Nanocarbon-Polyoxometalate Multilayer Composite for Pseudocapacitive Electrodes

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Introduction

One of the most common approaches to improve the energy density of electrochemical capacitors (ECs) is to add pseudocapacitive materials to those electrochemical double layer capacitive (EDLC) electrodes. Layer-by-layer (LbL) modification of carbon materials with electrochemical active molecules/species is a simple and effective method to develop such composites [1, 2]. The LbL deposition involves the adsorption of layers of oppositely charged molecules or species via electrostatic interaction. Polyoxometalates (POMs) are low cost materials that exhibit fast and reversible multi-electron transfer reactions [3]. Our objective is to leverage the various POM molecules to design and engineer high performance nanocarbon/polyoxometalate composite electrodes for ECs.

Experimental

Multi-wall carbon nanotubes (MWCNTs) from Arkema [4] were used as the EDLC substrate. Poly (diallyldimethylammonium chloride) (PDDA) was used as the polycation layer (Sigma-Aldrich). 10-Molybdo-2-vanadophosphoric acid ($H_5PMo_{10}V_2O_{40}$) and potassium 11-Tungsto-1-vanadophosphate ($K_4PW_{11}V_1O_{40}$) were used as the polyanion active layers. $H_5PMo_{10}V_2O_{40}$ and $K_4PW_{11}V_1O_{40}$ were synthesized in our laboratory [5 -6]. The chemical modification process is shown in Figure 1.

The composite materials were packed into a cavity microelectrode (CME) [7] and characterized in 1 M H_2SO_4 solution using cyclic voltammtery (CV). An EG&G 273 potentiostat and 3 electrode setup was utilized with the CME, Pt and Ag/AgCl serving as the working, counter and reference electrodes respectively.

Results and Discussion

Cyclic voltammograms of the bare and the single-layer $H_5PMo_{10}V_2O_{40}$ ($PMo_{10}V_2$) coated MWCNTs are shown in Figure 2. At a scan rate of 0.05 V/s, the volume specific capacitance values of singe-layer $PMo_{10}V_2$ coated MWCNTs increased by approximately 6 times compared to bare MWCNTs (ca. 0.15 F/cm^3). The increase in capacitance is due to the four reversible oxidation/reduction peaks of $PMo_{10}V_2$. The CV of single-layer $K_4PW_{11}V_1O_{40}$ ($PW_{11}V_1$) coated MWCNTs is also depicted in Figure 2 with an area specific capacitance that represents an increase of approximately 2 times compared to that of the bare MWCNTs. $PW_{11}V_1$ shows only one oxidation/reduction feature, however, it is a broad peak located at the upper end of the potential window where charge storage is most valuable. Furthermore, the oxidation/reduction peak of $PW_{11}V_1$ is highly reversible as indicated by the "mirror-imaging" of the positive and negative scans.

Although the reversible oxidation/reduction peaks in $PMo_{10}V_2$ and $PW_{11}V_1$ are suitable for ECs, they do not display a rectangular "capacitive" voltammogram. Thus, utilising the LbL process, we developed a multi-layer coating structure via repeating the polycation with different POM layers on MWCNTs. This is demonstrated in Figure 2, where $PMo_{10}V_2$ was the 1st POM (bottom layer) and $PW_{11}V_1$ was the 2nd (top) POM layer. It is clear that the resulting voltammogram of multi-layer coated MWCNTs is a combination of its individual single-layer components. The addition of the second POM layer ($PW_{11}V_1$) increased the volume specific capacitance by an additional 34% over the single-layer $PMo_{10}V_2$ coated MWCNTs and extended the pseudocapacitive charge storage window by approximately 80 mV. Furthermore, the multilayer coated MWCNTs displayed a more even distribution of charge throughout the potential window. This multilayer deposition technique is viable for designing and engineering the electrode surfaces through superimposing different types of ions and molecules to achieve desirable characteristics.

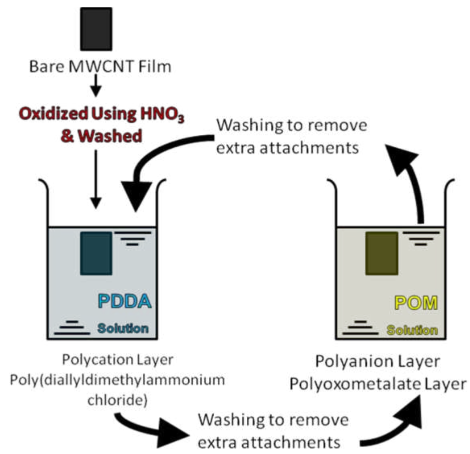

Figure 1: Schematic representation of the LbL process employed in this work.

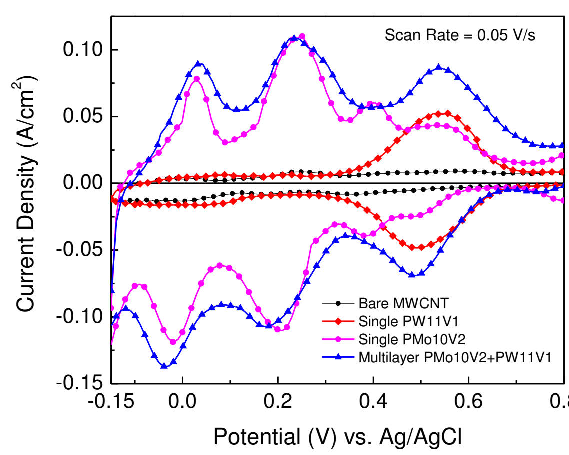

Figure 2: Cyclic voltammograms at 50 mV/s of bare MWCNTs in comparison with single-layer $PMo_{10}V_2$, single-layer $PW_{11}V_1$ and multi-layer coated MWCNTs.

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