POLYOXOMETALATES - CARBON NANOTUBES COMPOSITES FOR ELECTROCHEMICAL CAPACITORS

Tahmina Akter, Gurvinder Bajwa, and Keryn Lian

Department of Materials Science and Engineering, University of Toronto, Toronto, Ontario, Canada

Introduction

Electrochemical Capacitors (EC) are important energy storage devices as stand-alone or in hybrid energy systems for high power delivery. The key components in ECs are electrodes and electrolytes, which have been investigated extensively [1,2]. The electrodes are either based on electrochemical double layer (EDLC) or pseudocapacitance [1,2]. While the former are carbon-based with lower capacitance and lower cost, the latter can store more charge and tend to be more costly. Therefore, it is of great interest to develop composite materials that can leverage the performance advantages of both EDLC and psueducapacitive materials with low cost. We have developed a series of EDLC-pseudocapacitive composite electrodes via chemical modification of polyoxometalates (POMs) on multiwalled carbon nanotubes (MWCNT). Through this approach, we can increase the energy density by a few folds over the bare MWCNT. Moreover, this methodology enables us to design and tailor the deposited pseudocapacitive materials to achieve the optimum performance, which may impact other applications beyond the energy storage.

Experimental

The CNT modification was achieved through a layer-by-layer (LbL) molecular self-assembly technique that involves electrostatic interaction between alternately charged materials to produce multilayer films [3,4].

Two different types of polyoxometalates ($H_4SiMo_{12}O_{40}$ ($SiMo_{12}$) and $H_3PMo_{12}O_{40}$ (PMo_{12})) were used in diluted solutions for chemical modification. Other chemicals used for modification were HNO_3 (conc.) and poly (diallyl-dimethylammonium chloride) (PDDA). Most of the tests were carried out in 1 M H_2SO_4 electrolyte. Each LbL deposition on MWCNT was performed in three steps: HNO_3-PDDA-POM (with water rinsing in between each step). In addition to each single layer coating, we also superimposed PMo_{12} and $SiMo_{12}$ molecules to form a dual-layer structure as shown in Fig. 1. In the figure, the bottom active layer (BL) was PMo_{12} and the top active layer (TL) was $SiMo_{12}$. This sequence can also be reversed (i.e. BL was $SiMo_{12}$ and TL was PMo_{12}).

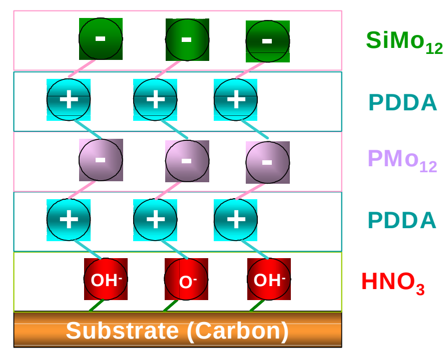

Fig. 1. A schematic diagram of LBL deposition of POM modification on CNT.

Three-electrode cell with cavity microelectrode (CME) as working electrode, Pt counter electrode and Ag/AgCl Sat. reference electrode were utilized. Electrochemical responses of bare and modified MWCNTs were investigated using cyclic voltammetry (CV) with an EG&G 273 potentiostat. All electrochemical tests were conducted in ambient condition.

Results and Discussion

Previous work has demonstrated that, with merely a single layer of POM modification, the capacitance of CNT was doubled with fast kinetics and good reversibility. Additional process development resulted in further increase in capacitance of single layer POM coating. Based on this result, we added a second layer with different POM molecule to form a dual-layer coating structure

Cyclic voltammograms of a bare MWCNT, a single-layer PMo_{12}, a single-layer $SiMo_{12}$, and a dual-layer (PMo_{12} BL + $SiMo_{12}$ TL) coated MWCNT are shown in Fig. 2. The capacitances of all POM modified MWCNTs electrodes showed 3 to 4 times increase from bare CNT. The oxidation/reduction peaks for single-layer PMo_{12} or $SiMo_{12}$ were almost overlapping except for reaction-3 (referred as Ox3 and Red3). Thus, Ox3 and Red3, can be used to differentiate the characteristics of PMo_{12} and $SiMo_{12}$. The CV profile of the dual-layer coating was also included in Fig. 2, which showed contributions from both PMo_{12} and $SiMo_{12}$. After applying the $SiMo_{12}$ layer on top of the PMo_{12} coated MWCNT, there was not only a further increase in the charge storage, but also a combined contribution of Ox3 and Red 3 from both molecules resulting a much broader Ox3 and red 3 than that of PMo_{12} or $SiMo_{12}$ alone. This suggests that by superimposing different molecules via LbL, one may be able to obtain contributions from both molecules to achieve desired performance.

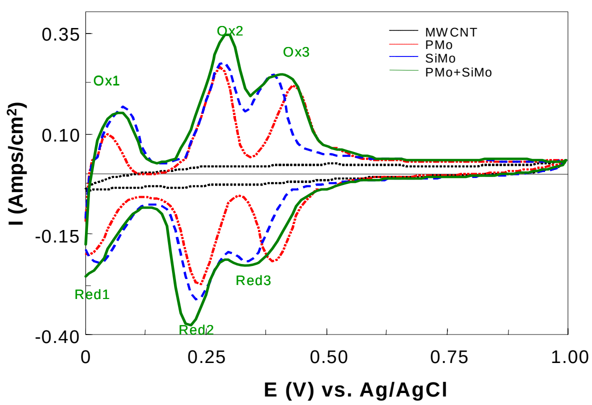

Fig.2. CV profiles of bare MWCNT, a single-layer PMo_{12} (red), $SiMo_{12}$ (blue) coated and a dual-layer (PMo_{12} + $SiMo_{12}$ TL) (green) coated MWCNT in 1M H_2SO_4.

Surface morphologies of the modified MWCNTs were also studied and compared with the bare CNT to understand the coating structures (Fig. 3). The SEM micrographs showed coverage of coatings on CNT. The coating thickness for the single layer was 3-4 nm and 10-12 nm for dual-layer coating. Considering the size of single PMo_{12} or $SiMo_{12}$ molecule to be 1.2 nm, the dual-layer coating may contain 8 to 10 POM molecules responsible for the 4 X increases in the capacitance.

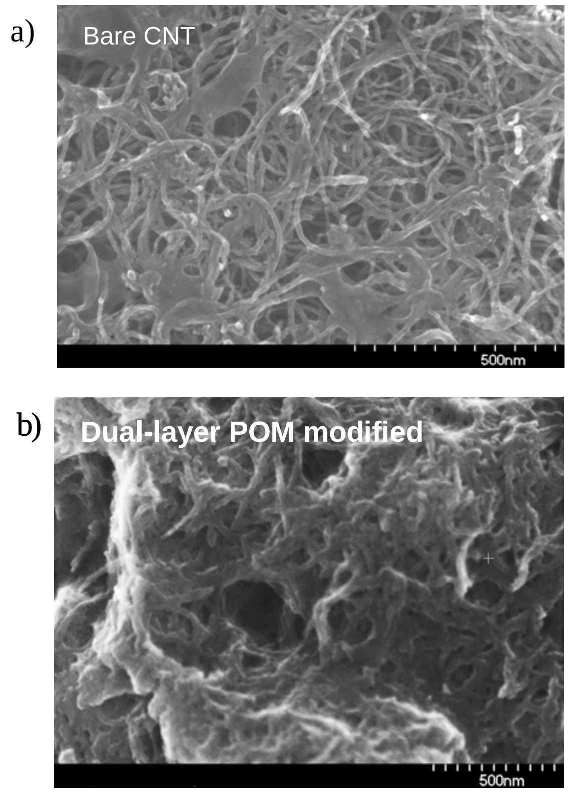

Fig.3, SEM micrographs of a) bare MWCNTs and b) POM modified MWCNTs.

Conclusions:

A simple and effective method to add pseudocapacitance to MWCNT through deposition of polyoxometalates (POMs) was demonstrated. By superimposing layers of different pseudocapacitive polyoxometalates, $SiMo_{12}$ and PMo_{12}, the POMs exhibited fast oxidation/reduction reactions and achieved an up to fourfold increase in specific capacitance when compared with the double layer capacitance of bare MWCNTs.

Reference:

1. P. Simon and Y. Gogotsi, Nature Materials, 7 (2008) 845-854.
2. B. Conway, Electrochemical Supercapacitors: Scientific, Fundamentals, and Technological Applications, Kluwer, New York, 1999.
3. M. Skunik, M. Chojak, I. A. Rutkowska, and P. J. Kulesza, Electrochimica Acta, 53, (2008) 3862-3869.
4. S. Park, K. Lian, and Y. Gogotsi, J. Electrochem. Soc.,156 (11), (2009) A921-A927.