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 (H₂PMo₁₀O₄₀V₂O₄₀) and potassium 11-Tungsto-1-vanadophosphate (K₆PW₁₁V₄₀O₄₀) were used as the polyanion active layers. H₃PMo₁₀O₄₀ and K₆PW₁₁V₄₀O₄₀ 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 H₂SO₄ solution using cyclic voltammetry (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 H₃PMo₁₀O₄₀V₂O₄₀ (PMo₁₀V₂) coated MWCNTs are shown in Figure 2. At a scan rate of 0.05 V/s, the volume specific capacitance values of single-layer PMo₁₀V₂ coated MWCNTs increased by approximately 6 times compared to bare MWCNTs (ca. 0.15 F/cm²). The increase in capacitance is due to the four reversible oxidation/reduction peaks of PMo₁₀V₂. The CV of single-layer K₆PW₁₁V₄₀O₄₀ (PW₁₁V₄₀) coated MWCNTs is also depicted in Figure 2 with an area specific capacitance that represents an increase of approximately 2 times compared to bare MWCNTs (ca. 0.15 F/cm²). The increase in capacitance is due to the four reversible oxidation/reduction peaks of PMo₁₀V₂. The CV of single-layer PMo₁₀V₂ coated MWCNTs shows only one oxidation/reduction peak, 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 PW₁₁V₄₀ coated MWCNTs is highly reversible as indicated by the “mirror-imaging” of the positive and negative scans.

Although the reversible oxidation/reduction peaks in PMo₁₀V₂ and PW₁₁V₄₀ 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 PMo₁₀V₂ was the 1st layer and PW₁₁V₄₀ was the 2nd 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 (PW₁₁V₄₀) increased the volume specific capacitance by an additional 34% over the single-layer PMo₁₀V₂ 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.

Reference:


