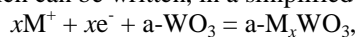


Solid-State Nano-composite Supercapacitors for Optical Modulation

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Conventional electrochromic devices rely upon the insertion of ionic species into a host lattice to effect changes in the optical properties of the materials. Such electrochromic coatings are being developed in applications for energy efficient, so-called "smart" dynamically-controlled windows, anti-glare automobile rearview mirrors and sunroofs as well as opto-electronic shutters. In particular, electrochromic windows can be used to control solar heat gain through windows and thereby reduce air-conditioning energy requirements in buildings and vehicles. A variable transmittance window coating, operated as part of an intelligent building energy management system, has been predicted to provide substantial energy savings. WO_3 , MoO_3 and Nb_2O_5 are well known electrochromic materials that show cathodic coloration with electron injection and charge-balancing H^+ or Li^+ ion insertion¹. As-deposited amorphous tungsten oxide films are transparent, but when ions such as H^+ or Li^+ and electrons are injected, the color of the films changes to dark blue. This color change in the films is believed to be directly related to the double injection/extraction of electrons and ions in the films, which can be written, in a simplified form, as



where $\text{M} = \text{H}, \text{Li}, \text{etc.}$

When lithium (or hydrogen) ions and electrons are inserted into $a\text{-WO}_3$ films, the electrons reduce W^{6+} ions to W^{5+} . Lithium or hydrogen ions are necessary to satisfy the charge neutrality condition inside the film. However, the result of ion insertion is a deleterious cyclic expansion and contraction of the bulk structure of the electrochromic material during use. This inherent cyclic process provides a degradation mechanism for the material that can limit the lifetime of an EC device.

Growing demands for power sources for transient high-power density have stimulated great interest in electrochemical capacitors in recent years. In general, an electrochemical capacitor of large specific capacitance results when an electrode material with large specific surface area is combined with a material that can be reversibly oxidized or reduced over a wide potential range². Carbon powders and conducting polymers have a large double layer capacitance and oxides of multivalent metals such as ruthenium and iridium exhibit large faradaic pseudocapacitance and these materials have often been studied for applications as supercapacitors. Electrochromic oxides such as NiO , WO_3 , MoO_3 and Nb_2O_5 appear to be suitable materials for electrochemical capacitors. These oxide materials contain multivalent metals that can be reversibly oxidized or reduced over a wide range of potential. More importantly, these materials can be made in highly porous forms resulting in high volumetric surface area.

In this paper, we report on an electrochromic phenomenon induced by charge/discharge of a solid-state electrochemical supercapacitor as opposed to ion-insertion. Nano-composites consisting of polycrystalline nano-particles of transition metal oxide surrounded by amorphous solid-state proton electrolytes were fabricated

by reactive co-sputtering from metal composite targets. Polycrystalline nano-particles (nickel oxides) within the composite play a role as an active electrochemical component while the surrounding amorphous metal oxide (tantalum oxides) acts as a proton electrolyte. This nano-composite structure offers the promise of creating a new class of solid-state supercapacitive electrochromic materials. The great potential of these materials is based on two interrelated properties.

- Nano-particles of transition metal oxides with a large surface area create high specific capacitances as well as optical modulation.
- Solid-state proton electrolytes (which basically fill in the pores between the nano-particles) increase the usage and accessibility of the total surface of nano-particles.

These nano-composites are projected to have a high charge capacity with improved response time (which is essential for a complementary counter electrode in EC devices) as compared to conventional electrochromic electrode materials. Our main objective is to synthesize a composite electrode with appropriately sized polycrystalline transition metal oxide nano-particles surrounded by an amorphous solid-state proton electrolyte.

Thin film nano-composites of polycrystalline nickel oxide/amorphous tantalum oxide electrolyte were deposited by reactive RF-magnetron sputtering in O_2 from a composite target. The thin films were prepared on indium tin oxide (ITO) coated glass for optical transmittance and electrochemical measurements and on polished stainless steel substrates for x-ray diffraction analysis, Raman spectroscopy, and TEM measurements. The composition of these nano-composites was evaluated by X-ray photoelectron spectroscopy (XPS) analysis and inductively coupled plasma (ICP) spectrometry. The average size of the nickel oxide nano-particles was adjusted by varying the RF sputtering power and the working pressure. The compositional ratio of the composite was adjusted by changing the surface ratio of the tantalum arrayed nickel target. The electrochemical characteristics of the resulting nano-composite $\text{NiO}/\text{Ta}_2\text{O}_5$ electrodes was examined in NaCl aqueous solutions using cyclic voltammetry as well as AC impedance spectroscopy.

References

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