METAL-OXIDE / CARBON NANOCOMPOSITES FOR USE IN SUPERCAPACITORS

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Introduction

Supercapacitors, also called electrochemical capacitors (EC), are rechargeable electrochemical energy storage devices, which offer a much longer life cycle and higher power density than batteries [1]. Their applications in hybrid electrical engines and power grid are growing. Transition metal-oxides exhibit fast and electrochemically-reversible Faradaic redox reactions to store charge in supercapacitors, but often suffer from low surface area and low electrical conductivity. The formation of highly conductive porous carbons decorated with inexpensive metal oxides should circumvent the disadvantages of pure metal oxide supercapacitors. In this work we deposited vanadium oxide nanoparticles or thin films of various thickness and microstructure on carbon nanotubes and other porous carbons via chemical vapor deposition (CVD) and atomic layer deposition (ALD) and studied their electrochemical properties, including specific capacitance, frequency response, power and energy density.

Experimental

Two electrode materials were investigated during the course of this study. A porous carbon peel made from high temperature annealed carbon black (95 wt.%) with a PTFE binder (5 wt%), and a multi-walled carbon nanotubes (MWCNT) paper made from MWCNTs which were boiled in nitric and sulfuric acid in a 1:1 ratio for 1 hour at 100°C were used. This acid purification step was done in order to introduce defects and surface functionalities onto the edge of the carbon nanotubes, which helps increase the rate of electron transfer and facilitates Vanadium Oxide deposition onto the MWCNTs [2]. The acid purification step also allows for the formation of a binder-free CNT electrode, since the filtered nanotubes are collected at the end of this step and form the paper. These materials were used as substrates for deposition of vanadium oxide via ALD and CVD.

Vanadium (V) tri-isopropoxy oxide [$VO(OC_3H_8)_3$] was used as a precursor for both the ALD and CVD processes. The precursor was heated to 60-80°C prior to deposition. The deposition temperature was 100°C for ALD and 300°C for CVD. In both cases, X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Energy-Dispersive X-Ray Spectroscopy (EDS) studies were conducted to characterize the microstructure and chemical composition of the samples.

The composite carbon-vanadium oxide electrodes were tested in 2016 stainless-steel coin cells. Both aqueous and organic electrolytes were used. Electrochemical measurements included electrochemical impedance spectroscopy, cyclic voltammetry and charge-discharge tests performed at different current densities.

Results and Discussion

SEM measurements showed uniform formation of vanadium oxide on a MWCNT paper (Fig. 1), in the case of ALD deposition. The CVD deposition resulted in thinner and less uniform coating (not shown). The smaller pore size in carbon peel electrode and more hydrophobic surface of the annealed carbon black resulted in thinner and non-uniform oxide deposition by using both methods employed. EDS measurements suggested that selected MWCNT paper samples contained over 80 wt.% of vanadium oxide.

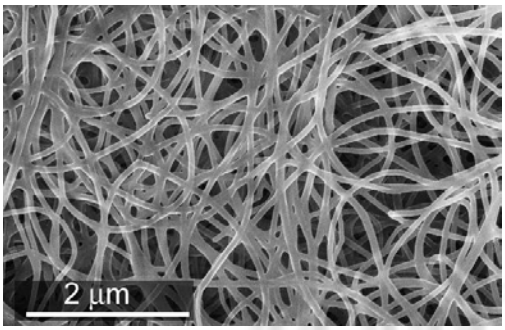

Fig.1. SEM micrograph of a CNT electrode coated with a uniform ALD layer of vanadium oxide.

XRD of the as-deposited ALD oxide films showed amorphous / nano-crystalline microstructure. The post-annealing process allowed us to change the microstructure of the deposited oxide and investigate effects of the microstructure on the capacity, capacity retention at high current densities and long-term cycle stability. Electrochemical measurements revealed stable performance of the selected MWCNT-vanadium oxide electrodes with capacities comparable to that previously observed in thin films and nanopowders.

Conclusions

Vapor deposition routes allow uniform deposition of metal oxides on the porous carbon surface, thus offering a novel route for the formation of binder-free electrodes with large thickness, controlled porosity, greatly improved electrical conductivity and cycle stability. The ability to precisely control the coating thickness and microstructure permits systematic studies of the ion intercalation and diffusion into the bulk of the electrodes.

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References

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