Electrochromic Properties of Mesoporous Tungsten and Niobium Oxides

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Mesoporous oxides possessing pore sizes from 2 to 30 nm have been widely investigated over the past several years. The most commonly produced materials are based on the use of various surfactants (cationic, anionic, nonionic) which serve as structure-directing agents and lead to the formation of supramolecular arrays. Mesostructured solids are synthesized by combining the structure-directing agents with sol-gel chemistry methods. Removal of the organic template by chemical or thermal methods leads to the mesoporous morphology in which the pores form ordered structures (lamellar, cubic, hexagonal) with an extremely narrow pore size distribution. While surfactant templated methods have been developed for several metal oxides, with the exception of SiO_2, there has been relatively little study of the functional properties of mesoporous oxides. The present paper describes the synthesis of mesoporous tungsten and niobium oxides and shows that the mesoporous morphology has a beneficial effect on their electrochromic properties.

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Mesoporous tungsten oxide and niobium oxide were synthesized by incoporating tri-block copolymer surfactants of the type poly (ethylene oxide)-*block*-poly (propylene oxide)-*block*-poly (ethylene oxide) into the precursor sol. The sol was prepared from the reaction of the corresponding chloride, WCl_6 or $NbCl_5$, with anhydrous ethanol. This sol was partially hydrolyzed prior to dip-coating on ITO coated glass. Solvent extraction in ethanol or calcination at temperatures above 300°C was used to remove the copolymer. The resulting mesoporous films exhibit similar morphology with an average pore diameter of ~ 5 nm and a narrow pore size distribution (± 1 nm). The materials possess surface areas in the range of 130 m^2/g. TEM images indicate that the pores are not ordered into specific phases. The presence of porosity in the plan-view TEM images suggests that the electrolyte will not have difficulty penetrating the porous electrode.

The electrochromic behavior of the mesoporous oxides was characterized using 0.1 M sulfuric acid as the electrolyte. The voltammetric responses are similar to those reported in the literature for WO_3 and Nb_2O_5; cathodic and anodic waves are observed which correspond to the insertion and extraction of protons for which coloration and bleaching of the respective films occurs. An interesting feature in the voltammetry for mesoporous tungsten oxide is the presence of multiple peaks which have been attributed to proton trapping/injection processes. The multiple peaks are most pronounced in the mesoporous tungsten oxide with the highest surface area.

The change in optical properties during coloration and bleaching is quite reversible as shown in Figure 1. The tungsten oxide exhibits its characteristic absorption in the red during reduction while the absorption change in the niobium oxide is fairly uniform throughout the visible spectrum causing the films to become dark grey during coloration. Both films exhibit nearly complete bleaching on oxidation. The coloration efficiencies are on the order of 25 cm^2/C and 15 cm^2/C for the mesoporous tungsten and niobium oxides, respectively. These values are consistent with the range reported in the literature for oxide systems.

While the electrochromic behavior for mesoporous tungsten and niobium oxides compares well with prior studies, there is one property where the mesoporous morphology has a significant effect. Chronoamperometry experiments indicate that the rates for the coloration and bleaching processes are enhanced for the mesoporous oxides as compared to standard sol-gel films (i.e. prepared without the copolymer template). The decrease in coloration time is particularly evident in the tungsten oxide material. In the bleaching response, both mesoporous films exhibit a sharp decrease in current after a finite period of time, indicating that the bleaching process is completed. It is proposed that the improved access of electrolyte to the oxide film via the mesoporous architecture, coupled with the high surface area of the film, are the key factors which contribute to the faster kinetics. The prospect of increasing the kinetics of the electrochromic response through the presence of controlled porosity may be significant for device applications.

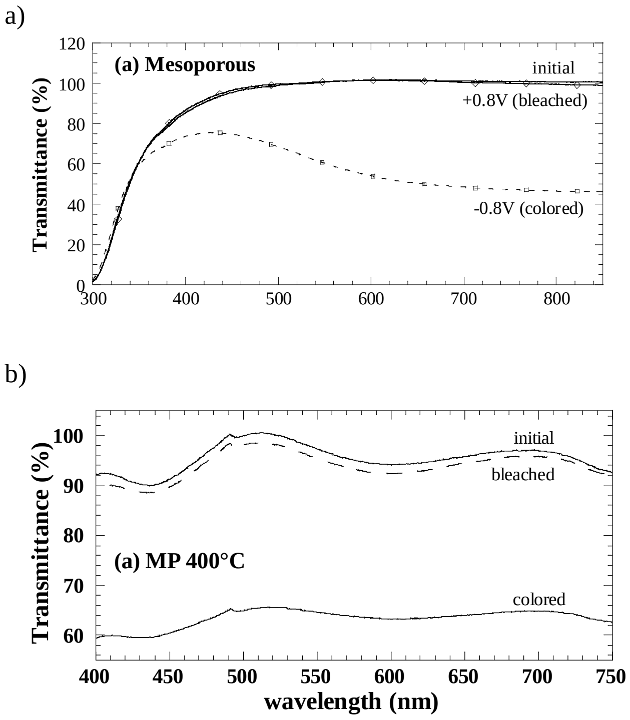

Figure 1. Optical transmittance spectra for mesoporous films; (a) tungsten oxide heated at 300 C; (b) niobium oxide heated at 400°C