Nanocarbon/Polyoxometalate Composite Electrodes for Electrochemical Capacitors

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Introduction

One of the 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 various POM molecules to design and engineer high performance nanocarbon/POM composite electrodes for ECs.

Experimental

Multi-wall carbon nanotubes (MWCNTs) (Arkema [4]) were used as the EDLC substrates. Poly (diallyldimethylammonium chloride) (PDDA) was used as the polycation layer (Sigma-Aldrich). Phosphomolybdic acid ($H_3PMo_{12}O_{40}$ or PMo_{12}) (Alfa Aeasar) and 10-Molybdo-2-vanadophosphoric acid ($H_5PMo_{10}V_2O_{40}$ or $PMo_{10}V_2$) were used as the polyanion active layer. $PMo_{10}V_2$ was synthesized in our laboratory [5]. The chemical modification process is shown in Figure 1.

The composite materials were packed into a cavity microelectrode (CME) [6] and characterized using cyclic voltammetry (CV) with an EG&G 273 potentiostat. A 3-electrode cell was utilized, where CME, Pt and Ag/AgCl were used as the working, counter and reference electrodes.

Results and Discussion

Cyclic voltammograms of the bare and the single-layer PMo_{12} coated MWCNTs are shown in Figure 2. At a scan rate of 0.05 V/s, the area specific capacitance of singe-layer PMo_{12} coated MWCNTs increased by approximately 245% compared to bare MWCNTs (ca. 0.5 F/cm^2). The increase in capacitance is due to the three reversible and "mirror-imaging" oxidation/reduction peaks of PMo_{12}. The CV of a single-layer $PMo_{10}V_2$ coated MWCNTs is also depicted in Figure 2, which had an area specific capacitance similar to that of single-layer PMo_{12} coated MWCNTs. Although both single-layer PMo_{12} and $PMo_{12}V_2$ exhibited similar capacitance values, $PMo_{12}V_2$ coated MWCNTs exhibited a more even distribution of charge within the potential window. This behaviour may be attributed to 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}.

The highly reversible oxidation/reduction peaks in PMo_{12} and $PMo_{12}V_2$ are suitable for ECs. However, they do not display a rectangular "capacitive" cyclic voltammogram. Thus, utilizing the LbL process, we developed a multi-layer coating structure via repeating the polycation but with different POM layers on MWCNTs. This is demonstrated in Figure 2, where PMo_{12} was the 1st POM (bottom layer) and $PMo_{10}V_2$ was the 2nd (top) POM layer. It is clear that the resulted voltammogram of multi-layer coated MWCNTs is a combination of its individual single-layer components. Furthermore, the area specific capacitance of this dual-layer coating increased an additional 65% over the single-layer coated MWCNTs. Therefore, this technique is viable for designing and engineering the electrode surfaces to achieve desirable properties through superimposing different types of POM molecules with various properties.

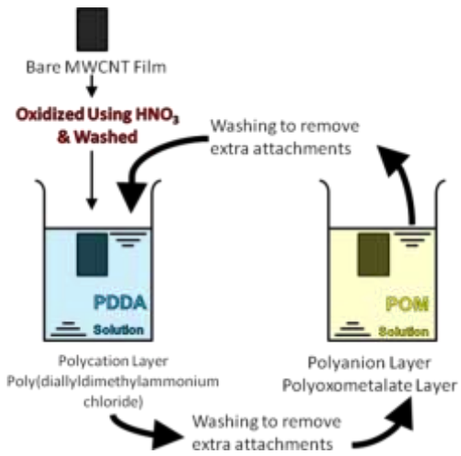

Figure 1: Schematic representation of the LbL process employed in this work.

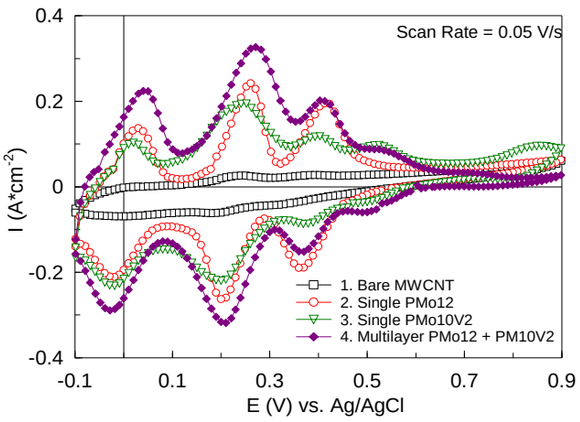

Figure 2: Cyclic voltammograms of bare MWCNTs in comparison with single-layer PMo_{12}, single-layer $PMo_{10}V_2$ and dual-layer coated MWCNTs.

Reference:

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