**SURFACE MODIFICATIONS OF NANOCARBON MATERIALS FOR
ELECTROCHEMICAL CAPACITORS**

By

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Abstract

Carbon nanomaterials have been investigated as electrode materials for high rate electrochemical capacitors (ECs). Multi-walled carbon nanotube (MWCNT) was found to be a good candidate and was further modified with additional pseudocapacitive polyoxometalates (POMs). A “layer-by-layer” (LBL) deposition technique was used to add POM active materials to CNT. MWCNTs were successfully coated with two different POMs, $(\text{SiMo}_{12}\text{O}_{40})^{-4}$ (SiMo_{12}) and $\text{PMo}_{12}\text{O}_{40}^{-3}$ (PMo_{12}). Even with merely a “single-layer” of POM, the modified MWCNTs exhibited more than 2X increase in capacitance compared with that of bare nanotubes. To further improve their electrochemical performances, the deposition sequence of the POM layers was adjusted to form “alternate layer” coating to modify MWCNT. Two coating sequences were developed with: Combination 1 (bottom layer PMo_{12} + top layer SiMo_{12}) and Combination 2 (bottom layer SiMo_{12} + top layer PMo_{12}). A synergistic effect on the capacitance and kinetics was observed for both combinations. X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM) also proved the successful coating of POMs on MWCNTs. The potential-pH relationship provided important insights in terms of the deposition mechanism and suggested that the bottom layer close to the electrode substrate was the dominating layer in alternate layer coated MWCNT electrodes.

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1 Literature Review

1.1 Electrochemical Capacitors

Electrochemical capacitors (ECs), also known as supercapacitors or ultracapacitors, have attracted significant attention for their applications as energy storage devices [1, 2] to supplement renewable energy such as photovoltaic, wind and fuel cells. As an electrochemical energy storage device, EC is composed of electrodes and electrolytes. The electrodes are the critical parts of EC and are also the center of this thesis. This chapter introduces the general concepts of ECs as well as the materials and process techniques involved in these devices. The role of the electrode materials and the electrolyte in determining the performance of these devices are also briefly described.

Figure 1-1 is a Ragone chart which illustrates the energy density and the power density of different energy storage devices. There are mainly three types of energy storage techniques: batteries, capacitors and ECs. Conventional capacitors can deliver high power, but their energy density is very low. The capacitance values of ECs are 20 to 200 times higher than conventional capacitors [3, 4]. Chemical energy storage devices (batteries) and ECs are the leading electrical energy storage devices today. However, batteries show somewhat slow power delivery or uptake. ECs can mitigate this limitation by providing much higher energy delivery or uptake within a few seconds (e.g. 10 kW/kg) [5, 6]. If the energy density is sufficiently high, it is possible to have high energy and high power ECs that can outperform batteries (the arrow in figure 1-1).

Figure 1-1. Specific power and energy for different energy storage devices.

Similar to batteries, ECs are configured with two electrodes immersed in electrolyte. ECs store charges at the electrode electrolyte interface, using low cost and high surface area carbon materials [7, 8, 9, 10, 11, and 12]. Because of the chemical and physical stability of the carbon electrodes, ECs can undergo millions of cycles without significant degradation of electrodes [5, 13]. In contrast, the energy storage mechanism of batteries involves chemical change between the charge and discharge state, which limits their life span [13]. Comparison of the properties of ECs and other energy storage devices are demonstrated in table 1-1.

Table 1-1. Comparison of the properties of different energy storage devices [8].

Characteristic	Electrolytic capacitors	Carbon ECs	Batteries
Specific energy (Wh kg ⁻¹)	< 0.1	1 – 10	10 – 100
Specific power (W kg ⁻¹)	>> 10,000	500 - 10,000	< 1000
Discharge time	10 ⁻⁶ to 10 ⁻³ s	s to min	0.3 - 3 h
Charging time	10 ⁻⁶ to 10 ⁻³ s	s to min	1 - 5 h
Charge/discharge efficiency (%)	~ 100	85 – 98	70 – 85
Cycle life (cycles)	Infinite	> 500,000	~ 1000
Max. voltage (Vmax) determinants	Dielectric thickness and strength	Electrode and electrolyte stability	Thermodynamics of phase reactions
Charge stored determinants	Electrode area and dielectric	Electrode microstructure and electrolyte	Active mass and thermodynamics

Since the anode and the cathode of ECs are connected in series in an EC device (figure 1-2), the overall capacitance C can be determined by the equivalent circuit consisting of anode capacitance, C_a , and cathode capacitance, C_c , according to the following equation [11]:

$$1/C = 1/C_a + 1/C_c \quad (\text{Eq. 1})$$

Figure 1-2. Schematic representation of an ECs and corresponding equivalent circuit, where C is the capacitance and R is the resistance [10].

There are two types of configuration in EC, symmetric and asymmetric. For a symmetrical capacitor, the anode and the cathode are identical; hence the overall capacitance is half of the capacitance value of the individual electrode. If the capacitor is built with different electrodes, then an asymmetric EC forms and the overall capacitance is dominated by the electrode with smaller capacitance. [14]. The energy (E) and the power (P) of supercapacitors can be calculated from the following

equations:

$$E = \frac{1}{2} CV^2 \quad (\text{Eq. 2})$$

$$P = V^2/4R, \quad (\text{Eq. 3})$$

Where C is the overall capacitance of the cell in Farads, V is the cell voltage or operating voltage and R is the equivalent series resistance (ESR) of the cell in ohms [8, 15].

Cell voltage is an important factor for both the specific energy and the specific power of ECs. Operating voltage is dependent on the stability of the electrolyte [8, 10, 12, and 16]. Aqueous electrolytes, such as acid (e.g., H_2SO_4) or alkali (e.g., KOH), possess high ionic conductivity (up to $\sim 0.8 \text{ S/cm}$). However, they have the disadvantage of limited voltage window of $\sim 1.23 \text{ V}$ [17]. Beyond this voltage limit, aqueous electrolytes are unstable and start to decompose.

Non-aqueous electrolytes allow the operating voltage window to be as high as about 2.5 V [12, 16, and 17]. Since the energy of supercapacitors is proportional to the square of the operating voltage, non aqueous electrolytes are being employed in many commercial ECs [8]. However, the electrical resistivity of a non-aqueous electrolyte is at least an order of magnitude higher than that of an aqueous electrolyte, which increases the internal resistance of the capacitors. High internal resistance limits the power capability of the ECs, thus limits their applications. Therefore, to develop high performance ECs, researchers have been focusing on the electrode materials both in their natural and modified forms for higher capacitance to improve their energy density. Commercialization of ECs of different specifications and form factors is now possible

by the advancement of electrode materials and electrolytes. A few examples of commercial ECs are shown in figure 1-3.

Figure 1-3. Examples of different commercial ECs [18].

1.2 Electrode Materials

Electrode materials play a major role in the energy density (capacitance) of ECs. There are two types of capacitance: a) electrochemical double layer capacitance (EDLC) and b) pseudocapacitance. Double layer capacitance arises from the charge adsorption on the electrode surface. Pseudocapacitance, originated from Faradic reactions, can be added to double layer by depositing electroactive materials to store more charges [5]. High surface area carbon materials are currently used for EDLCs, whereas metal oxides and conductive polymers are being used to add pseudocapacitance. These two sources of capacitance are described in the following sections.

1.2.1 Electrochemical Double Layer Capacitor

Double layer capacitors store charges electrostatically by reversible adsorption/desorption of ions from the electrolyte on to the electrodes that are electrochemically stable and possess high specific surface area (SSA). Charge separation takes place upon polarization at the electrode - electrolyte interface, hence producing an EDLC. The two electrodes and their interface systems in a single capacitor are illustrated in figure 1-4.

Figure 1-4. Schematic representation of an EDLC.

Since there is no electron transfer across the interface, this is known as the true capacitance [10] and can be expressed as follows [6]:

$$C_{DL} = \epsilon_r \epsilon_o A / t \quad (\text{Eq. 4})$$

Where ϵ_r is the dielectric constant of electrolyte, ϵ_o is the dielectric constant of vacuum, A is the surface area of electrode and t is the effective thickness of double layer. Therefore, the higher the specific surface area (SSA) of the electrode materials, the higher the double layer capacitance. The thickness of the double layer depends on the

electrolyte concentration and the size of the ions, which is usually 5 to 10 Å for concentrated electrolyte [5].

Active carbon materials are commonly employed for EDLCs because of the following unique chemical and physical properties [8]:

- High conductivity
- High surface area (> 2000 m²/g)
- Good corrosion resistance
- High temperature stability
- Controlled pore structure
- Processability and compatibility in composite materials
- Relatively low cost.

The SSA and the conductivity of the electrodes are critical to the performances of supercapacitor. Carbon and its various allotropes have been studied for their electrochemical properties and applications as electrode for ECs. The characteristics of some carbon materials that are commonly employed for high capacitance are briefly discussed and compared in the following sections.

1.2.1.1 Activated Carbon

Commercially available electrochemical capacitors (ECs) are EDLCs, which are dominantly activated carbon (AC) based [8]. The processes employed to increase the surface area are referred to as ‘activation’ and the resulted carbons are known as AC. Depending on the activation processes, the specific surface area of AC can be as high as

3000 m²/g [19]. The capacitance value of AC can vary from 15 to 50 μF/cm². Taking an average value of 25 μF/cm² and a specific surface area of 1000 m²/g for AC, the theoretically attainable capacitance can be 250 F/g [11, 12]. In reality, only a few tens of F/g of capacitance is achievable due to the limited accessible carbon surface to the electrolytes.

Since it is difficult to control the porosity and pore size during the activation process, AC has a broad distribution of pore size as shown in figure 1-5. Due to the non-optimized pore structure, most of the AC shows inconsistent capacitance values [6]. Carbon surfaces, often consist of micro pores (< 2 nm), are hardly-accessible or un-accessible for ions; especially for large sized ions such as ionic liquids. Micro pores cannot contribute to double layer capacitance in these cases [10].

Figure 1-5. Schematic representation of porous activated carbon particle with three classes of pores [11].

Moreover, longer activation time and higher temperature result in large and deep pores, which limit their application at high rate. This phenomenon can be explained by the RC transmission line equivalent circuit model as shown in figure 1-6 [7]. R and C represent the electrolyte resistance and double layer capacitance respectively. For a single-pore, the RC constant gives a unit time, which implies the time required for ions to access the pores. Charges stored deep in the pore are accessible by crossing a longer electrolyte path, results in higher series resistance as well as slow response [7]. Therefore, deep micro pores in AC are not desirable for ECs, which aim to deliver charge at high rate.

Figure 1-6. Schematic representation of a nanopore in a carbon electrode of an electrochemical capacitor [7].

1.2.1.2 Carbon Nanotubes

Carbon nanotube (CNT) has been considered as a promising electrode material for EDLC [5, 9, 11, 20, 21, 22, 23, and 24] because of their high surface area, high electrical conductivity, good physicochemical stability and excellent mechanical strength. Although the surface area of CNTs is less than AC, it predominantly contains “mesopores” (2-50 nm) [11], which are desirable for the double layer capacitance [8].

Carbon nanotubes are produced from the catalytic decomposition of hydrocarbons [25, 26]. Depending on the synthesis methods and parameters, CNTs can be prepared as single-wall carbon nanotube (SWCNT) or multi-wall carbon nanotube (MWCNT). Figure 1-7 represents the schematic diagram of SWCNT and MWCNT [27].

Figure 1-7. Schematic representation of (a) SWCNT and (b) MWCNT [27].

Single-wall carbon nanotube is essentially rolled single sheet of graphene, whereas MWCNT has multiple parallel layers of graphene sheets with an inter layer spacing of about 0.36 nm. The diameter of SWCNTs is 1-2 nm. For MWCNT, it has a range of 2-25 nm. The length of CNTs can vary from $>1\text{ }\mu\text{m}$ to a few millimetres depending on the synthesis process [27].

Thin MWCNT (5-20 nm) is one of the promising electrode materials which exhibit many properties of SWCNTs and have a higher production yield at a reasonable price. This makes them attractive over SWCNTs and for large volume commercial applications, where high conductivity is desirable [28].

The as-received nanotubes usually agglomerate in bundles and result in poor dispersion. To improve the dispersion properties, CNTs are functionalized by different methods [29, 30]. One way is to oxidize them in air [21] or to treat them with nitric (HNO_3) and sulphuric (H_2SO_4) acids [29]. These treatments create defective sites at the wall surface resulting in the formation of carboxyl and carbonyl groups, which can act as active sites for further functionalization [29, 31].

Behler et al. [28] and Osswald et al. [29] studied the effect of oxidation on some as-received thin MWCNTs. The CNTs are enriched in sp^2 hybridization and possess a electronic energy level that can be further occupied by functionalization [31]. However, Osswald et al. observed that the as-received nanotubes contained amorphous carbon (sp^3 hybridized) on the outer surface as shown in figure 1-8a (arrows). To remove the amorphous carbons, they oxidized and annealed the nanotubes and found: a) during

annealing, graphitization of MWCNTs took place and b) acid treatment resulted in oxidation of the surface. Graphitization lead to more ordered structure and removal of amorphous carbons (figure 1-8b), while acid treatment created defective cites (arrows in figure 1-8c) without damaging the overall MWCNTs structure.

Figure 1-8. TEM images of (a) as-received, (b) graphitized, and (c) nitric acid treated MWCNTs [29].

1.2.1.3 Nanodiamond (Onion like carbon)

Nanodiamond (ND) is the only carbon material that contains non-porous structure. Portet et al. examined the electrochemical performance of ND and onion like carbon (OLC) [20] and found that the as-received ND powders contained disordered carbons. These disordered carbons were removed by high temperature annealing. They reported that annealing could graphitize the ND. The transformation started at 1200°C at ND surface and completed at about 1800°C between which the graphitic shells grew from the surface toward the center to form OLC (figure 1-9). The specific surface area also increased due to the transformation from diamond structure to graphite. With the annealing temperature, the intensity of the defects decreased and the electrical

conductivity improved significantly due to increasing graphitization. This is because of the delocalization of π electrons in the graphitized structure that led to an increase in electronic conductivity. Indeed, Park et al. [32] reported a significant increase of sp^2 hybridization on OLC compared with ND.

Figure 1-9. High resolution TEM images of ND annealed at (a) 1200°C and (b) 1800°C [20].

1.2.1.4 Graphite Nanofiber

Graphite nanofiber (GNF) is another newly developed materials, which is produced by the decomposition of selected hydrocarbons on catalytic metal particles. GNF has a high surface area (50-700 m²/g). In the growth process, the hydrocarbon is chemisorbed on the metal surface and diffuses through the particle and precipitate at a specific crystal face to generate the nanofiber. These materials possess a unique combination of physical and chemical properties because of the presence of graphite platelets [33].

Through proper selecting the catalyst and controlling the reactions, it is possible to produce the nanofibers in several desired conformations, where the platelets are aligned

in a particular direction with respect to the fiber axis. Figure 1-10 represents some unique conformations of GNF [34]. The typical length of GNFs is in the range of 5-100 μm and the diameter varies from 5 to 1000 nm [33]. One of the most important features of these fibers is the presence of a large number of edges. These edges are the available sites for physical and chemical interactions, making of these crystalline solids chemically active [33, 34]. This is one of the unique properties of GNF over the conventional graphite and nanotubes, as the edges, but not the basal planes are exposed in the former. In these structures, the graphite sheets are oriented perpendicular to the growth axis and the minimum inter layer spacing is 0.355 nm [35].

Figure 1-10. Schematic representations of the three unique conformations of GNF [34].

In table 1-2, the double layer capacitances of different carbon materials including AC are summarized. The data are selected from the high rate performances only for these materials. It can be seen from the table that AC possess very low specific capacitance at high rate, in spite of the high energy density at low rate [36]. ND, OLC and MWCNT

are promising at high rate.

Table 1-2. Specific capacitances of different carbon materials at high rate.

Electrolyte	Capacitance from	F (Hz)	Material	Spec. Cap. (F/cm²)	Spec. Cap. (F/gm)	Ref.
1 M H ₂ SO ₄	Electrodes*	1	ND	0.6		32
			OLC	0.6		
			MWCNT	0.1		
1 M H ₂ SO ₄	Electrodes*	1	MWCNT		11	37
4 M H ₂ SO ₄	Electrodes*	1	MWCNT		17	38
7 M KOH			MWCNT		~ 0	
AN (aniline) +1.5M NEt ₄ BF ₄	Cell**	1	AC + 0-30% DWCNT (double wall CNT)	0.03 - 0.05		39, 40
AN+1.5M NEt ₄ BF ₄	Cell**	1	95% AC + 5% binder	0.02		36
Propylene Carbonate				~ 0		
AN+1.5M NEt ₄ BF ₄	Cell**	1	AC + 0-30% MWCNT	0.03-0.05		41

*Three electrodes were employed: working, reference and counter electrodes.

** Two working electrodes were employed, where cell capacitance is half of the capacitance of electrode.

1.2.2 Pseudocapacitor

Electrochemical double layer capacitors can be complemented by adding pseudocapacitance, which is induced by reversible Faradaic charge transfer reactions. It is known that the EDLCs may contain 1-5% of their capacitance as pseudocapacitance due to the Faradaic reactivity of the surface oxygen functional groups on carbon. The presence of these surface functional groups on the carbon surface [10] is related to the preparation or pre-treatment of the carbon materials. On the other hand, the specific capacitance of the pure pseudocapacitive materials can be 10 to 100 times higher than those for double layer alone [12]. The requirements of pseudocapacitance are fast and reversible redox reactions, multiple electron transfer with overlapped potentials, good conductivities and chemical stabilities.

The commonly studied pseudocapacitive materials are: i) transition metal oxides such as ruthenium dioxide (RuO_2) [42, 43] or manganese dioxide (MnO_2) [44 - 46], ii) hetero polyoxometalate (POM) such as Keggin type POMs [37, 49 – 51, 52, 53], and iii) conductive polymers such as polyaniline [54, 55]. They are described briefly in the following sections.

1.2.2.1 Transition Metal Oxides

Amongst all the transition metal oxides, RuO_2 is by far the most ideal pseudocapacitive electrode material. This is attributed to their high specific capacitance, long cycle life, good electrochemical stability and high conductivity [5]. Conway et al. [50] observed that the cyclic voltammogram (CV) of RuO_2 (figure 1-11) was close to that of an ideal

capacitor. In the voltammogram, RuO₂ exhibited highly reversible, multiple electron transfer redox reactions. The capacitance is almost independent of the potential, hence the charging/discharging current is almost constant [47, 48] due to the overlapping of the Faradaic oxidation/reduction reactions.

Figure 1-11. Cyclic voltammetry profile for RuO₂ electrode in 0.1M H₂SO₄ [47].

Hu et al. reported that the nano sized hydrous RuO₂/carbon composites exhibited specific capacitance as high as 1350 F/g [42], which is the highest reported value so far. However, the specific capacitance of hydrous RuO₂ was found to decrease with annealing temperature and with decreasing structural water content [5, 43]. Moreover, the limited resources and the cost of the precious metal (Ru) impede the commercial application of RuO₂ as electrode materials.

Hydrous MnO₂ is an attractive candidate for pseudocapacitor due to the low cost of raw material. Manganese is also more environmentally friendly than many other transition

metal oxides [5]. However, oxide materials themselves are poor electrical conductor. Moreover, most of the metal oxides are not stable in acid solution and can only be used in neutral solutions [44], which might induce higher electrolyte resistance.

1.2.2.2 Conductive Polymers

Conductive polymers are another good example of pseudocapacitive materials. Conductive polymers are cheap, with fast doping and un-doping (oxidation and reduction) process and can be applied as the active material for ECs [5, 10, and 54]. These materials are expected to provide the following advantages:

- i. Devices of various and flexible shape
- ii. Light weight devices due to their low density
- iii. High specific capacitance

If the conductive polymer is coated on high surface conductive materials such as carbon, they can produce an inorganic-organic hybrid electrode material for EC. Due to the high surface area of carbon materials, an enhancement of specific capacitance can be expected on these hybrid materials [3]. However, it was found that gradual degradation of these composite materials occurred and the capacity faded away when they are cycled repeatedly [11, 55]. Swelling and shrinking of the electro-active polymers might be the reason for this degradation [5].

1.2.2.3 Polyoxometalate (POM)

Polyoxometalate (POM) is a class of transition metal oxide cluster, which has attracted many research interests in recent years. In general, POMs can be divided into three classes:

- i. Heteropolyanions: these are metal oxide clusters that contain a central hetero atom such as phosphorous (P), silicon (Si) or boron (B) [56 – 58].
- ii. Isopolyanions: these are metal oxide framework without internal hetero atoms. As a result, they are less stable compared to their heteropolyanions [58].
- iii. Mo blue and Mo brown reduced POM clusters [58].

The heteropolyanions have many interesting properties including, a) high stability for most of their redox states, b) the possibility of tuning the redox potential by changing the heteroions and/or addenda ions without affecting their structure, c) the ability of incorporating various transition metal cations into the heteropolymetalate structure, and d) the potential of multiple electron transfer with fast kinetics during the oxidation/reduction reactions. Therefore, POMs are attractive for many applications including for electrode surface modifications [32, 56, and 59].

Keggin type POM is the best known structural form with a general formula of $\{XM_{12}O_{40}\}^{n-}$, in which the heteroatom is surrounded by twelve addenda atoms (e.g. molybdenum (Mo) or tungsten (W)) and forty oxygen atoms (figure 1-12). These POMs, when in contact with protons from acid solution (e.g. H_2SO_4), self assemble into heteropolyacid. In electrochemistry, Keggin-type POMs are the most common electrode materials with relative low cost.

Figure 1-12. Schematic representation of Keggin type POM.

For either of the molybdenum and tungsten complexes, the Keggin anion carrying a greater ionic charge is considered to be more basic. With identical anionic charge, there is a big difference between the electrochemical responses of molybdenum and tungsten complexes. For instance, in acidic electrolyte, $[PMo_{12}O_{40}]^{3-}$ undergoes successive two electrons reductions (2, 2 and 2 electrons) while $[PW_{12}O_{40}]^{3-}$ is reduced by 1, 1 and 2 electrons [51, 56, and 60]. Thus, molybdenum based Keggin structures are known to be more effective catalysts for multi-electron oxidation [65]. The pseudocapacitance arises from the multiple electron transfer reactions of POMs [20, 13, 40]. The reactions can be expressed as follows:

For $XMo_{12}O_{40}^{n-}$ (X = P or Si):

For $\text{XW}_{12}\text{O}_{40}^{n-}$ ($\text{X} = \text{P}$ or Si):

The reduction potentials for both the molybdenum based and tungsten based Keggin type POMs are tabulated in table 1-3.

Table 1-3. Reduction potentials for different Keggin type POMs [51].

	Reduction potentials (V) vs. reference		
POMs	1st reaction	2nd reaction	3rd reaction
$\text{SiMo}_{12}\text{O}_{40}^{4-}$	-0.025	0.175	0.3
$\text{PMo}_{12}\text{O}_{40}^{3-}$	-0.05	0.175	0.325
$\text{SiW}_{12}\text{O}_{40}^{4-}$	-0.275	-0.475	-0.625
$\text{PW}_{12}\text{O}_{40}^{3-}$	-0.1	-0.45	-0.65

Sadakane et al. reviewed the electrochemical properties of POMs as electro-catalysts [56]. They reported that the reduction potential of Keggin type heteropolymolybdates and heteropolytungstates decreased linearly with an increase in the negative charge of the heteropolyanions. It was also revealed that the redox potentials of the POMs were dependent on the pH of the solution and they shifted to more positive potential with decreasing in pH. This potential-pH relationship is closely related to the reactions 1 to 6.

1.3 Surface Modification

Since POMs are water soluble, they need to be deposited and bonded on a substrate. Many researchers have investigated the surface modification of POMs on different carbon materials and the relationship between the POM modification and carbon surface structure [32, 51, 52, and 61]. Surface modification of CNT via POM is one of the recent interests in the field of electrochemistry [32, 37, 49, 50, 53, and 59].

Although, extensive research has been accomplished regarding surface modification of carbon materials for higher capacitance, relatively few studies have been focusing on the high rate performances of the electrodes [32, 36, 38, 55, and 62]. In most of the cases, the electrochemical performances of modified electrodes were very good at slow rate, but gradually deteriorate at high rate. High rate performances of the electrodes are important for ECs and a thorough research is necessary. Table 1-4 summarizes the specific capacitances of some of the approaches in this field at high rate. Most of these works were based on CNT modification and these modifications involved different types of pseudocapacitive materials.

Surface modification by POMs can be achieved by different modification techniques [63] such as electrochemical treatment or chemical modification. These methods are described briefly in the following section.

Table 1-4. Electrochemical performances of modified carbon materials at high rate.

Electrolyte	Capacitance from	F (Hz)	Material	Spec. Cap. (F/cm ²)	Spec. Cap. (F/gm)	Ref.
1 M H ₂ SO ₄	Electrodes	1	ND + PMo ₁₂	0.65		32
			OLC + PMo ₁₂	0.76		
			MWCNT + PMo ₁₂	0.4		
1 M H ₂ SO ₄	Electrodes	1	MWCT + PMo ₁₂		18.5	37
4 M H ₂ SO ₄ 7 M KOH	Electrodes	1	MWCNT*		37	38
			MWCNT*		24.5	
			MWCNT * Ammoxidized		50	
			MWCNT*		30	
			MWCNT Ammoxidized		19	
			MWCNT* Ammoxidized		32	
1 M H ₂ SO ₄	Cell	1	PANI + MWCNT		100	55
0.5 M KCl	Electrodes	1.2	MWCNT + PPy	1		62

*Activated with KOH.

1.3.1 Electrochemical Modification

The electrochemical modification requires an external power supply, chemically compatible electrodes and electrolyte. This method often involves the cyclic voltammetry (CV) to monitor and control the flow of current as well as applied voltage [52]. Liu et al. deposited POM-polycation multilayer on carbon surface using electrochemical method [52]. This treatment often results in good adhesion, hence low resistance and high capacitance [63]. However, this method is not suitable to work with powder electrode materials such as AC and CNT and it usually takes long operation time.

1.3.2 Chemical Modification via Layer by Layer Deposition

The layer-by-layer (LbL) deposition is a molecular self assembly technique which involves electrostatic interaction between alternately charged material to produce multilayer films [32, 52, 64 – 67]. Because of the electrostatic interaction between the layers, charge reversal is a crucial step to ensure the surface readiness for the next layer.

Often, polyelectrolytes are used as a supporting layer to maintain the charge neutrality in the multilayer structure. There can be two scenarios for the charge balance. In the first case, also known as intrinsic compensation, a polymer positive charge is balanced by a negative charge from another polymer. In the alternative mechanism, also known as extrinsic compensation, polymer charge is balanced by salt counterions used to construct the multilayers (figure 1-13) [64, 66].

Figure 1-13. Intrinsic and extrinsic charge compensation [66].

Surface modification of carbon materials can be accomplished via LbL deposition as shown in figure 1-14. During the process, the non-stoichiometry induced in the interface enables the multilayers to form and propagate i.e., the increment per layer is controlled by the excess surface charge [66].

Figure 1-14. Schematic representation of LbL deposition using poly(diallyldimethylammonium chloride) (PDDA) and POM [32].

Because of the electrochemical inertness and low chemical reactivity, the surface of the carbon materials require to be pretreated to improve the adhesion between the carbon surface and the deposited layers [50]. One way to improve the activity of carbon surface is to treat them with oxidizing agents such as nitric acid (HNO_3) or sulfuric acid (H_2SO_4) solutions [29].

Nitric acid is used to oxidize the electrode by generating oxygen containing functional groups and to clean the surface by dissolving the catalyst particles [29]. It enhances the hydrophilicity of the carbon surface. As the POMs are negatively charged ions, a positive or polycationic layer is needed to hold the layers strongly by electrostatic force. Poly (diallyldimethyl-ammonium chloride (PDDA) has been used extensively as the cationic layer [32, 50, 64 – 67]. By repeating the polycationic and POM layers, deposition of multi layer POM on the surface of carbon have been demonstrated.

Martel et al. examined the redox systems associated with Keggin type heteropolymolybdates and heteropolytungstates deposited on a glassy carbon surface [51]. During the oxidation and reduction reactions, the POMs underwent multiple electrons transfer. They found that the reduction of tungsten based POMs occurred at more negative potentials than that of molybdenum based POMs. By utilizing four different POMs ($\text{PMo}_{12}\text{O}_{40}^{3-}$, $\text{PW}_{12}\text{O}_{40}^{3-}$, $\text{SiMo}_{12}\text{O}_{40}^{4-}$ and $\text{SiW}_{12}\text{O}_{40}^{4-}$) and two different cationic layers (methyl viologen and meso-tetra(4N-methylpyridyl porphyrin)), they fabricated various multilayer deposited carbon electrodes. It was shown in their study that, by increasing the coating layers on glassy carbon, the current response of the electrode also increased as shown in figure 1-15 [51].

Figure 1-15. Cyclic voltammetry of POM coated glassy carbon. The numbers indicate the number of POM layers [51].

Wang et al. observed similar trend after depositing multiple layers of POMs on indium tin oxide (ITO) coated glass slides [64]. They utilized PDDA as the positive layer and either SiMo_{12} or PMo_{12} as negative layer to fabricate the multilayers. For both POMs, they found that the anodic peak current increased linearly with the deposited layers (figure 1-16). For PMo_{12} coated sample, the anodic peak current maintained the linearity with increasing scan rate, indicating a charge transport controlled process. On the other hand, SiMo_{12} coated sample could not maintain the linearity with scan rate, suggesting a diffusion controlled process.

Figure 1-16. Cyclic voltammogram of LbL buildup for (a) $\text{PMo}_{12}/\text{PDDA}$ and (b) $\text{SiMo}_{12}/\text{PDDA}$ deposited sample [64].

Park et al. compared POM deposition on ND and OLC [32]. They found that OLC, enriched with sp^2 hybridization, showed good activity toward POM LbL deposition. They further performed confirmation tests on MWCNTs, which has a high concentration of sp^2 unsaturated bonds and controlled pore structure. Accordingly, CNT could be a good candidate for surface modification to add pseudocapacitance. CVs with highly reversible redox peaks were obtained after a single layer PMo_{12} coating on the MWCNT surface (figure 1-17). This result supports the argument that POMs are suitable pseudocapacitive material for adding capacitance to MWCNTs. And this was also the foundation of current project.

Figure 1-17. CV of P_{Mo}₁₂ coated MWCNT in 1M H₂SO₄ at 1 V/s [32].

2 Objectives

Carbon electrode materials are very promising for high rate and power applications in electrochemical capacitor (EC). Surface modification of the carbon materials is a low cost approach to enhance the capacitance. However, limited work has been reported based on the modification of carbon via layer by layer (LbL) deposition for EC applications [64]. In this project, different carbon materials were screened. The selected material was modified using polyoxometalates (POMs) with several variations via LbL deposition to enhance the performance for EC. Our objectives were to develop high power and high energy density electrode materials. Specifically, we would like to accomplish the following:

1. To select a carbon electrode material with good conductivity and high double layer capacitance for EC.
2. To enhance the pseudocapacitance by chemical modification of the surface of the selected carbon material.
3. To optimize the modification technique and to adjust the POM layer sequences to further improve the electrochemical performances.
4. To develop an understanding of the LbL coating mechanism through electrochemical analyses and surface characterizations.

3 Experimental

This section covers the experimental set-up, electrochemical and surface analyses of the electrode materials that have been employed in this project. Cavity micro electrode (CME) has been used for electrochemical analyses, which is also included here. In addition, the electrode film fabrication and their chemical modification processes are described.

3.1 Electrode Materials

Both SWCNT and MWCNT have been investigated in this project. The MWCNTs were provided by the Drexel University Nanomaterials group. These are small tubes with a diameter range of 5-20 nm, which have advantages in terms of mechanical and thermal properties over larger MWCNTs [28]. SWCNTs were provided by the Waterloo Institute of Sustainable Energy (WISE) group. Graphite nanofibers (95%) were purchased from Aldrich and their diameters are in the range of 80-200 nm. These nanofibers are 0.5-20 μm long and have about 4% metal catalyst.

3.2 Electrode Film Fabrication

The powder materials were fabricated into film using 8% poly tetrafluoro ethylene (PTFE) solution as a binder. The binder was dispersed in isopropyl alcohol (IPA) ultrasonically and mixed with the carbon electrode materials. This mixture was then dried until the IPA evaporated and the mixture became a dough. This dough of electrode materials was then passed through a pasta roller to make a film. These films were then used as substrates for chemical modification, electrochemical and surface analyses.

3.3 Working Electrodes

Cavity micro electrode (CME) was employed in this project for the electrochemical analyses of the electrode materials. The construction procedure for CME is described elsewhere [68] and the schematic is shown in figure 3-1. The powder or the film of the electrode materials can be grinded into the cavity (figure 3-1b) of the CME. The other end of the wire (silver wire) is connected to the external circuit for the electrochemical analysis (figure 3-1a).

Figure 3-1. Schematic representation of a cavity micro electrode (CME).

3.4 Procedures for Chemical Modifications

The polyoxometalates $\text{H}_4\text{SiMo}_{12}\text{O}_{40}$ (SiMo_{12}), $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (PMo_{12}), $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (PW_{12}), and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (SiW_{12}) (Alfa), were dissolved as individual diluted solutions (6 mmol/L) for chemical modifications. Other chemicals used for modification were aqueous solution of HNO_3 (conc.), 4 wt% poly (diallyldimethylammonium chloride) (PDDA) (Sigma-Aldrich). MWCNTs were coated with the POM solution in three steps deposition in the order of HNO_3 (2 min)- H_2O (2 min)-PDDA(10 min)- H_2O (2 min)-POM solution (5 min)- H_2O (2 min) as summarized in table 3-1.

Table 3-1. The coating parameters employed in this study.

Chemicals	Concentration	Time
HNO ₃	Concentrated	2 min
PDDA	4 wt%	10 min
POM	6 mmol/L	5 min

3.5 Electrochemical Cell

A three-electrode cell was utilized in this project for the electrochemical analyses of the modified and bare electrode materials. CME was employed as working electrode; platinum and Ag/AgCl Sat. electrode were used as counter and reference electrodes respectively. Electrodes results verifications were also performed by constructing a two-electrode cell, where two CMEs were connected in series to emulate a capacitor configuration. Most of the tests were carried out using 1 M H₂SO₄ electrolyte. Electrochemical responses of bare and modified MWCNTs were investigated using cyclic voltammetry (CV) with an EG&G 273 potentiostat controlled by a Corrware software.

3.5.1 Electrochemical Analysis: cyclic voltammetry

Cyclic voltammetry (CV) is a commonly used electrochemical characterization method to study the ECs. During the CV test, voltage is applied to the working electrode and corresponding current output that flows through the electrode is recorded. This current response is plotted against the applied voltage to form a cyclic voltammogram. Figure 3-2 represents a typical cyclic voltammogram, where the arrows indicate oxidation and

reduction region with anodic and cathodic peaks respectively.

Figure 3-2. Typical cyclic voltammogram; i = current, E = potential, p = peak, a = anodic and c = cathodic.

Cyclic voltammetry gives an overall understanding for the characterization of a system in terms of: (i) the reversibility of the charge/discharge processes, (ii) the distinction between any significant stages during the charge/discharge processes, (iii) the total amount of charges accumulated over a potential range, (iv) the voltage window for an electrode material between which it can accept or dispose the charges, and (v) the dynamic behavior of an electrode material for charge/discharge with increasing sweep rate [69].

The shape of the voltammogram is very important to determine the electrochemical response. An ideal double layer capacitive behavior can be represented as rectangular shape as shown in figure 3-3 [10]. The sign of the current reverses immediately for ideal capacitor as the potential sweep reverses. For this type of response, the current output is

independent of the potential. For the capacitor with high resistance, the current output depends on the potential and the voltammogram forms a tilted shape (indicated as #2). Electrode materials with pseudocapacitance show a deviation from rectangular shape (indicated as #3) with oxidation/reduction peaks that represent Faradaic charge transfer reactions (indicated as #4).

Figure 3-3. Cyclic voltammograms of ECs for different characteristics [10].

For an ideal capacitor, the capacitance can be calculated from the following equation:

$$C = I/v, \quad (\text{Eq. 5})$$

Where I is the current and v is the sweep rate in V/s. Sweep rate is related to the frequency response of the cell i.e. how fast an EC can be charged and discharged. When the voltammogram deviates from the ideal shape, the capacitance of the cell can be measured by integrating the charge (Q) for a voltage (V) window as shown by the equation below:

$$C = Q/V \quad (\text{Eq. 6})$$

In this project, the cyclic voltammetry was carried out from a low sweep rate of 50 mV/s to a high rate of 500 mV/s or higher.

3.5.2 Charge/Discharge Test

In the charge/discharge (CD) test, a constant current is applied to a two-electrode cell and the voltage responses are reported as shown in figure 3-4. Thus, the performance of the electrode materials in a capacitor cell can be investigated. For instance, by measuring the slope of the discharge curve, the cell capacitance can be calculated using the following equation:

$$C = I/(dU/dt) \quad (\text{Eq. 7})$$

Where C is the capacitance, I is the discharge current, and dU/dt is the slope of the discharge curve. In addition, the equivalent series resistance (ESR) can also be measured with the following equation:

$$ESR = V_{IR} / (I_{\text{charge}} + I_{\text{discharge}}) \quad (\text{Eq. 8})$$

Where, V_{IR} is from the initial voltage drop (IR). CD curve with and without significant IR effect are compared in figure 3-4 [70].

Figure 3-4. Schematic diagram for CD test of EC, with and without IR drop [70].

3.6 Surface Analysis and Characterization

Scanning electron microscopy (SEM) micrographs were obtained using Hitachi S-5200 for the morphologies of both the modified and bare MWCNT surfaces.

X-ray photoelectron spectroscopy (XPS) was conducted to characterize the surface chemistries of the bare and modified nanotubes. This method provides the information of the chemical bonding on the bare and coated nanotubes surfaces. XPS was conducted on Leybold (Specs) Max 200 with a monochromatic Aluminum (Al) $K\alpha$ X-ray source. The overall distribution of detected surface elements were collected in atomic percentage and the 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.

4 Results and Discussion

4.1 Electrochemical Analysis by CME

Traditional electrochemical testing on powder materials requires several days to prepare and analyze each sample due to the electrode preparation, where powders are made into film with a binder and pressed onto metal mesh current collectors. Thus, it is impractical to use conventional large area electrodes for fast screening of materials or for studying large number of electrode materials in various electrolytes. Moreover, additional effects from the mesh/electrode interface may cause unpredictable and inconsistent results, which further complicate the electrochemical tests [69].

The cavity microelectrode (CME) can be applied for fast electrochemical analyses of carbon materials. As the CME technique relies on a small amount of materials (a few micrograms), one can study the rate of charge transfer without the interference of mass transfer such as diffusion [69]. It is also a very cost effective way to study powder materials.

In this project, CME was employed so that we could focus on the electrode materials only. As mentioned earlier, the exposed end of CME was the platinum (Pt) wire and there was a cavity at the tip of this wire. The electrode material was ground and packed into the cavity (figure 4-1) and contacted with the Pt wire electrically. The calculation regarding the depth of cavity and the volume of the packed sample are included in appendix A.

Figure 4-1. CME, (a) before and (b) after sample packing.

One of the issues with our CME tests is the reproducibility and repeatability. To address this concern, the peak current distribution of MWCNT of 27 experiments with the same CME was recorded. As shown in figure 4-2, the peak current in the range of 0.35 to 0.41 μA was obtained most of the times (12 out of 27). The average value of these results was considered as the representative peak current of MWCNT. In this work, all of the experiments were conducted in a similar fashion and only the average of the most consistent results (including the standard deviation) was taken into account. Since all of the results were based on relative comparison, CME is suitable for such studies.

Figure 4-2. CME peak current distributions for MWCNT.

4.2 Carbon Materials Selection

Different types of electrode materials were screened based on their cost, availability, conductivity and capacitance. The materials were graphite, GNF, MWCNT and SWCNT. Figure 4-3 shows the comparison of the CV profiles for these materials. Graphite powder is conductive but with the smallest surface area ($3\text{--}5\text{ m}^2/\text{gm}$) amongst all the electrode materials, thus the lowest specific capacitance (about 0.2 F/cm^2 at 50 mV/s). For this reason, graphite was used only as a baseline material in our experiment. On the other hand, GNF had a higher capacitance than graphite (about 0.5 F/cm^2 at 50 mV/s). However, GNF was difficult to handle as they were too coarse and hard to be packed in the CME. The sharp redox peaks of GNF in the voltammogram were due to the functional group present on the carbon surface [12]. Since the edges of graphene sheets are exposed in GNF, they possess a surface area which is chemically active and thus,

higher peak current (figure 4-3).

Figure 4-3. CVs of GNF, MWCNT and SWCNT at 50 mV/s in 1M H_2SO_4 .

The capacitance for SWCNT was much higher ($>2 \text{ F}/\text{cm}^2$ at 50 mV/s) than the others. This was due to a high surface area and easy ionic access within a single rolled up graphene sheet of SWCNT. However, the challenge of SWCNTs is the poor dispersion, which limited their useful surface area. In this project, the resistivity of SWCNT was also found to be the highest compared to that of GNF or MWCNT. The resistance is given by the reciprocal of the slope of the tangent of the CV curve as it crosses the abscissa [71]. MWCNT, on the other hand, showed a capacitance value of $0.62 \text{ F}/\text{cm}^2$ at low rate and possessed the lowest value of resistance.

Furthermore, to understand the rate responses of these nano-materials, CV was conducted at higher potential sweep rate (figure 4-4). At a sweep rate of 500 mV/s, the CV profiles for GNF and SWCNT were distorted, whereas the CV for MWCNT remained relatively rectangular (figure 4-4). Even though the specific capacitance was the highest for SWCNT at low rate (figure 4-3), it became very resistive at high rate (figure 4-4). For GNF, the difference between the oxidation and reduction peak potentials (peak separation) was higher than that at low rate. This was an indication of the resistive nature of the nanofibers at high rate [12]. MWCNT showed the best conductivity among the nano carbon materials. In addition, the CV of the MWCNT resembled to that of an ideal capacitor at high rate. Table 4-1 summarizes the specific capacitances of these electrode materials at different scan rates. It is worth noting from the table that while SWCNT and GNF lost their abilities to store and deliver charge at high rate, MWCNT could retain a reasonable level of their capacitance from low to high rate (over 80% at 500 mV/s and over 70% at 1 V/s). This suggests that MWCNT could be a good material for ECs.

The stability of the carbon electrodes is also an important property for better performance of ECs. Thus the electrode materials were subjected to repeated potential cycling to evaluate their cycle life. In the cycle life test, MWCNT showed excellent stability. After 5000 cycles the nanotubes did not show any significant degradation (figure 4-5). Therefore, MWCNTs were chosen in this project for further investigation.

Figure 4-4. CVs of GNF, MWCNT and SWCNT at 500 mV/s in 1M H₂SO₄.

Figure 4-5. CVs of MWCNT at 500th, 1000th, 1500th, 2000th, 2500th, 3000th, 3500th, 4000th, 4500th, and 5000th cycles at 1 V/s in 1M H₂SO₄.

Table 4-1. Specific capacitances (with the standard deviation) of different electrode materials at different scan rate.

Material	Sweep rate V/s	Specific capacitance F/cm ²
GNF	0.05	0.54 ± 0.02
	0.5	0.34 ± 0.01
	1	0.26 ± 0.01
SWCNT	0.05	2.01 ± 0.43
	>0.1	Resistive
MWCNT	0.05	0.62 ± 0.04
	0.5	0.5 ± 0.03
	1	0.45 ± 0.03

4.3 Surface Modification of Selected Material

In order to further enhance the capacitance of MWCNT, we performed chemical modifications on the nanotubes using POMs. We employed LbL approach for all the modifications. In this project, both tungsten based [$\text{H}_3\text{PW}_{12}\text{O}_{40}$ (PW_{12}) and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (SiW_{12})] and molybdenum based [$\text{H}_4\text{SiMo}_{12}\text{O}_{40}$ (SiMo_{12}), $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (PMo_{12})] Keggin type hetero polyoxometalates were screened for their pseudocapacitive properties. The nanotubes were first modified by a single-layer of POM. In the subsequent approach, additional layers of POMs were deposited on the MWCNTs. In

the following sections, all of these modification techniques together with the electrochemical responses are described.

4.3.1 Single layer Coating

4.3.1.1 Electrochemical Behavior

Figure 4-6 are the voltammograms of bare and POM modified MWCNTs. There were total of four POM coating chemistries and each one was coated only once on the respective CNT substrate to form a “single-layer”.

Figure 4-6. CVs of MWCNT in 1M H₂SO₄, before and after single layer modification by PMo₁₂, SiMo₁₂, PW₁₂, and SiW₁₂. The sweep rate = 50 mV/s.

The area under the CV represents the total charge stored/released during charging/discharging processes, respectively. Clearly distinct CV profiles were observed on molybdenum and tungsten based POMs coated MWCNTs. Compared to the bare MWCNT, the one coated with PMo_{12} and SiMo_{12} showed higher charge storage reflected by the oxidation/reduction peaks. Little improvement was achieved on PW_{12} and SiW_{12} coated nanotubes relative to the bare counterparts. The redox peaks are the characteristics of both PMo_{12} and SiMo_{12} coated samples. From the literature review (table 1-3), we know that the redox peaks for tungsten based POMs appear at very negative potentials. Although they are potentially useful for energy storage, the negative potential range was beyond the scope of this project. Therefore, PMo_{12} and SiMo_{12} were selected as the modifier for MWCNTs.

Figure 4-7 depicts the voltammograms of the bare MWCNT and PMo_{12} or SiMo_{12} single-layer coated MWCNT films at two different potential sweep rates. The coated electrodes showed significantly higher capacitance than that of bare MWCNT. At low rate (50 mV/s), the capacitance values for both PMo_{12} and SiMo_{12} modified MWCNT films were about 0.95 F/cm^2 (figure 4-7a), which was over 50% higher than the capacitance of bare nanotubes. At a high sweep rate of 2 V/s, the specific capacitances for PMo_{12} and SiMo_{12} coated samples were 0.58 F/cm^2 and 0.57 F/cm^2 respectively, which was about 40% higher compared to bare MWCNT (figure 4-7b and table 4-1). The reversibility of the oxidation/reduction peaks were investigated using an incremental increase of potential as shown in figure 4-8. At this low sweep rate, each pair of peaks showed good reversibility, suggesting a relatively fast kinetics for both oxidation and reduction reactions. This was also an indication of their suitability for

ECs [47]. However, the peaks became less reversible at high rate (figure 4-7b).

Although it was reported in the literature that the peak potentials for PMo_{12} and SiMo_{12} were almost identical, we found that the redox peak positions were quite different (figure 4-7a and table 4-2) compared to the literature value listed in table 1-3. This difference might be due to the interaction between the polyelectrolyte (PDDA) and the POM molecules. As an intermediate layer, the PDDA polymer chain can have point contact to form a POM monolayer, or can wrap around the molecules to form more dangling loops [64]. In the latter case, more than one POM molecule can be adsorbed in the dangled PDDA loops and form deposited clusters. While the previous reported work was on glassy carbon (GC), which has a smooth surface, the current work was on high surface area MWCNT. As the nanotubes are much rougher than the surface of glassy carbon, it was more likely that the PDDA chains formed more dangling loops and wrapped around the POM clusters. This wrapping effect might cause more interaction between PDDA and POM, which led to a different degree of POM exposure to the electrolyte. This might result in different peak potential from those reported in literature.

Table 4-2. Redox peak positions for PMo_{12} and SiMo_{12} coated MWCNTs.

POMs	1 st reaction		2 nd reaction		3 rd reaction	
	Ox	Red	Ox	Red	Ox	Red
$\text{PMo}_{12}\text{O}_{40}^{3-}$	0.067 V	0.025 V	0.286 V	0.260 V	0.466 V	0.420 V
$\text{SiMo}_{12}\text{O}_{40}^{4-}$	0.067 V	0.013 V	0.250 V	0.230 V	0.350 V	0.325 V

Figure 4-7. CVs for bare, single layer SiMo₁₂ and PMo₁₂ coated MWCNT at a) 50 mV/s and b) 2 V/s in 1M H₂SO₄. The peak identifications are shown in (a), Ox = oxidation, Red = reduction.

Figure 4-8. CVs with incremental increase in voltage for a) PMo₁₂ and b) SiMo₁₂ coated samples in 1M H₂SO₄. The sweep rate = 50 mV/s.

4.3.1.2 Surface Morphology and Chemistry

Surface morphologies of bare and coated CNTs were studied to understand the coating structures and surface chemistry. In the SEM images in Figure 4-9, clearly distinct morphologies were observed for the “single-layer” modified versus the bare MWCNTs. The diameters of the bare and the modified nanotubes were calculated from the figure. The diameters of the bare nanotubes were around 13-14 nm. The coating thickness was measured from the difference in the diameter of nanotubes before and after the modification, and was found to be 3-4 nm for both PMo_{12} and SiMo_{12} coated samples. Knowing that the diameter of the $\text{PMo}_{12}/\text{SiMo}_{12}$ molecules is 1.1 nm, a single-layer coating of 2-3 molecules for either PMo_{12} or SiMo_{12} was assumed. The dangling loop formation of PDDA chain explained the deposition of multiple POM molecules as clusters. The surface features of the coated nanotubes proved a successful single-layer modification. Further comparison of the SEM images for the PMo_{12} and SiMo_{12} modified nanotubes suggested that the PMo_{12} coatings existed as small continuous clusters, while SiMo_{12} had a relatively even coating morphology.

Figure 4-9. SEM images of (a) bare, (b) PMo_{12} coated and (c) SiMo_{12} coated MWCNT.

The elemental compositions from the XPS spectra are listed in table 4-3. Phosphorous (P) and silicon (Si) were not included in the table due to their very low content. The broad scan analyses showed that the carbon content on the surface decreased and replaced by O and Mo after modification (appendix B). Initially, the nanotube surface consisted of 99 wt.% carbon and 1 wt.% oxygen. The carbon content on the nanotube surface decreased to 35 wt.% for PMo_{12} and 29 wt.% for SiMo_{12} coating, suggesting a relatively high coverage of coating in merely one coating.

High resolution XPS spectra were acquired on carbon C 1s for modified and bare MWCNTs and were illustrated in figure 4-10. The C 1s spectrum was deconvoluted to show the ratio of sp^2 and sp^3 carbon as well as various functional groups such as

hydroxyl and carbonyl [32, 72 – 74]. It was mentioned earlier in sections 1.2.1.2 and 1.2.1.3 that the sp^2 hybridized carbon represents the available electronic state (delocalized π electrons) that can be occupied for functionalization. In this case, the decrease of sp^2 carbon implies the increase in surface coverage. Therefore the carbon sp^2 peak (binding energy of 284.46 eV) was used as an indicator to track the variation of surface coverage before and after coating. After a single-layer coating (figure 4-10a), the peak intensity of sp^2 carbon decreased significantly, indicating the presence of coating on MWCNTs. The spectra analyses on Mo and O suggested that the CNT surface was mostly covered with Mo^{6+} (with small amount of Mo^{5+}) and oxygen species such as O^{2-} , OH^- and adsorbed H_2O (figure 4-10b and 4-10c). Comparing the O and Mo ratio in table 4-3, the ones coated with PMo_{12} had the ratio in the range of 3.3, which coincided with the O:Mo ratio in the Keggin structure. However, $SiMo_{12}$ had a ratio of 2.6, indicating the possibility of some changes in their structure.

Table 4-3. Elemental quantification of bare and modified MWCNTs.

	Bare		PMo_{12} coated		$SiMo_{12}$ coated	
Element	atom%	wt.%	atom%	wt.%	atom%	wt.%
C	99	99	60	35	57	29
O	1	1	31	24	31	21
Mo			9	41	12	50

Figure 4-10. XPS spectra for (a) bare and single layer modified carbon C1s, (b) O1s for PMo₁₂, and (c) Mo3d for PMo₁₂ coated MWCNT. (b) and (c) were similar for SiMo₁₂ coated MWCNT (shown in appendix B).

4.3.2 Alternate Layer Coating: initial approach

4.3.2.1 Electrochemical Behavior

One of the criteria of desirable pseudocapacitive material is overlapped multiple electron transfer, which results in a flat “capacitor-like” CV profile as observed on RuO₂ [47]. The “single-layer” PMo₁₂ and SiMo₁₂ showed enhanced charge storage but with distinct peaks. Thus, our next goal was to develop a technique to drive the POM coating chemistry to achieve the above mentioned CV response. Examining the peak potentials

in figure 4-7a and table 4-2, it was noticed that the oxidation/reduction peaks occurred at different potentials for PMo_{12} and SiMo_{12} coated CNTs. Three distinct reduction peaks were observed for PMo_{12} coated MWCNTs at low sweep rate, whereas four distinct reduction peaks were observed for SiMo_{12} coated MWCNTs. From these different peak potentials, we attempted to engineer a more overlapped CV profile over a voltage range, using mixed PMo_{12} and SiMo_{12} solutions. For instance, the first peak was expected to appear at around 0.25 V for SiMo_{12} and the following peak would appear for PMo_{12} at around 0.3 V. As the peaks were close to each other, they might overlap to show a flatter profile over that potential range. Initial trial used mixtures of the two POM solutions at different rates (50% PMo_{12} + 50% SiMo_{12} , 40% PMo_{12} + 60% SiMo_{12} , and 60% PMo_{12} + 40% SiMo_{12}) to coat the nanotubes. As the two solutions were mixed together, the deposition preference of SiMo_{12} and PMo_{12} was random and inconsistent depending on the deposition preference (appendix C).

Our next project was to deposit the two POMs alternately onto the MWCNTs. To obtain the combined effect via LbL, the CNT electrode can be first coated with PMo_{12} followed by SiMo_{12} or vice versa. Therefore, two Combinations were named for this purpose and, in both cases, SiMo_{12} and PMo_{12} were applied alternatively with different sequence. Figure 4-11 shows the voltammograms of alternate layer coated MWCNT samples. The voltammogram of the bare MWCNT was also included in the figures for comparison. In Combination 1 (figure 4-11a), PMo_{12} was applied first as the bottom layer (BL) followed by the top layer (TL) of SiMo_{12} . After the addition of a SiMo_{12} layer, Combination 1 showed little increase in current and capacitance (0.95 F/cm^2) compared with its single PMo_{12} layer coating. For Combination 2 (figure 4-11b), in

which the SiMo₁₂ was first coated followed by PMo₁₂, more than 60% additional capacitance (1.01 F/cm²) was obtained over bare MWCNT. More importantly, a different CV profile was obtained with shifted peaks (figure 4-11b).

Figure 4-11. CVs for alternate layer coated nanotubes in 1M H₂SO₄ at 50 mV/s, a) Combination 1 and b) Combination 2.

It was encouraging to see an increase in capacitance via LbL and it is also very important to ensure that the capacitances of the electrodes can be retained from low to high rates (or frequencies). Figure 4-12 reveals the capacitances of bare and modified MWCNTs as a function of voltage scan rate. In general, a flat profile is desirable, so that the energy can be delivered at low and high rates. Two significant observations can be summarized: a) the POM modified CNTs showed higher capacitance compared to bare nanotubes, with the Combination 2 having the highest capacitance value; and b) these modified MWCNTs can retain the capacitance at high rate. Even at a sweep rate as high as 1 V/s, the Combination 2 exhibited about 75% higher capacitance (0.79 F/cm^2) than that of bare MWCNT (0.45 F/cm^2). The Combination 2 had the best performance both at low and high rate.

Figure 4-12. Comparison of the high rate performances of bare and modified MWCNTs.

4.3.2.2 Surface Morphology

Figure 4-13 shows the SEM images of Combination 2 and the bare nanotubes. From the morphological variation of the bare and modified nanotubes, it was clear that the MWCNTs were coated with POM clusters. The crystalline appearance of the modified sample (figure 4-13b) resembled that of single layer PMo_{12} coated MWCNT (figure 4-9b). This might be due to the presence of PMo_{12} as the top layer in Combination 2. However, the coating thickness was found to be similar to that of single-layer, i.e. 3-4 nm. This is in agreement with the relative small increase in capacitance after the 2nd layer coating. The reason could be the repulsive interactions between the two layers of POMs, which will be addressed in the next section.

Figure 4-13. SEM images of a) bare and b) BL- SiMo_{12} + TL- PMo_{12} (Combination 2) coated MWCNTs.

4.3.3 Alternate Layer Coating: improved process

4.3.3.1 Electrochemical Behavior

Although the alternate coating showed certain improvement, it showed some inconsistencies and did not reach the expected performance. Thus we attempted to

improve the LbL coating process. The standard practice for LbL deposition was to immerse the nanotubes sequentially in “positive layer solution - H₂O - negative layer solution - H₂O” and repeat. However, this might create issues in our process. Since CNT has high surface area, it might have high water adsorption. The lone pair electron from the adsorbed water molecules remained in the first layer coating, which could repel the negatively charged POM. The polar water molecules could neutralize the surface positive charge from PDDA and resulted in weak adsorption of POM in the subsequent layer. If the coated CNT was dried after the deposition of the first layer to remove the adsorbed water, one would expect an improved performance with the second layer. Therefore, the modified nanotubes were air dried (overnight) after the first layer coating to remove about 80 wt.% water, and then followed by deposition of the second layer.

The resulted electrochemical responses are shown in figure 4-14. After drying the coated sample, we saw a further improvement for even “single-layer” coating (1.66 F/cm² and 1.23 F/cm² for PMo₁₂ and SiMo₁₂ coating, respectively), before adding the second layer. For Combination 1, after applying the second SiMo₁₂ layer on the air dried PMo₁₂ coated CNT, significant increase in capacitance was observed. A specific capacitance of 2.68 F/cm² was achieved, which was almost three times higher than the previous result (0.95 F/cm²). Specific capacitance of 1.93 F/cm² was obtained with Combination 2, which was also higher than previous reported values (1.01 F/cm²). For both Combination 1 and 2, the CV profiles were somewhat different from their single-layer counterparts as shown in figure 4-14. These results suggested a contribution from both PMo₁₂ and SiMo₁₂. Figure 4-15 shows the oxidation/reduction peaks reversibility of these two Combinations. Compared to the reversibility of the single-layer coated

films (figure 4-8), the two Combinations also maintained the reversibility.

Figure 4-14. CVs for alternate layer coated nanotubes in 1M H₂SO₄, a) Combination 1 and single-layer PMo₁₂ and b) Combination 2 and single-layer SiMo₁₂. For both cases, the second layer was applied after drying the first layer. The sweep rate = 50 mV/s.

Figure 4-15. CVs with incremental increase in voltage in 1M H_2SO_4 for a) Combination 1 and b) Combination 2. The sweep rate = 50 mV/s.

To verify the contribution from PMo_{12} and SiMo_{12} in the alternate layers, the MWCNTs were also modified using double layer of POMs i.e. two layers (2L) of PMo_{12} or two layers of SiMo_{12} (figure 4-16). For comparison, CV of MWCNT was also included. Comparing figures 4-16 and 4-7, the following observations can be derived:

1. The 2L coatings of PMo_{12} and SiMo_{12} remained the same CV profiles as the respective “single-layer”, i.e. no new peaks were observed.
2. The 2L coating increased the capacitance from their respective “single-layer”. The PMo_{12} showed a greater increase in capacitance but with slower kinetics (less reversible), while SiMo_{12} had a less increase in capacitance but with fast kinetics (good reversibility).
3. Both Combinations 1 and 2 had CV profiles that showed contributions from PMo_{12} and SiMo_{12} .
4. The capacitance values for both Combinations 1 and 2 increased significantly, especially for Combination 1, which demonstrated the highest capacitance among all the chemistries investigated in this work.
5. Even with a high capacitance, the CV kinetic responses of Combination 1 and 2 were still fast. This is different from the results of 2L PMo_{12} and suggested a synergistic effect between PMo_{12} and SiMo_{12} in their alternate LbL deposition.

Figure 4-16. CVs for a) 2L PMo₁₂, 2L SiMo₁₂ coated samples and Combination 1 and b) 2L PMo₁₂, 2L SiMo₁₂ coated samples and Combination 2 in 1M H₂SO₄. The sweep rate = 50 mV/s.

Figure 4-17. CVs for alternate layer coated nanotubes at 500 mV/s in 1M H₂SO₄.

Specific capacitances of alternate and double layer coated samples are listed in table 4-4. These values are also compared with the bare electrode materials listed in table 4-1. With the alternate layer coating, we could achieve even higher capacitance than SWCNTs with better conductivity and kinetics (figure 4-16 vs. 4-3). However, with the increase of sweep rate, the kinetics of alternate layer became more irreversible and resistive, especially at 500 mV/s and beyond (figure 4-17). This might be due to the increase in coating thickness resulted from improved adhesion after a “dried” first layer. Since the POM layer was thicker, the mass transfer such as diffusion could become dominant at high rate. A sharp decrease in capacitance was observed for Combination 1 (about 40%) than that of Combination 2 (about 26%) from low to high rate (table 4-4).

Table 4-4. Specific capacitances of the modified (with drying process) and bare MWCNTs in 1M H₂SO₄ at 50 mV/s and 500 mV/s. Standard deviation for these average values are also included.

Material	Sweep rate V/s	Specific capacitance F/cm²
Combination 1	0.05	2.68 ± 0.34
	0.5	1.6 ± 0.00
Combination 2	0.05	1.93 ± 0.20
	0.5	1.43 ± 0.13
2L PMo ₁₂ on MWCNT	0.05	2.38 ± 0.25
	0.5	1.45 ± 0.18
2L SiMo ₁₂ on MWCNT	0.05	1.43 ± 0.30
	0.5	0.92 ± 0.17
SWCNT	0.05	2.01 ± 0.43
	0.5	Resistive
MWCNT	0.05	0.62 ± 0.04
	0.5	0.5 ± 0.03

4.3.3.2 Surface Morphology and Chemistry

Surface morphology of the alternate layer POM coated samples were also examined and compared with bare nanotubes (figure 4-18). Unlike the “single-layer” coating in figure 4-9, there was little difference in morphology between Combinations 1 and 2. For Combination 1, the coating thickness was about 12 nm, while it was about 10 nm for Combination 2. Apparently, the coating thickness with the “dried process” was almost three times higher than that of single layer (figure 4-9) and previous alternate layer coated samples (figure 4-13). The increase of the thickness of the POM was proportional to the increase of capacitance, when refer to figure 4-13, 4-18, and table 4-4.

Figure 4-18. SEM images of a) bare and b) BL- PMo_{12} + TL- SiMo_{12} (Combination 1), and c) BL- SiMo_{12} + TL- SiMo_{12} (Combination 2) coated MWCNTs. The top layer POM was applied on a dried 1st layer coating.

The XPS results in table 4-5 showed that, for both Combinations, the surface carbon content decreased significantly, translated in higher surface coverage of POM coating (75 wt.% and 60 wt.% for Combination 1 and Combination 2, respectively). This was also clearly shown in the decreased intensity of carbon C 1s spectra after coating, obtained from the high resolution XPS (figure 4-19). Moreover, the Combination 1 showed the highest surface coverage so far. All of these were in good agreement with the finding of enhanced capacitance in electrochemistry.

Table 4-5. Elemental composition of bare and alternate layer (with dry film) coated MWCNTs.

	Bare		Combination 1 coated		Combination 2 coated	
Element	atom%	wt. %	atom%	wt. %	atom%	wt. %
C	99	99	51	25	67	40
O	1	1	36	23	25	21
Mo			13	52	8	39

Figure 4-19. XPS spectra for bare and alternate layer modified carbon C1s. For both alternate layer coated samples, the top layer of POM was applied on the “dried” bottom layer POM modified MWCNTs.

4.4 Coating Chemistry

Using LbL, we can modify the MWCNT with pseudocapacitive POMs and obtain high capacitance and good electrochemical performance. By adjusting the process condition and deposition sequence, the deposited POM showed synergistic effect. Surface morphology and XPS analyses confirmed the presence of POM coatings on MWCNT substrates. However, it was still not clear how POMs, specially the alternate layers, react during the oxidation and reduction. According to the literature [56], the oxidations and reductions of PMo_{12} and SiMo_{12} are pH dependent, that is to say, the electron transfer in the reactions are accompanied by proton (H^+) transfer. As a result, the charge storage and delivery will depend on the concentration of the proton or acidity. Indeed, examining the reactions in section 1.2.2.3 one can see that, for every two electron transfer, there are two protons as well. According to the Nernst equation, this can lead to

a V vs. pH relationship of 59 mV/pH [56]. Therefore, we investigated the electrochemical behavior of deposited POMs as a function of pH in this work as well.

4.4.1 Single-Layer Coating

Single-layer PMo_{12} and SiMo_{12} coated nanotubes were first analyzed in H_2SO_4 electrolyte with concentrations of 1, 0.1 and 0.01 M. Both PMo_{12} and SiMo_{12} showed higher capacitance in high concentration (or low pH) solution (figure 4-20). As shown in reaction 1-3 (section 1.2.2.3), the redox process of both SiMo_{12} and PMo_{12} involves two electrons and two protons. At high pH, the concentration of the electrolyte was low, which resulted in less available protons for reaction. Consequently, the two-electron waves were split into one-electron waves as reported by Sadakane et al [13] earlier. This phenomenon reduced the amount of charge transfer, thus lower the pseudocapacitance.

Figure 4-20. Variation of capacitance with pH for “single-layer” coating at 50 mV/s.

It was also reported that the redox peak potential changed towards negative direction with a slope of $\sim (-0.059)$ V/pH with pH. However, this value was obtained on electrodes with smooth surface (e.g. glassy carbon) only [64, 75]. To obtain the pH dependence for “single-layer” coated nanotubes, we selected two pairs of characteristic peaks, peaks 2 and 3 as labeled in figure 4-21(a) and (b). In our experiments, both of the PMo_{12} and SiMo_{12} coated samples showed potential-pH relationships that were deviated from the reported -59 mV/pH. All of the potentials with pH as well as the slopes of the potential-pH dependence obtained from this work are reported in table 4-6 and 4-7. One example for PMo_{12} coated sample is given in figure 4-22(a) and (b) to illustrate the trend and the others are included in the appendix D.

Figure 4-21. CVs with incremental increase in voltage for a) PMo_{12} and b) SiMo_{12} coated CNT in 1 M H_2SO_4 at 50 mV/s.

Figure 4-22. a) Variation of peak potentials with pH and b) the linear part of the potential-pH curve for PMo₁₂ coated MWCNT.

At pH from 0 to 1, both samples revealed a trend of peak potential decrease with the increase of pH. At pH from 1 to 2, the peak potentials became independent of pH. The difference between the literature and our work could be attributed to the different surfaces (smooth GC vs. CNTs), which will lead to different interactions between

PDDA and POM. When the PDDA chain wrapped up around the POM molecules, a stronger attraction and interaction occurred. More importantly, these potential-pH relationships were unique to the PMo_{12} or SiMo_{12} modified CNTs. They can be used as indicators when deconvolute the potential-pH relations of Combinations 1 and 2.

4.4.2 Alternate Layer Coating

The change in the oxidation/reduction peak potential was also examined for both Combinations 1 and 2 in the same manner as “single-layer” coating. The peaks of interest for the two Combinations are shown in figure 4-23. The potentials of peak 2 in figure 4-23 were very similar to the ones in figure 4-21. Thus, it may be difficult to differentiate the “signature” from peak 2 for PMo_{12} and SiMo_{12} . Peak 3 was broader than in pure PMo_{12} and SiMo_{12} and seemed to have the contributions from both PMo_{12} and SiMo_{12} . Therefore, peak 3 could be a stronger indicator to reveal the chemistry of the alternative coatings.

Figure 4-23. CVs with incremental increase in voltage for a) Combination 1 and b) Combination 2 in 1M H_2SO_4 at 50 mV/s.

For both Combinations 1 and 2, the overall trend for potential-pH dependence were similar to that obtained on PMo_{12} and SiMo_{12} (figure 4-22 and appendix D). At pH 0 to 1, the peak potential decreased with pH. At pH 1 to 2, the peak potential became independent to pH. Tables 4-6 and 4-7 summarize the peak potentials and their trend (slopes) of PMo_{12} , SiMo_{12} , Combination 1 and Combination 2. From the tables, we can see that the trend in potential-pH for the Combination 2 was very close to that of single layer SiMo_{12} (appendix D). This suggests that the bottom layer SiMo_{12} was electrochemically the dominating layer in the kinetics of Combination 2. On the other hand, the trend in peak 3 potentials vs. pH for Combination 1 were close to that of single-layer PMo_{12} coated nanotubes (table 4-6 and 4-7), again suggesting that the bottom layer (PMo_{12}) was the dominating layer. Therefore, when coating POMs alternately, the layer that was close to the electrode substrate (bottom layer) was expected to dictate the kinetics and the electrochemical behavior. This discovery is significant as it can provide guidance for future chemical modifications.

Table 4-6. Peak potentials for modified MWCNTs at different pH.

Peak potentials (V)	Ox 2	Red 2	Ox 3	Red 3
<i>1L-PMo₁₂</i>				
pH=0	0.296	0.225	0.453	0.378
pH=1	0.279	0.149	0.434	0.337
pH=2	0.289	0.125	0.441	0.326
<i>1L-SiMo₁₂</i>				
pH=0	0.305	0.260	0.397	0.358
pH=1	0.253	0.175	0.350	0.275
pH=2	0.252	0.161	0.355	0.273
<i>Combination 1</i>				
pH=0	0.273	0.156	0.407	0.292
pH=1	0.243	0.110	0.381	0.240
pH=2	0.239	0.112	0.368	0.234
<i>Combination 2</i>				
pH=0	0.260	0.221	0.405	0.313
pH=1	0.221	0.145	0.345	0.245
pH=2	0.231	0.146	0.347	0.247

Table 4-7. Slope of the potential-pH curve for different modified MWCNTs.

Samples	Slope of potential-pH graph (V/pH)			
	<i>Ox 2</i>	<i>Red 2</i>	<i>Ox 3</i>	<i>Red 3</i>
1L-PMo ₁₂	-0.017	-0.076	-0.019	-0.042
1L-SiMo ₁₂	-0.052	-0.085	-0.047	-0.083
Combination 1	-0.030	-0.046	-0.026	-0.052
Combination 2	-0.038	-0.076	-0.059	-0.082

4.5 Validation Using Two-Electrode Cell

So far, our studies were focusing on electrodes only. It is necessary to verify the performance at a “capacitor” device level. Two-electrode cell was constructed to mimic a capacitor using the alternate layer coated nanotubes. Their responses were also compared with that of bare MWCNTs. Figure 4-24 shows the CVs for bare and modified nanotubes at 50 mV/s and 500 mV/s. Both Combinations 1 and 2 behaved like capacitor at low as well as high rate with somewhat rectangular shape. Moreover, both Combinations showed higher capacitance than bare nanotubes, agreeing with the results in the electrode studies. The specific capacitance was higher for Combination 1 than Combination 2 at both low and high rate. However, the capacitance decreased more rapidly for Combination 1 (about 53%) than that of Combination 2 (about 38%) from low to high rate. This also proved that the order of performance in a cell was consistent with that observed from the electrodes (table 4-4).

Figure 4-24. CVs for a two-electrode cell for bare and alternate layer coated MWCNTs in 1M H₂SO₄ at a) 50 mV/s and b) 500 mV/s.

Charge-discharge (CD) tests were performed (figure 4-25) to mimic real application in ECs. CD is a complementary method to CV. It can also be used to calculate the cell capacitance from the slope of the discharge curves (Eq. 7) and to verify the CVs (figure 4-24) obtained from the cell. Again, the capacitance was found to be about four times increased after the modification with Combination 1. Similar to the CVs (figure 4-24), the capacitance obtained from CD was higher for Combination 1, which decreased rapidly at high rate. Although the capacitance was lower for Combination 2, they could retain the capacitance at high rate. At high current density, the cells from Combinations 1 and 2 showed identical capacitance.

The equivalent series resistance (ESR) was also calculated using the voltage drop of discharge curve for both Combinations. The bare MWCNT showed lower ESR ($2.7 \Omega\text{cm}^2$) than that for both Combinations 1 and 2 at high rate. Although the resistance was slightly higher after POM modification, it did not increase significantly ($3.7 \Omega\text{cm}^2$ and $3 \Omega\text{cm}^2$ for Combinations 1 and 2, respectively). However, Combination 1 showed higher ESR than Combination 2, which was consistent with the previous observation in table 4-4. Indeed, at high rate and high discharge current (figure 4-24b and 4-25b) the Combination 2 performed equal or better than Combination 1.

Figure 4-25. CD responses of a cell before and after coating at a constant current of a) 10 mA/cm² and b) 100 mA/cm².

Although the reported results were based on CME, they have demonstrated capacitive behavior for both EDLC (MWCNT) and pseudocapacitor (Combination 1 and 2). The capacitors by CME also correctly showed the trend of chemical modifications and rate responses of the modified MWCNT. We believe that we can leverage the results from CME to scale-up for larger scale applications.

5 Summary and Conclusion

The main objective of this project was to develop high power and high energy density electrode materials by chemical modifications. We have accomplished this and reached the following conclusions:

1. Three types of carbon nanomaterials, including GNF, SWCNT and MWCNT, have been evaluated in this work. Among these three materials, MWCNT is the promising electrode material for high rate and power applications for EC.
2. MWCNT surface was successfully modified by LbL deposition with Keggin-type POMs such as PMo_{12} and SiMo_{12} with added pseudocapacitance. With merely a “single-layer” PMo_{12} or SiMo_{12} coating, more than two times increases were observed compared with that of bare MWCNT.
3. A scheme of PMo_{12} and SiMo_{12} alternate layer coating to modify MWCNT was developed with two coating sequences: Combination 1 (bottom layer PMo_{12} + top layer SiMo_{12}) and Combination 2 (bottom layer SiMo_{12} + top layer PMo_{12}). Further improvement on capacitance was obtained with these Combinations. The highest specific capacitance of 2.68 F/cm^2 was achieved with Combination 1, which is over four times higher than that of bare MWCNT and has exceeded the value of SWCNT.
4. Both of Combinations 1 and 2 showed improved electrochemical performance with broader oxidation/reduction peaks in CV profiles. The PMo_{12} contributed more in charge storage capacity, whereas SiMo_{12} maintained better kinetics of modified samples. When deposit them alternatively on MWCNT, a synergistic effect on the capacitance and kinetics was observed on both Combinations.

5. X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM) showed significant changes in surface chemistry and morphology, and proved the successful coating of POMs on MWCNTs.
6. The electrochemical behavior of PMo_{12} and SiMo_{12} modified MWCNT was analyzed in electrolytes with different pH. The potential-pH relationship provided important insights in terms of POM LBL deposition mechanism and suggested that the bottom layer close to the electrode substrate was the dominated layer in alternate layer coated MWCNT electrodes.
7. Two-electrode capacitor cells with bare and POM modified MWCNTs were assembled and tested to validate the results from single electrode studies. A similar trend was obtained, which verified the positive impact of the chemical modifications on MWCNT in this work.

6 Future Work

Following approaches are recommended to further optimize the coating technique:

1. **Improving the deposition processes:** Knowing that the bottom layer is the dominating layer in alternate layer coating, electrochemical performances of the modified MWCNTs can be tailored by varying the process parameters during depositing the two layers. For instance, depositing SiMo_{12} for longer time as the bottom layer might improve the reversibility, while the top layer of PMo_{12} might boost up the capacitance of the Combinations.
2. **Developing alternative function POM molecules:** Keggin-type POMs with different heteroatom can be employed to modify the MWCNTs. Different heteroatom rather than P or Si might have different effect on the characteristic of POMs, which can be modified further to expand the voltage window of the operation with more overlapped oxidation/reduction reactions. It is also worth applying POMs with different structure rather than Keggin-type, such as Dawson-type heteropolyanions ($\text{X}_2\text{M}_{18}\text{O}_{62}^{n-}$). Through these studies, the origins and mechanisms of the synergistic effect between PMo_{12} and SiMo_{12} may be deduced. It may also be extended to other POM systems.
3. **Investigating alternative cationic layers for LbL processes:** Different cationic species such as transition metal complexes, metalloporphyrine, $[\text{Fe}(\text{bpy})_3]^{2+}$, $[\text{Cu}(\text{bpy})_2]^{2+}$, $[\text{Ru}(\text{bpy})_3]^{3+}$ etc. rather than PDDA can be applied, which not only will provide the positive charge but also will react to contribute to obtain improved performance to be “more capacitor-like” with more overlapped oxidation/reduction peak distribution in CV.

7 References

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8 Appendices

Appendix A: CME volume

If there were no effect of the cavity of the CME, the area of the powder would be the same as the area of the platinum tip, which was calculated to be 0.000707 cm^2 . To calculate the volume of the packed material in the cavity of CME, the depth of cavity need to calculate. The depth of cavity was measured to be 0.035 cm . Knowing the density of CNT (1.33 gm/cm^3), the mass of the packed nanotubes in the cavity can also be estimated. Hence, specific capacitance in F/cm^3 as well as F/gm can be calculated. For instance, the specific capacitance of Combination 1 can be expressed as follows:

$$\text{Area of the platinum tip} = 0.000707 \text{ cm}^2$$

$$\text{Depth of cavity of CME} = 0.021 \text{ cm}$$

$$\text{Volume of the cavity (volume of packed CNT)} = 14.85 \text{ } \mu\text{cm}^3$$

$$\text{Density of CNT } (\rho) = 1.33 \text{ gm/cm}^3$$

$$\text{Mass of the packed CNT} = 19.75 \text{ } \mu\text{gm}$$

$$\text{Capacitance for MWCNT} = 0.44 \text{ mF}$$

$$\begin{aligned} \text{Specific capacitance for MWCNT} &= 0.62 \text{ F/cm}^2 \\ &= 29.5 \text{ F/cm}^3 \\ &= 22.2 \text{ F/gm} \end{aligned}$$

$$\text{Capacitance for Combination 1} = 1.89 \text{ mF}$$

$$\text{Specific capacitance for Combination 1} = 2.68 \text{ F/cm}^2$$

$$=127.6 \text{ F/cm}^3$$

$$= 95.94 \text{ F/gm}$$

Appendix B: XPS broad scan

Figure B-1. XPS spectra for a) bare, b) PMo₁₂ coated and SiMo₁₂ coated MWCNT.

Figure B-2. XPS spectra of a) O1s and b) Mo3d for SiMo₁₂ coated MWCNT.

Appendix C: mixed solution effect

Figure C. CVs for MWCNTs modified with mixed solution.

Appendix D: potential-pH graph

Figure D-1. a) Variation of peak potentials with pH and b) the linear part of the potential-pH curve for SiMo₁₂ coated MWCNT.

Figure D-2. a) Variation of peak potentials with pH and b) the linear part of the potential-pH curve for Combination 1.

Figure D-3. a) Variation of peak potentials with pH and b) the linear part of the potential-pH curve for Combination 2.