V2O5 XEROGELS IN 1-ETHYL-3-METHYLMIDAZOLOM
CHLORIDE/ALUMINUM CHLORIDE MOLTEN SALTS

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ABSTRACT

Inert electrodes coated with V2O5 xerogels have been studied in room temperature molten salts comprised of mixtures of 1-ethyl-3-methylimidazolium chloride and aluminum chloride. In Lewis neutral melts V2O5 xerogel electrodes were stable, but in acidic melts V2O5 appears to be leached out of the gel into the melt. Cyclic voltammetry and differential pulse voltammetry was used to examine NaCl and LiCl buffered neutral melts. In the positive potential range there are one or two couples that may be due to the reversible insertion and release of Na\(^+\) and Li\(^+\) from the gels. SEM with energy dispersive spectra is being used to try to verify the insertion of Na\(^+\) into the gels as V2O5 is reduced.

INTRODUCTION

Because of their layered structure, vanadium pentoxide gels are excellent hosts for intercalation of a wide variety of inorganic and organic guest spcies [1]. Currently, extensive work is underway on the use of these gels for insertion of lithium ion as potential cathode materials for insertion batteries [2-4]. A specific energy density of 1600 wh/kg has been reached by using a V2O5 aerogel as a cathode for lithium ion batteries [5]. These works involve organic solvents such as propylene carbonate and inorganic lithium salts as the electrolyte. We are interested in extending the use of V2O5 cathodes to room temperature molten salts. Room temperature molten salts comprised of mixtures of 1-ethyl-3-methylimidazolium chloride (EMIC) and aluminum chloride are ionic liquids at room temperature and can serve as both solvent and electrolyte. They also have wide potential windows, wide operating temperature ranges, low density and good conductivity. Thus, using V2O5 xerogels as cathode hosts for intercalation of metal cations such as Li\(^+\), Na\(^+\), Al\(^3+\), and Mg\(^2+\) with room temperature molten salts could lead to high energy density ion batteries. Haas and coworkers have demonstrated that Mg\(^2+\) can be intercalated into V2O5 xerogels in a MgCl2 buffered melt [6]. As the first stage of our work, we report here a survey of the electrochemistry of V2O5 xerogels in acidic, neutral, and neutral buffered melts as well as AFM and SEM results from preliminary attempts to observe Li\(^+\) and Na\(^+\) insertion.
EXPERIMENTAL

$\text{V}_2\text{O}_5$ xerogels were synthesized by protonation of sodium metavanadate via the sol-gel route [3]. The gels were aged for at least 2 months to make them homogeneous. After aging, the gels were coated onto Pt and Ni electrodes either by spin coating or by dip coating. The coated electrodes were dried under vacuum at ambient temperature for 24 to 48 hours. The water content was estimated to be about $\text{V}_2\text{O}_5\cdot 0.5\text{H}_2\text{O}$. Components of the melts were synthesized and purified based on published methods.

Electrochemical measurements were carried out in a Vacuum Atmospheres Corp. glove box under dry nitrogen or argon. An EG&G Princeton Applied Research (PAR) Model 263A potentiostat/galvanostat interfaced to a personal computer using PAR Model 270 software was used. Three-electrode cells were set up with various $\text{V}_2\text{O}_5$ xerogel electrodes as working electrodes and Pt foil used as the auxiliary electrode. For the fundamental melt studies, the reference electrode consisted of an Al wire in an $N=0.60$ $\text{EMIC/AlCl}_3$ melt ($N=\text{mole fraction AlCl}_3$). For the lithium insertion studies, a lithium wire in a fritted tube with LiCl buffered melt was used as the reference electrode and lithium foil was used as the counter electrode.

Atomic force microscopy experiments were conducted with a Digital Instruments NanoScope Model IIIa Scanning Probe. SEM images and EDS spectra were recorded using a Philips 505 SEM equipped with an EDAX PV9100 X-ray microanalysis system.

RESULTS AND DISCUSSION

The physical properties of the spin-coated $\text{V}_2\text{O}_5$ xerogel electrodes where similar to those reported by Livage [1] and Smyrl and coworkers [2-5]. By microscopy the films were estimated to be about 1 μm thick and thermogravimetric analysis indicated a stoichiometry of about 0.5 moles of water per mole of $\text{V}_2\text{O}_5$. Figure 1 is an AFM image of one of the gels on an electrode surface. It shows deep cavities, which shrink if the gel is vacuum dried for prolonged times.

The voltammogram of a $\text{V}_2\text{O}_5$ xerogel electrode in a Lewis acidic melt ($N>0.5$) is shown in Figure 2. The large reduction and oxidation couple is expected for acidic melts and corresponds to the reduction of $\text{Al}_2\text{Cl}_6^-$ and the subsequent oxidation of $\text{Al}^0$. The small prewaves are also believed to be due to aluminum processes. At this current scale no other peaks can be seen in the positive potential range. Figure 3 is a blow up of the positive potential range and exhibits two broad peaks that may be due to vanadium(V) reduction. This conclusion is supported by the spectrum shown in Figure 4. Under some conditions $\text{V}_2\text{O}_5$ appeared to be leached out of the gel and the resulting spectrum was similar to those for $\text{VOCl}_3$ and $\text{VOF}_3$ dissolved in neutral unbuffered melt [7].
Figure 5 compares voltammograms for a V$_2$O$_5$ xerogel electrode and a bare Pt electrode in a neutral unbuffered melt. Whereas proton reduction peaks can be seen in the range from 0.0 to -1.0V, with corresponding oxidation peaks, for the Pt electrode, the voltammogram for the xerogel electrode is flat in this region. Thus, proton reduction is not favored at the xerogel electrode. The oxidation waves for each electrode probably result from reduction processes at the negative limit. Figure 6 compares voltammograms for these two electrodes in a NaCl buffered neutral melt. The xerogel electrode shows large background currents in comparison to the Pt electrode, probably due to the expanded surface area. Comparing the response of the xerogel electrode in the unbuffered and buffered melts (Figures 5 and 6, respectively) suggests that redox processes might be hidden under the large background present in the buffered melt voltammogram.

In order to improve resolution, the positive portion of the voltage range was examined using differential pulse voltammetry. Figure 7 shows a negative scan (A) and a positive scan (B) for the xerogel electrode in a NaCl buffered melt. These scans suggest that two reversible couples may be present. Smyrl and coworkers\(^3\) have studied the electrochemistry of V$_2$O$_5$ xerogel electrodes in propylene carbonate and have observed insertion of up to 3.3 equivalents of Li$^+$ per mole of V$_2$O$_5$. They interpreted this to mean that vanadium (V) was reduced to vanadium (III) giving a four electron change per mole of V$_2$O$_5$. Since this is a change of two oxidation states, it is reasonable to expect two reduction peaks, and two oxidations if the processes are reversible.

Evidence of Li$^+$ insertion was sought by examining LiCl buffered melts. For these experiments a Li$^+$/Li reference electrode was used. It consisted of a Li wire inserted into a tube containing LiCl buffered melt. The Li$^+$/Li reference electrode was found to give potentials 1.181V positive of the Al$^{3+}$/Al couple in an N=0.6 melt reference electrode used in the other experiments. Figure 8 shows voltammograms of a V$_2$O$_5$ xerogel electrode in both a neutral unbuffered melt and a LiCl buffered melt. The trace for the buffered melt shows a very broad reduction and a corresponding broad oxidation. Broad shoulders might suggest a second reduction and a second oxidation peak, but these are not well resolved. The same electrode was examined in the two melts using differential pulse voltammetry. Figure 9 displays these curves and demonstrates that the reduction and oxidation peaks occur with very little peak potential separation. Novak and coworkers [ref. 6, Figure 12] show a broad redox couple for a V$_2$O$_5$ xerogel electrode in a MgCl$_2$ buffered EMIC/AlCl$_3$ melt that looks much like the couple reported here. They suggested that it corresponds to Mg$^{2+}$ insertion and release. Thus, the processes shown in Figures 8 and 9 may be due to Li$^+$ intercalation.

To try and verify the insertion of cations into the V$_2$O$_5$ xerogels in these melt systems, scanning electron microscopy with energy dispersive spectra was used. Although lithium is too light to be detected, the EDS system is capable of detecting sodium. Figure 10 is the EDS plot for a V$_2$O$_5$ xerogel electrode dipped into a NaCl buffered melt and then...
rinsed in acetonitrile three times. This blank spectrum shows only significant amounts of nickel, the base electrode (the lowest energy spike and the two highest energy peaks marked) and vanadium, from the gel (two peaks marked). The marker for sodium indicates where a peak for sodium would be expected, but no peak is present. Small peaks for aluminum and silicon may be present in the baseline at low energy (compare to Figure 11). Figure 11 shows the spectrum recorded after electrolysis at 0.0V for 60 minutes in order to insert sodium. New peaks appeared for both sodium and chlorine. Since the same rinse procedure was used, chlorine from NaCl would not be expected, but cannot be ruled out. The chlorine could be from AlCl₃, NaCl, or both. Clearly, the system is capable of detecting sodium, but we cannot conclude at this time that insertion has occured.

CONCLUSIONS

The voltammetric data presented here suggest that one or two reversible processes occur for V₂O₅ xerogel electrodes in NaCl and LiCl buffered melts. These results agree with those reported for MgCl₂ buffered melts [6]. SEM/EDS experiments will be continued in order to try and verify the insertion of Na⁺ and Li⁺. Insertion will also be studied by quartz crystal microbalance experiments. Such data will also help to determine the number of cations inserted per electron involved in the reduction of vanadium. These studies should help determine the feasibility of using V₂O₅ xerogel cathodes and room temperature molten salts in high energy density batteries.

ACKNOWLEDGEMENTS

We wish to thank Dr. Richard E. Edelmann for assistance with the SEM experiments and Dr. John F. Rakovan for help with the AFM measurements. This work was supported by a State of Ohio Academic Challenge Grant.

REFERENCES

[1] J. Livage, Chem. Mater., 3, 578 (1991).
[2] H.-K. Park and W. H. Smyrl, J. Electrochem. Soc., 141, L25 (1995).
[3] H.-K. Park, W. H. Smyrl and M. D. Ward, ibid., 142, 1068 (1995).
[4] D. B. Le, S. Passerini, A. L. Tipton, B. B. Owens and W. H. Smyrl, ibid., 142, L102 (1995).
[5] D. B. Le, S. Passerini, J. Guo, J. Ressler, B. B. Owens and W. H. Smyrl, ibid., 143, 2099 (1996).
[6] P. Novak, W. Scheifele, F. Joho and O. Haas, ibid., 142, 2544 (1995).
[7] D. M. Ryan and T. L. Riechel, unpublished results.
Figure 1. AFM image of a spin-coated V$_2$O$_5$ xerogel on a Ni electrode.

Figure 2. Cyclic voltammogram of a V$_2$O$_5$ xerogel on a Pt electrode in a Lewis acidic EMIC/AlCl$_3$ melt (N=0.60). Scan rate: 100 mV/sec.
Figure 3. The positive potential portion of the voltammogram in Figure 2, with an expanded current scale.

Figure 4. Visible spectra of an acidic (N=0.60) EMIC/AlCl₃ melt, (A) blank, and (B) after voltammograms were recorded on the melt using a V₂O₅ xerogel coated Pt electrode.
Figure 5. Cyclic voltammograms of a V$_2$O$_5$ xerogel on a Pt electrode in a neutral unbuffered EMIC/AICI$_3$ melt (A), and a bare Pt electrode in the same melt (B). Scan rate: 100 mV/sec.

Figure 6. Cyclic voltammograms of a V$_2$O$_5$ xerogel on a Pt electrode in a neutral NaCl buffered EMIC/AICI$_3$ melt (A), and a bare Pt electrode in the same melt (B). Scan rate: 100 mV/sec.
Figure 7. Differential pulse voltammograms of a V$_2$O$_5$ xerogel on a Ni electrode in a neutral NaCl buffered EMIC/AlCl$_3$ melt. (A) Negative scan, (B) positive scan. Scan rate: 10 mV/sec.

Figure 8. Cyclic voltammograms of a V$_2$O$_5$ xerogel on a Ni electrode in EMIC/AlCl$_3$ melts: (A) neutral LiCl buffered melt, and (B) neutral unbuffered melt. Li$^+$/Li reference electrode; Li foil counter electrode. Scan rate: 100 mV/sec.
Figure 9. Differential pulse voltammograms of a V$_2$O$_5$ xerogel on a Ni electrode in EMIC/AlCl$_3$ melts: (A) neutral LiCl buffered melt, and (B) neutral unbuffered melt. Li$^+$/Li reference electrode; Li foil counter electrode. Scan rate: 10 mV/sec.

Figure 10. SEM/EDS spectrum of a V$_2$O$_5$ xerogel on a Ni electrode before electrolysis.
Figure 11. SEM/EDS spectrum of a V$_2$O$_5$ xerogel on a Ni electrode after electrolysis in a neutral NaCl buffered EMIC/AlCl$_3$ melt.