

FINAL REPORT DE-FG02-01ER15221

Electrochemistry of Nanostructured Intercalation Hosts

William H. Smyrl, Principal Investigator

Pillared V₂O₅ Aerogels and Xerogels

We found that both self-standing films and powders of highly amorphous V₂O₅ are composed of interconnected networks of solid material that form thin solid walls which separate the interpenetrating pore network. In order to form the porous nanostructured host, pore water in the bicontinuous hydrogel precursor was replaced with acetone (or dioxane, or acetonitrile, or methyl formate) which was then replaced with liquid CO₂ in preparation for the supercritical drying step. Our fundamental thermodynamic studies showed that the ARG material had very high specific energy (i.e., 1600 Wh/kg) that was higher than that of the xerogel (XRG) material formed from the precursor V₂O₅ hydrogel. However, the intercalation capacities were equal for both. The thermodynamic studies for both ARG and XRG forms were carried out by electrochemical coulometric titration and by chemical lithiation, and the results are shown in Figure 3.1. Forming the intermediate acetone organogel caused pillaring of V₂O₅ that was responsible for the enhancement of the specific energy over that of the xerogel dried from the hydrogel state. We have found (8) that compact xerogel films formed from the organogel (O-XRG) stage have the same equilibrium potential vs. composition as for the ARG.

The pillaring of V₂O₅ was caused by a small amount of acetone that was retained in the structure after supercritical drying (about 0.2 moles/mole of V₂O₅, analysis by

Galbraith Laboratories). Other pillared V_2O_5 materials have been formed in an analogous manner in the organogel state with the solvents listed in Table II. Also listed is the interlayer spacing found from XRD studies. The interlayer spacing for unpillared $V_2O_5 \cdot 0.5 H_2O$ is 0.88 nm (37). All the listed organic species pillar V_2O_5 to about 1 - 1.2 nm interlayer spacing. It is important to note that the pillaring species are retained in the structure throughout subsequent electrochemical insertion/release cycling. In Figure 3.2 is shown the thermodynamic equilibrium potential versus the insertion concentration (moles Li^+ / mole V_2O_5) for four of the pillaring species, including acetone for reference. It is clear that within experimental error, all of the pillared materials have similar thermodynamic properties. That is, pillaring increases the equilibrium potential at any Li^+ concentration. We have not yet determined the effect of larger pillaring distances. The relationship between voltage vs moles of Li^+ ions for dioxane, acetonitrile, and methyl formate aerogels were determined by chemical lithiation. Since we have already shown that the thermodynamic properties determined by chemical lithiation are equivalent to electrochemical insertion of Li^+ ions for acetone- pillared vanadium pentoxide, we propose that the same will be true for the other three materials, but it is yet to be shown.

Polyvalent Intercalation in V_2O_5 Aerogel

We demonstrated that amorphous, pillared V_2O_5 aerogel (ARG) is a facile universal host for intercalation of both univalent and polyvalent cations. It was found that the capacity for intercalation is 4 equivalents of Li^+ ions, 4 equivalents of Mg^{+2} ions,

3.33 equivalents of Al³⁺ ions, and 2.5 equivalents of Zn²⁺ ions, all determined per mole of V₂O₅. The intercalation was reversible

Pillaring Agent	Moles Li ⁺ / Mole ARG	
	0	1
Acetone	12.46 Å	10.94 Å
1,4 Dioxane	14.20	10.86
Acetonitrile	12.11	11.33
Methyl Formate	10.92	10.81
Dimethoxymethane	10.53	
Acetaldehyde	13.20	
Nitromethane	10.72	
Propionitrile	11.63	
Methyl Ethyl Ketone	12.45	

Table II. Interlayer d-Spacing of Pillared V₂O₅ Materials

as demonstrated by repeated release and re-insertion of the polyvalent cations over several cycles in anhydrous electrolytes in electrochemical cells (5). Further study is necessary to fully understand this reversibility and the rate of insertion and release. There appear to be at least two reasons why the V₂O₅ (ARG) has high experimental capacities for the polyvalent cations. First, the ARG has small pore wall dimensions (of the order of 10-15 nm) and thus small diffusion distances in the solid. This leads to rapid intercalation into the solid host (diffusion effect) and is probably a major reason for the great enhancement over the xerogel where diffusion distances (defined by the particle

size of the xerogel powder) are often 10 micrometers or larger. Previous work in other laboratories found only low intercalation capacities for the polyvalent cations and this was influenced by kinetic limitations. The increased interlayer spacing in the aerogel material facilitates cation (i.e., Mg^{+2}) insertion as well and alters the site energy for polyvalent cations in the host (thermodynamic effect) which promotes higher capacity. We conclude that these results provide a firm basis to indicate that barriers to intercalation of polyvalent cations are eliminated in pillared aerogels of V_2O_5 .

X-ray Absorption Spectroscopy Studies of Intercalation Sites in V_2O_5

X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) measurements were carried out on vanadium pentoxide aerogels that had been intercalated with lithium ions. In the pre-edge peak region of the XAS results, it was found that the energy position of the peak changed very little with lithium content above 1 Li^+ ions/mole V_2O_5 . This was in contrast to our previous work with vanadium pentoxide xerogels where the peak changed in a linear fashion with lithium content. The surprising result in the ARG clearly indicates that the correlation of oxidation state of vanadium in the aerogel as measured by the V pre-edge position is not observed for the aerogel materials. Analysis of the XANES portion of the XAS spectra showed that there was a gradual lengthening of the vanadyl bond, which forces vanadium to move into the plane of the 4 oxygens at the base of the pyramidal structure - which is in the opposite direction from all the previous work with crystalline and xerogel V_2O_5 materials. Interpretation of the XAS spectra is a continuing effort.

To pursue the unusual behavior for the aerogel, it was decided that XAS work with zinc intercalated samples would help to reveal the local structure around the intercalated species. Lithium is too light to yield spectra for the analysis of interest. XANES spectra at the vanadium k-edge of $Zn_xV_2O_5$ did not show any substantive change as a function of increasing amounts of intercalated Zn^{+2} ions, thus indicating the absence of interactions between the intercalated ions and the vanadium ions. To study the structural sites of the polyvalent ions, EXAFS (extended X-ray absorption fine structure) spectra were measured at the Zn k-edge. The EXAFS analysis showed that the Zn^{+2} ions are 4-fold coordinated by almost coplanar oxygens. In addition, differences in the bond distances in the first shell of the inserted Zn^{+2} have been observed. The first-shell Zn-O bond length shortened and the EXAFS Debye-Waller factor increased with intercalation level. The coordinating oxygens belong to the same V_2O_5 layer, and the Zn sites are in quasi coplanar positions with them. This leaves the interlayer space between V_2O_5 layers almost free. The empty interlayer spacing is then available for further ion insertion - at concentrations above 2 equivalents of Zn^{+2} per mole of V_2O_5 . At larger intercalation levels, a general atomic disorder is induced in the structure and more work is needed to complete our understanding. We conclude that Zn^{+2} ions that occupy intercalation sites within the V_2O_5 bilayer are highly reversible (mobile), and that these are preferred sites in the pillared aerogels. Apparently these are the same sites that are occupied by Mg^{+2} and Al^{+3} in the same host. This site is also occupied by Zn^{+2} and Cu^{+2} in xerogels formed from the hydrogel precursor (4).

Subcritical and Solvent Exchange Drying of V_2O_5 Aerogels

Aerogel processing involves exchanging water in the vanadium pentoxide hydrogel with acetone followed by a second fluid exchange with liquid carbon dioxide, and finally the CO₂ from the pores is removed above the critical point. We explored the use of subcritical conditions, i.e., removal of liquid carbon dioxide at temperatures just below the critical point where the surface tension is very low but not zero. The BET surface area of the material dried in subcritical CO₂ was found to be lower, about 300 m²/g, instead of 450-500 m²/g typically found for the aerogel. A second variation of the drying was to use hexane instead of liquid carbon dioxide to follow acetone in the processing. Liquid hexane was then removed from the pores by heating at about 80°C to form aerogels. The BET surface area of the aerogel-like V₂O₅ is typically about 200 m²/g. The latter material has the lowest surface area of the sequence, but only the smallest pores have been lost and the mesopores are preserved. Since the smallest pores, with pore diameters of 1 nm or smaller, are not favored for electrochemical reactions because they are less accessible than mesopores, the aerogel-like processing yields a more interesting host material. A basic understanding of these processes will result in the ability to prepare customized porous nanostructures for optimal rate behavior.

The new aerogel-like processing still yielded amorphous material with no loss of lithium intercalation capacity, i.e., 4 equivalents of Li⁺ per mole of V₂O₅. The rate at which Li⁺ ions may be inserted is also very high, which again is consistent with the thin solid walls in the network that provide short diffusion distances in the solid state. Impedance results show that diffusion in the solid state is fast and does not limit the overall rate of insertion. The high rate studies were done with low mass loadings on electrodes, typically less than one microgram.

Doped V₂O₅ Xerogels and Aerogels

In order to enhance the rate of insertion, another avenue of research was pursued in which the electronic conductivity of amorphous V₂O₅ was increased by doping. Silver and copper ion doping were found (1,2) to increase the conductivity of the solid by up to three orders of magnitude. The electrochemical performance of the doped material is excellent. Up to 2.2 equivalents of Li⁺ per mole of V₂O₅ were intercalated reversibly at high rates, with no loss of capacity over several hundred cycles (> 400) of insertion/release.

Li-Mn-O Aerogels

Aerogel forms of intercalation hosts were shown in our laboratory to be excellent for both high capacity and promising for high rate behavior. To extend the range of investigation, we recently investigated Li-Mn-O aerogels that were dried under low surface tension conditions. The lithiated manganese dioxide material was made by a sol-gel route. The inherent capacity for Li⁺ ion insertion in excess of 1.7 equivalents/Mn was demonstrated, with specific capacity and specific energy above 440 mAh/g and 1250 Wh/kg, respectively. This is significantly greater than the value of 150 mAh/g found in other forms of MnO_x.

Colloidal Crystal Routes to Porous Oxides and Metals

A final area of research was initiated jointly with Professor Andreas Stein in Chemistry at the University of Minnesota, in which a general chemical synthesis route was discovered for periodic, macroporous metals where 250-500 nm monodisperse voids

were surrounded by nanocrystalline metal walls. With pore sizes of a few hundred nanometers, the materials fill a gap in the range of accessible pore sizes between microporous (Raney nickel) or mesoporous metals (prepared from liquid crystalline phases) on the smaller end (less than 10 nm), and metal foams on the larger end (greater than hundreds of micrometers). One may expect to design porous structures for improved performance with the combination of porous electrode supports for solid electrolytes.

Summary of Research

We have shown that:

- (1) Li^+ ions are inserted reversibly, without diffusion control, up to the level of at least 4 moles Li^+ ions per mole for V_2O_5 , in the aerogel (ARG) form (500 m^2/g specific surface area) and aerogel-like (ARG-L) form (200 m^2/g specific surface area)(6,7,1,2);
- (2) polyvalent cations (Al^{+3} , Mg^{+2} , Zn^{+2}) may be intercalated reversibly into V_2O_5 (ARG) with high capacity (approaching 4 equivalents/mole V_2O_5 (ARG)) for each (5);
- (3) dopant cations such as Ag^+ and Cu^{+2} increase the conductivity of V_2O_5 (XRG) up to three orders of magnitude(3), they are electrochemically active – showing reduction to the metallic-state in parallel to intercalation of Li^+ ions – but are not released to the electrolyte upon oxidation and Li^+ ion release (Cu^{+2} ions are reduced to Cu metal and reoxidized to Cu^{+2} in Li^+ ion insertion/release cycles, but the copper ions are not released to the electrolyte over more than 400 cycles of the XRG form);
- (4) we have shown that Cu^{+2} ion (dopant) and Zn^{+2} ions (chemical insertion and dopant) occupy the same intercalation site in V_2O_5 xerogel and aerogel(4);
- (5) the reversible intercalation of Zn^{+2} , Mg^{+2} , and Al^{+3} in the ARG(11) indicates that these cations are “mobile”, but that Cu^{+2} ions and Ag^+ ions are “immobile” in the xerogel, i.e., the latter ions are not exchanged with the electrolyte in Li^+ ion intercalation cycling(3).

References

1. F. Coustier, S. Passerini, and W.H. Smyrl, Solid State Ionics **100** (1997) 247; F. Coustier, S. Passerini, J. Hill, and W.H. Smyrl, Mat. Res. Soc. Symp. Proc. **496** (1998) 353.
2. F. Coustier, S. Passerini, and W.H. Smyrl, J. Electrochem. Soc. **145**, (1998) L73.
3. F. Coustier, J. Hill, B.B. Owens, S. Passerini, and W.H. Smyrl, J. Electrochem. Soc. **146** (1999) 1355.
4. E. Frabetti, G.A. Deluga, W.H. Smyrl, M. Giorgetti, and M. Berrettoni, J. Phys. Chem. **108**, 3765-3771(2004).
5. D.B. Le, S. Passerini, F. Coustier, J. Guo, T. Soderstrom, B.B. Owens, and W.H. Smyrl, Chem. Mater. **10** (1998) 682.
6. D.B. Le, S. Passerini, A.L. Tipton, B.B. Owens, and W.H. Smyrl, J. Electrochem. Soc. **142** (1995) L202.
7. D.B. Le, S. Passerini, J. Guo, J. Ressler, B.B. Owens, and W.H. Smyrl, J. Electrochem. Soc. **143** (1996) 2099.
8. D.B. Le, Ph.D. Thesis, University of Minnesota.

Recent Publications from the DOE Sponsored Research

1. "Doped V₂O₅-based Cathode Materials: Where Does the Doping Metal Go? An X-ray Absorption Spectroscopy Study," M. Giorgetti, M. Berrettoni, W.H. Smyrl, Chemistry of Materials **19**(24) (2007) 5991-6000.
2. "X-ray Absorption spectroscopy Study of Cu_{0.25}V₂O₅ and Zn_{0.25}V₂O₅ Aerogel-like Cathodes for Lithium Batteries", E. Frabetti, G.A. Deluga, W.H. Smyrl, M. Giorgetti, M. Berrettoni, J. Phys. Chem. **108**, 3765-3771(2004).
3. "Metal Site Determination in Doped V₂O₅ Arg-Like Cathodes for Lithium Battery", E. Frabetti, G.A. Deluga, W.H. Smyrl, Electrochemical Society Proceedings, **2003-20** (2003) 383-390.