ELECTROCHEMISTRY OF VANADIUM OXIDES IN ROOM TEMPERATURE MOLTEN SALT ELECTROLYTES

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ABSTRACT

The electrochemistry and UV-visible spectroscopy of several high oxidation state vanadium oxides have been investigated in room temperature molten salts formed by mixing 1-methyl-3-ethylimidazolium chloride with AlCl3. V2O5, NaVO3, Na3VO4, V2O4, and V2O3 were studied in acidic, basic, neutral, neutral-buffered, and neutral-buffered-protonated melts. Most of these compounds have limited solubility of about 5mM or less. Cyclic voltammograms of V2O5 in the acidic melt show two reduction peaks at 1.7 and 0.5V. Upon reduction of the 1.7V peak a new absorption peak is observed at 510nm in the visible spectrum. This is believed to correspond to a V(IV) species, but comparison to V2O4 is difficult because of that compound’s low solubility. Neither of the two reduction peaks for V2O5 are reversible. The monosodium V(V) salt, NaVO3, is more soluble than the trisodium salt, Na3VO4, in all cases. In acidic melt it exhibits peaks similar to those for V2O5, except that the more positive peak is shifted to about 1.3V. V2O5 and NaVO3 are the best candidates for battery cathodes, but neither exhibit reversible electrochemistry as needed for a secondary cell.

INTRODUCTION

Room temperature chloroaluminate molten salts have been considered as electrolytes for primary and secondary batteries [1-3]. Sodium, lithium, and aluminum have been studied as possible battery anodes with these electrolytes, while the electrochemistry and spectroscopy of numerous transition metals have been reported in order to evaluate their use as possible cathodes [4,5]. Only a few vanadium species have been investigated in such systems. An early study examined V2O5 in a LiCl-KCl melt at 450°C [6]. Recently a few studies have appeared in which V2O5 and other oxides were examined in xerogels [7-9] at or near room temperature. In one case [9] a chloroaluminate melt doped with magnesium chloride was used at 80°C. We report here a survey of the electrochemistry and UV-visible spectroscopy of vanadium oxides in the (III), (IV), and (V) oxidation states studied in acidic, basic, and neutral melts of 1-methyl-
3-ethylimidazolium chloride (MEICl) and AlCl₃. The purpose is to evaluate the feasibility of using such materials as cathodes in cells incorporating room temperature chloroaluminate molten salt electrolytes.

**EXPERIMENTAL**

Cyclic voltammetry and controlled potential coulometry were performed using a Bioanalytical Systems (BAS) Model 100A Electrochemical Analyzer. A three electrode cell was employed using BAS Pt, W, and glassy carbon working electrodes for the voltammetry experiments. A Pt mesh electrode was the working electrode for the coulometric experiments. The reference electrode consisted of an Al wire in a 0.6 mole fraction AlCl₃ melt. The auxiliary electrode was a Pt flag. All measurements were made in a Vacuum Atmospheres glove box under a dry nitrogen atmosphere.

Preparation of the acidic, basic, neutral, and neutral-buffered melts of MEICl/AlCl₃ have been described previously [1-3]. The neutral-buffered-protonated melt was made by adding triethanolamine.HCl to the neutral-buffered melt as given in ref. [3]. The vanadium oxides studied, V₂O₅, NaVO₃, Na₃VO₄, V₂O₄, and V₂O₃, were obtained from Aldrich or Alfa/Aesar.

UV-visible spectroscopy was carried out using a Hewlett Packard Model 8452A diode array spectrometer and quartz cuvettes.

**RESULTS AND DISCUSSION**

Our initial studies focused on the vanadium (V) oxides and V₂O₅ in particular. A Lewis neutral melt (N=0.5, the mole fraction of AlCl₃) was made by mixing equal molar amounts of 1-methyl-3-ethylimidazolium chloride with AlCl₃. The light orange V₂O₅ did not readily dissolve. After heating to 80°C, sonicating, and stirring overnight, a suspension of <10mM V₂O₅ was obtained. The cyclic voltammogram of this suspension is shown in Figure 1. The rest potential shifted positively from that of the blank melt and two peaks appeared, a reduction peak at 0.5V and an oxidation peak at 1.2V. The oxidation peak only arises after scanning through the reduction peak. Thus, the two peaks are related, although they clearly do not constitute a reversible couple. Because of the small currents observed, the species responsible for these peaks are not certain.

To explore the solubility of V₂O₅ in a Lewis acidic melt, enough V₂O₅ was placed in an N=0.55 melt to make a 10mM solution. Although this material also did not dissolve completely even after prolonged stirring, upon filtration to remove the undissolved solid, an orange solution resulted. As shown in Figure 2, the voltammogram of this solution has a rest potential of about 1.9V, which is more positive than that for the suspension of this
reagent in the neutral melt. Furthermore, a new reduction peak appeared at 1.7V. Controlled potential electrolysis was carried out on this solution at 1.55V. After several hours a large residual current remained. The number of coulombs recorded was not useful data because the exact concentration of material was not known. The resulting voltammogram, Figure 3, shows that the species responsible for the 1.7V reduction peak has been consumed. Comparison of UV-visible spectra recorded before and after the electrolysis step also show a significant difference. Figure 4 is the spectrum of V_2O_5 before electrolysis. Three large absorbance peaks are observed below 400 nm, and the rest of the visible spectrum is blank. After electrolysis, the resulting spectrum (Figure 5) shows that of the three peaks below 400 nm only the lowest wavelength peak is still present. (Shoulders for the other two peaks are still evident.) Also, a new peak is present at 510 nm. We believe that this is due to a vanadium (IV) species. Attempts to study V_2O_4 for comparison have been fruitless because this compound is essentially insoluble.

V_2O_5 has also been examined in other melt compositions. In a basic melt (N=0.45) solubility is very low and there are no reduction peaks within the voltage window established by Cl^- oxidation. In a neutral melt buffered with NaCl the voltage window is over 4V wide, but no activity is observed. In a neutral buffered melt with protons added (0.060M triethanolamine.HCl, as in ref. [3]) the plating and stripping of sodium was observed, but no redox activity attributable to vanadium was evident.

Two vanadium (V) sodium salts were also investigated. The monosodium salt, NaVO_3, dissolved completely at a concentration of 30mM in a neutral melt, but over time deposited a white solid believed to be either NaCl or NaAlCl_4. (Both are known to be insoluble in neutral melts.) The voltammogram of this solution is shown in Figure 6. The reduction peak at 0.5V and the oxidation peak at 1.2V appear to be due to the same species as observed for V_2O_5 in neutral melt (Figure 1) but with larger currents as expected. Na_3VO_4 was only slightly soluble in neutral melt, but its voltammograms exhibited the same two peaks.

The solubility of NaVO_3 in acidic melt is about 7mM. The voltammogram of such a solution is shown in Figure 7. This voltammogram is similar to that of V_2O_5 in acidic melt (Figure 2) in that there are two reduction peaks in the positive potential range. The more positive peak is shifted to about 1.3V, as compared to 1.7V for V_2O_5. Because reduction peaks this far positive are not observed in the voltammograms for any of the lower oxidation state vanadium oxides, these peaks are believed to be reduction of vanadium (V).

Results for Na_3VO_4, V_2O_5, and V_2O_3 show little because of the very slight solubility of these compounds in the various melts. Further work is underway to identify the dominant vanadium (V) species present in acidic melts of V_2O_5 and NaVO_3. Neither of these compounds appear to be useful for reversible cathodes, but may find use in primary cells.
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Figure 1. Cyclic voltammogram of a <10mM V₂O₅ suspension in a Lewis neutral MEICl/AlCl₃ melt at a Pt working electrode. Scan rate 0.1V/sec.

Figure 2. Cyclic voltammogram of a filtered V₂O₅ solution in a Lewis acidic MEICl/AlCl₃ melt at a Pt working electrode. Scan rate 0.1 V/sec.

Figure 3. Cyclic voltammogram of the V₂O₅ solution in Figure 2 after controlled potential electrolysis at 1.55V. Scan rate 0.1V/sec.
Figure 4. UV-visible spectrum of $V_2O_5$ in a Lewis acidic MEICI/AlC$_3$ melt.

Figure 5. UV-visible spectrum of $V_2O_5$ in a Lewis acidic MEICI/AlCl$_3$ melt after electrolysis at 1.55V.
Figure 6. Cyclic voltammogram of 30 mM NaVO$_3$ in a Lewis neutral MEICl/AlCl$_3$ melt at a Pt working electrode. Scan rate 0.1V/sec.

Figure 7. Cyclic voltammogram of 7 mM NaVO$_3$ in a Lewis acidic MEICl/AlCl$_3$ melt at a Pt working electrode. Scan rate 0.1V/sec.