

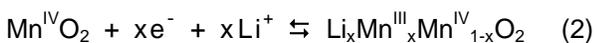
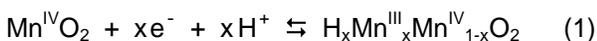
Spectroelectrochemical Characterization of Charge Transport at Thin Films of Nanostructured Mesoporous Oxides

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Manganese and vanadium oxides are mixed electron-cation conductors, which when prepared as nanostructured mesoporous materials exhibit a range of properties upon cation insertion that have applications in energy storage (batteries, ultracapacitors), electrochromics, sensing, and catalysis. Nanostructured mesoporous architectures with electrically conductive oxides can be attained by sol-gel chemistry with controlled removal of the pore fluid.

Recent work on sol-gel-derived nanoscopic, highly mesoporous, networked charge-insertion oxides has revealed that these architectures store charge in three ways, via: (1) double-layer capacitance; (2) energy-specific insertion of cations (as would be seen in a standard insertion battery material); and (3) pseudocapacitance. Materials that blend all three mechanisms of charge storage are innately hybrid and should provide future functions now served by the physical/electrical coupling of battery and capacitor in applications that require both high peak power and sustained low power. The ability to store both battery-like and ultracapacitor-like charge is attributed to the disorder present in these nanomaterials.^[1]

Manganese oxide is an anodically coloring electrochromic material (at ~ 500 nm),^[2] where the conversion of Mn (IV) to Mn (III) during the cation-insertion process is accompanied by a decrease in the optical absorbance. Vanadium pentoxide has two electrochromic features; one centered at ~400 nm (anodically coloring) and ~1000 nm (cathodically coloring).^[3] Charge storage is accomplished in such mixed-conducting oxides by cation/electron insertion. The reaction for Mn, for inserting either H⁺ or Li⁺, can be written as:



Characterization of these architectures first as nanomaterials and then as charge-storage materials requires an array of physical, structural, and chemical approaches. A time-honored electroanalytical approach is proving especially fruitful in sorting out the nature of these disordered, high-surface-area materials. Spectroelectrochemical characterization of sol-gel-derived thin films of manganese dioxide and vanadium pentoxide provides an independent measure of the electronic state of the Mn or V in

the oxide during electrochemically driven cation insertion in nonaqueous and aqueous electrolytes.^[2,4]

We exploit these electrochromic properties in the characterization of cation-insertion reactions at ITO-supported films of sol-gel-derived manganese oxide and vanadium pentoxide where the pore-solid architecture of the mixed-conducting oxide is varied from xerogel to ambigel to aerogel. Although the electrochemical response (current, charge) at these high-surface-area materials is complicated by such effects as double-layer charging and electrolyte decomposition, the optical absorbance responds only to changes in the electronic state of the oxide, as seen in Figure 1.

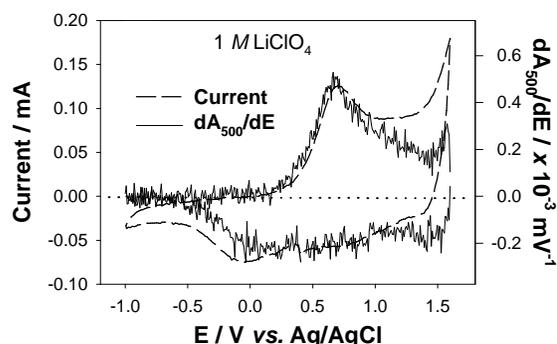


Figure 1. Spectroelectrochemical response at an ITO-supported thin-film electrode of Na_{0.44}MnO₂ · xH₂O ambigel in 1 M LiClO₄/propylene carbonate electrolyte (scan rate = 4 mV/s). Dashed line denotes the voltammetric current; solid denotes the absorbance as a function of time (and applied potential) at λ = 500 nm; dotted line denotes zero on both axes.

The spectral and electrochemical signatures for these materials demonstrate that charge is stored in these nanoscale architectures in electrochemically distinct sites beyond those associated just with Mn(III/IV) or V(IV/V) electron-transfer chemistry. By varying the insertion cation, polymorphic nature of the oxide, and degree of disorder, the character of charge storage in nanoscale mesoporous materials can be spectroelectrochemically probed en route to designing improved properties for electrochemical power sources.

ACKNOWLEDGMENTS

This work was supported by the Office of Naval Research. W.D. was an ASEE-NRL Summer Faculty Fellow (2001).

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