Materials for EDLCs

Equation 4 suggests that double layer capacitance is proportional to the area of the electrode/electrolyte interface. Carbon materials, due to their high specific surface area, high conductivity and low cost, have been extensively studied as the electrode material for EDLCs [1,4,5,29]. Table 3-2 shows the properties and structure of six different carbon materials, onion-like carbon (OLC), carbon nanotubes (CNTs), graphene, activated carbon, carbide-derived carbon and template carbon. It can be observed that there is a general trade-off between performance and cost. There is also a trade-off between conductivity and volumetric capacitance. The following project focused on the application of two carbon materials as the electrode material, CNTs and OLC. The purpose of this project was to use these double layer materials as a substrate for thin film pseudocapacitive coatings. In addition to good charge storage, these carbon materials must also exhibit good electrical conductivity and surface adhesion. The properties of these carbon materials are discussed in sections 3.2.2.1 and 3.2.2.2.

Table 3-2: Properties and structures of different carbon materials used in EDLCs [29].

<table>
<thead>
<tr>
<th>Material</th>
<th>Carbon onions</th>
<th>Carbon nanotubes</th>
<th>Graphene</th>
<th>Activated carbon</th>
<th>Carbide derived carbon</th>
<th>Templated carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimensionality</td>
<td>0-D</td>
<td>1-D</td>
<td>2-D</td>
<td>3-D</td>
<td>3-D</td>
<td>3-D</td>
</tr>
<tr>
<td>Conductivity</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>Low</td>
<td>Moderate</td>
<td>Low</td>
</tr>
<tr>
<td>Volumetric Capacitance</td>
<td>Low</td>
<td>Low</td>
<td>Moderate</td>
<td>High</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Cost</td>
<td>High</td>
<td>High</td>
<td>Moderate</td>
<td>Low</td>
<td>Moderate</td>
<td>High</td>
</tr>
<tr>
<td>Structure</td>
<td>✪</td>
<td>✪</td>
<td>✪</td>
<td>✪</td>
<td>✪</td>
<td>✪</td>
</tr>
</tbody>
</table>

3.2.2.1 Carbon Nanotubes

Within the last decade, carbon nanotubes (CNTs) have been extensively studied as the electrode material for EDLCs [1,4,5,11]. These materials not only have fascinating structural features, but also have high specific surface area, high electrical conductivity, good physicochemical stability and excellent strength. CNTs are produced from the catalytic decomposition of hydrocarbons [30]. Depending on the synthesis method, CNTs may be prepared as single-wall carbon nanotubes (SWCNTs) or multi-wall carbon nanotubes (MWCNTs). Both of these are schematically represented ✪.
in figure 3-2. SWCNTs consist of a single rolled sheet of graphene, and have a tube diameter of approximately 1-2nm. Alternatively, MWCNTs consist of multiple parallel layers of graphene rolled into a tube. The inter-layer spacing in MWCNTs is approximately 0.36 nm, which results in a tube diameter that ranges from 2-25nm. Depending on the synthesis method, the length of CNTs can range from a few micrometers to a few millimeters [31]. In comparison to MWCNTs, SWCNTs have higher specific surface area and conductivity but are much more expensive. Therefore, MWCNTs are much more practical for large volume commercial applications.

Figure 3-2: Schematic representation of A) single-wall carbon nanotubes and B) multi-wall carbon nanotubes [31].

MWCNTs are expected to have a high concentration of sp² hybridized carbon, which is desirable for further functionalization of the surface. However, CNTs tend to be agglomerated and they may also contain sp³ hybridized carbon on the outer surface. The diamond structure is not desirable for this application because sp³ is a saturated bond. In order to improve the dispersion and adhesion properties, CNTs may be functionalized using many different methods. They may be oxidized in air, or treated with a strong acid (HNO₃ or H₂SO₄) [32,33]. Oxidation of the
surface introduces carboxyl and carbonyl functional groups, which act as active sites for further functionalization [32,34].

Osswald et al [32] studied the oxidation of MWCNTs in air and acids, while varying the treatment time and/or temperature. It was found that the as-received MWCNTs display amorphous carbon (sp\(^3\) hybridized) on the surface (figure 3-3a). In order to remove this amorphous carbon, the as-received MWCNTs were annealed and treated with acid. During annealing graphitization took place and resulted in an ordered structure and removal of amorphous carbon (figure 3-3b). During acid treatment the surface was oxidized and functional groups were generated without damaging the overall structure of MWCNTs (figure 3-3c).

![Figure 3-3: Transmission Electron Microscopy (TEM) images of a) as-received b) graphitized and c) nitric-acid oxidized MWCNTs. The arrows in a) indicate amorphous carbon on the surface, which are successfully removed by annealing (b). Subsequently, acid treatment results in the oxidation of the outer walls and introduces defective sites (arrows in c) [32].](image)

3.2.2.2 Onion-like Carbon

Onion-like carbon (OLC) was first discovered in 1980 [35], but has recently gained interest as a potential electrode material for EDLCs [14,36-39]. The precursor of OLC is nanodiamond (ND), which can be produced inside of a steel chamber using the detonation of carbon-containing explosives such as trinitrotoluene (TNT) and hexogen [40]. ND has a nanocomposite structure which contains mostly sp\(^3\) hybridized carbon and a very small amount (0.3~5%) of sp\(^2\) hybridized carbon. OLC is formed via vacuum annealing from ND [41]. Typical conditions for
vacuum annealing include temperatures above 1200°C and a vacuum pressure higher than 10^{-6} torr. During this process, sp³-bonded ND is gradually transformed into sp²-bonded carbon nanosphere particles of 5-10 nm in size [37]. These particles are often interconnected because of the sintering of agglomerated diamond powder at elevated temperatures. Figure 3-4 shows Transmission Electron Microscopy (TEM) images that demonstrate the formation of OLC which was vacuum annealed at various temperatures [37]. The as-received ND mostly contains sp³ hybridized diamond cores and some sp² hybridized graphite shells [37,40]. After annealing at a temperature of 1200°C, the sp² hybridized graphite shells become highly visible (figure 3-4a), indicating the transformation of ND into OLC. Annealing at a higher temperature of 1800°C results in complete transformation of ND into OLC (figure 3-4b).

![Figure 3-4: TEM images of ND that was vacuum annealed for the production of OLC at an annealing temperature of a) 1200°C and b) 1800°C [37].](image.jpg)

Annealing of ND to form OLC results in two-dimensional conducting paths which lead to a significant increase in the electrical conductivity (from 0.025 to 4 S/cm) [37]. Furthermore, OLC offers a specific surface area of approximately 500-600 m²/g that is fully accessible to ion adsorption. Due to this high electrical conductivity, OLC has proven to be an excellent EC electrode material for high rate and high power applications. OLC electrodes assembled in a microsized electrochemical capacitor device were able to be cycled at a scan rate of 200 V/s [17]. The cyclic voltammogram of this device at a scan rate of 100 V/s is illustrated in figure 3-5, which demonstrates an ideal "rectangular" profile.
Figure 3-5: Cyclic voltammogram of microsized electrochemical capacitor device that was developed by Pech et. al. to demonstrate the high power capabilities of OLC electrodes [42].

Table 3-3 lists the area specific capacitance of MWCNTs and OLC. These values were obtained from literature that uses a similar three electrode cell to the one that was employed in this project. Both these material demonstrate similar capacitance values. However, OLC is able to demonstrate a similar capacitance at a much higher scan rate (5 V/s versus 0.05 V/s).

Table 3-3: Area specific capacitance of MWCNTs and OLC using a three electrode cell in 1M H₂SO₄ electrolyte and cavity micro electrode (CME) as the working electrode. Platinum and Ag/AgCl Sat. were used as the counter and reference electrodes, respectively.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Specific Capacitance (F/cm²)</th>
<th>Scan Rate (V/s)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNTs</td>
<td>1 M H₂SO₄</td>
<td>0.6</td>
<td>0.05</td>
</tr>
<tr>
<td>OLC</td>
<td>1 M H₂SO₄</td>
<td>0.5</td>
<td>5</td>
</tr>
</tbody>
</table>
3.3 Pseudocapacitance

3.3.1 Charge Storage Mechanism of Pseudocapacitance

EDLCs are low cost; however they have low specific capacitance. Alternatively, the specific capacitance of pure pseudocapacitive materials is 10 to 100 times higher than double layer materials [20]. Therefore, EDLCs may be complemented by the addition of pseudocapacitance in order to increase the overall capacitance of the electrode material. Pseudocapacitors store charge by reversible Faradaic charge transfer reactions on the surface of the electrode [1,5]. In pseudocapacitance, there is exchange of charge across the double layer, rather than a static separation of charge across a finite distance as in the case of EDLC. This concept is schematically represented in figure 3-6, where charge (ne⁻) is exchanged in the oxidation/reduction reaction, and the energy storage is via chemical reactions; analogous to that of a battery [5].

![Figure 3-6: Schematic representation of an oxidation/reduction reaction that generates pseudocapacitance.](image)

Even in EDLCs, approximately 1-5% of the capacitance is due to Faradaic charge transfer reactions of oxidized functional groups present on the surface of carbon electrodes [4,19]. The capacitance generated by pure pseudocapacitive materials such as ruthenium dioxide (RuO₂) is much greater than what is generated by these surface functional groups. RuO₂ represents the ideal pseudocapacitor due to its high specific capacitance, long cycle life, good electrochemical stability and high conductivity [1,5,23]. RuO₂ exhibits a rectangular “capacitive” profile (figure 3-7) that is ideal for electrochemical capacitors [43]. For this material, the charging/discharging
current is constant, which is a result of several overlapping Faradaic oxidation/reduction reactions. It has been reported that nano-sized hydrous RuO$_2$/carbon composites can generate a specific capacitance as high as 1350 F/g [23]. However, the high cost associated with the precious metal ruthenium has impeded the commercial use of RuO$_2$ as an electrode material for ECs. Research has focused on low cost pseudocapacitive alternatives to RuO$_2$ and some of these alternatives are discussed in section 3.3.2 and 3.3.3.

Figure 3-7: Cyclic voltammogram profile of a RuO$_2$ electrode in 1M H$_2$SO$_4$ aqueous electrolyte, which shows an ideal "rectangular" profile. [43].

### 3.3.2 Common Pseudocapacitive Materials

Transition metal oxides such as manganese dioxide (MnO$_2$) is an attractive candidate for pseudocapacitors due to its low cost [5,44]. MnO$_2$ exhibits capacitance as high as 200 F/g [45], however this material was not used in this project because of three reasons. First, MnO$_2$ has poor conductivity. Also, MnO$_2$ cannot be deposited using the LbL process due to its insolubility in water and inability to covalently bond with the substrate. Preparation of MnO$_2$ composites is
long and complex, because the oxidation state, solution pH and substrate microstructure have to be controlled for successful disposition [46,47]. Lastly, MnO₂ is only compatible with alkaline electrolytes; which impedes its usage with proton conducting solid polymer electrolytes [45].

Another example of commonly studied pseudocapacitive materials is conductive polymers. Conductive polymers have the advantages of high specific capacitance, light weight, and ability to be formed in various flexible shapes [5]. However, their applications for this project were also limited due to three reasons. First, they have poor conductivity compared to metallic pseudocapacitance materials. Also, the deposition of conductive polymers is complex since they must be polymerized onto the substrate [48]. Lastly, swelling and shrinking of these electroactive polymers results in the degradation of their capacitance as they are repeatedly cycled [5].

For the following project, pseudocapacitive materials known as polyoxometalates (POMs) were investigated. Amongst several alternatives to exploit the redox activity of materials in ECs (e.g. MnO₂ [45] and polyaniline [49,50]), POMs are promising due to their well-known reversible and multiple electron electrochemical reactions, their stability and low cost.

3.3.3 Polyoxometalates

Polyoxometalates (POMs) constitute a subset of metal oxide clusters with an unmatched range of physical and chemical properties. These compounds not only have a range of diverse structures, but also have a wide range of sizes from nanometers to a few micrometers. The versatile range of structure, size, photochemistry, redox chemistry, and charge distribution makes polyoxometalate chemistry one of the key emerging areas in inorganic chemistry [51]. Until 2010, there are over 500 papers published each year involving POM chemistry and this number is increasing rapidly [22].

POMs have diverse properties such as catalytic activity and high stability of their redox states. These materials have the ability to act as an electron reservoir, thus giving rise to mixed valence state species [52,53]. These attributes make POMs particularly advantageous for applications in electrochemical storage devices such as ECs.
POMs are polyoxoanions of the early transition elements, primarily vanadium (V$^{5+}$), molybdenum (Mo$^{6+}$) and tungsten (W$^{6+}$) [22]. Transition elements such as niobium (Nb$^{5+}$) and tantalum (Ta$^{5+}$) may also form POMs [54]. In general, these materials are based on metal oxide building blocks with a general formula of [MO$_x$]$_n$, where M is the transition metal oxide and $x$ can range from 4 to 7 [22]. These structural combinations lead to many thousands of compounds in the polyoxometalate category. POM clusters are anionic and can be complexed with cations as linkers, making their chemistry even more diverse and complex. It is possible to classify POMs into three broad categories:

1. Heteropolyanions are by far the most explored class of POMs. These consist of a high atomic proportion of one type of transition metal, the “addenda atoms”, and a small atomic proportion of other types of atoms that are referred to as “heteroatoms”. The addenda atom is usually the transition metals vanadium, molybdenum, tungsten and to a lesser extent, niobium, tantalum, rhenium and iodine in their highest oxidation states. There are over 60 other elements, most non-metals and transition metals, which can function as the heteroatom. Much of the research related to heteropolyanions has great emphasis on the Keggin [XM$_{12}$O$_{40}$]$^{n-}$ and Wells-Dawson [X$_2$M$_{18}$O$_{62}$]$^{n-}$ anions (where M is the addenda atom and X is the heteroatom) [22,51].

2. Isopolyanions contain the same metal oxide framework as heteropolyanions without the internal heteroatom. Although isopolyanions are unstable compared to heteropolyanions, they can be used as basic building blocks due their physical properties such as high charge [22].

3. Molybdenum blue and molybdenum brown reduced POM clusters are high-nuclearity metal-oxygen anions that have unique wheel-shaped structures. These species are the most recently discovered POMs with considerable research devoted to rationalize and control the formation of these supramolecules [22,54].

The focus of this project was on the first, heteropolyanions, because [22]:

1. They are by far the most explored subset of POM clusters.
2. They have high stability.
3. They exhibit several fast and reversible oxidation/reduction reactions with multiple electron transfer.
4. Their redox potential can be tuned by substituting the heteroatom and/or addenda atom, without affecting their structure.

5. Various transition metal cations can be incorporated into the heteropolymetalate structure.

Heteropolyanions with Keggin structure (figure 3-8) are by far the most common. Discovered by J.F. Keggin in 1933 [55], they have the general formula of \( \{XM_{12}O_{40}^{n-}\} \), in which the central heteroatom is surrounded by twelve addenda atoms and forty oxygen atoms. Some Keggin structure POMs are commercially available and these materials are relatively low cost [11].

![Keggin structure POMs](image)

**Keggin Type \([MX_{12}O_{40}]^{n-}\)**  
M: heteroatom (e.g. \(P^{5+}\) or \(Si^{4+}\))  
X: addenda atom (e.g. Mo or W)

*Figure 3-8: A schematic representation of the Keggin structure POMs.*

Keggin structure POMs with molybdenum as the addenda atoms (\([XM_{12}O_{40}]^{n-}\)), also known as heteropolymolybdates, possess desirable properties for applications as electrode material for ECs. Examples of these molybdenum based Keggin structure POMs are phosphomolybdic acid, \(PMO_{12}O_{40}^{3-}\) (PMo12), and siliconomolybdic acid, \(SiMo_{12}O_{40}^{4-}\) (SiMo12). These two POMs have been investigated due to their stability and commercial availability [11,14,15,25]. Both of these POMs demonstrate reversible redox reactions with multiple-electron transfers. There are three general oxidation/reduction reactions experienced by these POMs [13]:
The pseudocapacitive behavior of POMs, particularly their reaction reversibility and electron transfer mechanism, has been studied by many research groups [13,16,25,52,56]. Martel et al studied the characteristics of PMo$_{12}$ and SiMo$_{12}$ multilayer films deposited on glassy carbon electrodes [13]. Cyclic voltammograms of these composite materials are shown in figure 3-9 and their reduction potentials are listed in table 3-4.

\[
\begin{align*}
\text{XMo}_{12}\text{O}_{40}^{\text{n}^-} + 2\text{e}^- + 2\text{H}^+ & \rightleftharpoons \text{H}_2\text{XMo}_{12}\text{O}_{40}^{\text{n}^-} \quad \text{(Reaction 1)} \\
\text{H}_2\text{XMo}_{12}\text{O}_{40}^{\text{n}^-} + 2\text{e}^- + 2\text{H}^+ & \rightleftharpoons \text{H}_4\text{XMo}_{12}\text{O}_{40}^{\text{n}^-} \quad \text{(Reaction 2)} \\
\text{H}_4\text{XMo}_{12}\text{O}_{40}^{\text{n}^-} + 2\text{e}^- + 2\text{H}^+ & \rightleftharpoons \text{H}_6\text{XMo}_{12}\text{O}_{40}^{\text{n}^-} \quad \text{(Reaction 3)}
\end{align*}
\]

*Figure 3-9: Cyclic voltammograms of A) PMo$_{12}$ coated glassy carbon electrodes and B) SiMo$_{12}$ coated glassy carbon electrodes. The numbers represent the number of POM layer that were deposited. Each cyclic voltammogram was obtained at scan rate = 0.01 V/s and 0.5M H$_2$SO$_4$ electrolyte [13].*
Table 3-4: Reduction potentials for PMo$_{12}$ and SiMo$_{12}$ deposited glassy carbon electrodes [13].

<table>
<thead>
<tr>
<th>POMs</th>
<th>Reaction 1</th>
<th>Reaction 2</th>
<th>Reaction 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>[PMo$<em>{12}$O$</em>{40}$]$^{3-}$</td>
<td>0.325 V</td>
<td>0.175 V</td>
<td>-0.05 V</td>
</tr>
<tr>
<td>[SiMo$<em>{12}$O$</em>{40}$]$^{4-}$</td>
<td>0.3 V</td>
<td>0.175 V</td>
<td>-0.025 V</td>
</tr>
</tbody>
</table>

3.4 Modification of Carbon with Polyoxometalates

POMs are water soluble and display a high affinity towards carbon. The amount and strength of POM adsorption on a carbon substrate depends on the surface structure, surface area and origin of the substrate [57,58]. A number of recent studies have focused on the modification of carbon surfaces with polyoxometalates [11,13,14,25]. Carbon materials may be modified with POMs using several methods. These methods are discussed in more detail in section 3.4.1 and 3.4.2.

3.4.1 Common Modification Techniques

Mixing of the carbon materials with polyoxometalates is perhaps the simplest and fastest method [59,60]. Pan et al fabricated polyoxometalate-modified CNTs by ultrasonically mixing the two powder materials [59]. In this method, the particles are physically bonded, thus these composites may not have long term stability. Furthermore, particles may form agglomerates leading to inhomogeneous properties.

Another method is electrochemical modification. This method required the use of an external power supply and a set of chemically compatible electrode and electrolyte. The method involves a cyclic voltammetry (CV) technique in order to monitor and control the amount of voltage and current through the electrode. This method has been successfully used to deposit POMs onto the surface of carbon electrodes [61]. Martel et al used electrochemical modification to deposit POMs onto grassy carbon electrodes (figure 3-9) [13]. Although this treatment results in good adhesion, it required long operating times and is not suitable for working with powder electrode materials such as activated carbon (AC), MWCNTs and OLC. Thus, the method that was used in this project is Layer-by-layer (LbL) chemical modification.
3.4.2 Chemical Modification: Layer-by-Layer Technique

The LbL chemical modification technique has been extensively used for the modification of carbon electrodes with POMs [11,14,25,62-65]. Wang et al demonstrated the application of the LbL technique to modify glassy carbon electrodes with POMs (figure 3-10) [64].

![Cyclic voltammograms](image)

*Figure 3-10: Cyclic voltammograms of a) PMo$_{12}$/PDDA modified glassy carbon and b) SiMo$_{12}$/PDDA modified glassy carbon [64].*

This process is schematically represented in figure 3-11. The LbL deposition technique involves the adsorption of a single species in each adsorption step. The driving force behind this multilayer assembly is the electrostatic interaction between alternately charged molecules. This technique is used in many laboratory processes due to several advantages: (1) low cost; (2) environmentally friendly; (3) very simple yet allows extensive control of structure, order and functionality; (4) a very diverse range of materials may be used in the LbL technique [54].
POMs are negativity charged ions; therefore an intermediate polycation layer is required in order to hold POM molecules onto the substrate. There are a number of polycation species that have been studied for this application, including methyl viologen [13], meso-tetra(4N-methylpyridyl porphyrin) [13], alkyl-silane [66] and poly (diallyldimethylammonium chloride) (PDDA) [11,14,25,54,62]. In this project, PDDA was used as the polycation layer due to its effectiveness and relatively low cost. PDDA polymer chains form a continuous structure on the substrate so that POM molecules may be entrapped into the polymer.

There are two models that are used to represent the microstructure of POM/PDDA multilayer films [54]. Figure 3-12 represents these models in the case of glassy carbon, which has flat surface. Under low ionic strength, polymer chains are compact and flat and POM clusters adapt a stratified structure (figure 3-12a). Under high ionic strength, polymer chains dangle around and the POM clusters are dispersed in the polymer matrix (figure 3-12b). The second model may be used to represent the microstructure in this project. However, the materials used in this study (MWCNTs and OLC) have a rough surface compared to glassy carbon.

One of the key strategies associated with the LbL process is the ability to form multi-layer coatings by repeating the polycation and POM layers [54]. Thus, this technique may be used to design and engineer the surface to achieve the desirable properties by leveraging different types of POM molecules and their properties. However, the addition of each subsequent layer will also
increase the resistance, especially in the case of PDDA layers. In order to conserve the high power capabilities of ECs, the number of layers must be restricted.

Figure 3-12: Proposed microstructures of POM/PDDA multilayer under A) low ionic strength and B) High ionic strength [54].

Carbon surfaces are electrochemically inert and have low chemical reactivity. As discussed earlier, the surface of carbon materials may contain sp³ hybridized carbon, which is resistant to further functionalization. For LbL, sp² hybridized carbon is the preferred structure. In order to improve adhesion between the substrate and the coating, pretreatment of the carbon substrate is essential. Acid treatment using nitric acid (HNO₃) or sulfuric acid (H₂SO₄) has shown to be very effective in improving the surface activity of carbon [32]. For example, HNO₃ generates oxygen containing functional groups and enhances the hydrophilicity of the carbon substrate [32].

Both MWCNTs and OLC have previously been chemically modified with POMs using the LbL technique [11,14]. Cyclic voltammograms of POM modified MWCNTs and OLC are presented in figure 3-13 and figure 3-14, respectively. The area specific capacitance values of bare
MWCNTs, single-layer PMo$_{12}$ coated MWCNTs and multi-layer coated MWCNTs (PMo$_{12}$ bottom layer and SiMo$_{12}$ top layer) are reported to be 0.62 F/cm$^2$, 1.66 F/cm$^2$ and 2.68 F/cm$^2$, respectively [11]. Subsequently, the area specific capacitance values of bare OLC and single-layer PMo$_{12}$ coated OLC are reported to be 0.5 F/cm$^2$ and 0.6 F/cm$^2$, respectively [14].

Figure 3-13: Cyclic voltammograms of bare, single-layer PMo$_{12}$ coated and multiple-layer coated MWCNTs (indicated as S1 with PMo$_{12}$ as bottom layer and SiMo$_{12}$ as top layer) [11].

Figure 3-14: Cyclic voltammogram of bare and single-layer PMo$_{12}$ coated OLC [14].
4 Experimental

4.1 Electrode Material

The electrode material consisted of two active components, a carbon substrate and a POM coating. The following section describes how each of these components was synthesized and then combined to produce a composite material.

4.1.1 Carbon Substrate Fabrication

MWCNTs, OLC and graphite have been investigated in this project. MWCNTs and OLC were provided by the Nanomaterials Group at Drexel University. The graphite fine powder was purchased from Sigma-Aldrich. MWCNTs were produced by chemical vapour deposition (CVD) using an iron catalyst [32,67]. These MWCNTs have a relatively small diameter ranging from 5-20 nm; resulting in superior mechanical and thermal properties compared to larger diameter MWCNTs [67]. OLC was produced by annealing ND in a vacuum furnace at a temperature of 1800ºC [37].

The "as received" MWCNT powder and OLC powder were fabricated into a film to ensure ease of chemical modification and consistent results. A film was formed using 4 wt% polytetrafluoroethylene (PTFE) as the binder. Binder was ultrasonically dispersed in isopropyl alcohol (IPA) and mixed with carbon powder. This mixture was then formed into dough and passed through a pasta roller to form the film. The film had an approximate thickness of 100 µm. The use of this thin film is advantageous for research purposes and the majority of this work was completed using a film substrate. However, the use of this film is not practical for real world applications. Therefore, a small part of this project involved the LbL modification of large sized graphite electrodes. The details of these graphite electrodes may be found in appendix A [68].
4.1.2 Polyoxometalate Synthesis

A total of five different Keggin-type POMs were investigated in this project. Two of these, phosphomolybdic acid (PMo\textsubscript{12}) and silicomolybdic acid (SiMo\textsubscript{12}) were purchased from Alfa Aesar and Sigma-Aldrich, respectively. Additionally, three vanadium substituted phosphomolybdic acids (PMo\textsubscript{(12-x)}V\textsubscript{x}) were synthesized using a method derived from the work of Tsigdinos et al.\cite{69}. These POMs involve 1, 2 and 3 vanadium addenda atoms substituted in for the respective number of molybdenum addenda atoms:

1. 11-Molybdo-1-vanadophosphoric acid or PMo\textsubscript{11}VO\textsubscript{40}\textsuperscript{4-} (PMo\textsubscript{11}V)
2. 10-Molybdo-2-vanadophosphoric acid or PMo\textsubscript{10}V\textsubscript{2}O\textsubscript{40}\textsuperscript{5-} (PMo\textsubscript{10}V\textsubscript{2})
3. 9-Molybdo-3-vanadophosphoric acid or PMo\textsubscript{9}V\textsubscript{3}O\textsubscript{40}\textsuperscript{6-} (PMo\textsubscript{9}V\textsubscript{3})

The general outline of the synthesis methods is presented in figure 4-1 and a more detailed description is included in appendix B.

\begin{center}
\textbf{Figure 4-1: Experimental synthesis of vanadium substituted phosphomolybdic acids.}
\end{center}
4.1.3 Procedure for LbL Chemical Modification

The POMs PMo$_{12}$, SiMo$_{12}$, PMo$_{11}$V, PMo$_{10}$V$_2$ and PMo$_9$V$_3$ were all dissolved in distilled water to form a 10 mmol/L dilute solution. Other chemicals used for the LbL modification were 4 wt% poly (diallyldimethylammonium chloride) (PDDA), aqueous HNO$_3$ (conc.) and 1 wt% ZONYL FSO-100; all commercially available (Sigma-Aldrich).

MWCNT film and OLC film was coated using the process described in figure 4-2. Large sized graphite electrodes were coated using the same process, but ZONYL was used for surface activation instead of HNO$_3$. The parameters of this process are summarized in table 4-1. A total of three “single-layer” and four “multi-layer” coating chemistries were investigated in this project (figure 4-3).

Figure 4-2: The details of the layer by layer process that was used in this study.
Table 4-1: *The LbL coating parameters that were employed in this study.*

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Concentration</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO$_3$ or ZONYL</td>
<td>Concentrated</td>
<td>2 min</td>
</tr>
<tr>
<td>ZONYL</td>
<td>1 wt%</td>
<td>10 min</td>
</tr>
<tr>
<td>PDDA</td>
<td>4 wt%</td>
<td>10 min</td>
</tr>
<tr>
<td>POM</td>
<td>10 mmol/L</td>
<td>20 min</td>
</tr>
</tbody>
</table>

Figure 4-3: Schematic representation of all the coating chemistries that were used in this project.
4.2 Electrochemical Analysis

4.2.1 Cavity Microelectrode

A cavity microelectrode (CME) was used as the working electrode to determine the electrochemical kinetics of powder materials. The construction process of the CME is described elsewhere [70] and a schematic representation of CME is shown in figure 4-4. The materials in powder or film form were packed into the platinum end cavity (figure 4-4b); while the opposite end (silver wire) was connected to an external circuit for electrochemical analysis. After each set of tests, the powder or film in the cavity was removed by ultrasonic cleaning. The clean cavity was then used for another set of tests. In comparison with conventional large surface electrodes, CME is an effective method for screening a large number of powder samples rapidly, reliably, and efficiently. In no way would a CME replace conventional methods for electrochemical characterization; however it is a complementary tool that can be used to quickly assess and compare the performance of materials. Results showing the consistency of CME are presented in appendix C.

![Figure 4-4: A schematic representation of a cavity microelectrode (CME).](image)

4.2.2 Electrochemical Cell and Instrumentation

A conventional three-electrode cell was utilized for this project, with CME as the working electrode, Ag/AgCl as the reference electrode, and platinum as the counter electrode. Majority of the tests were carried out in 1 M H₂SO₄ solution. The cell was connected to an EG&G 273...
potentiostat (Corrware software) for Cyclic Voltammetry (CV) tests. Additionally, CV and Charge/Discharge (CD) tests were conducted using large sized graphite electrodes in a two-electrode cell with 0.5 M H$_2$SO$_4$ electrolyte.

### 4.2.3 Cyclic Voltammetry

CV is a frequently used technique to study the electrochemical properties of ECs. In a CV test, voltage is applied to the working electrode and the corresponding current is recorded. This current at the working electrode is plotted versus the applied voltage to form a cyclic voltammogram. Figure 4-5 is representative a typical cyclic voltammogram. The arrows indicate the direction of oxidation and reduction regions with the respective anodic and cathodic peaks.

*Figure 4-5: A typical cyclic voltammogram; $i =$ current, $E =$ potential, $p =$ peak, $a =$ anodic and $c =$ cathodic.*
CV provides an overall understanding of the characterization of the system in terms of: (i) the reversibility of the charge/discharge process; (ii) the distinction between any noticeable stages in the charging and/or discharging process; (iii) the total amount of charge accumulated over a potential range; (iv) the voltage window between which the electrodes can accept or dispose of charge, and (v) the dynamic behaviour of the electrode for charge acceptance and disposal with increasing scan rate [71].

An ideal capacitor has a rectangular CV profile; as represented in figure 4-6 (label #1). In the ideal case, the current output is independent of the potential as the sign of the current reverses instantly as the potential scan reverses. In the case of resistance capacitor, the current output becomes dependent on the potential, results in a tilted shape (label #2). Lastly, electrode materials with pseudocapacitance show a deviation from the rectangular shape (label #4) due to oxidation/reduction peaks that represent redox reactions (i.e reversible Faradaic reactions).

![Figure 4-6: Typical charge/discharge CV characteristics of an electrochemical capacitor][19]
Based on the above diagram, if a capacitor exhibits ideal behaviour, the capacitance \((C)\) is simply:

\[
C = \frac{I}{v}
\]  

(5)

where \(I\) is the capacitive current and \(v\) is the scan rate in V/s. However, if a capacitor deviates from the ideal behaviour, its capacitance is calculated by integrating the charge \((Q)\) over the given voltage window \((V)\):

\[
C = \frac{Q}{V}
\]  

(6)

Capacitance values reported in literature are commonly in units of mass specific capacitance (F/g). In this project, the fabricated electrodes are for thin and flexible ECs that use thin-film electrodes and solid polymer electrolytes. In these applications the weight of the active material used is negligible and the area is more important [28]. Therefore, all capacitance values reported in this project are area specific capacitance. Also, volume specific capacitance values may be found in appendix G.

### 4.2.4 Charge/Discharge

In a charge/discharge (CD) test, a constant-current is applied to a two-electrode cell and the voltage response is monitored. This analysis allows the capacitance to be calculated for the electrode materials within a capacitor cell [72]. The cell capacitance can be calculated from the slope of the discharge curve:

\[
C = \frac{I}{\left(\frac{dV}{dt}\right)}
\]  

(7)

where \(C\) is the cell capacitance, \(I\) is the discharge current and \(dV/dt\) is the slope of the discharge curve. CD is a complementary tool to CV and may also be used to calculate the capacitance.
4.3 Surface Analysis and Characterization

A total of four different surface analysis and characterization techniques were used in this project. First of all, powder X-ray Diffraction (XRD) was conducted to study the structure and different phases present in the synthesized materials. XRD was conducted using a Philips XRD system with monochromatized Cu-Kα anode whose basic components are a PW 1830 HT generator, a PW 1050 goniometer, a PW3710 control electronics, and X-Pert system software. Secondly, Energy-dispersive X-ray Spectroscopy (EDX) was conducted using a Hitachi S-4500 in order to study the stoichiometry of the synthesized POMs. Also, Scanning Electron Microscopy (SEM) micrographs were obtained using Hitachi S-4800. These micrographs displayed information about the surface morphology of bare and coated MWCNTs. Finally, X-ray Photoelectron Spectroscopy (XPS) was conducted in order to characterize the surface chemistries of both bare and coated MWCNTs. XPS was conducted using Leybold (Specs) Max 200 with a monochromatic aluminum (Al) Kα X-ray source. The overall distribution of detected surface elements were collected in atomic percentage and chemical bonding information was obtained in both low and high energy resolution modes. All XPS spectra were calibrated with respect to the C1s peak at 284.6 eV. It should be noted that XRD and EDX was performed on POM powder materials, while SEM and XPS was performed on POM coated MWCNTs.
Chapter 5
Results and Discussion

5 Results and Discussion

5.1 Analysis of the Layer by Layer Technique

Past work has shown that layer-by-layer (LbL) deposition is an effective technique for the fabrication of POM/carbon composites [11,12,14-16,66]. However, the role of each individual layer in the LbL technique has not been extensively studied. The following section examined the properties and function of each individual layer. This work aimed to establish the importance of all three steps in the LbL process (figure 5-1).

Figure 5-1: Overview of the LbL process.

5.1.1 Surface Pre-treatment

The first step in the LbL process, surface pre-treatment, is essential to improve the adhesion between the substrate and coating. The importance of pre-treatment is demonstrated in figure 5-2. Single-layer PMO$_{12}$ coated MWCNTs that were not pre-treated have significantly low
oxidation/reduction peak currents in comparison to the ones that were pre-treated prior to application of the active POM layer. Acid pre-treatment has been extensively used in previous work involving the LbL deposition of POMs onto carbon substrates [11,14-16]. In the following project concentrated nitric acid was used, which oxidizes the substrate to generate oxygen containing functional groups [32,73]. Although the acid treatment worked well, it is not ideal due to the safety and environmental effects associated with acids.

An alternative to acid treatment is the use of surfactants. Surfactants are used in many applications to improve surface tension and wetting properties [74,75]. As a pre-treatment agent, a fluorinated surfactant (ZONYL FSO-100) worked nearly as well as acid treatment (figure 5-2). The use of this material is especially important for the pre-treatment of large sized electrodes, where the use of high amount of acid is not ideal. Furthermore, a low concentration (1 wt%) of ZONYL was effective, whereas a highly concentrated acid was used to achieve similar results.

Figure 5-2: Cyclic voltammograms of single-layer PMo$_{12}$ coated MWCNTs with 1) no-pretreatment, 2) pre-treatment using concentrate HNO$_3$ and 3) pre-treatment using ZONYL FSO-100.
5.1.2 Polycation Intermediate Layer

POM ions are negatively charged, thus an intermediate polycation layer is essential in the LbL process. PDDA worked exceptionally well as a polycation layer. As confirmed in figure 5-3, single-layer PMO$_{12}$ coated MWCNTs that did not have this intermediate polycation layer displayed significantly lower oxidation/reduction peak currents.

![Figure 5-3: Cyclic voltammograms of 1) bare MWCNTs 2) single-layer PMO$_{12}$ coated MWCNTs without PDDA layer and 3) single-layer PMO$_{12}$ coated MWCNTs with PDDA layer.](image)

5.1.3 Polyanion Active Layer

POMs were used as the polyanion active layer. Figure 5-4 shows the voltammograms of bare MWCNTs versus MWCNTs that were coated with commercial POMs (PMO$_{12}$ and SiMo$_{12}$). These coating chemistries involved a single polyanion layer (POM) on top of a single polycation layer (PDDA); they were referred to as "single-layer" coatings (see figure 4-3). MWCNTs modified by single-layer PMO$_{12}$ (figure 5-4a) and single-layer SiMo$_{12}$ (figure 5-4b) stored a higher amount of charge, which was reflected by the significant increase in current density. At a scan rate of 0.05 V/s, the area specific capacitance values for PMO$_{12}$ modified and SiMo$_{12}$
modified MWCNTs were 1.76 F/cm$^2$ and 1.50 F/cm$^2$, respectively. These values were over 200% higher than that of bare MWCNTs (0.51 F/cm$^2$). Furthermore, three reversible and "mirror-imaging" oxidation/reduction peaks were observed. Although these highly reversible oxidation/reduction peaks are suitable for ECs, they did not display overlapping peaks as seen in the rectangular "capacitive" cyclic voltammogram of RuO$_2$ [43], an issue to be addressed in section 5.3.

The observed oxidation/reduction peaks are the characteristic peaks of PMo$_{12}$ and SiMo$_{12}$, and their peak potentials are listed in table 5-1. These peak potential values were slightly different from the ones reported in literature, where glassy carbon (GC) electrodes were modified with POMs [13]. This difference may be due to the interaction between PDDA molecules and POM molecules. As the intermediate layer, PDDA polymer chains may either have point contact to form a POM monolayer, or the chains may wrap around the molecules to form dangling loops [64]. In the latter case, more than one POM molecule may be adsorbed onto the dangled polymer chain. Furthermore, MWCNTs have a higher surface roughness than GC, which would result in a higher amount of polymer dangling loops to form. The degree of wrapping might directly affect the degree of POM exposure to the electrolyte. Furthermore, POMs are adsorbed onto PDDA through an electrostatic attraction and the difference in adsorption energies may lead to different potentials. The values reported in table 5-1 are however much closer to a similar study, where MWCNTs were modified with POMs using the same LbL technique [11,15].

| Table 5-1: Oxidation/reduction peak potentials of commercial POMs (PMo$_{12}$ and SiMo$_{12}$). |
|-----------------------------------|---|---|---|---|---|---|
|                                 | Ox-1 | Red-1 | Ox-2 | Red-2 | Ox-3 | Red-3 |
| PMo$_{12}$O$_{40}^{3-}$          | 0.385 V | 0.364 V | 0.229 V | 0.203 V | 0.012 V | 0.000 V |
| SiMo$_{12}$O$_{40}^{4-}$         | 0.326 V | 0.315 V | 0.225 V | 0.210 V | 0.021 V | 0.003 V |
Figure 5-4: Cyclic voltammograms of bare MWCNTs in comparison with a) single-layer PMo$_{12}$ coated MWCNTs and b) single-layer SiMo$_{12}$ coated MWCNTs.
5.2 OLC: Alternative Carbon Substrate

Onion-like carbon (OLC) is an attractive carbon substrate that may also be modified by POMs using the LbL technique. OLC has proven to be an excellent EC electrode material for high rate and high power applications. There was also similar work where POMs are deposited onto an OLC substrate using the LbL technique [14]. To our best knowledge this is the only other work that has reported on POM modified OLC. The following section demonstrates the performance of OLC/POM composite electrodes in comparison with MWCNT/POM composite electrodes.

5.2.1 Electrochemical Behaviour of OLC/POM Composites

Figure 5-5 shows the voltammograms of both single-layer PMO\textsubscript{12} coated OLC and single-layer PMO\textsubscript{12} coated MWCNTs. Three interesting observations were derived from figure 5-5. First of all, PMO\textsubscript{12} coated OLC have the same three reversible oxidation/reduction peaks as PMO\textsubscript{12} coated MWCNTs. Secondly, although the current density of the three peaks were similar for both materials, PMO\textsubscript{12} coated MWCNTs displayed slightly higher charge storage. At a scan rate of 0.05 V/s, the area specific capacitance values for PMO\textsubscript{12} coated OLC and PMO\textsubscript{12} coated MWCNTs were 1.62 F/cm\textsuperscript{2} and 1.76 F/cm\textsuperscript{2}, respectively. OLC has a solid structure that is less porous compared to MWCNTs. Thus, the lower capacitance values of OLC may be attributed to its lower porosity. Lastly, the solid structure of OLC is also why PMO\textsubscript{12} coated OLC displays higher conductivity, which was confirmed by observing that its oxidation/reduction peaks are more reversible and "mirror-imaging".

The capacitance value obtained for PMO\textsubscript{12} coated OLC was much higher than the value that was reported in literature (0.6 F/cm\textsuperscript{2} at a scan rate of 5 V/s) [14]. To the best of our knowledge, these results show the best example of POM modified OLC using the LbL technique.
5.2.2 Performance of Single-Layer OLC/POM Composites

While single-layer PMO$_{12}$ coated MWCNTs performed better at a scan rate of 0.05 V/s, single-layer PMO$_{12}$ coated OLC performed much better at a scan rate of 2 V/s (figure 5-6). MWCNTs became resistive at 2 V/s, while OLC maintained its high performance due to its superior conductivity. Even at a scan rate of 2 V/s, the three reversible oxidation/reduction peaks were still visible for PMO$_{12}$ coated OLC. Furthermore, the PMO$_{12}$ coated OLC was able to store a higher amount of charge at higher scan rates. Figure 5-7 compares the area specific capacitance values of both materials at different scan rates. MWCNTs retained a higher capacitance value up until a scan rate of approximately 1.2 V/s, while OLC provided a higher capacitance value at higher scan rates. The high rate performance of OLC is attributed to its solid structure, which does not contain any pores [37].

These results demonstrated the superior overall performance of OLC relative to MWCNTs. OLC is able to deliver a similar area specific capacitance to MWCNTs, while its conductivity is much
higher. Therefore, OLC is a material of considerable interest for electrodes that deliver both high energy densities (high capacitance) and high power densities (low electrode resistance).

Figure 5-6: Cyclic voltammograms of single-layer PMo$_{12}$ coated OLC in comparison with single-layer PMo$_{12}$ coated MWCNTs at a scan rate of 2 V/s.

Figure 5-7: Area specific capacitance of single-layer PMo$_{12}$ coated OLC and MWCNTs at various scan rates.
5.3 Multi-Layer Coating Using Commercial POMs

One of the criteria for an ideal pseudocapacitive material is to have numerous, overlapping and multiple electron transfer oxidation/reduction peaks, which results in a rectangular "capacitive" cyclic voltammogram as observed for RuO$_2$ [43]. Single-layer PMo$_{12}$ and SiMo$_{12}$ coated MWCNTs showed enhanced charge storage with very distinct peaks (figure 5-8a). One solution to achieving a "capacitive" voltammogram is to form a "multi-layer" coating, which combines the pseudocapacitance from the distinct peaks of different POMs.

5.3.1 Electrochemical Behaviour of Multi-Layer Sequence-1

Both PMo$_{12}$ and SiMo$_{12}$ have the same Keggin structure, but with different heteroatoms. Changing the heteroatom from phosphorus to silicon resulted in a difference in the oxidation/reduction potentials (table 5-1). The peak potentials of PMo$_{12}$ and SiMo$_{12}$ are labeled from high to low as shown in figure 5-8a. The second and third peaks have identical peak potentials; the first pair of peaks (labeled as 1a for SiMo$_{12}$, and 1b for PMo$_{12}$) has approximately a 0.06 to 0.07 V shift. Therefore, it is of interest to combine and leverage the different electrochemical properties of these two POMs to further achieve higher performance and, specifically, to exploit the effect of superimposing the two molecules on MWCNTs.

Figure 5-8b shows the voltammograms for multi-layer coated MWCNTs versus single-layer coated MWCNTs. In this case, the multi-layer sequence has PMo$_{12}$ as the bottom polyanion layer and SiMo$_{12}$ as the top polyanion layer. This sequence is referred to as sequence-1 (see figure 4-3 for more details on other multi-layer sequences). The cyclic voltammogram of multi-layer sequence-1 was a combination of the both single-layer PMo$_{12}$ and single-layer SiMo$_{12}$. This multi-layer voltammogram was developed from the overlapping peak potentials of both PMo$_{12}$ and SiMo$_{12}$, strongly suggesting the collective contributions from both POMs. As a result the multi-layer sample displayed a slightly better “capacitive” cyclic voltammogram. The multi-layer sample also had a further increase in capacitance over its single-layer counterparts. At a scan rate of 0.05 V/s, the area specific capacitance values for multi-layer sequence-1 MWCNTs was 2.45±0.08 F/cm$^2$. An increase of approximately 380% compared to bare MWCNTs and an increase of approximately 40% compared to single-layer PMo$_{12}$ coated MWCNTs. These values
were similar to previous work. However, they are much more consistent; reflected by their lower standard deviation [11,15].

![Figure 5-8: Cyclic voltammograms of a) bare, single-layer PMo\textsubscript{12} coated and single-layer SiMo\textsubscript{12} coated MWCNTs and b) multi-layer sequence-1 (PMo\textsubscript{12} as bottom and SiMo\textsubscript{12} as top layer) coated MWCNTs.](image)

*Figure 5-8: Cyclic voltammograms of a) bare, single-layer PMo\textsubscript{12} coated and single-layer SiMo\textsubscript{12} coated MWCNTs and b) multi-layer sequence-1 (PMo\textsubscript{12} as bottom and SiMo\textsubscript{12} as top layer) coated MWCNTs.*
5.3.2 Electrochemical Behaviour of Multi-Layer Sequence-2

Section 5.3.1 showed the results for multi-layer sequence-1 where PMo$_{12}$ is the bottom polyanion layer and SiMo$_{12}$ is the top polyanion layer. The reversed sequence may also be used, where SiMo$_{12}$ is the bottom layer and PMo$_{12}$ is the top layer (sequence-2). Figure 5-9 shows the cyclic voltammograms for single-layer PMo$_{12}$, single-layer SiMo$_{12}$, multi-layer sequence-1 and multi-layer sequence-2 MWCNTs. It can be seen that sequence-2 was very similar to sequence-1. At a scan rate of 0.05 V/s, the area specific capacitance value of multi-layer sequence-2 was 2.27 F/cm$^2$.

![Cyclic voltammograms of single-layer PMo$_{12}$, single-layer SiMo$_{12}$, multi-layer sequence-1 and multi-layer sequence-2 coated MWCNTs.](image)

**Figure 5-9:** Cyclic voltammograms of single-layer PMo$_{12}$, single-layer SiMo$_{12}$, multi-layer sequence-1 and multi-layer sequence-2 coated MWCNTs.

5.4 Single-Layer Coating Using Synthesized PMo$_{(12-x)}V_x$

To this point, only commercially available POMs have been studied as the polyanion layer. There are a limited amount of commercially available POMs that may be used for applications as the electrode material for ECs. Thus, it is essential to study other POMs that can be synthesized in the laboratory. In this work, vanadium substituted phosphomolybdic acids (PMo$_{(12-x)}V_x$) were
synthesized and applied as the polyanion layer. These POMs have the same Keggin-type structure as PMO\textsubscript{12}, except a certain number of molybdenum atoms are substituted by vanadium atoms. These materials are attractive because a literature review showed that they have potential to fill in the gaps in electrochemical properties but they have not been extensively studied.

5.4.1 Electrochemical Behaviour of Synthesized PMO\textsubscript{(12-x)V\textsubscript{x}}

Three different vanadium substituted POMs were investigated: H\textsubscript{5}PMo\textsubscript{11}VO\textsubscript{40} (PMO\textsubscript{11}V), H\textsubscript{5}PMo\textsubscript{10}V\textsubscript{2}O\textsubscript{40} (PMO\textsubscript{10}V\textsubscript{2}), and H\textsubscript{6}PMo\textsubscript{9}V\textsubscript{3}O\textsubscript{40} (PMO\textsubscript{9}V\textsubscript{3}). Figure 5-10 shows the voltammograms for single-layer PMO\textsubscript{12}, PMO\textsubscript{10}V\textsubscript{2}, and PMO\textsubscript{9}V\textsubscript{3} MWCNTs. For these synthesized materials, rather than having charge concentrated at three potentials, there was a distribution of charge as the vanadium content increases. This resulted in a more “capacitive” cyclic voltammogram, compared to that of commercial PMO\textsubscript{12}. Although, all three cases of these synthesized POMs worked well for this application, further discussion will focus only on one, 10-Molybdo-2-vanadophosphoric acid (PMO\textsubscript{10}V\textsubscript{2}).

![Figure 5-10: Cyclic voltammograms of synthesized POMs in comparison to commercially available PMO\textsubscript{12} at a scan rate of 0.05 V/s.](image)

*Figure 5-10: Cyclic voltammograms of synthesized POMs in comparison to commercially available PMO\textsubscript{12} at a scan rate of 0.05 V/s.*
5.4.2 Electrochemical Behaviour of PMo$_{10}$V$_2$

Figure 5-11 shows the voltammograms for single-layer PMo$_{12}$ and PMo$_{10}$V$_2$ coated MWCNTs. PMo$_{10}$V$_2$ coated MWCNTs demonstrated a more capacitive electrochemical behaviour compared to that of PMo$_{12}$ coated MWCNTs, yet they stored a similar amount of charge. At a scan rate of 0.05 V/s, the area specific capacitance value of PMo$_{10}$V$_2$ coated MWCNTs was 1.77 F/cm$^2$, which was similar to that of PMo$_{12}$ coated MWCNTs (1.76 F/cm$^2$). The even charge distribution associated with PMo$_{10}$V$_2$ may be attributed to peak broadening and additional redox reactions. There were a total of four redox peaks for PMo$_{10}$V$_2$, and these peaks were broader compared to the redox peaks of PMo$_{12}$.

![Cyclic voltammograms of bare, single-layer PMo$_{12}$ and single-layer PMo$_{10}$V$_2$ coated MWCNTs.](image)

*Figure 5-11: Cyclic voltammograms of bare, single-layer PMo$_{12}$ and single-layer PMo$_{10}$V$_2$ coated MWCNTs.*

The electrochemical properties of synthesized PMo$_{10}$V$_2$ have been studied previously {{17 Barth,Marek 1999}}. Adopted from literature, the voltammograms of PMo$_{12}$ and PMo$_{10}$V$_2$ are shown in figure 5-11. These results represented a composite material where polyaniline, a conductive polymer, was doped with the two different POMs. It should be noted that polyaniline is a pseudocapacitive material and exhibits redox reactions of its own [19].
Two similarities can be observed when comparing the results from this study (figure 5-11) and literature (figure 5-12). In both cases, the PMO_{10}V_2 exhibited broader redox peaks and showed an enhanced "rectangular" voltammogram. Also, the redox peak at approximately 0.22 V in figure 5-11 were the dominate peaks for both PMO_1V_2 modified MWCNTs and PMO_{10}V_2 modified polyaniline.

There were also differences between the results in literature and this study, notably the peak potentials of the peak at approximately 0 V in figure 5-11. This peak was at the same potential as PMO_{12} for this study, however results from literature showed slightly different peak potentials for PMO_{12} and PMO_{10}V_2 modified polyaniline. These differences may be due to the difference in substrates (carbon versus conducting polymer) and processing methods (LbL coating versus doping).

Surface coverage of each coated sample was calculated from the peak current ($I_p$), which follows the following theoretical relationship:

$$I_p = \frac{n^2 F^2 A \nu \Gamma}{4RT}$$  \hspace{1cm} (8)

where $n$ is the number of electrons, $F$ is Faraday’s constant (96485 C/mol), $\nu$ is the scan rate (V/s), $A$ is the electrode area (cm$^2$), $\Gamma$ is the surface coverage (mol/cm$^2$), $R$ is the ideal gas constant (8.31 J/mol*K) and $T$ is the temperature (K) [76]. The electrode area ($A$) is not the geometric area of the electrode, but the real specific surface area ($S_{BET}$) of the active material. MWCNTs have a $S_{BET}$ of 200 m$^2$/g and a density of 1.33 g/cm$^3$ [37]. From equation (8), surface coverage was calculated to be $1.6 \times 10^{-11}$ mol/cm$^2$ for PMO_{12} coated MWCNTs and $1.3 \times 10^{-11}$ mol/cm$^2$ for PMO_{10}V_2 coated MWCNTs. The maximum theoretical surface coverage can be estimated to be $1.4 \times 10^{-10}$ mol/cm$^2$ assuming full coverage onto flat accessible surfaces (e.g. gold, graphite) [77,78].
5.4.3 Performance of Single-Layer Coatings

Figure 5-13 presents the area specific capacitance values of all single-layer coating chemistries in comparison with bare MWCNTs at a low rate (0.05 V/s) and high rate (1 V/s). All single-layer chemistries had significantly higher capacitance compared to bare MWCNTs. Also, all MWCNT samples, including bare MWCNTs, experienced a decrease in capacitance when the scan rate was increased from 0.05 V/s to 1 V/s. While the scan rate increased by twenty times, the decrease in capacitance was 15% to 25% for single-layer coated MWCNTs compared to 37% for bare MWCNTs. Therefore, modification of MWCNTs using the LbL process significantly increased the capacitance while retaining the conductivity. The voltammograms of all single-layer coating chemistries at scan rate of 1 V/s can be found in appendix D.
Figure 5-13: Area specific capacitance of bare MWCNTs in comparison with single-layer coated MWCNTs at a scan rate of 0.05 V/s and 1 V/s.

The amount of charge stored by PMo_{12} coated and PMo_{10}V_{2} coated MWCNTs was very similar. Furthermore, the ability of these coated electrodes to retain the capacitance at high rate was also very similar. Although PMo_{12} performed slightly better at high rates in terms of area specific capacitance, this performance may be attributed its commercial purity. On the other hand, the broader distribution of PMo_{10}V_{2} redox peaks gives it a much enhanced “capacitive” behaviour.

5.5 Structural and Compositional Characterization of Synthesized PMo_{10}V_{2}

In the previous section, cyclic voltammetry demonstrated the encouraging electrochemical properties for synthesized PMo_{12}V_{2} compared to that of the commercial PMo_{12}. Literature review has shown that information on this particular material is very limited. Therefore, it is of great interest to characterize the structural and compositional properties of PMo_{12}V_{2}. The
structural properties were studied using XRD. The composition properties were studied using EDX and further confirmed using XPS.

5.5.1 XRD of PMo\textsubscript{10}V\textsubscript{2}

XRD patterns for both PMo\textsubscript{12} and PMo\textsubscript{10}V\textsubscript{2} powder materials are shown in Figure 5-14. The commercial PMo\textsubscript{12} XRD patterns was included as the baseline for Keggin-type POM crystals. The major diffraction peaks at approximately 2\(\theta\) = 6.7° and 2\(\theta\) = 26.7° are typical features of the Keggin structure [80]. In the case of the synthesized material, PMo\textsubscript{10}V\textsubscript{2}, the two major peaks appeared shifted by approximately +1.5°. This shift was also observed in the PMo\textsubscript{10}V\textsubscript{2} XRD pattern reported in previous work (figure 5-15) [81]. The close resemblances of the XRD pattern from literature with the pattern reported in this work provide certainty about the identity of these materials. However, the reason for shift in the major peaks of PMo\textsubscript{10}V\textsubscript{2} in comparison to commercial PMo\textsubscript{12} must be investigated.

Synthesized PMo\textsubscript{10}V\textsubscript{2} contains vanadium which may cause changes in the lattice parameters. Furthermore, XRD studies of dehydrated POMs have shown that the patterns of these species is highly dependent on the amount of water molecules attached to the POM anions [82]. Therefore, the shift in major diffraction peaks may be attributed to the difference in water molecules attached to synthesized PMo\textsubscript{10}V\textsubscript{2} versus commercial PMo\textsubscript{12}. In our case, the PMo\textsubscript{10}V\textsubscript{2} was crystallized in ambient conditions, which was likely to contain a higher amount of water.

In additional to providing information on the structure of the synthesized PMo\textsubscript{12}V\textsubscript{2}, XRD also provided information on the purity of the synthesis. Appendix E compares the XRD patterns of the synthesized product versus the used reactants. It is clear from this analysis that none of the three reactants were present in the final product. However, there might be side products such as VO\textsubscript{x} present in the synthesized PMo\textsubscript{10}V\textsubscript{2}. Appendix E also contains the XRD patterns for PMo\textsubscript{11}V and PMo\textsubscript{9}V\textsubscript{2}, the other two POMs that were synthesized in this project.
Figure 5-14: XRD patterns for commercial PMo$_{12}$ and synthesized PMo$_{10}$V$_2$.

Figure 5-15: XRD pattern a) for PMo$_{10}$V$_2$ and PMo$_{10}$V$_1$ from literature [81] and b) for PMo$_{10}$V$_2$ from this study.
5.5.2 EDX of PMo$_{10}$V$_2$

EDX analysis of commercial PMo$_{12}$ powder material showed that the atomic percent ratio of addenda atoms to hetero atoms matches the theoretical value of 12:1 (table 5-2). Therefore, EDX is an appropriate method to study the stoichiometry of synthesized PMo$_{10}$V$_2$ (figure 5-16). As expected, EDX analysis confirmed the presence of P, Mo and V in synthesized PMo$_{10}$V$_2$ powder. Table 5-2 shows the atomic percent ratio of addenda and hetero atoms for PMo$_{10}$V$_2$. The experimental value of 18:1 for (Mo + V):P was higher than theoretical value of 12:1. This higher percentage together with the fact that the experimental ratio of 3.7:1 for Mo:V was lower than the theoretical value of 5:1, suggests the presence of intermediate vanadium oxide phases in the product. These intermediate oxides may be removed through further purification during the synthesis process.

Figure 5-16: EDX spectra and SEM morphology of PMo$_{10}$V$_2$ crystals.
Table 5-2: Theoretical and experimental atomic % ratios of addenda atoms (Mo and V) and hetero atoms (P) present in both commercial PMo$_{12}$ and synthesized PMo$_{10}$V$_2$.

<table>
<thead>
<tr>
<th></th>
<th>PMo$_{12}$</th>
<th>PMo$_{10}$V$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mo:P</td>
<td>(Mo+V):P</td>
</tr>
<tr>
<td>Theoretical</td>
<td>12 : 1</td>
<td>12 : 1</td>
</tr>
<tr>
<td>Experimental</td>
<td>12.6 : 1</td>
<td>18.1 : 1</td>
</tr>
</tbody>
</table>

5.5.3 XPS of PMo$_{10}$V$_2$

XPS analysis was performed on bare, single-layer PMo$_{12}$ coated and single-layer PMo$_{10}$V$_2$ coated MWCNT films. Broad-survey XPS spectra were acquired for the elements C1s, O1s, F1s, P2p, Mo3d, and V2p. F1s was from the PTFE binder that was used to make the film. P2p was not analyzed due to its very low content. The overall elemental composition of each film before and after LbL modification is shown in figure 5-17. Before coating, the carbon content of bare MWCNTs was 90.5 at.% carbon and 2.9 at.% oxygen. After coating, the carbon content decreased by 43.5 at.% and 36.7 at.% for PMo$_{12}$ coated and PMo$_{10}$V$_2$ coated MWCNTs, respectively. The oxygen content increased by 32.0 at.% and 22.7 at.% for PMo$_{12}$ coated and PMo$_{10}$V$_2$ coated MWCNTs, respectively. The decrease in carbon and increase in oxygen content suggests a relatively high amount of surface coverage for coated MWCNTs. Also, PMo$_{10}$V$_2$ coated MWCNTs had lower surface coverage, which was due to a higher amount of PTFE binder, causing poor adhesion between the coating and substrate. There was also an introduction of 12.6 at. % and 8.2 at.% molybdenum for PMo$_{12}$ coated and PMo$_{10}$V$_2$ coated MWCNTs, respectively. Additionally, 0.7 at. % vanadium was present in PMo$_{10}$V$_2$ coated MWCNTs.
Comparisons between the theoretical and experimental stoichiometry ratios for PMo$_{12}$ and PMo$_{10}$V$_2$ are shown in table 5-3. The experimental values for the ratio of addenda atoms to heteroatoms (Mo:P and (Mo+V):P) and oxygen to addenda atoms (O:Mo and O:(Mo+V)) deviated from the theoretical values. However, the results for both PMo$_{12}$ and PMo$_{10}$V$_2$ were very similar. Furthermore, these results were different from EDX analysis, where the bulk properties of POM powder materials were analyzed rather than the surface properties of POM coated MWCNT films. During the LbL process, there is selective adsorption of POM anions, while the bulk powder material contains both POM clusters and intermediate metal oxides.

Table 5-3: Theoretical and experimental atomic% ratios for the different elements present in commercial PMo$_{12}$ and synthesized PMo$_{10}$V$_2$.
High resolution C1s XPS spectra that were acquired for bare and coated MWCNTs (appendix F) demonstrated the presence of sp\(^2\) hybridized carbon, sp\(^3\) hybridized carbon and various functional groups such as hydroxyl and carbonyl [14,25,73]. The binding energies of these functional groups are listed in table 5-4. As discussed earlier, sp\(^2\) hybridized carbon represents the available electronic state (delocalized π electrons) that may be occupied for functionalization. For coated MWCNTs the decrease in sp\(^2\) hybridized carbon at 284.5 eV [25], implies the high degree of surface coverage (figure 5-18).

The sp\(^2\) hybridized carbon decreased when MWCNTs were coated, but there was an increase in the various functional groups (appendix F). These groups on the surface of coated MWCNTs may be attributed to the pre-treatment step during the LbL process, where nitric acid oxidizes the bare MWCNTs by introducing oxygen containing functional groups. The PDDA layer may also contribute to this increase of functional groups.

![C1s XPS spectra for bare, single-layer PMo\(_{12}\) coated and single-layer PMo\(_{10}\)V\(_{2}\) coated MWCNTs. This peak at 284.5 eV represents sp\(^2\) hybridized carbon.](image)

Figure 5-18: C1s XPS spectra for bare, single-layer PMo\(_{12}\) coated and single-layer PMo\(_{10}\)V\(_{2}\) coated MWCNTs. This peak at 284.5 eV represents sp\(^2\) hybridized carbon.
In both cases of single-layer coated MWCNTs, there was an increase in the oxygen content. Approximately 66-69 at.% of the oxygen observed for coated MWCNTs was oxides, which was most likely due to Mo(VI) oxides from the PMo$\text{_{12}}$ and PMo$\text{_{10}}$V$_2$ molecules (figure 5-19a) [57,83,84]. For coated MWCNTs there was also an increase in the molybdenum content. Most of this elemental molybdenum (84-90 at.%) was Mo$^{6+}$, in the form of MoO$_3$ (figure 5-19b).

Figure 5-19: a) O1s XPS spectra and b) Mo3d XPS spectra for single-layer PMo$_{12}$ and PMo$_{10}$V$_2$ coated MWCNTs.
Table 5-4: XPS binding energies and surface functional groups for a) bare b) single-layer PMo$_{12}$ coated and c) single-layer PMo$_{10}$V$_2$ coated MWCNTs.

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Binding Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a) Bare</td>
</tr>
<tr>
<td><strong>C1s</strong></td>
<td></td>
</tr>
<tr>
<td>sp$^2$ Carbon (C-C)</td>
<td>284.5</td>
</tr>
<tr>
<td>sp$^3$ Carbon (C-C)</td>
<td>285.5</td>
</tr>
<tr>
<td>Hydroxyl (C-OH/C-O-C)</td>
<td>286.9</td>
</tr>
<tr>
<td>Carbonyl (&gt;C=O)</td>
<td>287.9</td>
</tr>
<tr>
<td>Carbonate (-O-(C=O)-O-)</td>
<td>292.2</td>
</tr>
<tr>
<td><strong>O1s</strong></td>
<td></td>
</tr>
<tr>
<td>Oxygen (O)</td>
<td>531.1</td>
</tr>
<tr>
<td>Oxygen (MoO$_3$)</td>
<td>-</td>
</tr>
<tr>
<td>Hydroxyl (C-OH/C-O-C)</td>
<td>532.5</td>
</tr>
<tr>
<td>Carbonate (-O-(C=O)-O-)</td>
<td>534.0</td>
</tr>
<tr>
<td>Water (H$_2$O)</td>
<td>-</td>
</tr>
<tr>
<td><strong>Mo3d</strong></td>
<td></td>
</tr>
<tr>
<td>Mo$^{6+}$ (MoO$_3$)</td>
<td>-</td>
</tr>
<tr>
<td>Mo$^{5+}$</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-</td>
</tr>
<tr>
<td>Mo$^{5+}$</td>
<td>-</td>
</tr>
<tr>
<td><strong>V2p</strong></td>
<td></td>
</tr>
<tr>
<td>V$^{5+}$ (V$_2$O$_5$)</td>
<td>-</td>
</tr>
<tr>
<td>V$^{4+}$</td>
<td>-</td>
</tr>
</tbody>
</table>
Only PMo$_{10}$V$_2$ coated MWCNTs contained oxidized vanadium. The V2p XPS spectra is illustrated in figure 5-20. Approximately 81 at.% of this vanadium was $V^{5+}$ in the form of $V_2O_5$ and the remaining is $V^{4+}$.

![Figure 5-20: V2p XPS spectra for single-layer PMo$_{10}$V$_2$ coated MWCNTs.](image)

XRD, EDX and XPS demonstrated the structure and surface composition of synthesized PMo$_{10}$V$_2$. The results for this POM were very similar to commercial PMo$_{12}$, with the expected difference being the presence of vanadium. Therefore, these results provide supporting evidence regarding the properties of the synthesized PMo$_{10}$V$_2$. The next section will explore the application of synthesized PMo$_{12}$V$_2$ in multi-layer coatings.

### 5.6 Multi-Layer Coating Using Synthesized PMo$_{10}$V$_2$

MWCNTs that were coated with a single-layer of PMo$_{10}$V$_2$ showed an enhanced "capacitive" cyclic voltammogram while maintaining the conductivity. Therefore, it is of interest to investigate multi-layer coatings that involve this synthesized POM. The following section will investigate two sequences, sequence-3 (PMo$_{12}$ as bottom layer and PMo$_{11}$V$_2$ as top layer) and sequence-4 (PMo$_{11}$V$_2$ as bottom layer and SiMo$_{12}$ as top layer).
5.6.1 Electrochemical Behaviour of Multi-Layer Sequence-3 and 4

Figure 5-21 shows the voltammograms of bare, single-layer PMo$_{12}$ coated, single-layer SiMo$_{12}$ coated and multi-layer sequence-3 coated MWCNTs. The cyclic voltammogram of sequence-3 was a combination of both PMo$_{12}$ and PMo$_{10}$V$_2$ chemistries. The cyclic voltammogram of multi-layer sequence-4 is shown in figure 5-22, and which was a combination of both PMo$_{10}$V$_2$ and SiMo$_{12}$. At a scan rate of 0.05 V/s, the area specific capacitance values of multi-layer sequence-3 coated and multi-layer sequence-4 coated MWCNTs was 2.91 F/cm$^2$ and 2.53 F/cm$^2$, respectively. Similar to the results for sequence-1 and sequence-2, these multi-layer sequences also showed a significantly enhanced capacitance compared to their single-layer counterparts.

![Figure 5-21: Cyclic voltammograms of single-layer PMo$_{12}$ and PMo$_{10}$V$_2$ MWCNTs in comparison with multi-layer sequence-3 MWCNTs.](image)

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5.6.2 Performance of Multi-Layer Coatings

Figure 5-23 shows the area specific capacitance of all multi-layer coating chemistries in comparison to bare MWCNTs. At a scan rate of 0.05 V/s and 1 V/s, the increase in capacitance for all multi-layer coated MWCNTs was significantly higher (380-470 % of bare MWCNTs) than the observed values for single-layer coated MWCNTs (194-247 % of bare MWCNTs). As expected, all multi-layer samples exhibited a decrease in capacitance when the scan rate was increased to 1 V/s (29-36% decrease from 0.05 V/s). The decrease was slightly more significant compared to single-layer coated MWCNTs (19-25% decrease from 0.05 V/s). This was simply because of the decrease in conductivity as more layers are coated onto MWCNTs. However, this decrease in capacitance was still very competitive with bare MWCNTs (37% decrease from 0.05 V/s). Furthermore, the high rate performance significantly exceeded the values reported in previous work [11,15]. The cyclic voltammograms of all multi-layer chemistries at a scan rate of 1 V/s can be found in appendix D.
Figure 5-23: Area specific capacitance of bare MWCNTs in comparison with all multi-layer coated MWCNTs at a scan rate of 0.05 V/s and 1 V/s.

Long cycle life is one of the advantages of ECs. Therefore, the cycle life of these composite materials was analyzed. Figure 5-24 shows the cycle life of multi-layer sequence-1 coated MWCNTs for up to 5000 cycles. Two observations may be made from figure 5-24. First of all, the rate of charge decay decreases with the number of cycles, which indicates a leveling-off effect. Secondly, in addition to the decrease in pseudocapacitance, the double layer capacitance region of the voltammogram also decreases. Although the amount of charge stored decayed as the number of cycles increased, this charge decay may be largely attributed to the mass loss from the CME working electrode in a liquid cell.
Figure 5-24: Cycle life analysis of multi-layer sequence-1 coated MWCNTS (scan rate = 0.2 V/s).

5.6.3 Surface Characterization

The morphologies of various MWCNT composites were obtained using a SEM. Figure 5-25 shows the SEM images of bare, PDDA only coated, single-layer PMo$_{10}$V$_2$ coated and multi-layer sequence-3 coated MWCNTs. Distinct morphologies were observed for the four different cases, suggesting that MWCNTs were coated with POM clusters. The bare and PDDA only coated MWCNTs had smooth surfaces; while the POM coated MWCNTs had rough surfaces. The diameter of MWCNTs increased with each successive layer, demonstrating the effectiveness of the LbL process. Bare MWCNTs had a diameter of approximately 14 nm, which is the same value that has been reported in previous work [11,15]. Using the diameter values listed in figure 5-25, it was found that the thickness of the PDDA layers was approximately 2-3 nm, while the thickness of the POM layers was approximately 3 nm.
Figure 5-25: SEM images of a) bare, b) PDDA only coated, c) single-layer PMo$_{10}$V$_2$ coated and d) multi-layer sequence-3 coated MWCNTs. Approximations of the tube diameter is also indicated for each case.

5.7 Scaling Up For Device Fabrication

Thus far all the presented results have been obtained using a cavity micro electrode (CME). Although an effective method for screening a large number of powder samples rapidly and efficiently, CME cannot be used for the fabrication of actual EC devices. Thus, the following section investigates the LbL chemical modification of large sized graphite electrodes (appendix A) for EC devices.
5.7.1 Single-layer PMo$_{10}$V$_2$ Coated Graphite Electrodes

Figure 5-26a illustrates the cyclic voltammograms of single-layer PMo$_{10}$V$_2$ coated graphite electrodes in comparison with uncoated graphite electrodes. These results were obtained in a 3-electrode cell for studying single electrodes. The coated graphite electrodes stored a higher amount of charge compared to uncoated graphite electrodes. At a scan rate of 0.05 V/s, the area specific capacitance values for bare and single-layer PMo$_{10}$V$_2$ coated graphite electrodes were 7.5 mF/cm$^2$ and 21.4 F/cm$^2$, respectively. The percentage of capacitance increase (185%) was slightly lower than the value of single-layer PMo$_{12}$ coated MWCNTs obtained using a CME (247%). This discrepancy may be attributed to the lower porosity and lower specific surface area of graphite. These results demonstrated the effectiveness of the LbL process and its potential to be used for large scale applications.

Two-electrode cells were constructed to mimic a capacitor using bare electrodes and single-layer PMo$_{10}$V$_2$ coated electrodes, respectively. Figure 5-26b shows the voltammograms of these two devices for comparison. The PMo$_{10}$V$_2$ enhances the capacitance of the device, as the PMo$_{10}$V$_2$ coated electrode cell stored a higher amount of charge while maintaining capacitive electrochemical behavior. At a scan rate of 0.05 V/s, the area specific capacitance values for the bare electrode cell and the PMo$_{10}$V$_2$ coated electrode cell was 2.8 mF/cm$^2$ and 9.7 mF/cm$^2$, respectively. Going from a single-electrode cell to a two-electrode cell, the capacitance values decreased by 63% and 55% for bare graphite and coated graphite, respectively. In the case of a symmetrical cell, the overall capacitance of the cell should be half of each individual electrode. This suggests that both two-electrode cells represented a slightly asymmetrical cell, more so in the case of bare graphite electrodes.

The high rate performance of these cells was also investigated. Figure 5-27 illustrates the cyclic voltammograms of the two-electrode cells at a scan rate of 1 V/s. Even at this increased scan rate, single-layer PMo$_{10}$V$_2$ coated graphite electrodes demonstrated a capacitive “rectangular” profile. The area specific capacitance values for the bare electrode cell and the PMo$_{10}$V$_2$ coated electrode cell was 1.7 mF/cm$^2$ and 4.4 mF/cm$^2$, respectively. In comparison to values reported at 0.05 V/s, the specific capacitance at 1 V/s decreased by 39% for bare electrodes and 55% for PMo$_{10}$V$_2$ coated electrodes. Nonetheless, PMo$_{10}$V$_2$ coated electrodes displayed a 159% increase in area specific capacitance over bare electrodes.
Figure 5-26: Cyclic voltammograms of bare graphite electrodes and single-layer $\text{PMo}_{10}\text{V}_2$ coated graphite electrodes in a) single-electrode cell and b) two-electrode cell. The scan rate is 0.05 V/s.

Figure 5-27: Cyclic voltammograms of bare graphite electrodes and single-layer $\text{PMo}_{10}\text{V}_2$ coated graphite electrodes in a two-electrode cell. The scan rate is 1 V/s.
5.7.2 Charge/Discharge

Constant-current charge/discharge (CD) tests were performed on the large sized graphite electrode cell. The CV and CD of a two-electrode cell are shown in figure 5-28a and 5-28b, respectively. From the CV test, the area specific capacitance of bare and PMo$_{10}$V$_2$ coated graphite electrodes was calculated to be 1.8 mF/cm$^2$ and 4.2 mF/cm$^2$, respectively. Using the CD response, area specific capacitance values were calculated for bare (2.0 mF/cm$^2$) and single-layer PMo$_{10}$V$_2$ coated graphite electrodes (5.4 mF/cm$^2$). Therefore, the CD test confirmed that the application of POM coatings onto the surface of carbon electrodes improved the specific capacitance. It should be noted that the results in this section were obtained using a different cell to that of section 5.7.1.

![Figure 5-28: a) CD response of two-electrode cell before and after coating at a constant current of 0.4 mA/cm$^2$ and b) Cyclic voltammogram of two-electrode cell before and after coating at a scan rate of 1 V/s.](image)

Figure 5-28: a) CD response of two-electrode cell before and after coating at a constant current of 0.4 mA/cm$^2$ and b) Cyclic voltammogram of two-electrode cell before and after coating at a scan rate of 1 V/s.
Chapter 6
Conclusions

6 Conclusions

The primary objective of this work was to add pseudocapacitive material to the double layer electrodes in order to increase the specific energy (by increasing capacitance) of ECs, while maintaining high specific power (maintaining low ESR). This objective has been accomplished via the LbL chemical modification of carbon substrates with polyoxometalates. The following conclusions have been reached:

1. A robust process has been developed to chemically modify nanocarbon materials.

2. Each layer in the LbL technique was found to affect the subsequent layers and the final properties of the composite material. The chemistries were optimized and the process has led to consistent and homogenous coating properties.

3. The properties of the carbon substrate also impact the final properties of the composite. POM coated OLC retained its high conductivity after LbL deposition and showed better high rate performance than that of POM coated MWCNTs. PMo$_{12}$ coated OLC demonstrated good performance for scan rates of up to 2 V/s.

4. LbL deposition of single-layer POMs (PMo$_{12}$, SiMo$_{12}$ and PMo$_{10}$V$_2$) onto the surface of MWCNTs increased the area specific capacitance by almost three folds over that of uncoated material (scan rate of 0.05 V/s). The synthesized PMo$_{10}$V$_2$ coated MWCNTs achieved similar capacitance and exhibited a more “rectangular” cyclic voltammogram compared to commercial PMo$_{12}$ coated MWCNTs.

5. XRD, EDX and XPS provided additional structural and compositional information about the synthesized PMo$_{10}$V$_2$.

6. MWCNTs were modified with four multi-layer coating chemistries: sequence-1 (bottom layer PMo$_{12}$ + top layer SiMo$_{12}$), sequence-2 (bottom layer SiMo$_{12}$ + top layer PMo$_{12}$),...
sequence-3 (bottom layer PMo$_{12}$ + top layer PMo$_{10}$V$_2$) and sequence-4 (bottom layer PMo$_{10}$V$_2$ + top layer SiMo$_{12}$). At a scan rate of 0.05 V/s, multi-layer coating chemistries increased the area specific capacitance by 380-470 % compared to bare MWCNTs and by approximately 40% over single-layer coated MWCNTs. The highest area specific capacitance value was attained by sequence-3 (2.91 F/cm$^2$). In addition to increased capacitance at 0.05 V/s, multi-layer coated MWCNTs retained 64-71% of its capacitance at 1 V/s. This performance was very competitive with bare MWCNTs, which retained only 63% of their capacitance.

7. The diverse range of multi-layer coating chemistries also demonstrates the versatility of the LbL technique and its ability to be used to design and engineer the surface to reach the desirable properties by leveraging different types of POM molecules and their properties.

8. To test the validity of this process for large scale applications, large sized graphite electrodes were modified with PMo$_{12}$. The LbL deposition of PMo$_{12}$ on large sized graphite electrode enhanced their performance. At a scan rate of 0.05 V/s, coated electrodes achieved an area specific capacitance of 185% higher than uncoated electrodes. A two-electrode cell was constructed using these electrodes and CV and CD confirmed the superior performance of PMo$_{12}$ coated electrodes over that of uncoated electrodes.
7 Future Work

The following approaches are recommended for further investigations in this topic:

1. Investigation of alternative POM molecules: There are many POMs that are yet to be explored for this particular application. Keggin-type POMs with different combination of heteroatoms or addenda atoms may be explored. Furthermore, other structures such as the Dawson-type \((X2M18O62n-)\) also remain to be explored for this application.

2. Investigation of alternative cationic layers: Different polycation species such as transition metal complexes and methaloporphyrine may be explored. PDDA works well as the polycation layer; however it has high resistance and does not contribute to the overall capacitance. Therefore, polycation molecules that have good conductivity and exhibit pseudocapacitance are of high interest.

3. Fabrication of solid electrolyte devices: The successful LbL deposition of POMs onto the surface of thin film electrodes was demonstrated in this work. These electrodes may be used to develop thin and flexible solid EC devices.
References


Appendices

Appendix A: Large Graphite Electrodes

Large graphite electrodes were fabricated using the literature by Park et. al [68]. A schematic of these electrodes is shown in figure A-1. In this work, the active material is graphite mixed with 10% cross-linked 10 wt% poly(vinyl alcohol) (PVA), where glutaric acid (GA) is the cross linking agent. The PVA was cross-linked by heat treatment and improves the adhesion between stainless steel and graphite.

![Figure A-1: Schematic representation of large graphite electrodes that were coated using the LbL process.](image)

Appendix B: Synthesis of PMo\(_{(12-x)}\)V\(_x\)

Vanadium substituted phosphomolybdic acids were synthesized using the work of Tsigdinos et al [69]. All required materials are commercially available (Alfa Aesar). Figure B-1 shows the images of all synthesized POMs in dilute solutions.

Materials:

- Na\(_2\)HPO\(_4\)
- Sodium metavanadate
- Distilled Water
- Sulfuric acid conc.
- Na$_2$MoO$_4$.2H$_2$O
- Ethyl ether

Procedure for 11-molybdo-1-vanadophosphoric acid (H$_4$[PMo$_{11}$VO$_{40}$] nH$_2$O):

1. Dissolved 1.42g of Na$_2$HPO$_4$ in 20 mL of water and marked as solution A.

2. Dissolved 1.22g of sodium metavanadate (NaVO$_3$.xH$_2$O) in 20 mL water by boiling and mixing the two solutions together and marked as solution B.

3. Mixed solution A with solution B. Cooled and acidified the mixture using 1 mL concentrated sulphuric acid. Slowly added the sulphuric acid drop wise. The mixture was a red color at this point.

4. Dissolved 26.6g of Na$_2$MoO$_4$.2H$_2$O in 40 mL water and added it to the mixture.

5. To the mixture, slowly (drop wise) added 17 mL of concentrated sulphuric acid with vigorous stirring of the solution. The dark red colour changed to a light red.

6. Transferred the mixture to a tap funnel to perform extraction of the heteropoly acid by adding 80 mL of ethyl ether. Vibrate, deflate and leave until separation. In this extraction, the heteropoly etherate is present as the middle layer; while the bottom layer is a yellow water solution.

7. Once separated, passed a stream of air through the heteropoly etherate layer to free it of ether. The remaining orange solid was dissolved in 10 mL water.

8. Allowed the concentrated solution to crystallize.

9. The final orange crystals were filtered, washed with water and air dried.

10. The final yield should was 5.6g.

The above procedure is specifically for H$_4$[PMo$_{11}$VO$_{40}$] nH$_2$O. The procedures for H$_4$[PMo$_{11}$VO$_{40}$] nH$_2$O and H$_4$[PMo$_{11}$VO$_{40}$] nH$_2$O were very similar and the variations for their preparation are listed in Table A-1.
Table A-1: Quantity of reactants needed for the preparation of different molybdovanadophosphoric acids.

<table>
<thead>
<tr>
<th>Step</th>
<th>PMo$_{11}$V</th>
<th>PMo$_{10}$V$_2$</th>
<th>PMo$_9$V$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Na$_2$HPO$_4$</td>
<td>1.42 g in 20 mL</td>
<td>0.71 g in 10 mL</td>
<td>0.71 g in 5 mL</td>
</tr>
<tr>
<td>2. Sodium metavanadate</td>
<td>1.22 g in 20 mL</td>
<td>2.44 g in 10 mL</td>
<td>3.66 g in 20 mL</td>
</tr>
<tr>
<td>3. H$_2$SO$_4$ (concld.)</td>
<td>1 mL</td>
<td>0.5 mL</td>
<td>0.5 mL</td>
</tr>
<tr>
<td>4. Na$_2$MoO$_4$•2H$_2$O</td>
<td>26.6 g in 40 mL</td>
<td>12.1 g in 20 mL</td>
<td>5.45 g in 15 mL</td>
</tr>
<tr>
<td>5. H$_2$SO$_4$ (concld.)</td>
<td>17 mL</td>
<td>8.5 mL</td>
<td>8.5 mL</td>
</tr>
<tr>
<td>6. Ethyl ether</td>
<td>80 mL</td>
<td>50 mL</td>
<td>40 mL</td>
</tr>
<tr>
<td>10. Final yield</td>
<td>5.6 g</td>
<td>3.5 g</td>
<td>0.72 g</td>
</tr>
</tbody>
</table>

Figure B-1: Images of synthesized POMs in 10mmol/L dilute solution.
Appendix C: Reproducibility of CME and LbL Process

The following section presents results that show the consistency of both the CME and the LbL process. Figure C-1 demonstrates the narrow distribution of specific capacitance values for bare MWCNTs tested using a CME. Figure C-2 demonstrates the narrow distribution of specific capacitance values for single-layer PMo$_{12}$ coated MWCNTs. Furthermore, figure C-3 shows twenty different CV profiles of single-layer PMo$_{12}$ coated MWCNTs and figure C-4 shows twelve different CV profiles of multi-layer sequence-1 coated MWCNTs.

![Figure C-1: Specific capacitance values of bare MWCNTs (scan rate = 50mV/s).](image1)

![Figure C-2: Specific capacitance values of single-layer PMo$_{12}$ coated MWCNTs (scan rate = 50mV/s).](image2)
Figure C-3: CV profiles of single-layer PMo$_{12}$ coated MWCNTs (scan rate = 50mV/s).

Figure C-4: CV profiles of multi-layer sequence-1 coated MWCNTs (scan rate = 50mV/s).
Appendix D: High Rate CVs

The CVs of all single-layer chemistries is presented in figure D-1 and the CVs of all multi-layer chemistries is presented in figure D-2.

Figure D-1: CVs of bare MWCNTs and all single-layer coated MWCNTs at a scan rate of 1 V/s.

Figure D-1: CVs of bare MWCNTs and all multi-layer coated MWCNTs at a scan rate of 1 V/s.
Appendix E: XRD Study of PMo$_{10}$V$_2$

Figure E-1 shows the XRD patterns on the synthesized product, PMo$_{10}$V$_2$, versus the three different reactants (Na$_2$HPO$_4$, sodium metavanadate and Na$_2$MoO$_4$•2H$_2$O). Figure E-2 contains the XRD patterns of commercial PMo12 in comparison to synthesized PMo$_{11}$V and PMo$_9$V$_3$. Figure E-3 contains XRD patterns of commercial PMo$_{12}$ in comparison to synthesized PMo$_{11}$V, PMo$_{10}$V$_2$ and PMo$_9$V$_3$.

Figure E-1: Comparison of XRD patterns of the final product, PMo$_{10}$V$_2$, versus the three different reactants used during the synthesis process.
Figure E-2 XRD patterns of commercial PMo_{12} in comparison to synthesized PMo_{11}V, PMo_{10}V_{2} and PMo_{9}V_{3}.
Appendix F: C1s XPS Spectra

Figure F-1 shows the C1s XPS spectra for bare MWCNTS, single-layer PMo$_{12}$ coated MWCNTs and single-layer PMo$_{10}$V$_2$ coated MWCNTs.

*Figure F-1: High resolution C1s XPS spectra of bare, single-layer PMo$_{12}$ coated and single-layer PMo$_{10}$V$_2$ coated MWCNTs. All three cases are to the same vertical scale.*
Appendix G: Volume Specific Capacitance Values

In order to calculate the volume specific capacitance it was assumed the CME has a cylindrical cavity, with a measured depth of approximately 0.03 cm. The diameter of this cavity is assumed to be the same as the platinum tip (0.25 mm).

Area of the platinum tip = 0.000491 cm$^2$

Depth of CME cavity = 0.03 cm

Therefore, these values may be used to calculate the volume specific capacitance. The volume specific capacitance values for all composite materials at a scan rate of 0.05 V/s are listed in this section.

*Table G-1: Volume specific capacitance of MWCNTs.*

<table>
<thead>
<tr>
<th></th>
<th>Area Specific Capacitance (F/cm$^2$)</th>
<th>Volume Specific Capacitance (F/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare</td>
<td>0.51</td>
<td>17.00</td>
</tr>
<tr>
<td>Single-Layer PMo$_{12}$</td>
<td>1.76</td>
<td>58.67</td>
</tr>
<tr>
<td>Single-Layer SiMo$_{12}$</td>
<td>1.50</td>
<td>50.00</td>
</tr>
<tr>
<td>Single-Layer PMo$_{10}$V$_2$</td>
<td>1.77</td>
<td>59.00</td>
</tr>
<tr>
<td>Multi-Layer Seq. 1</td>
<td>2.45</td>
<td>81.67</td>
</tr>
<tr>
<td>Multi-Layer Seq. 2</td>
<td>2.27</td>
<td>75.67</td>
</tr>
<tr>
<td>Multi-Layer Seq. 3</td>
<td>2.91</td>
<td>97.00</td>
</tr>
<tr>
<td>Multi-Layer Seq. 4</td>
<td>2.53</td>
<td>84.33</td>
</tr>
</tbody>
</table>
Table G-2: Volume specific capacitance of OLC.

<table>
<thead>
<tr>
<th></th>
<th>Area Specific Capacitance (F/cm²)</th>
<th>Volume Specific Capacitance (F/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare</td>
<td>0.57</td>
<td>19.00</td>
</tr>
<tr>
<td>Single-Layer PMO₁₂</td>
<td>1.62</td>
<td>54.00</td>
</tr>
</tbody>
</table>