SPECTROELECTROCHEMICAL STUDY OF MAGNESIUM ELECTROLYSIS

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The characteristics of laboratory scale magnesium electrolysis cells are being investigated by spectroscopic and electrochemical techniques. To determine the factors controlling 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% $MgCl_2$, 65% NaCl, 18% KCl and 6% $CaCl_2$. Cells operate at a temperature of 750°C and current densities of up to 2 A cm^{-2}. Spectral information 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. Recent results indicate that it is possible to monitor $MgCl_2$ concentration spectroscopically on-line in real time using $CaCl_2$ as a reference. Through cyclic voltammetry, which can also be performed in the same cell, valuable information about electrode kinetics and the existence of short-lived chemical species is being sought.

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].

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 the hydrous electrolytic process (Dow Chemical) is close to 80% [3]. However, the voltage efficiency of the electrolytic process is less than 50% in all cases, with the consequence that the power efficiency is typically 40% on the average [4]. Thus, at least in part, research efforts are directed at reducing the energy requirements of these extraction processes.

As part of a study of the causes of poor power 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 [5]. The results of the Raman work are combined with those of electroanalytical techniques in order to reveal the mechanisms and kinetic pathways that decrease power efficiency in magnesium cells.

Of particular interest in the present study was the determination of $MgCl_2$ concentration in the cell bath on-line in real time. Since $CaCl_2$ is present in the electrolyte but is not electroreduced, it was felt that it could serve as an internal standard. The purpose of the current phase of this study, then, was to investigate the possible use of $CaCl_2$ in this regard.

As for electroanalytical techniques, the electrode kinetics of magnesium reduction have been studied by cyclic voltammetry.

Literature

Reasons for the loss of current efficiency in magnesium cells are discussed in a recent review [6]. The monograph by Strelets contains additional information about the deleterious effects of various impurities in the electrolyte [7].

Raman spectra of pure $MgCl_2$ and solutions of $MgCl_2$ in alkali chlorides have been measured [5,8-13]. In contrast, in the analogous calcium chloride systems, there is only one reported Raman study, that of pure molten $CaCl_2$ [14].

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 [15] and one by Duan, Dudley, and Inman [16].

Experimental

A detailed description of the Raman instrumentation and the magnesium electrolysis cell can be found in previous reports [5,13,17].

The 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 [13].

In a typical experiment, the cell is charged with salt and assembled with the cap and electrodes in the glove box. The charged cell is placed in an electrical resistance furnace with windows [13], and the salt is 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 supporting electrolyte for magnesium electrolysis, i.e., $CaCl_2$-KCl-NaCl in the ratio of 6:18:65 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, Hewlett Packard Model 7004B, while fast scan responses were recorded on a digital computer, DEC MINC 23.

Results and Discussion

Figure 1 shows the Raman spectrum of pure molten $CaCl_2$ at 800°C. One sees a broad polarized band between 155 and 180 cm^{-1} which demonstrates that, just as $MgCl_2$, $CaCl_2$ has some tendency to form structural entities in the pure molten state. These results are in agreement with the earlier measurement by Brooker [14].

Figure 2 shows the Raman spectrum of 25 m/o $CaCl_2$ - 75 m/o CsCl at 840°C. CsCl was chosen as a solvent because it is a good ligand donor and as such would strongly promote complex formation. A sharp polarized peak at 194 cm^{-1} is clearly evident. The spectrum has been made smooth by means of the Savitzky-Golay technique, which also identifies peak positions by differentiation of the functional representation of the raw data.

The strong polarized peak of what is believed to be the $CaCl_4^{=}$ complex having been identified, the study turned to solutions of $CaCl_2$ in lighter alkali chlorides and finally in the supporting electrolyte for magnesium electrolysis.

Figure 3 shows the spectrum of 25 m/o in KCl. The peak at 194 cm^{-1} is evident but not as pronounced as in the CsCl solvent melt.

Figure 4 shows the spectrum of 25 m/o in NaCl. The peak at 194 cm^{-1} is not obvious at all. In the absence of the knowledge from the previous solvent melts, one would be tempted to conclude that $CaCl_2$ does not coordinate in NaCl solvent melts to form Raman active species. At the same time, with curve fitting and noise suppression techniques, it is possible to enhance the resolution of the spectra once one knows where to look. As a crude illustration of this, Figure 5 shows the spectrum of Figure 4 plotted with different scale factors.

It is instructive to see the effects of the mixed $MgCl_2$ - $CaCl_2$ system. For reference, Figure 6 shows the spectrum of pure molten $MgCl_2$ [5]. It has the predominant sharp peak at 205 cm^{-1}. Figure 7 shows the equimolar solution of $MgCl_2$ - $CaCl_2$. This represents essentially the superposition of Figure 1 and Figure 6, both in a physical sense and from the standpoint of data analysis. The peaks of pure $MgCl_2$ and $CaCl_2$ at 205 cm^{-1} and 180 cm^{-1} must be deconvoluted and the broad anomalous Rayleigh shoulder must be suppressed in order to derive quantitative information from these data. Efforts to accomplish this are underway.

Figure 8 shows the spectrum of a melt containing 33 m/o $CaCl_2$, 50 m/o KCl, 17 m/o KF. Two peaks are plainly evident where there was only one peak seen in the all-chloride melts described up to this point. Clearly, the fluoride coordinates more tightly around the central calcium cation giving a more precisely defined halocomplex, in all likelihood $CaF_4^{=}$. The main Raman peak has shifted from 194 cm^{-1} where it is found in the all-chloride melts to 205 cm^{-1} in the mixed chloride-fluoride melts.

Figure 9 shows resolution at low concentrations. This melt contains 6 w/o $CaCl_2$, 18 w/o KCl, 65 w/o NaCl, and 11 w/o KF. While they are not sharp, the calcium peaks are still detectable down to this concentration which represents the commonly found industrial value.

Signal to noise ratio is being enhanced by the Savitzky-Golay technique: a polynomial approximates local regions of raw data; then, weighting coefficients are convoluted with raw data to yield smoothed values. This technique reduces noise (high frequency fluctuations) by acting as a mathematical low pass filter.

Figure 10 shows a cyclic voltammogram for the deposition of magnesium on silver at 750°C from a melt containing 2 weight percent $MgCl_2$ 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 0.04 cm^2. The well defined trace shows clearly the reduction and oxidation processes. The residual current is extremely low and did not decrease with pre-electrolysis. This demonstrates that the dehydration procedure developed in this laboratory [13] gives material suitable for electroanalytical studies without further purification. The fact that the current does not increase sharply with the onset of reduction is consistent with the formation of a soluble reaction product which is expected under the circumstances, since magnesium alloys with silver under these conditions. 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. The equation given by Nicholson and Shain [18] predicts 98 mV if one assumes that the electron number is 2, while Figure 10 shows almost 170 mV. However, if one assumes an electron number of 1, the difference in peak potentials is calculated to be 196 mV which is much closer to the observed value of 170 mV. It is too early to state whether there is a monovalent species being reduced at the working electrode. In the meantime, it should be reported that other investigators also have taken data that correspond more closely to a one-electron reduction step than a two-electron reduction step [19]. The scan rate had essentially no effect on the peak potential; if anything, with both peaks there is a slight shift in the cathodic direction as scan

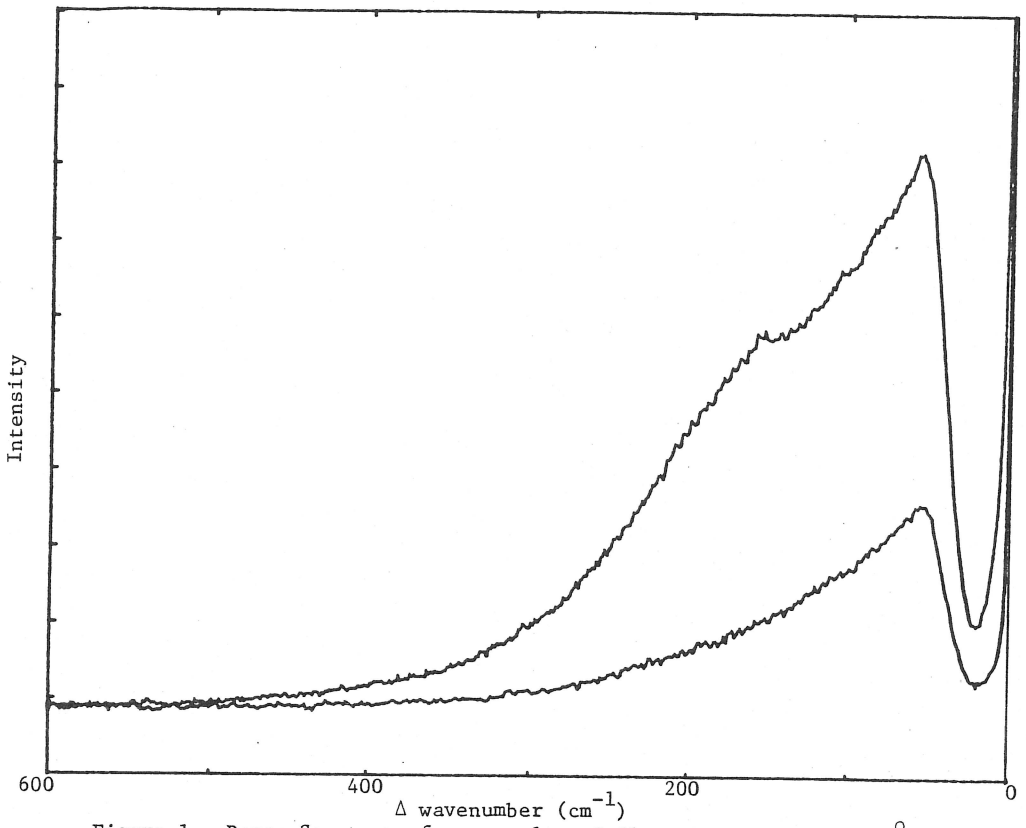

Figure 1. Raman Spectrum of pure molten $CaCl_2$. Temperature = 800°C. Excitation λ = 514.5 nm.

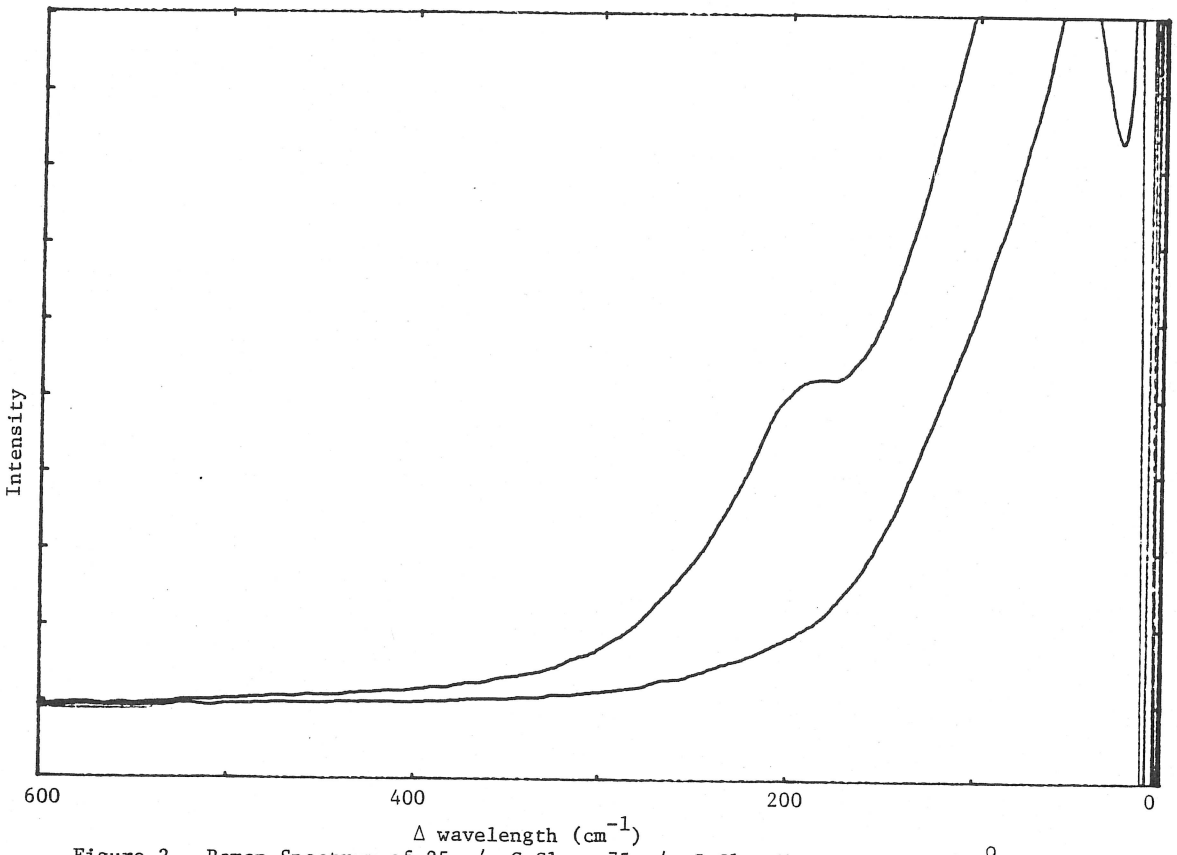

Figure 2. Raman Spectrum of 25 m/o $CaCl_2$ - 75 m/o CsCl. Temperature = 840°C. Excitation λ = 514.5 nm.

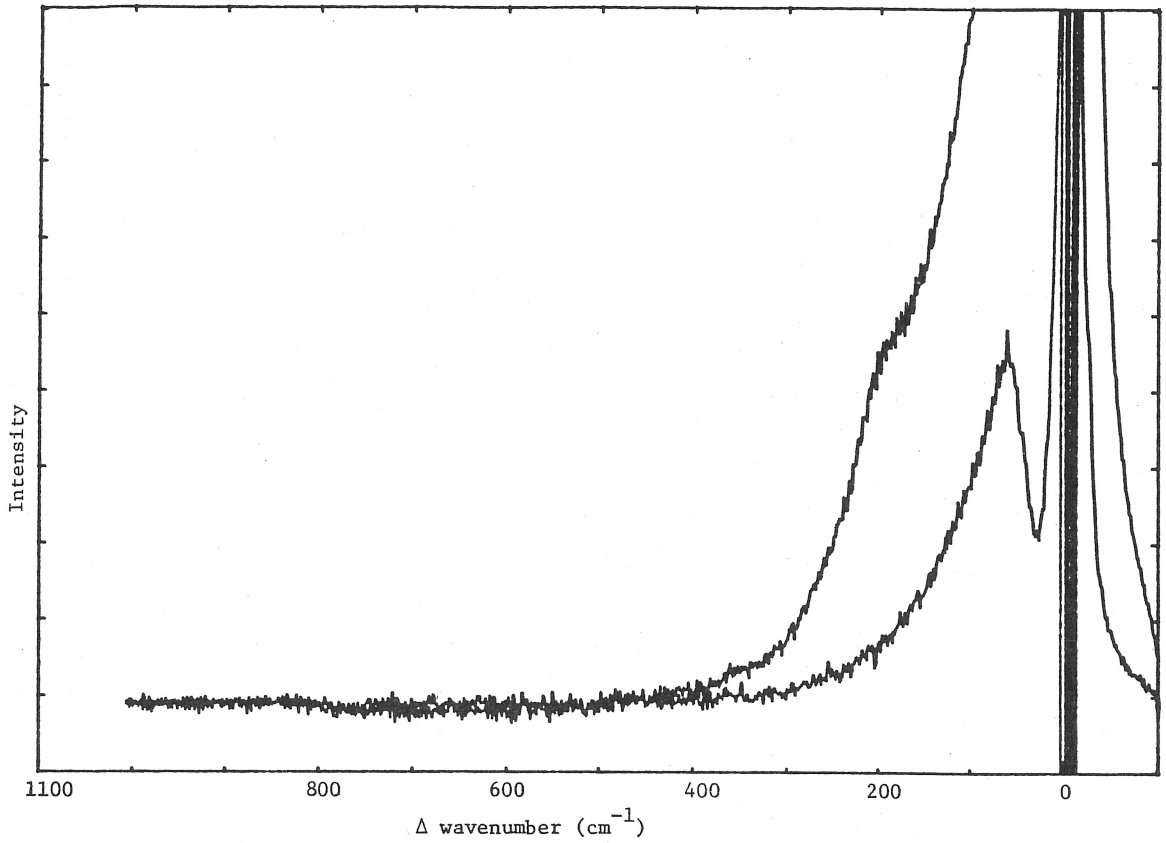

Figure 3. Raman Spectrum of 25 m/o $CaCl_2$ - 75 m/o KCl. Temperature = 800°C. Excitation λ = 514.5 nm.

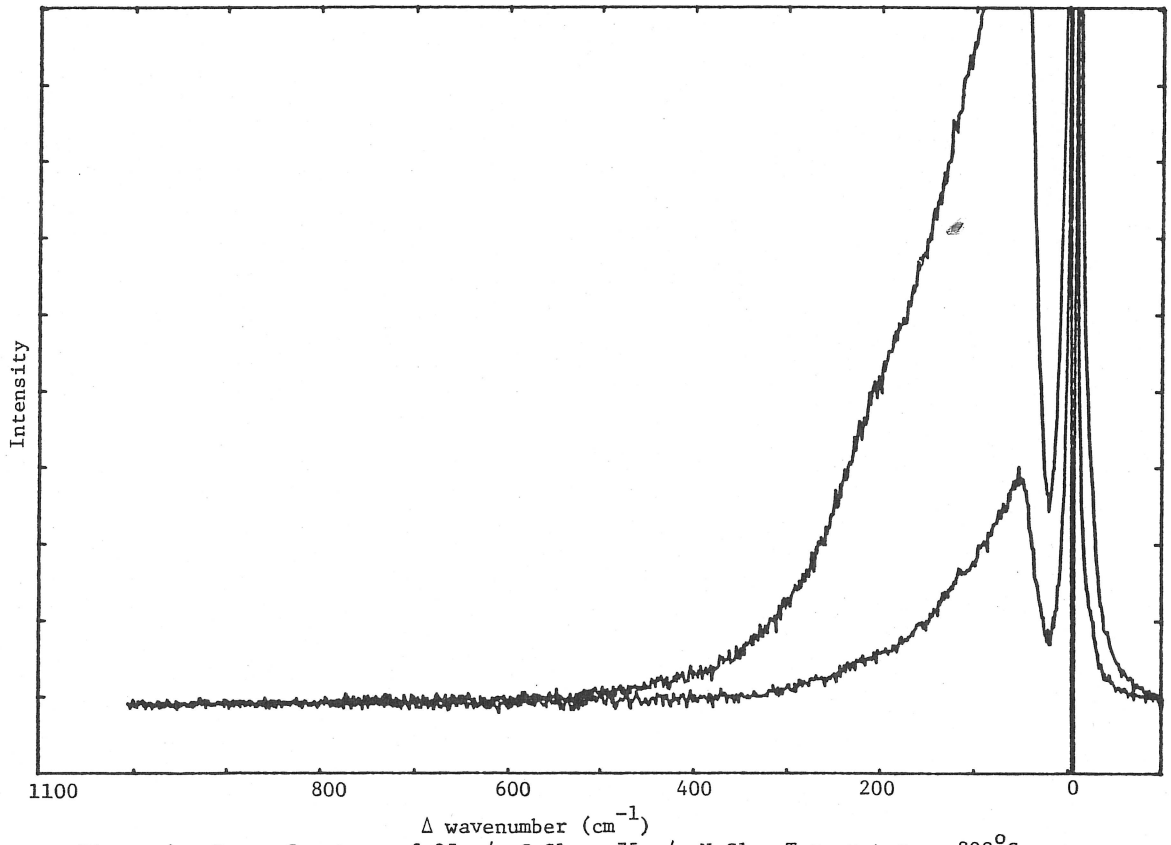

Figure 4. Raman Spectrum of 25 m/o $CaCl_2$ - 75 m/o NaCl. Temperature = 800°C. Excitation λ = 514.5 nm.

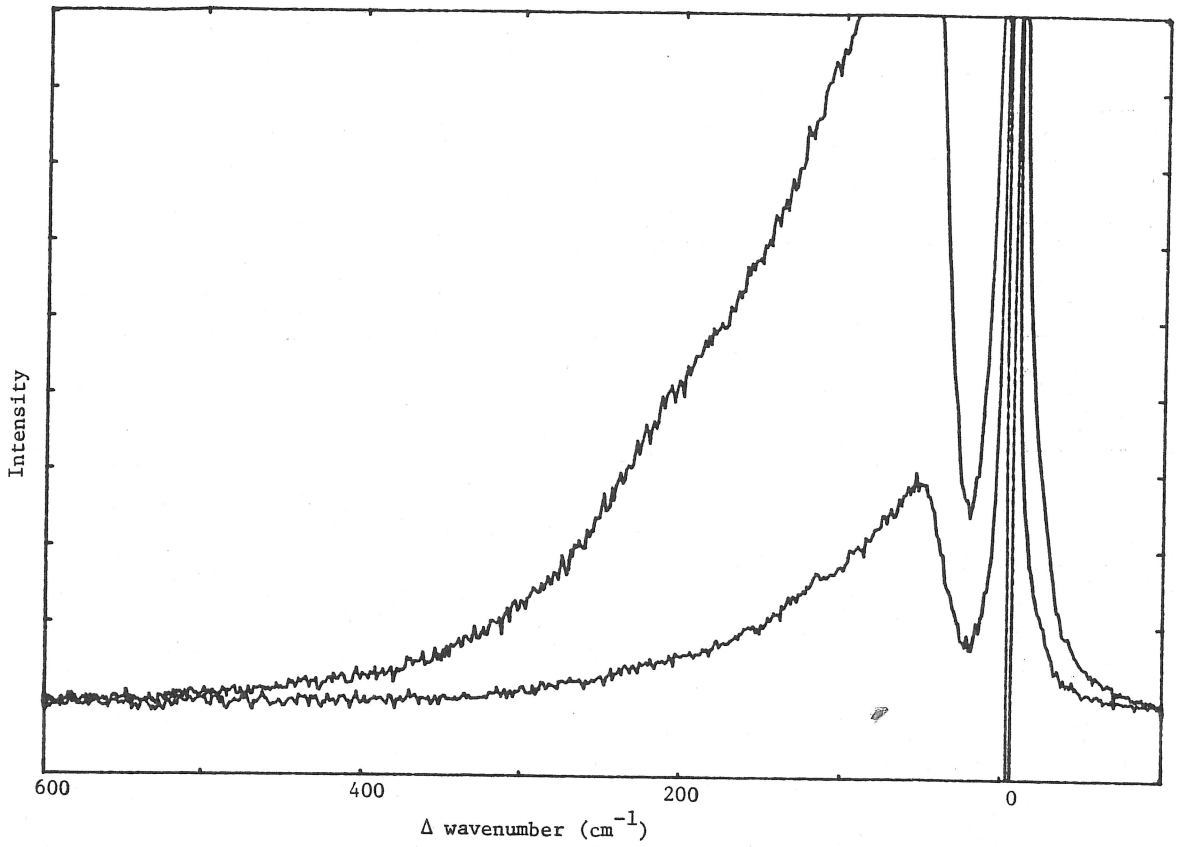

Figure 5. Raman Spectrum of 25 m/o $CaCl_2$ - 75 m/o NaCl. Temperature = 800°C. Excitation λ = 514.5 nm.

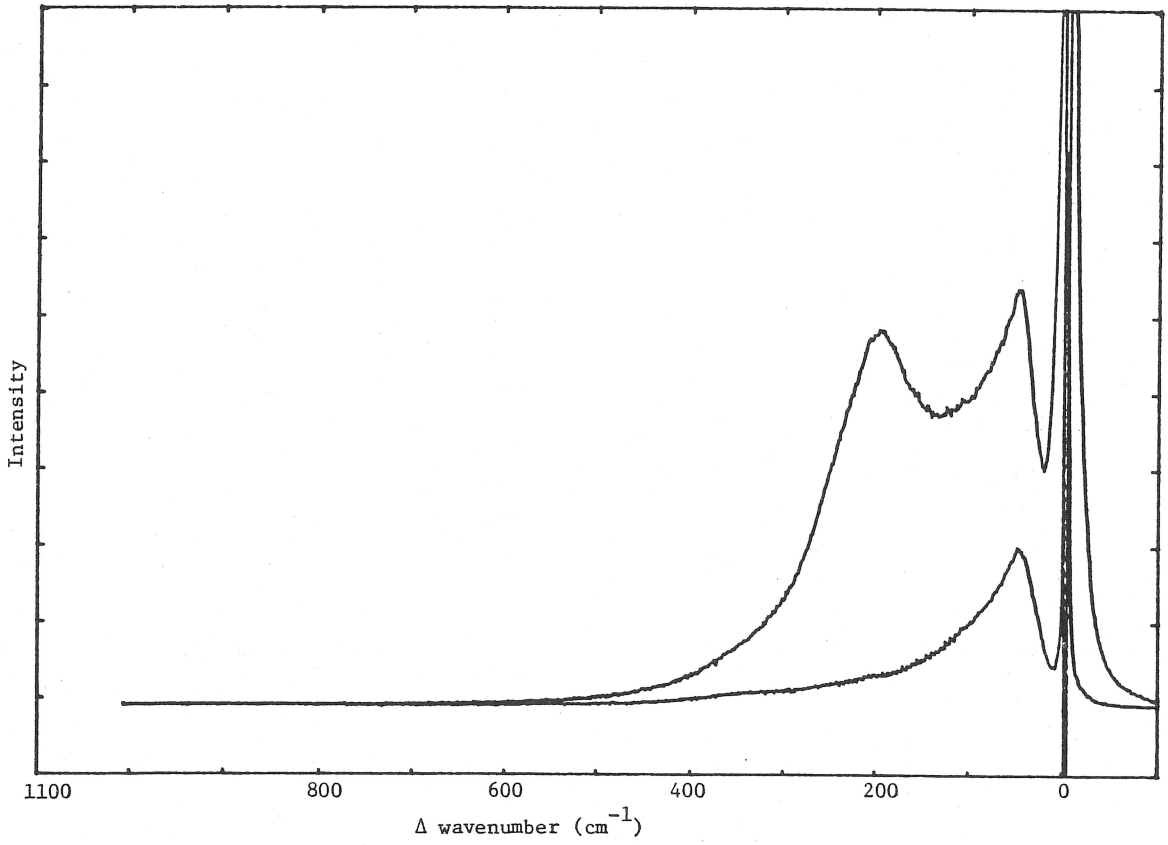

Figure 6. Raman spectrum of molten $MgCl_2$. Temperature = 750°C. Excitation λ = 514.5 nm.

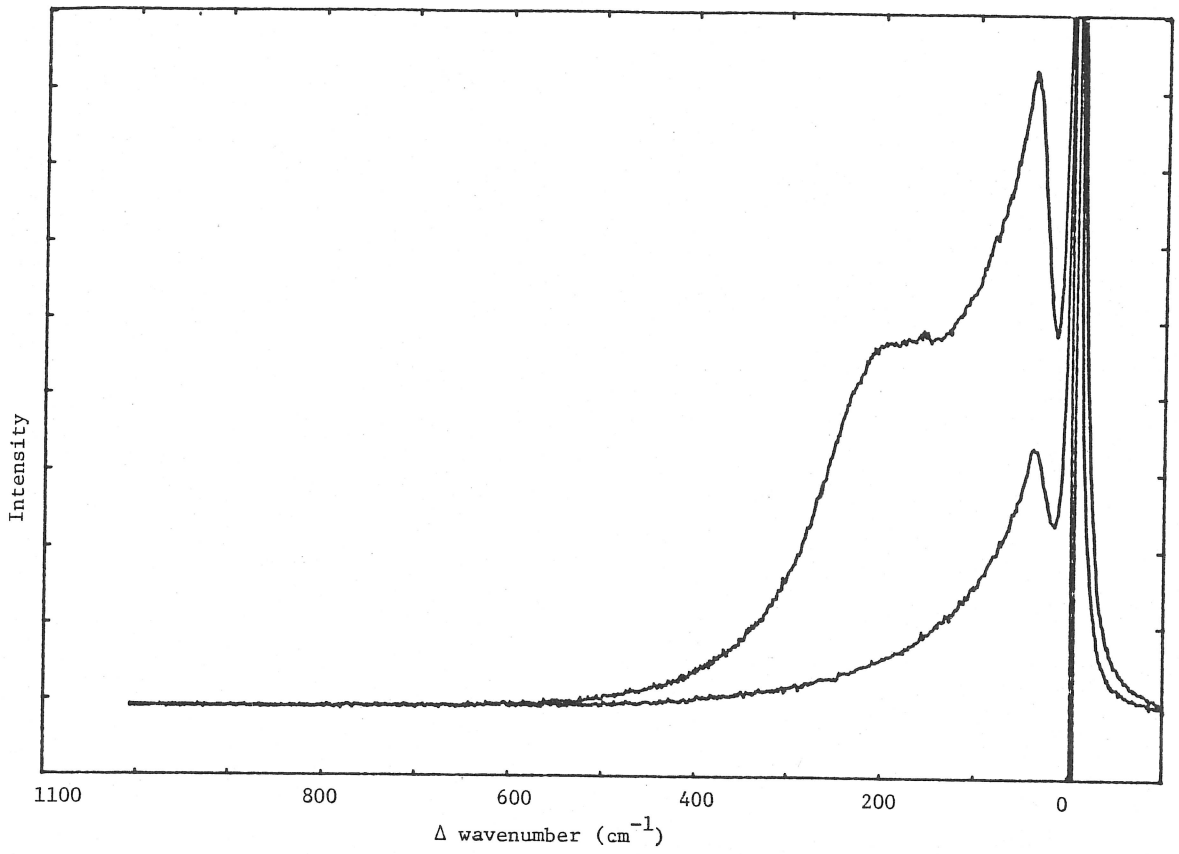

Figure 7. Raman Spectrum of Equimolar $CaCl_2$ - $MgCl_2$. Temperature = 800°C. Excitation λ = 514.5 nm.

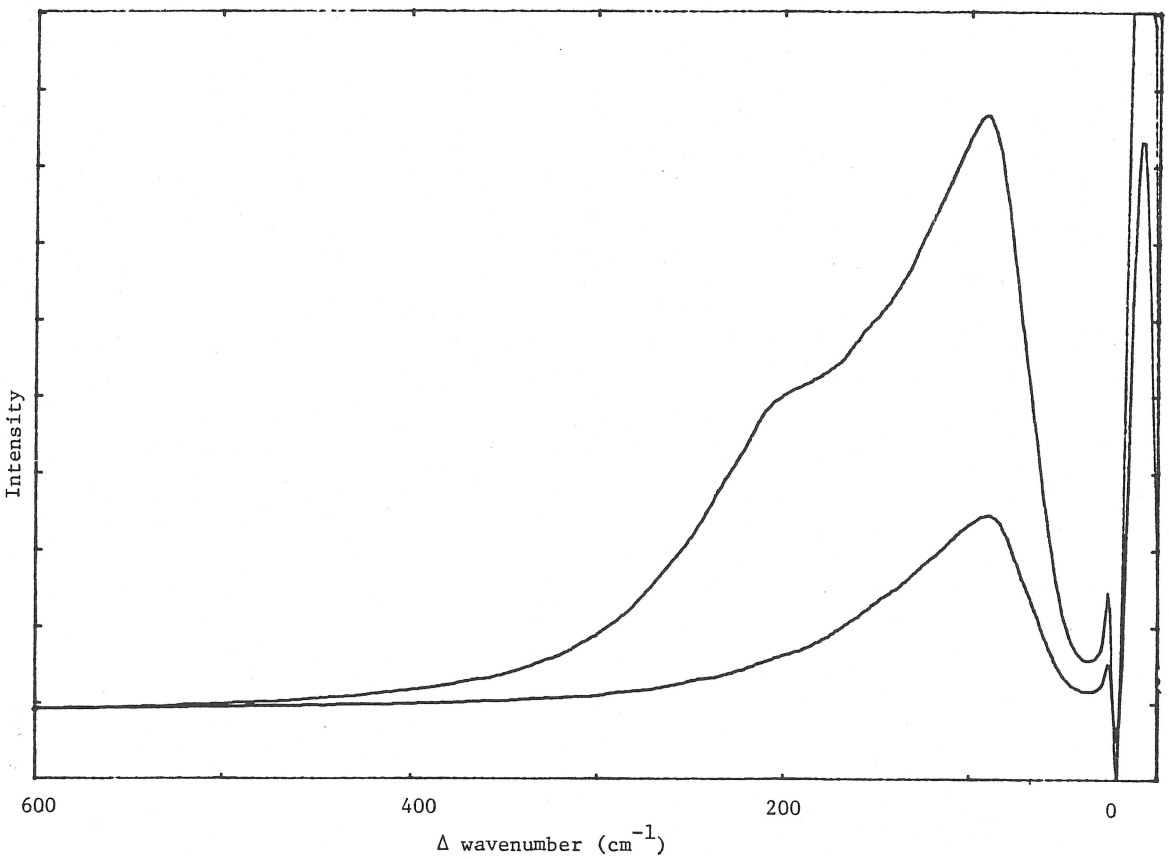

Figure 8. Raman Spectrum of 33 m/o $CaCl_2$ - 50 m/o KCl - 17 m/o KF. Temperature = 800°C. Excitation λ = 514.5 nm.

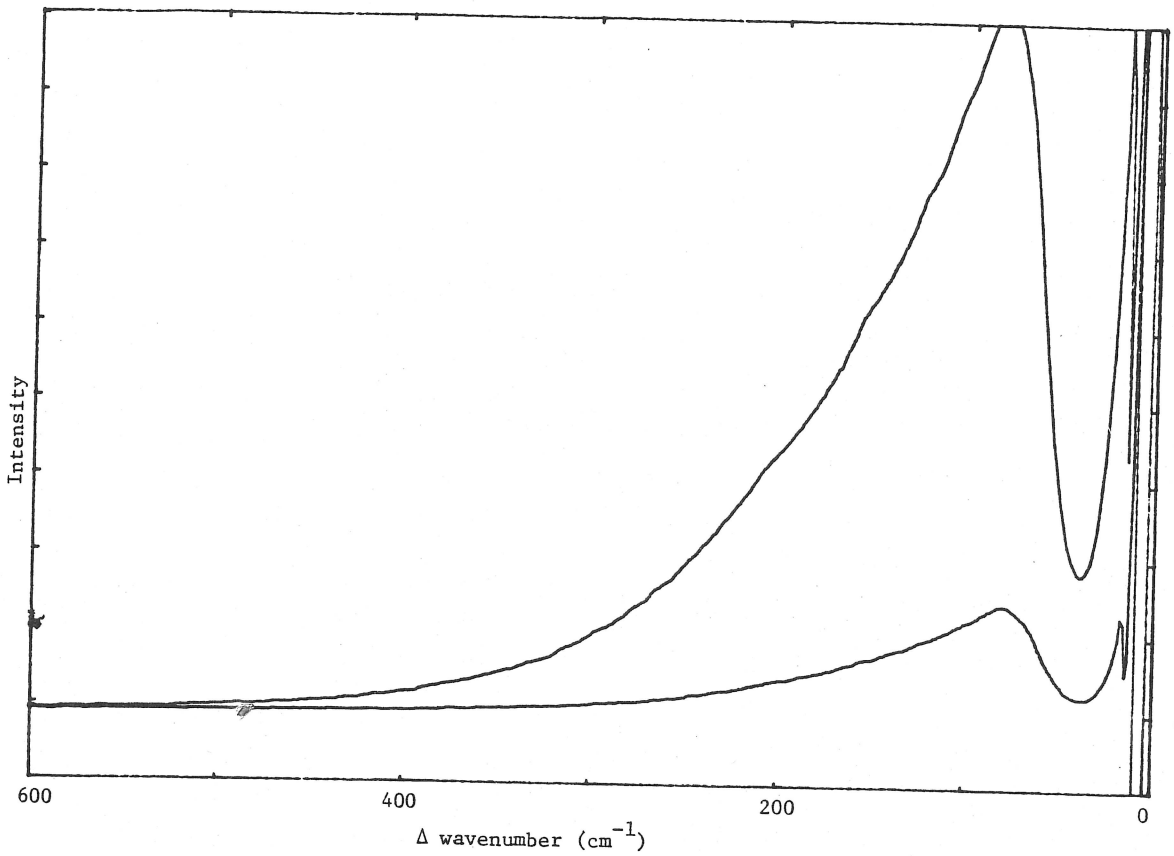

Figure 9. Raman Spectrum of 6 m/o $CaCl_2$ - 18 m/o KCl - 65 m/o NaCl - 11 m/o KF. Temperature=750°C. Excitation λ = 514.5 nm.

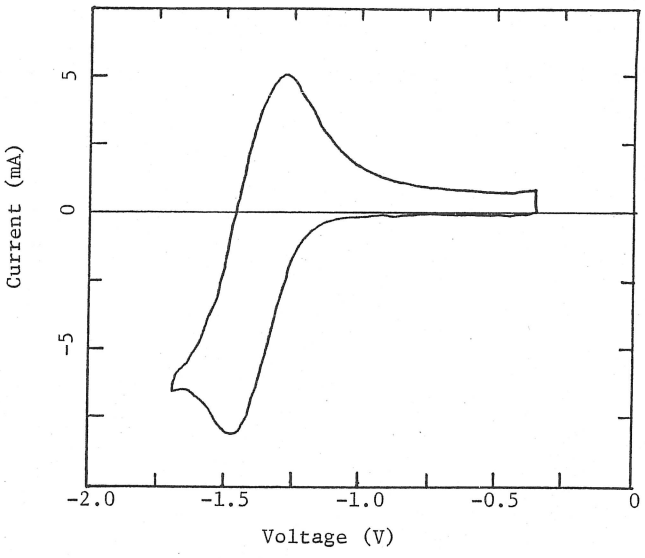

Figure 10. Cyclic Voltammogram of Magnesium Chloride. Scan Rate = 0.4 V s^{-1}. T = 750°C. Silver working electrode, A = 0.04 cm^2.

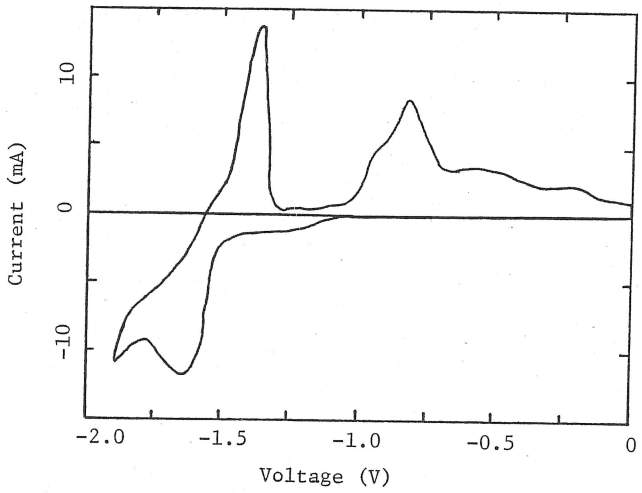

Figure 11. Cyclic Voltammogram of Magnesium Chloride. Scan Rate = 0.1 V s^{-1}. T = 750°C. Platinum working electrode, A = 0.04 cm^2.

rate increases. The cathodic peak current is linear in the square root of scan rate: over the range of experiments conducted, the current was diffusion controlled.

Figure 11 shows a cyclic voltammogram for the deposition of magnesium on platinum at 750°C from the same melt described in the previous paragraph. The scan rate was 0.1 V s^{-1} and the area of the working electrode was 0.04 cm^2. Magnesium alloys more readily with platinum than with silver as seen from the difference in the anodic oxidation peaks between Figures 10 and 11. Furthermore, in the case of a platinum working electrode, the cathodic peak potential shifted to more cathodic values as the scan rate increased, whereas the anodic peak potential remained unchanged. Figure 12 shows that glassy carbon almost completely represses magnesium deposition; instead, the cathodic wave is associated with the electrolysis of sodium.

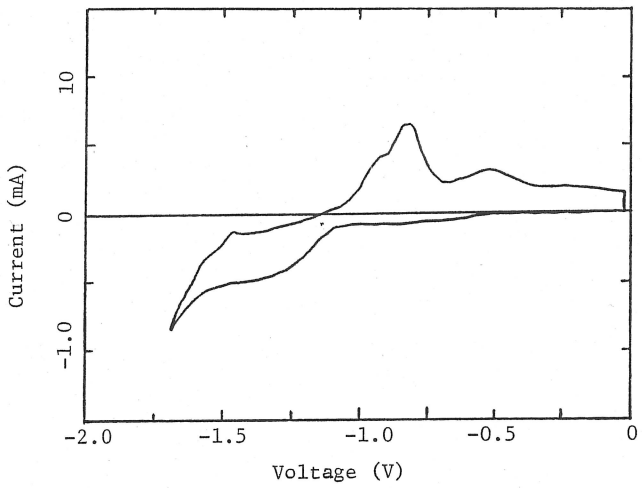

Figure 12. Cyclic Voltammogram of Magnesium Chloride. Scan Rate = 0.1 V s^{-1}. T = 750°C. Glassy carbon working electrode, A = 0.04 cm^2.

Conclusions

The basis for real time spectroscopic determination of $MgCl_2$ concentration in cell bath has been established through the identification of distinct Raman peaks for magnesium and calcium in molten chlorides. Cyclic voltammetry has shown magnesium deposition to be quasi-reversible. Efforts are underway to combine time based Raman spectroscopy with cyclic voltammetry to analyze the bath chemistry of the cathode boundary layer during the voltage scan in order to identify short-lived species.

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