**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 (H3PMO12O40) or PMo12 (Alfa Aesar) and 10-Molybdoo-2-vanadophosphoric acid (H3PMo10V2O40 or PMo10V2) were used as the polyanion active layer. PMo10V2 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 PMo12 coated MWCNTs are shown in Figure 2. At a scan rate of 0.05 V/s, the area specific capacitance of single-layer PMo12 coated MWCNTs increased by approximately 245% compared to bare MWCNTs (ca. 0.5 F/cm2). The increase in capacitance is due to the three reversible and "mirror-imaging" oxidation/reduction peaks of PMo12. The CV of a single-layer PMo10V2-coated MWCNTs is also depicted in Figure 2, which had an area specific capacitance similar to that of single-layer PMo12 coated MWCNTs. Although both single-layer PMo12 and PMo10V2 exhibited similar capacitance values, PMo10V2 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 PMo10V2, and these peaks were broader compared to the redox peaks of PMo12.

The highly reversible oxidation/reduction peaks in PMo12 and PMo10V2 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 PMo12 was the 1st POM (bottom layer) and PMo10V2 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. 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.

**Reference:**


