ELECTROCHEMICAL REDUCTION OF TiO\textsubscript{x} AT ROOM TEMPERATURE IN IONIC LIQUIDS

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ABSTRACT

The reduction of titanium oxide was achieved in ionic conducting electrolytes on oxidized titanium foils and on titanium oxide particles in a packed bed electrode configuration. The surface of a titanium foil oxidized in air at 550°C for 140 hrs was studied with cyclic voltammetry. The voltammetry showed a series of shallow waves in the negative potential region corresponding to reduction reactions occurring on the surface oxide. Changes observed in subsequent cycles clearly indicated that the oxide had undergone significant changes. To establish that titanium metal was obtained an experiment was run using TiO\textsubscript{2} particles in a packed bed configuration where no titanium metal was available to give false analytical signals. After the particles were exposed to conditions which were determined, from the voltammograms on the oxidized Ti foil, to lead to metallic titanium the particles were examined with x-ray photoelectron spectroscopy (XPS) to determine the presence of elemental titanium metal. A 20% conversion to elemental titanium was observed. Further experiments were carried out on the oxidation/reduction behavior of Ti\textsuperscript{3+} and Ti\textsuperscript{4+} ions in the ionically conducting electrolytes.

INTRODUCTION

The Kroll and Hunter processes are methods currently in use for the production of titanium metal from titanium dioxide (1,2). In these methods, TiO\textsubscript{2} is reacted with chlorine gas to produce titanium tetrachloride, a volatile corrosive liquid. This is reduced to titanium metal by reacting with metallic magnesium in the Kroll process or with metallic sodium in the Hunter process. Both processes are carried out at high temperatures in sealed reactors. Following this, a two-step refining process is carried out which includes vacuum distillation to remove the alkali metal and its chloride from the titanium metal.
The refining of titanium by electrochemical means has long been a sought after process. It has been shown in the literature that oxygen could be removed from titanium and titanium alloys using an electrochemical molten salt method (3). This has led to the development of a possible new method of extracting and refining titanium directly from the oxide ore (4,5). This process involves electrochemistry in a high temperature molten salt, molten CaCl₂ at ~ 800°C. In these publications two different mechanisms are proposed for the reduction of titanium oxides. In the first mechanism it is proposed that the Ca²⁺ ions are reduced to metallic Ca at the cathode. Then the Ca metal chemically reacts with the TiOₓ forming an oxygenated Ca species, CaO, which is soluble in the melt forming Ca²⁺ and O²⁻. The second mechanism proposed was the direct electrochemical reduction of the TiOₓ to Ti metal and an oxygen species such as O²⁻. This is followed by the migration of the O²⁻ to the carbon anode where it forms volatile species such as CO or CO₂.

In this paper the electrochemical reduction of TiO₂ to Ti metal at room temperature in ionic conducting electrolytes is demonstrated. Further, we report the electrochemical behavior of ionic titanium species (Ti³⁺ and Ti⁴⁺) dissolved in the electrolyte EMİ BF₄ at glassy carbon and platinum electrodes.

EXPERIMENTAL

Two different ionic conducting liquids were used in these experiments. The first was a mixture of 1-ethyl-3-methylimidazolium chloride (EMİC) and aluminum chloride (EMİC AlCl₃) and the other was 1-ethyl-3-methylimidazolium tetrafluoroborate (EMİ BF₄). The EMİ AlCl₃ was prepared by recrystallizing EMİC and subliming AlCl₃ in a closed tube and then mixing them in the proper ratios. For these experiments they were mixed together in a ratio of 0.8 to 1 to give a basic melt with a mole ratio, AlCl₃:EMİC, of 0.44. The second melt was 1-ethyl-3-methylimidazolium tetrafluoroborate obtained from TCI America. The as received material was purified by heating on a vacuum line at 100°C in a low 10⁵ torr vacuum. These electrolytes are air and moisture sensitive so all the experiments were carried out in a Vacuum Atmospheres dry box.

The electrochemical experiments were conducted in 3ml vial cells obtained from Cypress Instruments. Platinum and glassy carbon disc electrodes (1 mm diameter) were also obtained from Cypress Instruments. A PAR 283 potentiostat was used to control the potential in the experiments. The reference electrode used in the EMİC AlCl₃ electrolyte was an aluminum wire in a 1.5:1 acidic melt held in a capillary with Vycor sealed in one end. The reference used in the EMİBF₄ was Ag/AgCl in 0.1M EMİC/EMİ BF₄ also held in a Vycor sealed capillary.

The titanium foil electrodes were strips of titanium (0.25mm x 2mm x 10cm) cut from a titanium sheet of 99.99+% obtained from Alfa. The strips were placed in a furnace and oxidized in air at 550°C for 140 hrs. The titanium oxide granules 99.998+% (TiO₂ rutile) were obtained from Alfa and ground and sieved to obtain particles ~1mm in diameter. These particles were held in a platinum gauze basket in a packed bed configuration for the electrochemical experiments.
RESULTS AND DISCUSSION

In Figure 1 the initial cyclic for the oxidized Ti foil in the EMIC AlCl₃ melt is shown. The overall slope of the voltammogram is quite large and this suggests a significant IR drop, which arises from the air grown oxide covering the surface. Considering the cathodic-going portion of the voltammogram there are indications of at least three and possibly four cathodic waves, which indicate that there are some reduction reactions taking place on the surface of the oxide film. On the anodic return sweep three anodic waves are observed at ~0.5, ~0.25 and 0.0 V vs Al. At this point we do not know which reactions correspond to these three peaks. In the second voltammogram shown in Figure 1 (dashed curve) we held the oxidized Ti foil at ~1.6 V vs Al and then recorded the voltammogram. The first thing to notice is the large change in the overall slope of the voltammogram. This suggests that the conductivity of the sample has been significantly modified by the reduction of the sample. It could be that some portion of the oxide has been reduced to Ti metal or the conductivity of the oxide film has been significantly modified by the reduction reactions. Further, there are now two sharp anodic waves at ~0.5 and ~0.2 V vs Al and one minor wave at ~0.85 V vs Al observed. This behavior raises the question of whether the oxide is actually reduced to the metal, or the

Figure 1. Cyclic voltammograms for Ti foil oxidized in air at 550C for 140 hours at a sweep rate of 50 mV/sec in the EMIC AlCl₃ electrolyte. The solid line is the initial scan. The dashed scan was recorded after holding the sample at ~1.6V for 15 minutes and then recording the data shown.
surface Ti$^{4+}$ is being reduced to a lower oxidation state and the subsequent anodic waves are merely the reoxidation of the surface?

In order to determine if the titanium oxide was reduced to Ti metal a Pt guaze basket containing TiO$_2$ was placed in a vial cell containing EMIC AlCl$_3$ melt and the potential was set at -1.6 V vs Al. This value was chosen from the cyclics in Figure 1, which suggested the possibility that at -1.6 V the oxide on the Ti foil was being reduced to Ti metal. The sample was held at this potential for about 12 hours at which point the TiO$_2$ granules had turned black. The TiO$_2$ granules were washed hexane in the dry box, sealed in a vial, and removed from the dry box for XPS analysis. There was not a sufficient amount of sample for a diffraction experiment. The sample was further washed in water and ground into a gold foil to hold it in the XPS machine and reduce any charging which might occur during the experiment. Figure 2 shows the XPS data for the TiO$_2$ sample following the electrochemical reduction in EMIC AlCl$_3$ melt. The data clearly show the presence of both titanium metal and the original starting material TiO$_2$. The positions of the Ti 2p$^{3/2}$ in the Ti metal (453.5 eV) and in the TiO$_2$ (459 eV) agree well with the values quoted in the literature (6). The yield of Ti metal in this experiment was -20%. This data demonstrates that TiO$_2$ can be reduced directly to Ti metal at room temperature.

![XPS Data](image)

Figure 2. X-ray photoelectron spectrum showing the formation of titanium metal by electrochemical reduction of TiO$_2$ powder in the ionically conducting electrolyte EMIC AlCl$_3$ at -1.6V.

To investigate the source of the anodic waves in Figure 1 we examined the redox properties of the Ti$^{3+}$/Ti$^{4+}$ couple in EMIBF$_4$. This melt was chosen because trace amounts of moisture do not produce protons, as occurs in the EMIC AlCl$_3$ melt. A solution of 100 mM TiCl$_3$ in EMIBF$_4$ was used. Several days were required for complete...
dissolution of the TiCl₃. The data were recorded in the vial cell using a glassy carbon disc electrode. Figure 3a shows the cyclic for the Ti³⁺/Ti⁴⁺ couple in neat EMIBF₄. The scan began at −0.5V and went in the positive direction. At about 0.5V the oxidation of the Ti³⁺ to Ti⁴⁺ is seen. Following the reversal of the scan direction the reduction of the Ti⁴⁺ to Ti³⁺ occurs at ~0.4V. As the sweep proceeds in the negative direction a rather unusual behavior is observed beginning at ~−1V. A wave is observed which is quite broad and has what appear to be oscillations at its peak position. We have tentatively interpreted this phenomenon as the formation of an insoluble Ti²⁺ species, probably TiCl₂, on the surface. This deposit is not very conductive, leading to behavior which has been generally observed when filming occurs at the electrode surface.

![Figure 3a](image-url)

*Figure 3. Cyclic voltammograms for 100 mM TiCl₃ in EMI BF₄ ionically conducting electrolyte, sweep rate 100 mV/sec: 3a) cyclic for Ti³⁺ in neat EMI BF₄; 3b) cyclics showing the effects of adding chloride to the EMI BF₄.*

The titanium species tend to be more soluble in chloride containing electrolytes so chloride was added to the EMIBF₄ in the form of EMIC and the progression of the cyclic voltammograms as the concentration of chloride was increased is shown in figure 3b. With chloride additions, we see the Ti³⁺ / Ti⁴⁺ couple shift in the negative direction, behavior expected for formation of higher chloride complexes. In addition, the wave that was exhibiting the unusual behavior in the neat EMI BF₄ has now shifted negatively and become a well developed wave ~−1.6V. Based on the total amount of chloride added, the final voltammogram is that of the hexachlorotitanium species.
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