

## RAMAN SCATTERING STUDIES OF MAGNESIUM ELECTROLYSIS

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As part of a study of the causes of the loss of current efficiency in industrial magnesium 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 the cell, Raman spectra are taken *in situ* during electrolysis. The electrolyte consists of 11%  $\text{MgCl}_2$ , 65%  $\text{NaCl}$ , 18%  $\text{KCl}$ , and 6%  $\text{CaCl}_2$ . Cells operate at a temperature of  $750^\circ\text{C}$  and current densities up to  $2\text{ A/cm}^2$ . 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, and melt coloration, all of which are observed in these laboratory-scale cells.

### 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 2.8% of total generated electric power in the United States during the Year 1984[1]. 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. Thus, research efforts are directed at reducing the energy requirements of these extraction processes.

The electrolytic production of magnesium accounts for about 70% of the total magnesium production in the Western world[2]. Magnesium production by electrolysis requires 15 - 18 kWh/kg of magnesium metal. The current efficiency of the anhydrous electrolytic process (I.G. Farben - Norsk Hydro) exceeds 90%, while that of hydrous electrolytic process (Dow Chemical) is close to 80%[3].

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As part of a study of the causes of loss of current efficiency, Raman spectra of laboratory-scale magnesium 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. 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 magnesium cells. This paper reports some preliminary Raman data for the electrolysis of anhydrous magnesium chloride.

### Literature

Reasons for the loss of current efficiency are discussed in a recent review of the chemistry and electrochemistry of magnesium production[4]. More information is given in the monograph by Strelets[5]. Of particular concern to the Raman work is information on melt structure: magnesium does not exist as a discrete cation in chloride melts but instead in the form of the chlorocomplex,  $\text{MgCl}_4^{2-}$ [6-8]. Vibrational spectra confirm this[9-13]. However, the purpose of these studies was to determine the structure of molten salts, not to understand the electrolytic production of magnesium. 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  $\text{Ar}^+$  laser (Coherent Innova 90-4) or  $\text{Kr}^+$  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 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  $90^\circ$  and is imaged onto the vertical polarization analyzer ( $I_\perp$  always). The spectrometer slit width is  $100\text{ }\mu\text{m}$ , 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. All spectra reported in this article were obtained using the  $514.5\text{ nm}$  line of argon as exciting radiation.

The electrolysis cell is constructed of optical-grade square fused quartz tubing,  $1''$  on inside edge, joined to round tubing  $41\text{ mm}$  O.D. The cap is a compression fitting made of 304 stainless steel and has 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,  $1/8''$  dia., usually shrouded by a fused quartz tube,  $3/8''$  dia. For the cathode, mild steel,  $1/4''$  dia.,  $\text{TiB}_2$  single crystal,  $1\text{ mm}$  dia., or high-density graphite rod,  $1/8''$  dia., shrouded by an alumina tube,  $3/8''$  dia., have all been used.

The preparation of anhydrous salts for electrolyte formulation has been described previously[14].

In a typical experiment, the electrolysis 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.

### Results and Discussion

Figure 1 shows Raman spectra of pure molten  $\text{MgCl}_2$  at  $740^\circ\text{C}$ . There is a strong polarized peak at  $205\text{ cm}^{-1}$  and a weak depolarized peak at  $385\text{ cm}^{-1}$ . These results are essentially identical to those of Huang and Brooker[10]. The difference is that it took the authors of this report only 4 minutes using the OMA to measure these spectra which Huang and Brooker recorded for several hours. This shows the speed, accuracy, and sensitivity of the adapted instrumentation to be satisfactory.

Figure 2 shows Raman spectra of the melt, 78%  $\text{NaCl}$  and 22%  $\text{KCl}$ , at a temperature of  $840^\circ\text{C}$ . There are no "peaks" like those seen in Figure 1. However, the featureless traces in Figure 2 derive from inelastic scattering and are proper Raman spectra.

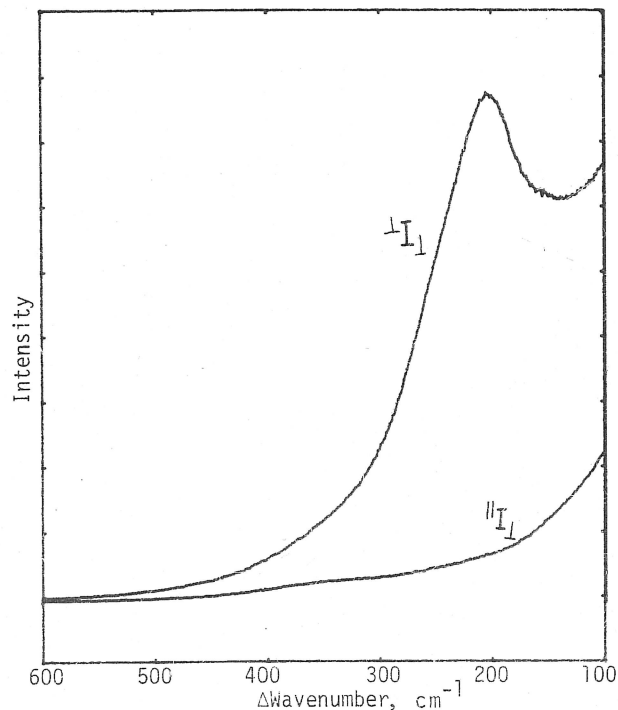


Fig.1 Raman spectra of molten magnesium chloride at  $740^\circ\text{C}$ .

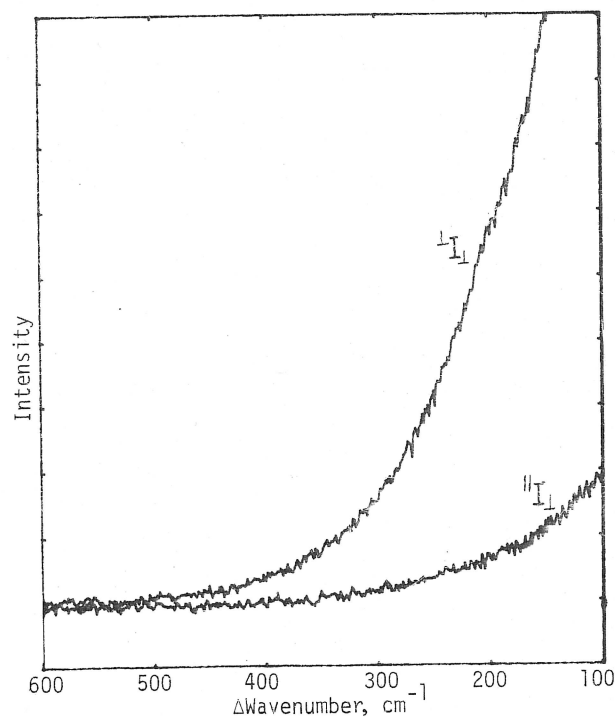


Fig.2 Raman spectra of molten 78w/o  $\text{NaCl}$  - 22w/o  $\text{KCl}$  at  $840^\circ\text{C}$ .

Figure 3 shows Raman spectra of the supporting electrolyte, 7%  $\text{CaCl}_2$ , 20%  $\text{KCl}$ , and 73%  $\text{NaCl}$ , taken at a temperature of  $850^\circ\text{C}$ . Somewhat surprisingly, the addition of  $\text{CaCl}_2$  to the alkali chloride melt did not give rise to any distinct peaks. It was hoped that one or more such peaks could be used as a standard for calibrating composition during electrolysis experiments. The  $\text{CaCl}_2$  content is not expected to change while magnesium is produced.

Figure 4 shows Raman spectra of a melt representative of industrial composition (11%  $\text{MgCl}_2$ , 6%  $\text{CaCl}_2$ , 65%  $\text{NaCl}$ , 18%  $\text{KCl}$ ) taken at a temperature of  $750^\circ\text{C}$  in the absence of current. The prominent polarized peak at  $205\text{ cm}^{-1}$  in pure  $\text{MgCl}_2$  has shifted to  $249\text{ cm}^{-1}$ . During electrolysis there was a decrease in peak height without change in wavenumber for the peak at  $249\text{ cm}^{-1}$ .

Figure 5(a) shows a photograph of the cell taken after 1 minute of electrolysis at a current density of  $100\text{ mA/cm}^2$ . The composition of the electrolyte was 11%  $\text{MgCl}_2$ , 6%  $\text{CaCl}_2$ , and 18%  $\text{KCl}$ . Temperature was  $750^\circ\text{C}$ . On the left is a  $1/4$ " graphite cathode; on the right is a  $1/8$ " graphite anode shrouded with fused quartz tubing. Streamers have begun to emanate from the cathode. Chlorine gas bubbles can be seen on the anode. Figure 5(b) shows the same cell as Figure 5(a) after approximately 5 minutes of electrolysis at a current density of  $100\text{ mA/cm}^2$ . It is evident that the streamers emanating from the cathode have grown over essentially the entire breadth of the cell. The electrolyte has become cloudy. Figure

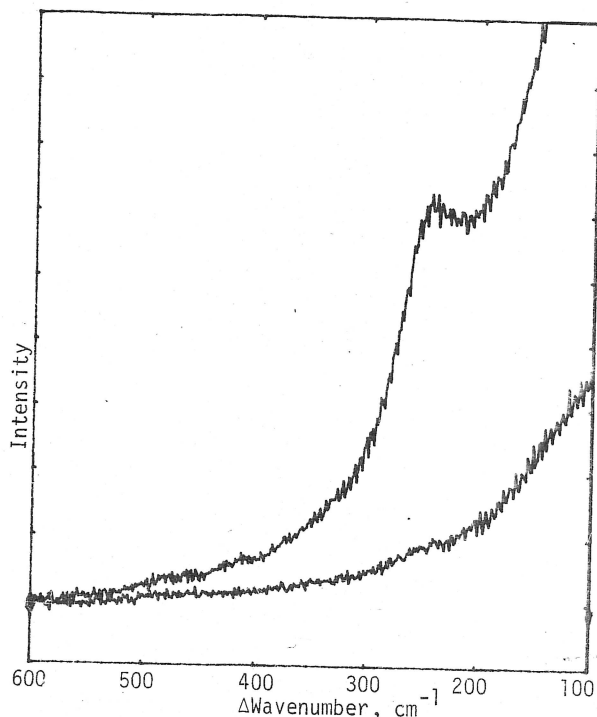


Fig.4 Raman spectra of molten 11w/o  $\text{MgCl}_2$  - 6w/o  $\text{CaCl}_2$  - 65w/o  $\text{NaCl}$  - 18w/o  $\text{KCl}$  at  $750^\circ\text{C}$ .

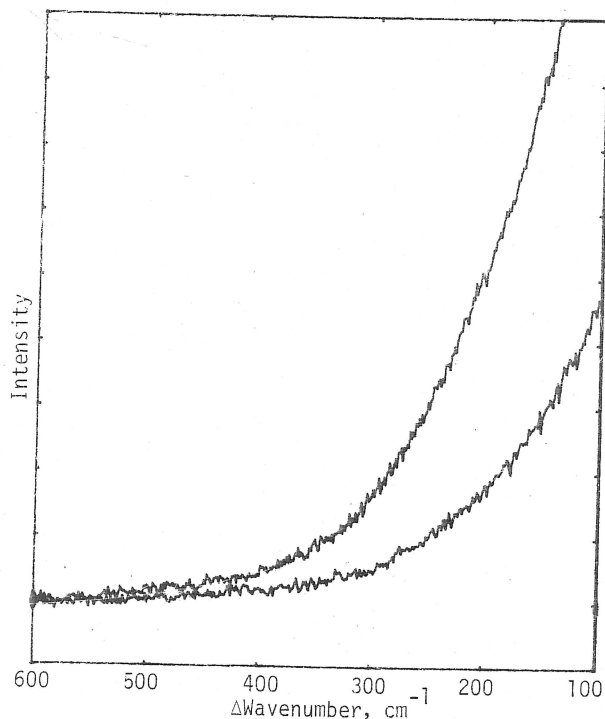


Fig.3 Raman spectra of molten 7w/o  $\text{CaCl}_2$  - 20w/o  $\text{KCl}$  - 73 w/o  $\text{NaCl}$  at  $850^\circ\text{C}$ .

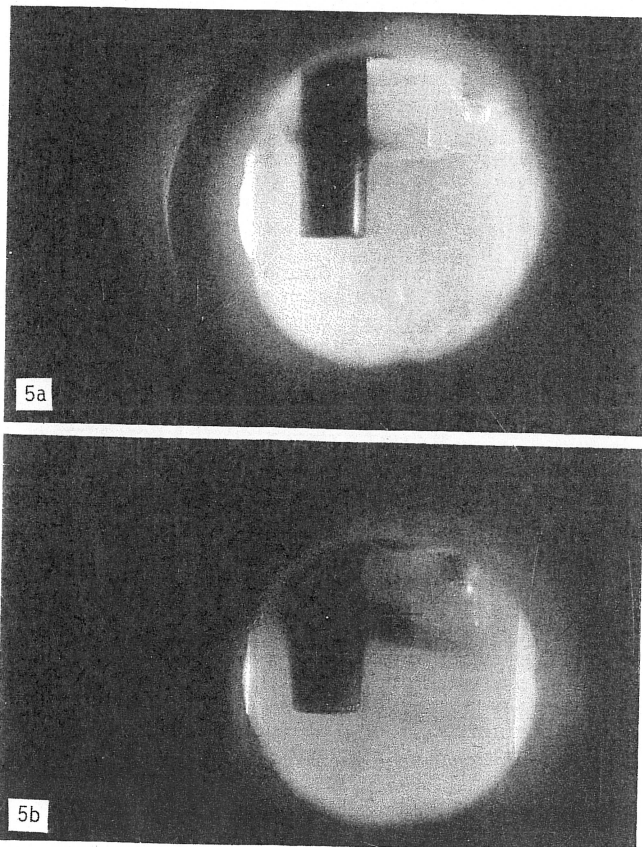


Fig.5 Streamer development in a laboratory-scale magnesium electrolysis cell. Electrolyte: 11w/o  $\text{MgCl}_2$  - 6w/o  $\text{CaCl}_2$  - 65w/o  $\text{NaCl}$  - 18w/o  $\text{KCl}$ .  $T = 750^\circ\text{C}$ . Current density =  $100\text{ mA/cm}^2$ . (a) after 1 minute; (b) after 5 minutes.

5(b) also shows the appearance of tiny droplets of magnesium on the tip of the cathode. Chlorine bubbles are seen to continue evolving on the anode. Attempts to take Raman spectra of the streamers have failed. There is a good possibility that the streamers are not Raman active. Other techniques, both spectral and electrochemical, will be used to study streamers further.

#### Conclusion

Some preliminary results of Raman scattering studies of laboratory-scale magnesium 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<sup>2</sup>. On the basis of the Raman scattering data it appears that it should be possible to measure the concentration of MgCl<sub>2</sub> in the electrolyte as a function of time. Efforts are underway to improve the spatial resolution of the system to permit the measurement of electrolyte concentration profiles.

#### Acknowledgement

This material was prepared with the support of the U.S. Department of Energy (DOE) Grant No. DE-FG07-82-CE40545. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of DOE.

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