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# RAMAN SCATTERING STUDIES OF MOLTEN SALT ELECTROLYSIS OF LIGHT METALS

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The adaptation of laser Raman scattering instrumentation to permit in situ investigation of laboratory-scale magnesium chloride and aluminum chloride electrolysis cells is described. For the systems,  $\text{MgCl}_2\text{-CaCl}_2\text{-KCl-NaCl}$  and  $\text{AlCl}_3\text{-NaCl-LiCl}$ , melt spectra are reported as well as spectra taken during electrolysis.

## Introduction

Molten salt electrolysis is used in the extraction of light metals. This is a very energy-intensive process. Indeed, the electrometallurgical industries are estimated to consume 5 percent of the total generated electrical energy in this country (1). It is somewhat ironic that the least dense structural metals, which can reduce energy consumption when used as materials of construction in transportation vehicles, are the most energy-intensive metals to produce. Therefore, it is to decrease net energy utilization that efforts are being made to reduce 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 processes (I. G. Farben - Norsk Hydro) exceeds 90%, while that of the hydrous electrolytic process (Dow Chemical) is closer to 80% (3). Essentially all aluminum is extracted in Hall-Héroult cells by the electrolysis of alumina dissolved in cryolite. Energy consumption is 12 kWh/kg of aluminum metal, with current efficiency exceeding 90%. 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 (4,5).

"Metal fog" formation and coloration of the normally transparent electrolyte are both associated with loss of current efficiency (6,7,8). As well, multiplicity of valence can decrease current efficiency through so-called redox looping. Aluminum is reported to be both trivalent and monovalent in chloride melts (9).

As part of a study of the causes of loss of current efficiency, Raman spectra of laboratory-scale molten salt electrolysis cells are being measured. Raman spectroscopy has been chosen because it is generally acknowledged to be the most powerful technique available for the study of complexing ionic species (10). The purpose of this paper is to describe the adaptation of laser Raman scattering instrumentation to permit *in situ* real time analysis of melt chemistry and thereby provide the basis for "fast Raman" spectroelectrochemistry in these systems. Results are presented from the investigations of the electrolysis of anhydrous magnesium chloride and the electrolysis of aluminum chloride. Apart from their intrinsic value, these results are in support of future work on the much more difficult to handle cryolite-based system.

## Literature

Magnesium and aluminum do not exist as discrete ions in chloride melts; instead, they are thought to form the chlorocomplexes  $MgCl_4^{2-}$  and  $AlCl_4^-$ , respectively (11-16). Vibrational spectra confirm this, in particular the Raman spectra of  $MgCl_2$  or  $AlCl_3$  in alkali or alkaline earth chlorides (15-22). However, the purpose of these studies was to determine the structure of molten salts, not to understand the electrolytic production of light metals. As a consequence, melt spectra were not taken during electrolysis, nor were they taken of melts resembling industrial compositions.

## Experimental

### Instrumentation

The schematic diagram of the instrumentation is given in Fig. 1. A mono-

chromatic linearly polarized laser (Innova 90-4) or Kr lamps: mirrors to polarization state sample in the cell ed later. Electrode (EG&G PARC, Model 1) a coulometer (EG&G

Figure 1.

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chromatic linearly polarized laser beam from either an Ar<sup>+</sup> laser (Coherent Innova 90-4) or Kr<sup>+</sup> laser (Coherent Innova 90-K) passes the optical instruments: mirrors to change beam direction, a polarization rotator to change the polarization state, and a focusing lens. The focused beam irradiates the sample in the cell which is held inside a specially designed furnace described later. Electrolysis is conducted galvanostatically with a potentiostat (EG&G PARC, Model 173). The charge passed during electrolysis is measured by a coulometer (EG&G PARC, Model 179).

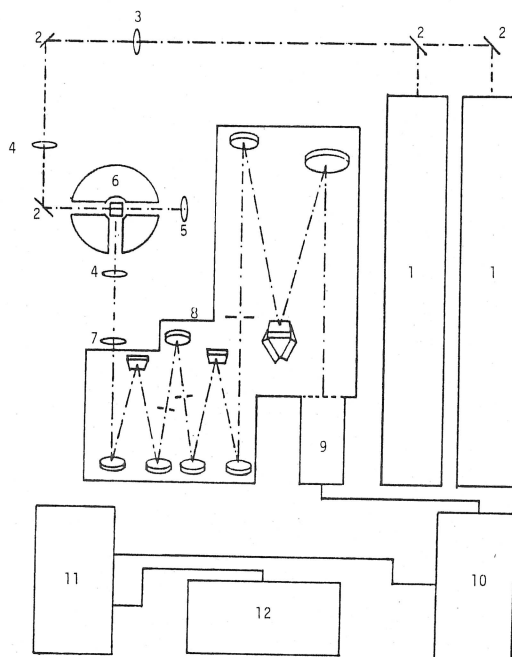


Figure 1. Schematic diagram of Raman instrumentation.

- (1) Lasers; (2) Mirrors; (3) Polarization rotator; (4) Lenses;
- (5) Power meter; (6) Furnace; (7) Polarization analyzer;
- (8) Spectrometer; (9) Detector; (10) Detector controller;
- (11) Optical multichannel analyzer (OMA); (12) Plotter

Most of the incident beam is transmitted unchanged and strikes a power meter (Newport Research, Model 185) which measures the transmitted power. The scattered beam is collected by a lens at 90° from the beam propagation direction, where the depolarization ratio can be most accurately measured (25).

The scattered light passes through a polarization analyzer and is focused onto the entrance slit of the spectrometer, which in this case is a triple monochromator (Spex Industries Triplemate 1403). In the spectrometer the beam is collimated, dispersed, and refocused onto an exit slit. At this stage much of the stray light is eliminated. The refocused light is again collimated and dispersed on the grating, which can be varied in order to change the resolution. The final mirror projects a flat image onto the focal plane, where it is seen by the detector, an intensified silicon photodiode array (EG&G PARC Model 1420-3). 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 plane of polarization of the exciting radiation is set by a polarization rotator ( $\perp I$  or  $\parallel I$ ). The beam then passes horizontally through the molten sample. The scattered radiation is collected at  $90^\circ$  and is imaged onto the vertical entrance slit of the spectrometer while passing through a 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. All spectra reported in this article were obtained using the  $514.5\ \text{nm}$  line of argon as exciting radiation.

Furnace. Specimens were heated by a method somewhat different from those previously employed in spectroscopic studies. This was due to the need to accommodate the laboratory-scale electrolysis cells, which are quite large compared to spectrocells commonly employed in such work. Specifically, an electrical resistance tube furnace was designed and built (Figure 2). It con-

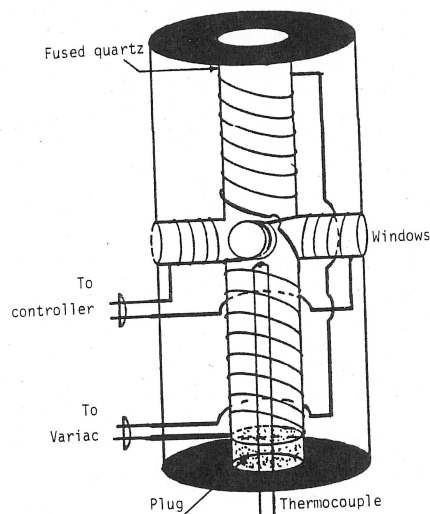


Figure 2. Furnace for Raman Scattering Studies of Molten Salt Electrolysis.

sisted of nichrome wire wrapped around a vertical fused quartz tube,  $5.1\ \text{cm}$  in diameter  $\times$   $30\ \text{cm}$  long, contained in a can packed with aluminosilicate insulating fiber. To permit irradiation and observation of the sample in the furnace, three sidearm tubes were connected to the vertical tube to serve as windows. Located in the same horizontal plane and in a tee configuration, the sidearms were heated by independently-controlled nichrome windings to maintain a constant temperature in the sample. The maximum operating temperature of this furnace was  $1273\ \text{K}$ .

Electrolysis cell. The cell is made of optical grade square fused quartz tubing,  $1\ \text{in}$  on edge, joined to round tubing  $41\ \text{mm}$  O.D. (Figure 3). 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  $1/8\ \text{in}$  dia. high density graphite rod shrouded by a  $1/4\ \text{in}$  fused quartz tube. For the cathode,  $1/4\ \text{in}$  mild steel or  $\text{TiB}_2$  for magnesium, or graphite,  $\text{TiB}_2$ , or liquid metal for aluminum, are used.

Figure 3. Spectrocell

#### Salt Preparation

For the magnesium KCl, NaCl, and  $\text{CaCl}_2$

For anhydrous Mg argon-atmosphere glove which was dried under vacuum for 8 h. The temperature is then increased and the tube is left for 8 h and deposits on the  $\text{MgCl}_2$  is removed in it is heated slowly  $\text{NH}_4\text{Cl}$  and water. At over the salt for 2 this,  $\text{MgCl}_2$  is sublimed.

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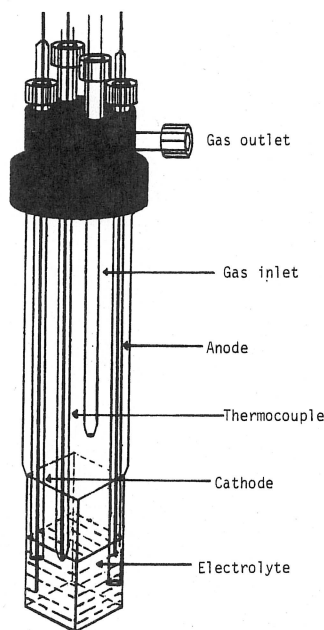


Figure 3. Spectrocell for Raman Scattering Studies of Molten Salt Electrolysis.

#### Salt Preparation

For the magnesium experiments the necessary salts are anhydrous  $\text{MgCl}_2$ ,  $\text{KCl}$ ,  $\text{NaCl}$ , and  $\text{CaCl}_2$ .

For anhydrous  $\text{MgCl}_2$ , the starting material is  $\text{NH}_4\text{Cl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . In the argon-atmosphere glove box the salt is charged into the fused quartz tube which was dried under vacuum at  $750^\circ\text{C}$ . The charged tube is heated to  $175 \pm 5^\circ\text{C}$  under vacuum for 8 hours. At this stage the moisture is removed. The temperature is then increased to  $340^\circ\text{C}$  very slowly ( $30^\circ\text{C}$  every two hours), and the tube is left for 8 hours at this temperature. At this stage  $\text{NH}_4\text{Cl}$  vaporizes and deposits on the wall of the upper part of the tube. The remaining powdery  $\text{MgCl}_2$  is removed in the glove box and transferred to another reactor in which it is heated slowly to  $550^\circ\text{C}$  ( $100^\circ\text{C}$  every 2 hours) to remove the remaining  $\text{NH}_4\text{Cl}$  and water. At this temperature, Ar gas bubbled through  $\text{SOCl}_2$  is passed over the salt for 24 hours to remove any oxides or hydroxychlorides. After this,  $\text{MgCl}_2$  is sublimed and deposits on the wall of the tube.

The preparation of  $\text{KCl}$ ,  $\text{NaCl}$ , and  $\text{CaCl}_2$  is simpler. The salt is dried under vacuum at  $150^\circ\text{C}$ ,  $300^\circ\text{C}$ , and  $500^\circ\text{C}$  for 5 hours at each temperature. The argon gas bubbled through  $\text{SOCl}_2$  is passed for 24 hours at  $550^\circ\text{C}$ . The salt, except for  $\text{CaCl}_2$ , is then sublimed at  $770^\circ\text{C}$ .  $\text{CaCl}_2$  has too low a vapor pressure for this procedure, so this last step is omitted and instead  $\text{SOCl}_2$  is passed for another 24 hours.

The necessary salts for  $\text{AlCl}_3$  electrolysis are  $\text{AlCl}_3$ ,  $\text{NaCl}$ , and  $\text{LiCl}$ .  $\text{AlCl}_3$  is very hygroscopic, subliming at a very low temperature ( $182^\circ\text{C}$ ). Analytical grade  $\text{AlCl}_3$  is sublimed 5 times under vacuum at  $170^\circ\text{C}$ . In the

glove box, this salt is then charged into a tube which was dried at 700°C. At 100°C, argon gas bubbled through  $\text{SOCl}_2$  is passed over the salt for 24 hours, and then the  $\text{AlCl}_3$  is sublimed under  $\text{SOCl}_2$  at 150°C. The salt is again sublimed under vacuum at 180°C without passing  $\text{SOCl}_2$ .

The procedure for  $\text{LiCl}$  purification is the same as that for  $\text{NaCl}$  or  $\text{KCl}$ .

#### Typical Experiment

The electrolytic cell is charged and assembled with the cap and electrodes in the glove box. The charged cell is placed in the furnace and the salt is melted under high purity argon.

#### Results and Discussion

Raman spectra measured for pure molten  $\text{MgCl}_2$  at 740°C in this laboratory (Figure 4) are essentially identical to those of C.-H. Huang and M. H. Brook-er (18).

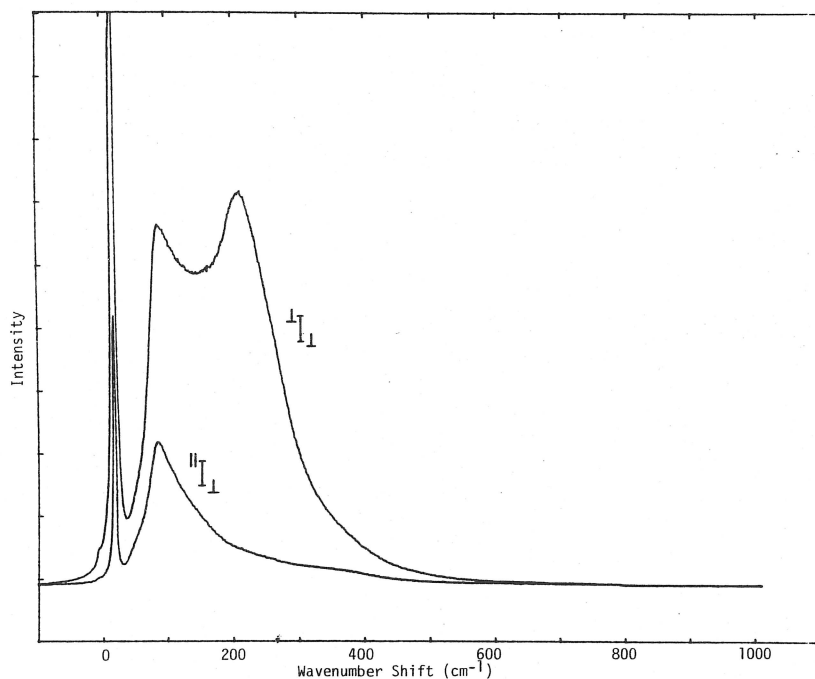


Figure 4. Raman spectra of pure molten  $\text{MgCl}_2$ .

The Raman spectra of molten  $\text{MgCl}_2$  in the industrial electrolyte (11%  $\text{MgCl}_2$ , 6%  $\text{CaCl}_2$ , 65%  $\text{NaCl}$ , 18%  $\text{KCl}$ ) show a peak shift (Figure 5). The peak shifted from 205  $\text{cm}^{-1}$  in pure molten  $\text{MgCl}_2$  to 249  $\text{cm}^{-1}$  in the industrial electrolyte.

Figure 6 shows the Raman spectra taken during electrolysis. There is a decrease in peak height without a change in wavenumber for the peak at 249  $\text{cm}^{-1}$ .

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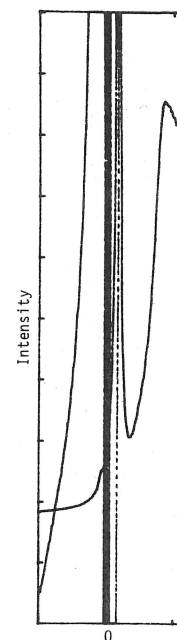


Figure 5. Raman spectra showing a peak shift.

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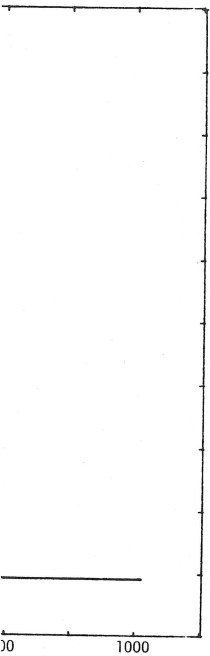
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Since the melts become milky due to fine scattering particles and colored from the apparently dissolved chlorine, the decrease in peak height cannot be said to be due to electrolysis only. A TiB<sub>2</sub> cathode instead of the mild steel cathode was tried, but the same was observed.

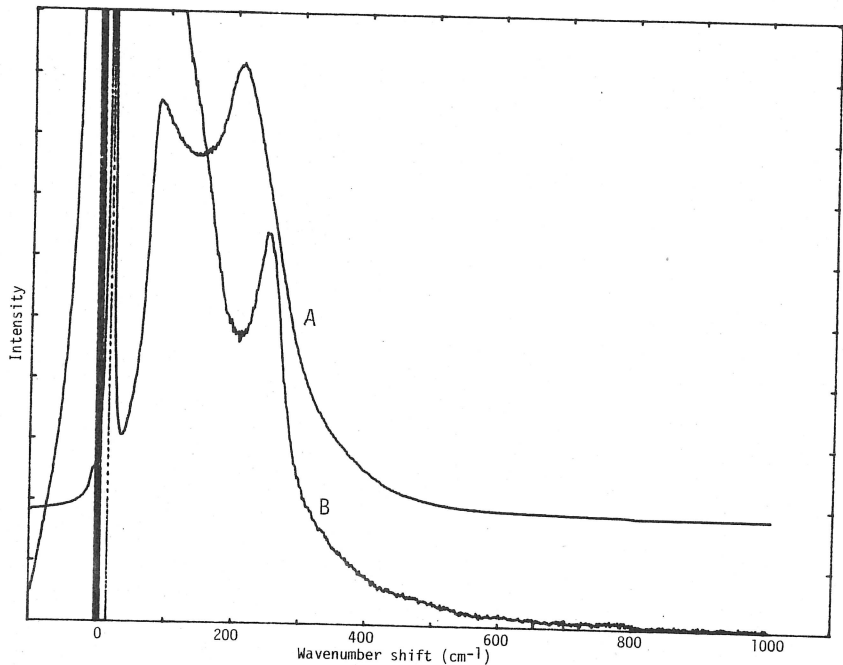


Figure 5. Raman spectra of MgCl<sub>2</sub> in pure molten state (A) and in industrial electrolyte (B).

Because AlCl<sub>3</sub> sublimes without melting at 182°C, Raman spectra of pure molten AlCl<sub>3</sub> cannot be obtained. The spectra for NaCl-LiCl melts do not show any peaks (Figure 7). Before electrolysis, the spectra for AlCl<sub>3</sub> in the NaCl-LiCl melt were taken at 610°C (Figure 8). These spectra show four distinct peaks, at 121 cm<sup>-1</sup>, 177 cm<sup>-1</sup>, 349 cm<sup>-1</sup>, and 485 cm<sup>-1</sup>. The peak at 349 cm<sup>-1</sup> is polarized, the others are not. These spectra look like those of CCl<sub>4</sub> (26) in that there are four peaks, one of them is polarized, and the others are not. By comparison, the conclusion is that aluminum coordinates with four chlorines to form a tetrahedrally coordinated tetrachloroaluminate ion, AlCl<sub>4</sub><sup>-</sup>.

In order to compare the peak height at different compositions and test the sensitivity of Raman spectroscopic instruments at reduced concentration, Raman spectra were taken of 10% and 1% AlCl<sub>3</sub> in equimolar compositions of NaCl-LiCl (Figure 9).

Figure 10 shows the spectra during electrolysis at 620°C taken at every 250 coulombs at the same position, near the graphite cathode. The peaks decrease in height with time. Because AlCl<sub>3</sub> vaporizes and white particles emanating from the cathode block the incident and scattered beams, this decrease cannot be attributed only to electrolysis. However, with the use of transmitted power figures and more elaborate data reduction techniques, it should be possible to separate these effects to permit the determination of aluminum concentration in the electrolyte.

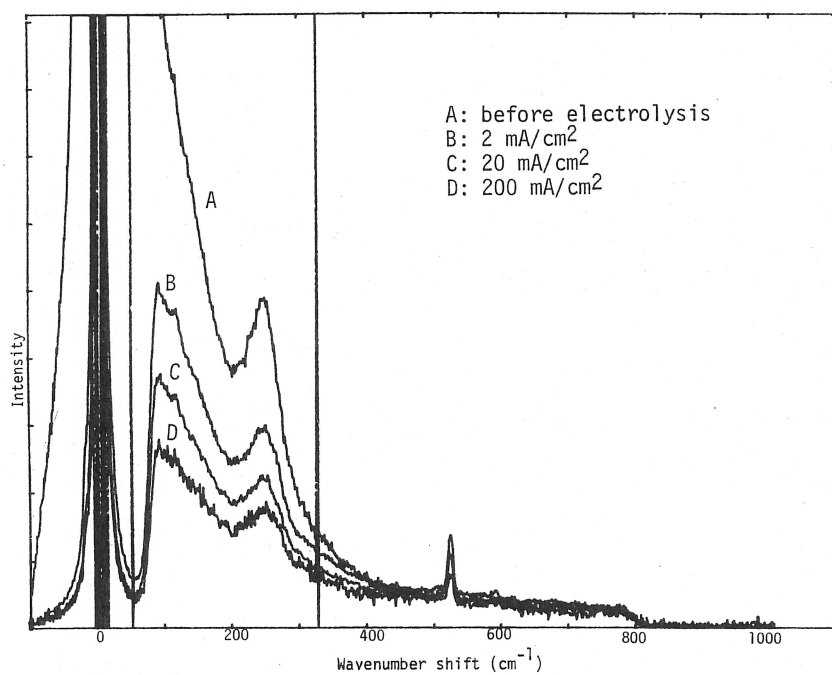


Figure 6. Raman spectra of 11% MgCl<sub>2</sub>-6% CaCl<sub>2</sub>-65% NaCl-18% KCl at 740°C.

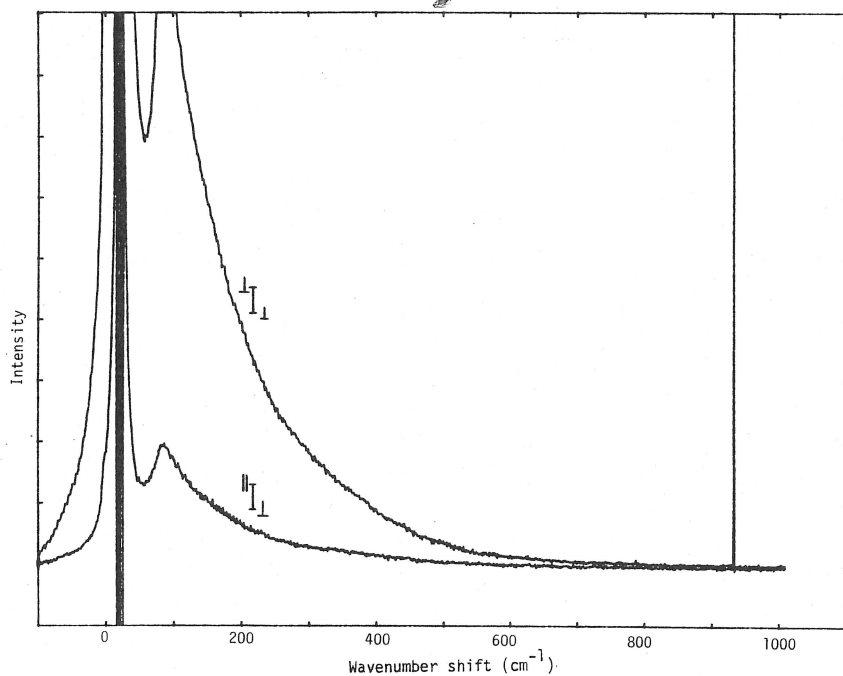


Figure 7. Raman spectra of 55% NaCl-45% LiCl.

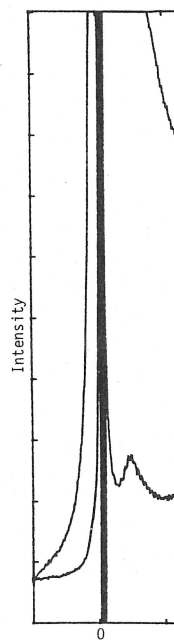


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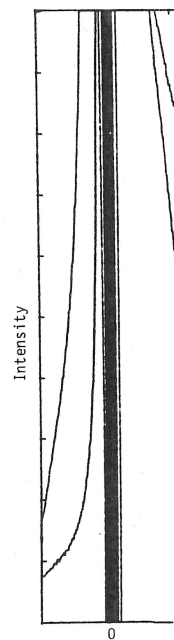
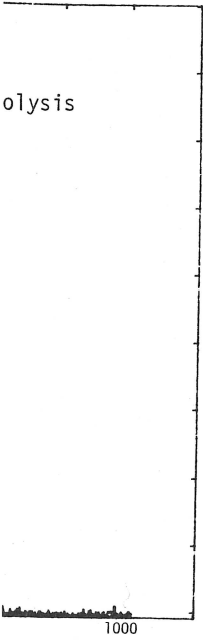


Figure 9. Raman sp



18% KCl at 740°C.

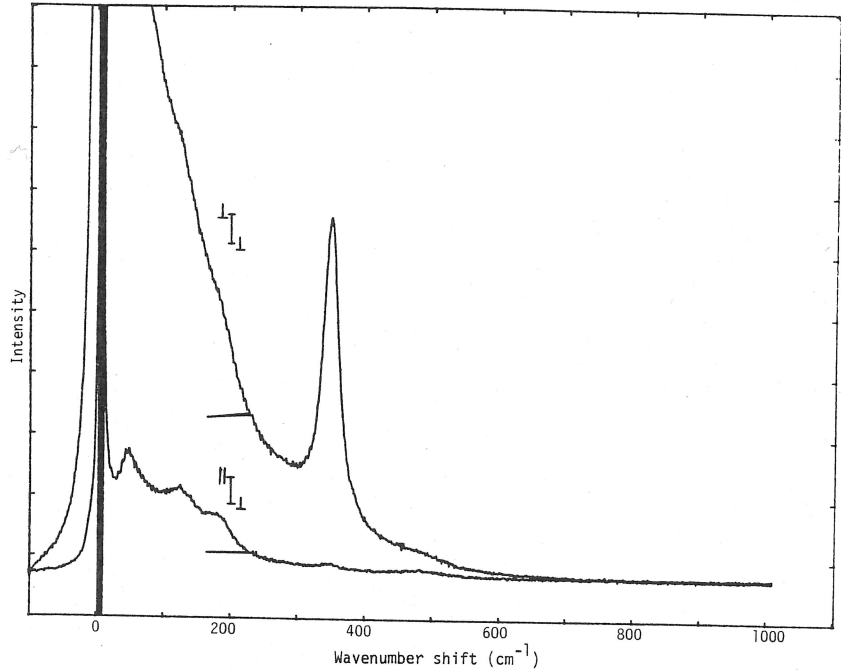
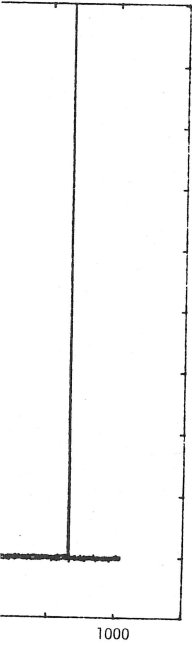


Figure 8. Raman spectra of 10%  $\text{AlCl}_3$ -50%  $\text{NaCl}$ -40%  $\text{LiCl}$  at 610°C.

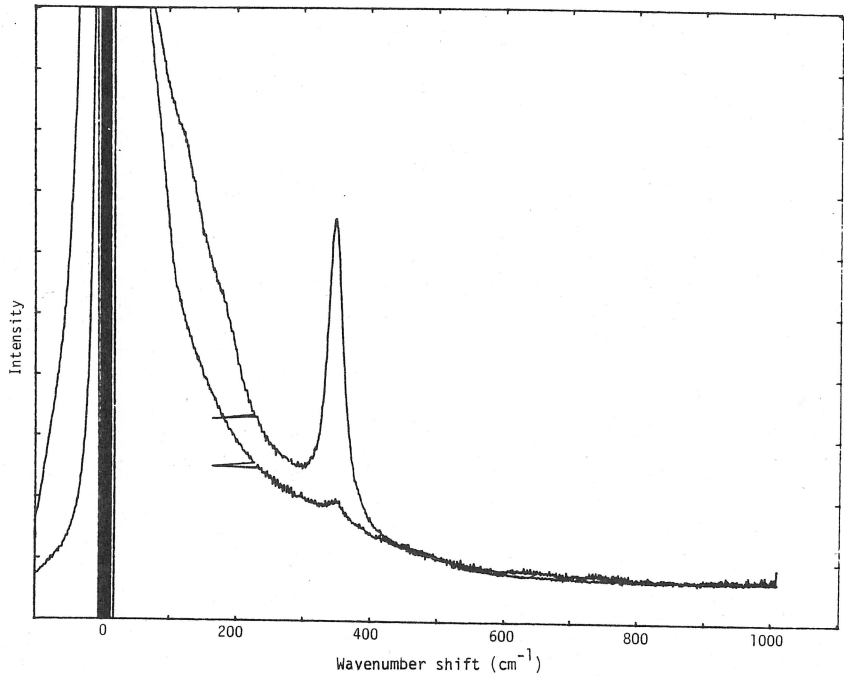


Figure 9. Raman spectra of 10% and 1%  $\text{AlCl}_3$  in equimolar  $\text{NaCl}$ - $\text{LiCl}$ .  $T=620^\circ\text{C}$ .

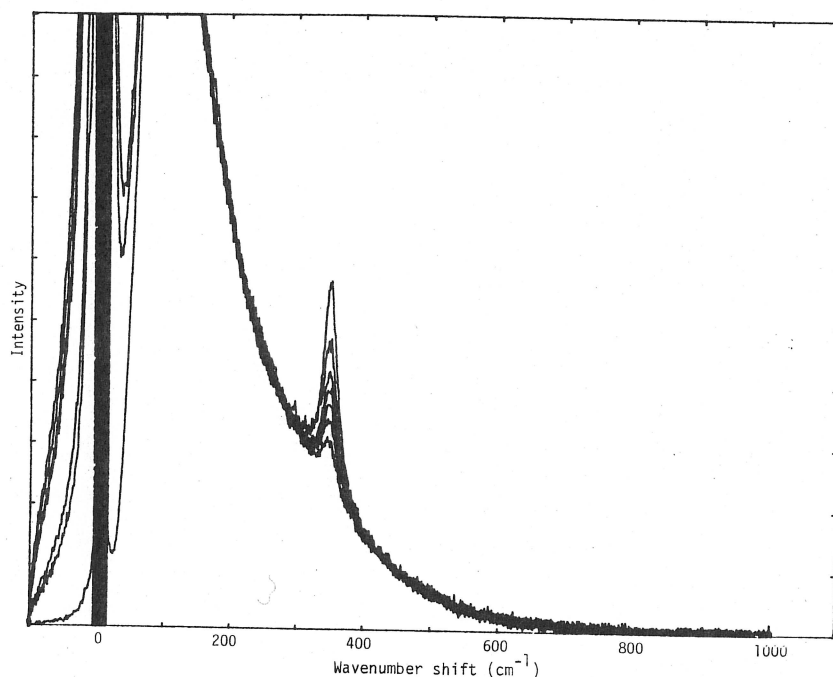


Figure 10. Raman spectra of 10%  $\text{AlCl}_3$ -50%  $\text{NaCl}$ -40%  $\text{LiCl}$  during electrolysis at every 250 coulombs.  $T = 620^\circ\text{C}$ . Current density =  $100 \text{ mA/cm}^2$ .

#### Conclusions

Laser Raman scattering instrumentation has been adapted to permit *in situ* investigation of laboratory-scale magnesium chloride and aluminum chloride electrolysis cells. The study is presently being broadened to include Hall cells. Furthermore, Raman spectra of refractory metal halides have been measured (27). On the basis of experience with the technique to date, it is felt that Raman spectroscopy could be used for spectroreducibility studies of multivalent metals in molten salts, as well as for spectrocorrosion studies of inert electrode materials.

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1. R. O. Loutfy, *J. Appl. Elec.*
2. M. C. Fleming, "An Assessment of the Electrolysis of Molten Salts," Department of Chemistry, University of Toronto, 1981.
3. N. Jarrett, *Treatises, J.* (1981), pp. 1-10.
4. A. S. Russell, *ment, "Metall."*
5. N. Jarrett, *Treatises, J.* (1981), pp. 1-10.
6. W. E. Haupin, *pp.* 273-275.
7. Kh. L. Strel'nikov, *Schmorak, Ke* 276-279.
8. A. Komora, *H. the Electrol.* 281-286.
9. T. Notoya, "Aluminum Chloride," *pp.* 2194-2195.
10. L. A. Woodward, "Raman Spectroscopy," *Raman Spectroscopy*, Plenum Press.
11. H. Flood and J. Chlond, *Chlorid - Al* chem., 59 (1981).
12. D. E. Neil, *ties of Molten Salts*, *J. Chem. Eng.*
13. O. J. Kleppa, *Binary Fused Salt Systems*, the Alkali Chlorides, (1966), pp. 1-10.
14. H. Gerding and J. NaCl, *AlCl<sub>3</sub> and NaCl*.
15. K. Balasubramanian, *and AlCl<sub>3</sub> in NaCl*.
16. E. Rytter, *H. Nucl. Chem.*,

## References

1. R. O. Loutfy and R. L. Leroy, "Energy Efficiency in Metal Electrowinning," *J. Appl. Electrochem.*, **8** (1978), pp. 549-555.
2. M. C. Flemings, G. B. Kenney, D. R. Sadoway, J. P. Clark, J. Szekely, "An Assessment of Magnesium Production Technology," report to the U. S. Department of Energy, Contract No. EX-76-A-01-02295, Feb. 1, 1981.
3. N. Jarrett, "Advances in the Smelting of Magnesium," in *Metallurgical Treatises*, J. K. Tien and J. F. Elliott, editors, AIME, Warrendale PA (1981), pp. 159-169.
4. A. S. Russell, "Pitfalls and Pleasures in New Aluminum Process Development," *Metall. Trans. B*, **12B** (1981), pp. 203-214.
5. N. Jarrett, "Advances in the Smelting of Aluminum," in *Metallurgical Treatises*, J. K. Tien and J. F. Elliott, editors, AIME, Warrendale, PA, (1981), pp. 137-157.
6. W. E. Haupin, "See-through Hall-Heroult Cell," *Aluminum*, **51**(4) (1975), pp. 273-275.
7. Kh. L. Strelets, *Electrolytic Production of Magnesium*, trans. by J. Schmorak, Keter Publishing House Jerusalem Ltd, Jerusalem, 1977, pp. 276-279.
8. A. Komora, H. Imanaga and N. Watanabe, "The Dispersion of Magnesium in the Electrolysis of  $MgCl_2$ -KCl Mixts," *Denki Kagaku*, **41**(4) (1973), pp. 281-286.
9. T. Notoya, "Recrystallization of Aluminum in the Molten Mixture of Aluminum Chloride and Sodium Chloride," *Electrochim. Acta*, **13** (1968), pp. 2194-2195.
10. L. A. Woodward, "General Introduction," pp. 1-43, and D. E. Irish, "Raman Spectroscopy of Complex Ions in Solution," pp. 240-250, in *Raman Spectroscopy, Theory and Practice*, H. A. Szymanski, editor, Plenum Press, New York, 1967.
11. H. Flood and S. Urnes, "Die Berechnung der Aktivitätsen in Magnesium Chlorid - Alkalichlorid -- Schmelzen aus Strukturmodellen," *Z. Elektrochem.*, **59** (1955), pp. 834-839.
12. D. E. Neil, H. M. Clark, and R. H. Wiswall, Jr., "Thermodynamic Properties of Molten Solutions of  $MgCl_2$ -KCl,  $MgCl_2$ -NaCl, and  $MgCl_2$ -KCl-NaCl," *J. Chem. Eng. Data*, **10**(1) (1965), pp. 21-24.
13. O. J. Kleppa and F. G. McCarty, "Thermochemistry of Charge-Unsymmetrical Binary Fused Halide Systems, II. Mixtures of Magnesium Chloride with the Alkali Chlorides and with Silver Chloride," *J. Phys. Chem.*, **70**(4) (1966), pp. 1249-1255.
14. H. Gerding and H. Houtgraaf, "The Raman Spectra of the Compounds  $NaCl \cdot AlCl_3$  and  $NOCl \cdot AlCl_3$ ," *Rec. Trav. Chim.*, **72** (1953), pp. 21-38.
15. K. Balasubrahmanyam and L. Nanis, "Raman Spectra of Liquid  $AlCl_3 \cdot KCl$  and  $AlCl_3 \cdot NaCl$ ," *J. Chem. Phys.*, **42**(2) (1965), pp. 676-680.
16. E. Rytter, H. A. Øye, S. J. Cyvin, B. N. Cyvin, and P. Klæboe, *J. Inorg. Nucl. Chem.*, **35** (1973), pp. 1185-1198.

17. K. Balasubrahmanyam, "Raman Spectra of Liquid  $MgCl_2$  and Liquid  $MgCl_2$ -KCl System," J. Chem. Phys., **44**(9) (1966), pp. 3270-3273.
18. C.-H. Huang and M. H. Brooker, "Raman Spectrum of Molten  $MgCl_2$ ," Chem. Phys. Letters, **43**(1) (1976), pp. 180-182.
19. M. H. Brooker, "A Raman Spectroscopic Study of the Structural Aspects of  $K_2MgCl_4$  and  $Cs_2MgCl_4$  as Solid Single Crystals and Molten Salts," J. Chem. Phys., **63**(7) (1975), pp. 3054-3060.
20. M. H. Brooker and C.-H. Huang, "Raman Spectroscopic Studies of Structural Properties of Solid and Molten States of the Magnesium Chloride-Alkali Metal Chloride Systems," Can. J. Chem., **58** (1980), pp. 168-179.
21. V. A. Maroni, "Vibrational Frequencies and Force Constants for Tetrahedral  $MgX_4^{2-}$  ( $X = Cl, Br$  and  $I$ ) in  $MgX_2$ -KX Melts," J. Chem. Phys., **55**(10) (1971), pp. 4789-4792.
22. G. Torsi, G. Mamantov and G. M. Begun, "Raman Spectra of the  $AlCl_3$ -NaCl System," Inorg. Nucl. Chem. Letters, **6** (1970), pp. 553-560.
23. H. A. Øye, E. Rytter, P. Klæboe, and S. J. Cyvin, "Raman Spectra of KCl- $AlCl_3$  Melts and Normal Coordinate Analysis of  $Al_2Cl_7^-$ ," Acta Chem. Scand., **25** (1971), pp. 559-576.
24. R. Fehrmann, J. H. von Barner, N. J. Bjerrum, and O. F. Nielson, "Chloro Complexes in Molten Salts. 8. Potentiometric and Raman Spectroscopic Study of the Systems  $NaCl$ - $AlCl_3$ - $Na_2O$ ,  $NaCl$ - $AlCl_3$ - $SeCl_4$ , and  $NaCl$ - $AlCl_3$ - $SeCl_4$ - $Na_2O$  at  $175^\circ C$ ," Inorg. Chem., **20** (1981), pp. 1712-1718.
25. N. E. Colthup, L. H. Daly, and S. E. Wiberley, Introduction to Infrared and Raman Spectroscopy, Academic Press, New York (1975), pp. 1-68.
26. D. P. Strommen and K. Nakamoto, Laboratory Raman Spectroscopy, John Wiley & Son, New York, 1984, pp. 76-92.
27. G. J. Kipouros, J. H. Flint, and D. R. Sadoway, "Raman Spectroscopic Investigation of Some Alkali-metal Hexachlorocompounds of Refractory Metals," submitted for publication to Inorganic Chemistry (1985).

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