

In Situ XAS Study of the Mechanism of Li Interaction with V₂O₅ Aerogel and Ambigel Cathodes

A. N. Mansour and P. H. Smith

Carderock Division, Naval Surface Warfare Center
West Bethesda, MD 20817-5700

M. Balasubramanian and J. McBreen

Brookhaven National Laboratory, Upton, NY 11973-5000

Nanophase V₂O₅ synthesized using sol-gel techniques has been considered a potential alternative to the cobalt and nickel oxide systems.^{1,2} The electrochemical performance of V₂O₅, however, depends on its structure (crystalline vs. amorphous) and morphology (particle size and surface area).^{3,4} The goal of this investigation is to examine the change in the oxidation state and local structure of V during electrochemical Li intercalation of V₂O₅ aerogel and ambigel cathodes.

Gels were prepared via the hydrolysis and condensation of vanadyl triisopropoxide.^{5,6} Cathodes were prepared by spraying a slurry of 75% V₂O₅, 20% carbon black, and 5% PVDF that was suspended in a solution of propylene carbonate and cyclohexane onto a 10 μm thick Al foil. The cathodes were then placed in a vacuum oven (100 μtorr) and allowed to dry at 220 °C for 16 hours. The cell consisted of a Li foil, a Celgard 2400 separator, a filter paper soaked with 1 M LiPF₆ in EC:DMC (1:1), and a V₂O₅ cathode. Cells were discharged at constant current at the C/20.2 rate for the aerogel cell and the C/21.6 rate for the ambigel cell in the voltage range 1.5-4.0 V vs. Li/Li⁺. The X-ray absorption spectroscopy (XAS) experiments were conducted on beamline X-11A at the National Synchrotron Light Source (NSLS).

A comparison of the first cycle voltage profiles for the aerogel and ambigel cathodes is shown in Figure 1. Both profiles are typical for an amorphous material due to the absence of voltage plateaus associated with crystalline phase transitions.⁷ Discharge capacities are 375 and 419 mAh/g for the aerogel and ambigel cells, respectively. Assuming 100% coulombic efficiency, an intercalation of 2.68 and 3.06 moles of Li per mole of V₂O₅ are calculated for the aerogel and ambigel cathodes, respectively.

The evolutions of the XANES spectra for the V₂O₅ aerogel and ambigel cathodes during the first cycle of discharge (Li insertion) are displayed in Figures 2 and 3, respectively. Clearly, the X-ray edge energy continuously shifts to a lower energy with the incremental increase in the lithium content of the V₂O₅ cathode. The negative energy shifts relative to V₂O₅ are consistent with the reduction of V(V) to a lower oxidation state upon Li insertion. On the basis of comparisons with XANES spectra for crystalline V₂O₃, VO₂, and V₂O₅, we conclude that during discharge, V(V) is initially reduced to V(IV) during the intercalation regime of 0-2 moles of Li per mole of V₂O₅ and then V(IV) is reduced to V(III) upon additional insertion of Li. The reduction of V(IV) to V(III) is confirmed by the emerging shoulder labeled by the arrow in Figures 2 and 3. Variations in the amplitude of the V-O correlation displayed by the Fourier transforms of EXAFS spectra (not shown here) indicates an increase in symmetry of the local structure of V in the lithiated cathodes.

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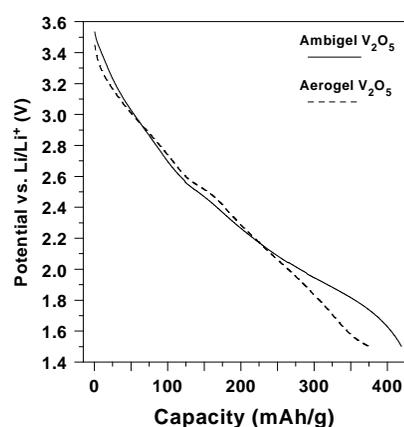


Figure 1. Voltage profiles for the first cycle of the Li/V₂O₅ aerogel and ambigel cells discharged at the C/20.2 and C/21.6 rates, respectively.

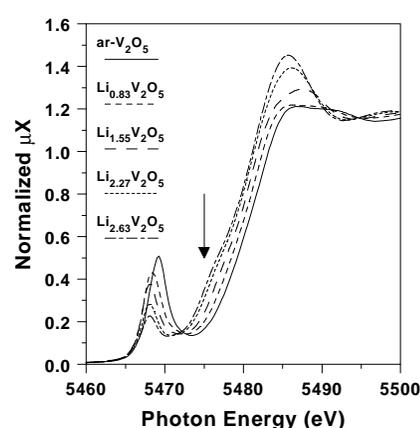


Figure 2. Normalized V K-edge XANES for a V₂O₅ aerogel cathode as a function of state of discharge.

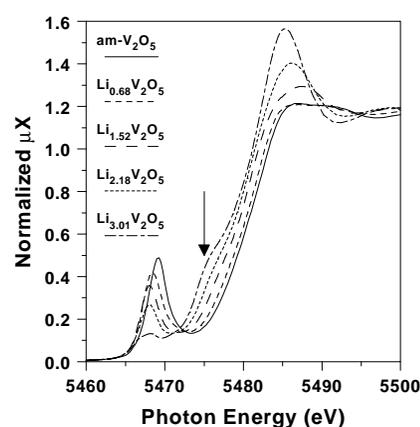


Figure 3. Normalized V K-edge XANES for a V₂O₅ ambigel cathode as a function of state of discharge.

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