

IN SITU RAMAN SPECTROSCOPIC INVESTIGATION OF MELT CHEMISTRY AND
ELECTRODE PROCESSES IN LABORATORY-SCALE ALUMINUM CELLS

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As part of a study of the causes of loss of current efficiency in industrial aluminum cells, the characteristics of laboratory-scale cells are being investigated by electrochemical and spectroscopic techniques. Specifically, to determine the factors that control the concentrations and spatial distributions of the various chemical species in both aluminum chloride and "Hall" cells, Raman spectra are taken in situ during electrolysis. Aluminum chloride cells with an electrolyte consisting of 5% AlCl_3 , 53% NaCl , 42% LiCl have been operated at current densities up to 2 A/cm^2 . Spectral information from all identifiable species is correlated with cell operating conditions in an attempt to understand the nature of such phenomena as metal fog, streamers, melt coloration and anode effect, all of which are observed in these laboratory-scale cells.

Introduction

It is somewhat ironic that the least dense structural metals, which can reduce net energy consumption when used as materials of vehicular construction, are among the most energy-intensive metals to produce. The production of primary aluminum is estimated to have consumed 2.6% of the total generated electrical energy in the United States during 1984 [1].

Virtually all aluminum is extracted in Hall-Héroult cells by the electrolysis of alumina dissolved in cryolite. Energy consumption is approximately 16 kWh/kg of aluminum metal. Current efficiency exceeds 90%; however, voltage efficiency, i.e., the ratio of decomposition potential to cell voltage, is closer to 30% [2]. The commercial production of aluminum by the electrolysis of aluminum chloride was developed by Alcoa in the 1970's; this process (the Alcoa Smelting Process) is reported to consume 30% less energy than Hall-cell based technology [2,3].

As part of a study of the causes of loss of current efficiency, Raman spectra of laboratory-scale aluminum chloride electrolysis cells are being measured. Commercially available laser Raman scattering instrumentation has been adapted to permit in situ real time investigation of melt chemistry and to provide the basis for "fast Raman" spectroelectrochemistry in this and other melt systems, notably cryolite. The results of the Raman work are combined with those of other techniques in order to reveal the mechanisms and kinetic pathways that decrease current efficiency in aluminum cells. This paper reports some of the Raman data for the electrolysis of aluminum chloride. As well, preliminary results are reported for cryolite melts not undergoing electrolysis.

Literature

Reasons for the loss of current efficiency are discussed by Grjotheim et al. [4]. Of particular concern to Raman studies is information on melt structure. Aluminum does not exist as a discrete cation in these melts. In chloride melts aluminum forms chlorocomplexes, predominantly AlCl_4 at industrial compositions [5-9]. In cryolite melts aluminum forms a variety of fluoro-complexes and oxyfluorocomplexes, principally AlF_6 and AlF_4 at industrial compositions [10-13]. In some of the studies cited, Raman spectra of these or closely related melts were measured. However, the purpose of these studies was to determine the structure of molten salts, not to understand the electrolytic production of aluminum. As a consequence, melt spectra were not taken during electrolysis, nor were they taken of melts resembling industrial compositions.

Experimental

A detailed description of the instrumentation is given in previous reports [14,15]. Very briefly, a monochromatic linearly polarized laser beam from either an Ar^+ laser (Coherent Innova 90-4) or Kr^+ laser (Coherent Innova 90-K) irradiates the electrolysis cell, which is held inside a specially designed furnace. The scattered light is focused onto the entrance slit of

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the spectrometer (Spex Industries Triplemate 1403). An intensified silicon photodiode array (EG&G PARC Model 1420-3) serves as detector. The amplified signal is digitized in the detector controller (EG&G PARC Model 1218) and transmitted as data to the optical multichannel analyzer (EG&G PARC, OMA, Model 1215).

The polarization state of the exciting radiation is set by a polarization rotator (\perp I or \parallel I). The beam then passes horizontally through the electrolysis cell. The scattered radiation is collected at 90° and is imaged onto the vertical polarization analyzer (I always). The spectrometer slit width is $100 \mu\text{m}$, equivalent to $\sim 6 \text{ cm}^{-1}$. Typically, the spectra were recorded for approximately 1 minute, corresponding to 200 scans on the OMA, which was calibrated using the emission lines of a neon lamp in the green. Spectra reported in this article were obtained using either the 514.5 nm or the 488.0 nm line of Ar^+ as exciting radiation.

The aluminum chloride electrolysis cell is constructed of optical grade square fused quartz tubing, 1" on the inside edge, joined to round tubing 41 mm OD. The cap is a compression fitting made of 304 stainless steel with ports for the cathode, anode, inert gas inlet, and thermocouple. The cap also has a sidearm for gas outlet. The anode is made of high-density graphite rod, $1/8$ " diameter, usually shrouded by a $3/8$ " dia. fused quartz tube. The cathode is high-density graphite rod, $1/8$ " dia., usually shrouded by a $3/8$ " dia. alumina tube. TiB_2 single crystal cathodes, 1 mm dia., and high-density polycrystalline TiB_2 cathodes have been used.

The preparation of anhydrous salts for the formulation of chloride electrolytes has been described previously [11].

In a typical electrolysis experiment the cell is charged with salt and assembled with the cap and electrodes in the glove box. The charged cell is placed in the electrical resistance furnace with windows [14], and the salt is melted under high purity argon.

A special cell has been designed and constructed for spectral studies of molten cryolite: a single crystal of sapphire in the shape of a tube, $1/2$ " ID and closed at one end. The cell cap is a compression fitting made of 304 stainless steel with ports for inert gas inlet and thermocouple. The cap also has a sidearm for gas outlet. With minor adaptation it is possible to conduct electrolysis in this cell.

Salt preparation consisted of heating pure Greenland cryolite in a vacuum to a temperature of 400°C for 24 hours.

Results and Discussion

Figure 1 shows Raman spectra of 55% NaCl - 45% LiCl taken at 700°C . This melt is the

supporting electrolyte in the Alcoa Smelting Process. There are no "peaks" like those seen in a spectrum such as that of CCl_4 [16]. However, the featureless traces in Figure 1 derive from inelastic scattering and are proper Raman spectra. All chloride spectra reported in this article were taken using the 514.5 nm line of Ar^+ .

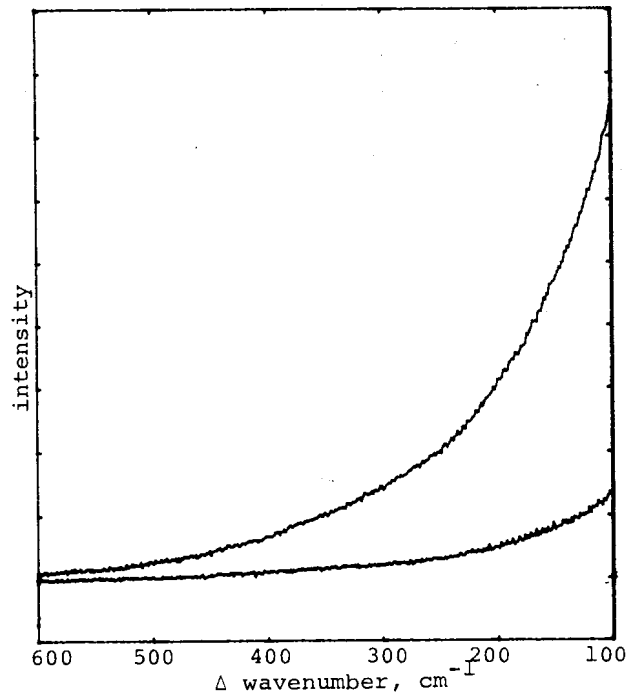


Figure 1. Raman Spectra of 55% NaCl -45% LiCl at 700°C (514.5 nm excitation).

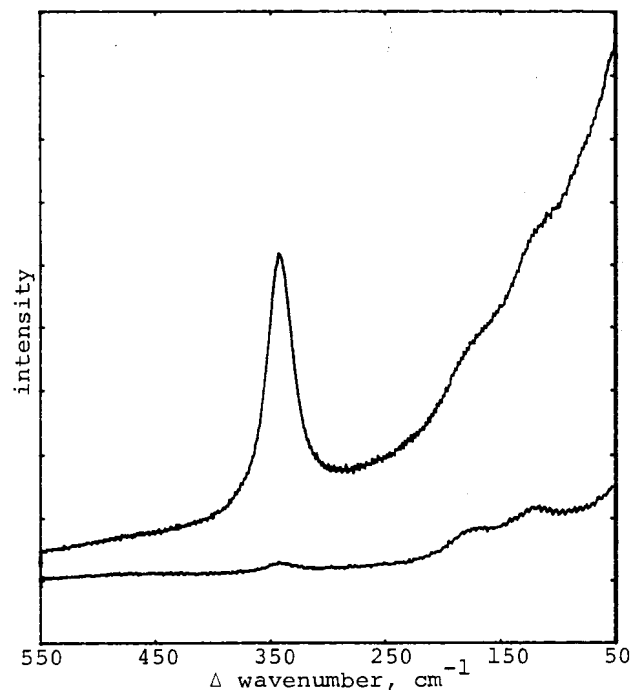


Figure 2. Raman spectra of 10% AlCl_3 -50% NaCl -40% LiCl at 610°C (514.5 nm excitation).

Because AlCl_3 at 1 atm. pressure sublimates at 182°C without melting, Raman spectra of pure molten AlCl_3 cannot be obtained. Fig. 2 shows Raman spectra of a melt representative of industrial composition (10% AlCl_3 - 50% NaCl - 40% LiCl) taken at a temperature of 610°C before electrolysis.

These spectra show four distinct peaks, at 121 cm^{-1} , 177 cm^{-1} , 349 cm^{-1} and 485 cm^{-1} . The peak at 349 cm^{-1} is polarized, the others are not. These spectra look like those of CCl_4 [16] in that there are four peaks, the strongest one of them polarized. On this basis, the Raman spectra are evidence of the fact that aluminum coordinates with four chlorines to form a tetrahedrally coordinated tetrachloroaluminate ion, AlCl_4^- .

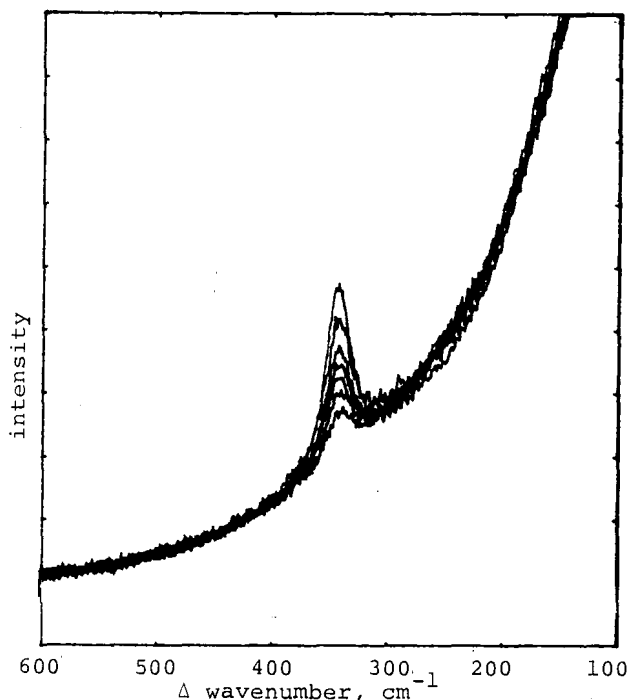


Figure 3. Raman spectra of 10% AlCl_3 -50% NaCl -40% LiCl during electrolysis. $T=620^\circ\text{C}$. Current density=100 mA/cm^2 . Successive traces every 250 Coulombs (514.5 excitation).

Figure 3 shows spectra taken during electrolysis of aluminum chloride at 620°C . Successive traces are separated by 250 coulombs. The spectral sample volume was located in the bulk electrolyte near the graphite cathode. The observed decrease in peak height of the line at 349 cm^{-1} is not due exclusively to the decrease in AlCl_3 concentration but rather includes the effects of AlCl_3 vaporization. Furthermore, during electrolysis, small white particles emanate from the cathode and block the incident and scattered light. Efforts are presently underway to use transmitted power data along with more elaborate data reduction techniques to separate these various effects to allow quantitative spectral analysis of AlCl_3 concentration in the electrolyte in real time as electrolysis proceeds.

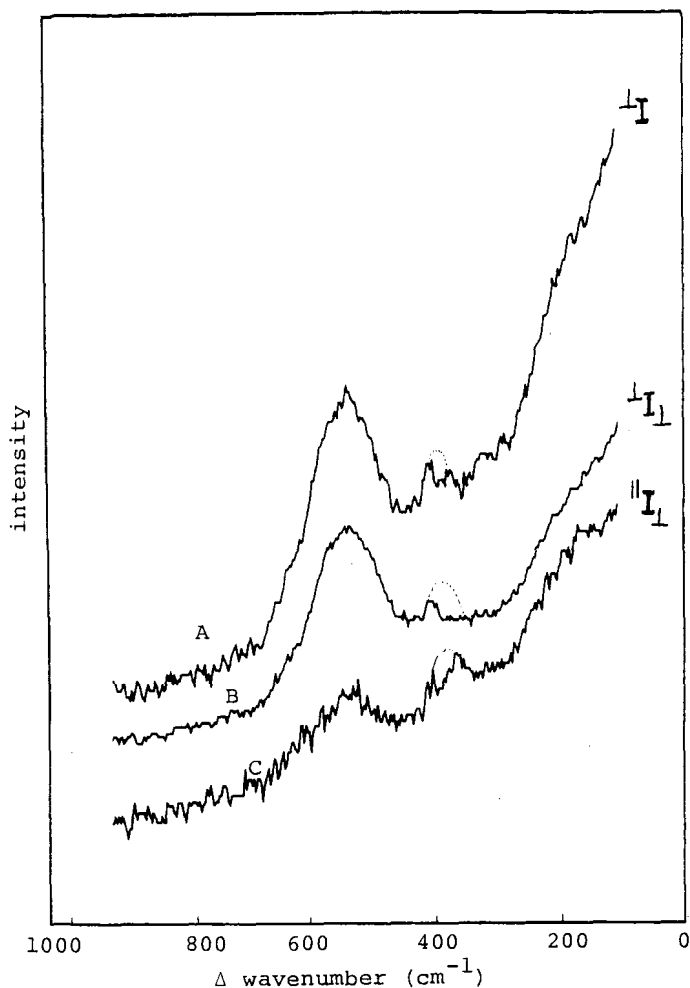


Figure 4. Raman spectra of Greenland cryolite at 1015°C (488.0 nm excitation).

Figure 4 shows the Raman spectra of cryolite taken at 1015°C using the 488.0 nm line of Ar^+ as exciting radiation. The different traces represent results for different polarization settings of incident radiation and analyzer. The uppermost curve was recorded without the polarization analyzer (\perp).

While these results are preliminary, it is evident that there is a strong polarized peak at 535 cm^{-1} and a weak depolarized peak at 390 cm^{-1} . This is in agreement with the data of Gilbert, Mamantov, and Begun, who explained this in terms of the presence of AlF_6^{3-} species [13]. The shoulder at about 625 cm^{-1} suggests dissociation of AlF_6^- into AlF_4^- for which this is the dominant peak [12].

Conclusions

Some preliminary results of Raman scattering studies of laboratory-scale aluminum chloride electrolysis cells have been presented. Metal fog, streamers, and melt coloration are all observed in these cells, which are operated at current

densities of up to 2 A/cm^2 . It appears that it should be possible to measure the concentration of AlCl_3 in the electrolyte as a function of time by Raman spectroscopy. Efforts are under way to improve the spatial resolution of the system to permit the measurement of electrolyte concentration profiles during electrolysis.

The preliminary results of Raman spectra of molten cryolite taken in sapphire cells are encouraging. However, it still remains to be demonstrated that this technique can be used to measure electrolyte composition during electrolysis in such melts.

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