

XAS Investigation of Heated Vanadium Pentoxide ($V_2O_5 \cdot nH_2O$) Aerogels and Ambigels

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Introduction: There has been a steady increase in the demand for high energy density rechargeable batteries over the last 30 years. Nanophase vanadium pentoxide ($V_2O_5 \cdot nH_2O$) synthesized using sol-gel techniques has been investigated as a viable cathode material for advanced Li batteries. Depending on drying and heating conditions, the material has been classified into xerogels, aerogels and ambigels. The electrochemical performance of $V_2O_5 \cdot nH_2O$ gels has been shown to be superior to that of crystalline material. The Li storage capacity of $V_2O_5 \cdot nH_2O$ gels depends on drying and heating conditions. In this report, we investigated the effect of heating conditions on the oxidation state and structure of $V_2O_5 \cdot nH_2O$ aerogels and ambigels.

Methods and Materials: XAS was used to examine the oxidation state and local structure of V in $V_2O_5 \cdot nH_2O$ aerogels and ambigels in the as prepared state as well as those heated under vacuum (100 μ Torr) at 114 and 220°C for 25 hours. Prior to the XAS measurements, the water content of the aerogels and ambigels was determined using thermogravimetry (TG). Vanadium pentoxide gels were prepared via the hydrolysis and condensation of vanadyl triisopropoxide $VO[OC_3H_7]_3$ using procedures well established in the literature.

Results: The composition of the aerogels and ambigels consists of about 2 and 1 mole of H_2O per mole of V_2O_5 in the pristine state and after heating at 114°C, respectively. TG analysis reveals the absence of loosely bound H_2O in the network of the aerogels and ambigels heated at 220°C. Analyses of XANES (Figures 1 and 2) and EXAFS spectra (not shown here) reveal that the oxidation state of V for aerogels and ambigels in the pristine state ($V_2O_5 \cdot 2.0H_2O$) as well as those heated at 114°C ($V_2O_5 \cdot 1.0H_2O$) is similar to that of V in orthorhombic V_2O_5 ; i.e., +5. The local structure of V under these conditions is similar to that of V in orthorhombic V_2O_5 except for a higher degree of local symmetry within the structure of the VO_5 square pyramid. Analysis of XANES and EXAFS spectra of aerogels and ambigels heated at 220°C, on the other hand, reveals the presence of both tetravalent and pentavalent V. The fractions of tetravalent V are estimated to be 0.29 ± 0.08 and 0.26 ± 0.08 for the aerogels and ambigels, respectively. The mixed valency can be in the form of a single phase with a solid solution of tetravalent and pentavalent V sites or a two-phase system with one phase containing tetravalent V and the other phase containing pentavalent V.

Conclusions: Heating $V_2O_5 \cdot nH_2O$ aerogels and ambigels under elevated temperatures leads to the loss of at least some H_2O and the reduction of pentavalent V. The thermal decomposition process must be fully understood in order to optimize the electrochemical performance characteristics of $V_2O_5 \cdot nH_2O$ aerogels and ambigels.

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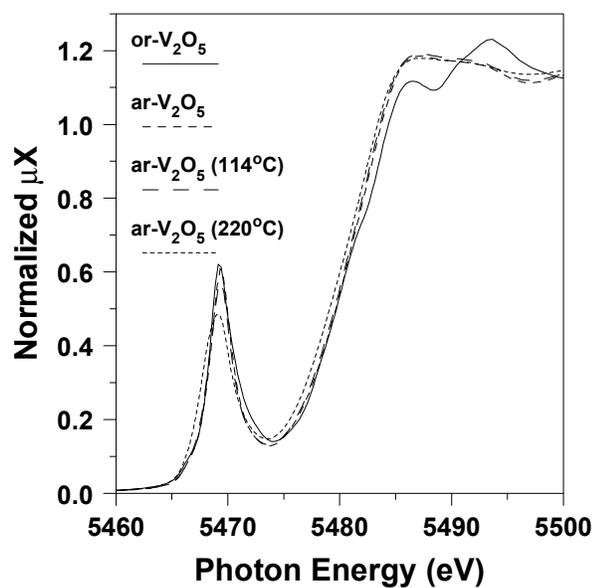


Figure 1. V K-edge XANES for $V_2O_5 \cdot nH_2O$ aerogels in the pristine state and after heating at 114 and 220°C for 25 hrs along with the reference spectrum of orthorhombic V_2O_5 .

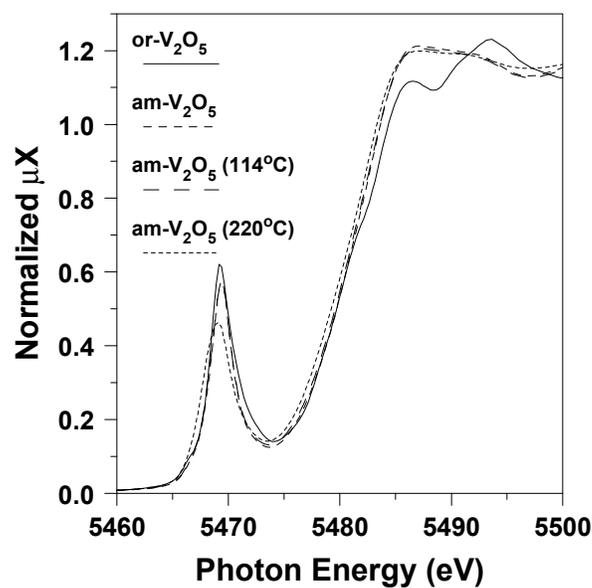


Figure 2. V K-edge XANES for $V_2O_5 \cdot nH_2O$ ambigels in the pristine state and after heating at 114 and 220°C for 25 hrs along with the reference spectrum of orthorhombic V_2O_5 .