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SPECTROSCOPIC AND ELECTROCHEMICAL STUDIES OF MOLTEN SALT ELECTROLYSIS OF ALUMINUM AND MAGNESIUM

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ABSTRACT

Chloride based electrolytes employed in the electrolytic production of aluminum and magnesium have been investigated by laser Raman spectroscopy and cyclic voltammetry. In solutions of composition approximating industrial conditions, aluminum and magnesium exist as tetrahedrally coordinated chloro-complexes, $AlCl_4^-$ and $MgCl_4^{2-}$, respectively. For both elements the electrodeposition of liquid metal was found to be quasi-reversible.

INTRODUCTION

The extraction of light metals is achieved for the most part by molten salt electrolysis, a very energy-intensive process. The production of primary aluminum and magnesium is estimated to have consumed 2.1% of total generated electric power in the United States during the year 1985 (1).

The characteristics of laboratory-scale aluminum and magnesium cells were investigated by spectroscopic and electrochemical techniques. The electrolytes were constituted to be representative of industrial conditions. Aluminum cells operated at a temperature of 700°C with an electrolyte of composition 5 wt % $AlCl_3$, 42 wt % LiCl, and 53 wt % NaCl. Magnesium cells operated at a temperature of 750°C with an electrolyte of composition 11 wt % $MgCl_2$, 65 wt % NaCl, 18 wt % KCl, and 6 wt % $CaCl_2$. The maximum current density was 2 A cm^{-2}.

As part of a study of the causes of poor power efficiency, Raman spectra of laboratory-scale aluminum chloride and magnesium chloride electrolysis cells were measured. Commercially available laser Raman scattering instrumentation was adapted to permit *in situ* real-time investigation of melt chemistry and to establish the basis for "fast Raman" spectroelectrochemistry in this and other melt systems (2). The results of the Raman work were combined with those of cyclic voltammetry in an attempt to reveal the mechanisms and kinetic pathways that decrease power efficiency in aluminum and magnesium cells and also to understand the nature of such phenomena as metal fog, streamers, and melt coloration, all of which were observed in these laboratory-scale cells.

LITERATURE

Reasons for the loss of current efficiency in aluminum cells (3,4) and magnesium cells (5,6) have been discussed in the literature.

Raman spectra of pure $MgCl_2$ and solutions of $MgCl_2$ in alkali chlorides have been measured (2,7-13). In contrast, in the analogous aluminum chloride systems spectra have been taken of $AlCl_3$ only in solution in alkali chlorides as pure $AlCl_3$ sublimes without melting under an applied pressure of 1 atmosphere (14-18).

Over the years, magnesium electrodeposition has rarely been the topic of electrochemical analysis. In the last decade there have been only two reports, one by Tunold (19) and one by Duan, Dudley, and Inman (20). As for aluminum chloride, it has been found primarily as a constituent of supporting electrolytes for use in electrochemical studies of other ions, particularly those of refractory metals (Groups 4,5, and 6). However, there have been some studies of the electrodeposition of aluminum in chloride melts (21-23).

EXPERIMENTAL

A detailed description of the Raman instrumentation and the laboratory-scale electrolysis cell can be found in previous reports (2,12,24).

Cyclic voltammetry was conducted in a fused quartz cell, 52 mm ϕ. The stainless steel cap had 7 fittings, 2 gas ports, and one 3/8" O.D. tube which accessed the cell by means of a 3/8" valve. The fittings were used for a thermocouple, a reference electrode, cathode and anode for pre-electrolysis, and for voltammetry a counter electrode and two working electrodes. The valved tube allowed melt composition to be regulated and sampled as well as the introduction of a new electrode, all without interruption of the experiment.

The preparation of anhydrous salts for electrolyte formulation has been described previously (12).

In a typical experiment, the cell was charged with salt and assembled with the cap and electrodes in the glove box. The charged cell was placed in an electrical resistance furnace with windows (12), and the salt was melted under high purity argon.

For pre-electrolysis, a platinum plate, 4 mm x 8 mm, and a glassy carbon rod, 1/8" ϕ, served as cathode and anode, respectively. For the working electrode, each of silver, gold, glassy carbon, tungsten, titanium diboride, and platinum was employed. The reference electrode was a silver wire immersed in a solution of AgCl (5 weight percent) in the appropriate supporting electrolyte: for magnesium electrolysis, $CaCl_2$-KCl-NaCl in the ratio of 6:18:65 by weight, and for aluminum electrolysis, NaCl-LiCl in the ratio of 50:40 by weight.

Cyclic voltammetry was conducted with an EG&G PARC Model 173 potentiostat/galvanostat and Model 175 universal programmer. Slow scan responses were recorded on an X-Y recorder, while fast scan responses were recorded on a digital computer.

RESULTS AND DISCUSSION

Figure 1 shows the Raman spectrum of aluminum chloride in its supporting electrolyte at a temperature of 700°C. Excitation was caused by radiation of wavelength, $\lambda = 514.5$ nm. Four distinct peaks have been identified: 125 cm^{-1}, 183 cm^{-1}, 349 cm^{-1}, and 483 cm^{-1}. The peak at 349 cm^{-1} is polarized; the others are depolarized. Such a pattern of peaks is indicative of tetrahedral coordination and suggests the presence of the tetrachloroaluminate complex, $AlCl_4^-$.

Figure 2 shows the Raman spectrum of magnesium chloride in its supporting electrolyte at a temperature of 750°C. Excitation was caused by radiation of wavelength, $\lambda = 514.5$ nm. Four distinct peaks have been identified: 107 cm^{-1}, 142 cm^{-1}, 249 cm^{-1}, and 351 cm^{-1}. The peak at 249 cm^{-1} is polarized; the others are depolarized. As was the case above with the aluminum chloride system, such a pattern is indicative of tetrahedral coordination and suggests the presence of the tetrachloromagnesate complex, $MgCl_4^{2-}$.

Figure 3 shows a cyclic voltammogram for the deposition of aluminum on gold at 700°C from a melt containing 1.5 wt % $AlCl_3$ in NaCl-LiCl in the ratio of 50:40 by weight. The reference electrode was silver wire immersed in a melt of AgCl-NaCl-LiCl (5:53:42 by weight). The counter electrode was glassy carbon. The area of the working electrode was 0.173 cm^2. The scan rate was 0.05 V s^{-1}. In Figure 3 the reduction and oxidation peaks are clearly evident and are separated by 56 mV which is close to the theoretical value of 62 mV for a simple reversible 3-electron reduction process (25). However, the ratio of the anodic peak current to the cathodic peak current is much greater than unity, so the process cannot be considered strictly reversible. The peak potentials did not change with scan rate. Thus, the reduction process of aluminum on gold appears to be quasi-reversible.

Figure 4 shows a cyclic voltammogram for the deposition of magnesium on silver at 800°C from a melt containing 2 wt % $MgCl_2$ in $CaCl_2$-KCl-NaCl in the ratio of 6:18:65 by weight. The scan rate was 0.4 V s^{-1}, and the area of the working electrode was 0.08 cm^2. The well defined trace shows clearly the reduction and oxidation processes. The residual current was extremely low and did not decrease with pre-electrolysis. The value of the potential difference between peak potentials for the cathodic and reoxidation processes is greater than would be expected for a simple reversible process (25). The scan rate had essentially no effect on the peak potential: if anything, both peaks seem to shift very slightly in the cathodic direction as scan rate increases.

For both the aluminum and the magnesium studies the cathodic peak current is linear in the square root of scan rate: over the range of experiments conducted in the present cell configuration, the current was mass transfer controlled by diffusion.

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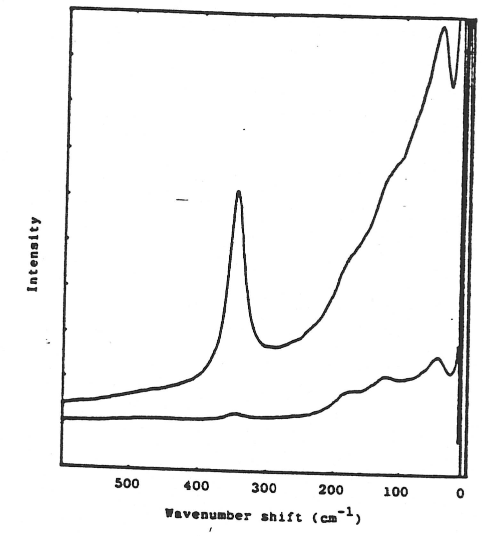

Figure 1. Raman spectrum of 10 wt % $AlCl_3$ - 40 wt % LiCl - 50 wt % NaCl. T = 700°C. $\lambda = 514.5$ nm.

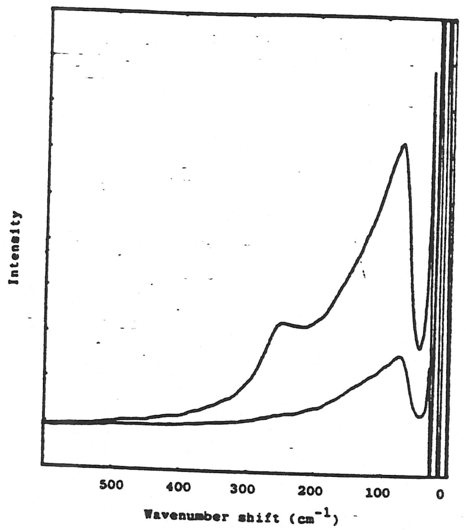

Figure 2. Raman spectrum of 11 wt % $MgCl_2$ - 6 wt % $CaCl_2$ - 18 wt % KCl - 65 wt % NaCl. T = 760°C. $\lambda = 514.5$ nm.

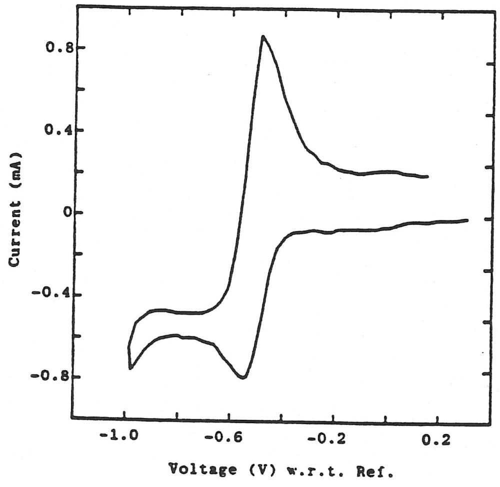

Figure 3. Cyclic voltammogram of 1.5 wt % $AlCl_3$ in LiCl - NaCl in a weight ratio 40:50. Working electrode: gold. Area: 0.173 cm^2. T = 700°C. Scan rate: 0.05 V s^{-1}.

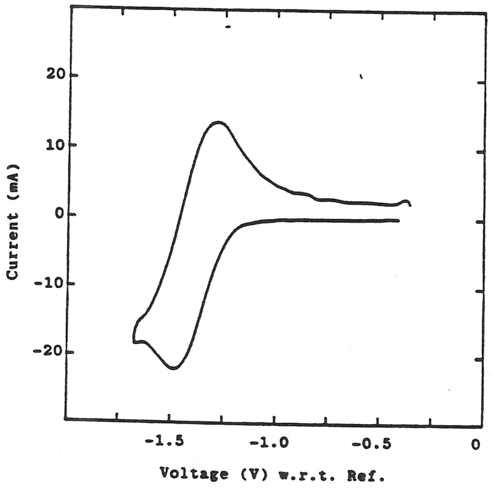

Figure 4. Cyclic voltammogram of 2.2 wt % $MgCl_2$ in $CaCl_2$ - KCl - NaCl in a weight ratio 6:18:65. Working electrode: silver. Area: 0.08 cm^2. T = 750°C. Scan rate: 0.4 V s^{-1}.