

# *In situ* Raman spectra of electrode products during electrolysis of $\text{HgCl}_2$ in molten $\text{LiCl-KCl}$ eutectic

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Modulation and photon counting Raman spectroelectrochemical methods have been applied for studying amorphous carbon electrode surfaces during the electrolysis of  $\text{HgCl}_2$  in  $\text{LiCl-KCl}$  eutectic at  $370^\circ\text{C}$ . A new Raman band measured at  $152\text{ cm}^{-1}$  was attributed to subvalent  $\text{Hg}_2\text{Cl}_2$  species. The Raman signal arises from the melt solvent having appreciable  $\text{Hg}_2\text{Cl}_2$  concentrations in the vicinity of the cathode.

## 1. Introduction

The species formed on, or in the vicinity of, the electrode surface during molten salt electrolysis are difficult to identify and the electrode processes are not fully understood. Metal fog has been observed (visually) in several systems and it seems to play an important role in reducing the current efficiency of metal production [1-6]. A potential technique for investigating electrode surfaces is Raman spectroscopy which has been applied for *ex situ* [7] or *in situ* [8] studies of room temperature solutions. Due to experimental difficulties *in situ* Raman spectroelectrochemical measurements have not been used so far for studies of electrodes in melts. However, studies of the species formed in the bulk molten salt electrolyte during electrolysis, have been reported [3, 4].

The present paper reports on Raman spectroelectrochemical measurements at amorphous carbon electrodes during the electrolysis of  $\text{HgCl}_2$  solutions in  $\text{LiCl-KCl}$  eutectic. Photon counting and modulation methods have been used for obtaining "backscattering" Raman spectra from the electrodes at  $370^\circ\text{C}$ .

The  $\text{HgCl}_2$  was chosen as solute because mercury is known to form in aqueous solutions, two well defined oxidation states  $\text{Hg}^{2+}$  and  $\text{Hg}_2^{2+}$ , which could be present during electrolysis. Furthermore the species formed by dissolving  $\text{HgCl}_2$ ,  $\text{Hg}_2\text{Cl}_2$  or  $\text{Hg}$  in different halide melts have been extensively identified and characterized by Raman spectroscopy [9-11] and thus may be used as reference for determining the possible species formed on the electrode. The electrochemistry of mercury in  $\text{LiCl-KCl}$  eutectic and in haloaluminate melts has been the subject of early investigations which are reviewed and summarized by Plambeck [12, 13]. The reversible potential for the  $\text{Hg(II)/Hg(O)}$  couple is reported as  $-0.62$  [14] or  $-0.5\text{ V}$  [12] while the presence and stability of  $\text{Hg(I)}$  in the  $\text{LiCl-KCl}$  eutectic has been questioned [14].

The Raman spectroscopic experiments conducted in the present work indicate that  $\text{Hg(I)}$  is stable in the  $\text{LiCl-KCl}$  eutectic in the presence of  $\text{Hg(II)}$  (as

$\text{HgCl}_4^{2-}$ ) and  $\text{Hg(O)}$ . Subvalent  $\text{Hg(I)}$  species were also detected spectroscopically in the vicinity of the cathode during the electrolysis of the  $\text{HgCl}_2/\text{LiCl-KCl}$  eutectic solutions.

## 2. Experimental details

The electrochemical cell was made from fused silica tubing 12 mm (int. dia.). Two amorphous carbon 3 mm rods were inserted through a Teflon cover from the top of the cell and were used as electrodes. The cell was filled with  $\sim 3\text{ g}$  of  $\text{LiCl-KCl}$  eutectic and known amounts of  $\text{HgCl}_2$  were added to give a concentration of  $\sim 1.33\text{ M}$ . The Teflon cover and electrodes on the top of the cell were sealed with epoxy and the seal was always kept outside the optical furnace used to obtain the Raman spectra. The lower part of the electrodes had a flat and polished area of about  $3\text{ mm} \times 3\text{ mm}$  which during the measurements was dipped into the melt.

Mercury (II) chloride (Merck) was purified by several sublimations in evacuated Pyrex tubes at temperatures between  $280$  and  $300^\circ\text{C}$ . The subchloride of mercury,  $\text{Hg}_2\text{Cl}_2$ , was prepared by mixing and reacting equimolar quantities of  $\text{Hg(O)}$  and  $\text{HgCl}_2$  in fused silica tubing. Details for the preparation of chemicals are given in [11] and in references therein. The  $\text{LiCl-KCl}$  eutectic was prepared by mixing and melting the anhydrous and oxide free component salts. All operations and handling of chemicals were made in a glove box or in gas tight containers under a nitrogen atmosphere. The gas over the melt in the electrochemical cell was also nitrogen at about 1 atm pressure.

A simple optical furnace made from two coaxial fused silica tubes was used. The inner tube (ext. dia. 18 mm, int. dia. 16 mm) was wound with nichrome wire while the outer tube (ext. dia. 51 mm, int. dia. 49 mm) was used for protection and thermal insulation. A variac and a thermocouple next to the electrochemical cell were used to control the furnace temperature. The temperature variation, in the area where the melt was placed, was less than  $1^\circ\text{C}$ .

A Par model 173 potentiostat connected with a Wavetek model 187 wave function generator was used to control the cell potential. For all electrochemical experiments the reference connection of the potentiostat was attached to the anode connection. The Raman spectra were excited with a spectra physics argon laser using mainly 250 mW of the 514.5 nm line. The beam was directed on the electrode flat surface through a cylindrical lens forming on the surface a focussed "line" about 2 mm long which was parallel to the slit of the monochromator. The angle between the normal to the surface and the incident beam was about 30°. The scattered radiation was collected with an  $F/1.4$  (80 mm dia.) lens in front of the slit and in a direction perpendicular to the incoming laser beam. The furnace containing the cell, the collecting and the focusing lenses were mounted on micropositioners allowing fine adjustments of the optics during the execution of the experiments. A Spex model 1403 double monochromator coupled with an RCA model C-31034 photomultiplier tube (PMT) was used to analyse the scattered radiation. The detection system included Par photon counting and rate meter electronics. For the modulation Raman experiments a Par model 5204 lock-in amplifier was used.

### 3. Results and discussion

Four different types of Raman experiments were conducted with the instruments described above.

#### 3.1. Experiments at open circuit potential

In these experiments the laser beam was focused on the electrode surface but no potential was applied on the electrodes. The image of the focussed "line" on the electrode was directed through the collecting lens into the entrance slit of the double monochromator and the Raman spectra were recorded using the photon counting system. Spectra obtained by this method for the pure LiCl-KCl solvent consisted of a 'Rayleigh' wing [for example 15] without any Raman bands. The addition however of small amounts of  $\text{HgCl}_2$  ( $\sim 1.33$  M) gave rise to a new band at  $\sim 270$   $\text{cm}^{-1}$  as shown in Fig. 1a. From the previous Raman studies of  $\text{HgX}_2$  solutions in alkali halide melts [9, 11, 16] it is evident that the 270  $\text{cm}^{-1}$  band is due to the formation of  $\text{HgCl}_4^{2-}$  species formed in the eutectic. The Hg-Cl stretching frequency for this 'tetrahedral' species has been found to be at 267 and 265  $\text{cm}^{-1}$  in the alkali chloride rich mixtures of the KCl-HgCl<sub>2</sub> [9] and the CsCl-HgCl<sub>2</sub> [11] systems, respectively.

#### 3.2. Constant potential experiments

After measuring the spectra of the solute/solvent (Fig. 1a) a constant potential of  $-1.05$  V was applied to the cell and the Raman spectra from the cathode surface were measured after 2 min. A current of about 30 mA was passing through the cell during electrolysis. A new band appeared in the spectrum at 154  $\text{cm}^{-1}$

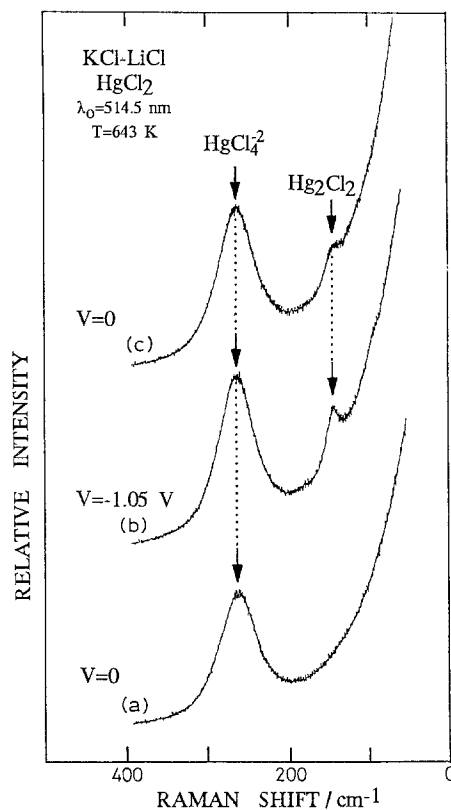


Fig. 1. Raman spectra from amorphous carbon electrodes in LiCl-KCl eutectic-HgCl<sub>2</sub> solutions at 370°C. Laser line ( $\lambda_0$ ) = 514.5 nm; spectral slit width (SSW) = 8.5  $\text{cm}^{-1}$ ; scan rate (SR) = 0.7  $\text{cm}^{-1}\text{s}^{-1}$ ; rate meter system: time constant ( $\tau$ ) = 0.1 s, range (R) =  $3 \times 10^3$ . (a) Spectrum at zero potential, (b) spectrum after reaching steady state with "constant" potential of  $-1.05$  V and (c) spectrum 1 min after opening the circuit.

(Fig. 1b) whose intensity did not change much as long as the potential was applied. At the same time on the surface of the anode, small gas bubbles (chlorine) were formed. The intensity of the 154  $\text{cm}^{-1}$  band dropped rather quickly and disappeared in a few minutes by interrupting the electrolysis. Figure 1c shows the intensity drop in a spectrum, that started 1 min after disconnecting the potential source.

The new band at 154  $\text{cm}^{-1}$  is attributed to subvalent mercury species formed on the cathode. A recent Raman study of  $\text{HgX}_2$ -Hg (X = F, Cl, Br, I) mixtures [10] has shown that the dissolution of Hg in molecular  $\text{HgX}_2$  melts leads to the formation of  $\text{Hg}_2\text{X}_2$  molecules. For the  $\text{HgCl}_2$ -Hg system the Hg-Hg stretching frequency of the linear  $\text{Hg}_2\text{Cl}_2$  molecule has been measured at 153  $\text{cm}^{-1}$  which is close to the band observed in our electrode experiments. It is thus likely that subvalent  $\text{Hg}_2\text{Cl}_2$  molecules are formed on the cathode during electrolysis. The solubility and stability of molecular species (like  $\text{Hg}_2\text{Cl}_2$ ) in ionic melts (like LiCl-KCl eutectic) is not expected to be high [17].

In separate nonelectrolytic experiments,  $\text{Hg}_2\text{Cl}_2$  was added into two different sets of cells containing CsCl and LiCl-KCl eutectic and the Raman spectra of the melt solution were measured. It was observed visually that when appreciable quantities of  $\text{Hg}_2\text{Cl}_2$  (over 0.1 M) were added, metallic Hg(O) was precipitated at

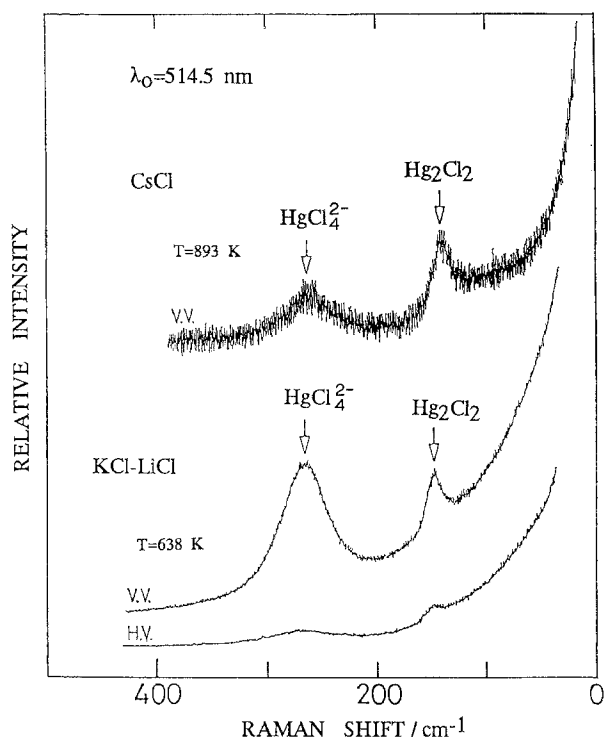
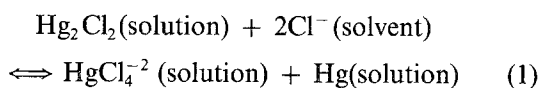


Fig. 2. Raman spectra of Hg<sub>2</sub>Cl<sub>2</sub> dissolved in molten salts.  $\lambda_0 = 514.5$  nm;  $SSW = 2$  cm<sup>-1</sup>;  $SR = 0.5$  cm<sup>-1</sup>s<sup>-1</sup>; rate meter:  $\tau = 0.1$  s in CsCl and 0.3 s in eut.,  $R = 3 \times 10^2$  in CsCl and  $1 \times 10^3$  in eut. The CsCl(l) contained "large" quantities ( $\sim 1.81$  M) of Hg<sub>2</sub>Cl<sub>2</sub>. In the eutectic  $\sim 0.55$  M of Hg<sub>2</sub>Cl<sub>2</sub> were added. The HgCl<sub>4</sub><sup>2-</sup> frequencies were at 264 and 268 cm<sup>-1</sup> for the CsCl and the eutectic, respectively. A similar small shift was also observed for the Hg<sub>2</sub>Cl<sub>2</sub> band on going from the CsCl ( $\sim 146$  cm<sup>-1</sup>) to the eutectic ( $\sim 151$  cm<sup>-1</sup>). These shifts were attributed to effects of the solvent cation [9–11].

the bottom of the cell. Figure 2 shows typical results from two such cells where Raman bands due to HgCl<sub>4</sub><sup>2-</sup> and to Hg<sub>2</sub>Cl<sub>2</sub> are present indicating an equilibrium between these species:



The solubility of Hg(O) in the eutectic is reported [18] to be less than  $1 \times 10^{-3}$  M and is presumably important for determining the equilibrium constant of the reaction and the stability of the Hg<sub>2</sub>Cl<sub>2</sub> solutions.

In view of these experiments it seems that in the electrolysis cell the Hg<sub>2</sub>Cl<sub>2</sub> formed on the cathode diffuses into the melt and is then partially decomposed according to Reaction 1. This mechanism accounts for the rapid disappearance of the 154 cm<sup>-1</sup> after switching off the cell voltage. In case that Hg<sub>2</sub>Cl<sub>2</sub> does not decompose it may diffuse in the anode area where it will be oxidized to form HgCl<sub>2</sub>. This creates a redox loop and the chlorine evolution at the anode is drastically reduced or stopped altogether. In the time scale of our experiments no such effect was observed.

### 3.3. Square wave modulation experiments

In these experiments the voltage applied between the two electrodes was modulated with a square wave pulse of variable frequency and amplitude. The optical geometry was the same as for the previous exper-

iments but the Raman spectra were obtained by connecting the lock-in amplifier with the PMT and using as reference the frequency of the square wave from the wave function generator. This technique permits measurements of Raman signal arising from species formed periodically on the electrode with the frequency of the applied potential. Species not sensitive to the applied potential, i.e. the solvent and the solute are not detected by this method. Figure 3a shows a typical modulation Raman experiment from the HgCl<sub>2</sub>/LiCl-KCl solutions.

The only band present is at  $\sim 152$  cm<sup>-1</sup> which, according to the above discussion, is due to subvalent mercury species. By changing the amplitude of the square wave from +0.2 V to -1.7 V modulated Raman signals were obtained. At higher voltage differences the focussed laser "line" on the cathode became "brighter" and the signal to noise ratio decreased rapidly. The modulation frequency for measuring spectra also had an upper value of about 2 Hz and a lower value the limit of our lock-in amplifier of 0.5 Hz. For frequencies higher than 2 Hz no spectra could be recorded.

### 3.4. Constant Raman shift experiments

These experiments were conducted by fixing the position of the monochromator at a certain wave number between 100 and 300 cm<sup>-1</sup> and then measuring the Raman intensity as a function of a trigonal wave potential applied on the electrodes. The photon counting system was used and the variation of potential and Raman intensity were simultaneously plotted on the same recorder chart. Fig. 3b shows typical spectra obtained with a 0.2 to -1.05 trigonal wave with frequency 0.03 Hz at four different fixed wave numbers. When the monochromator was set at the 270 cm<sup>-1</sup> peak of the HgCl<sub>4</sub><sup>2-</sup> species the application of the trigonal potential resulted in no changes of the Raman signal. In contrast, when the experiment was performed by setting the monochromator at the 152 cm<sup>-1</sup> peak of Hg<sub>2</sub>Cl<sub>2</sub>, drastic Raman intensity changes occurred which were almost parallel to the changes of the trigonal potential. Thus when the potential had its minimum value at -1.05 V the Raman intensity passed through a maximum. At frequencies around the 152 cm<sup>-1</sup> peak (for example 180 and 120 cm<sup>-1</sup> see Fig. 3b) the Raman intensity changes were much weaker while at frequencies around the 270 cm<sup>-1</sup> peak the trigonal potential had no effect on the Raman intensities.

The results obtained by all the above methods indicate that the subvalent Hg<sub>2</sub>Cl<sub>2</sub> species can be detected by Raman spectroscopy on the electrodes during electrolysis. The fact, however, that no modulation Raman signal could be measured at square wave frequencies higher than 2 Hz, suggests that the scattering does not arise from a Hg<sub>2</sub>Cl<sub>2</sub> species on the surface of the electrode. The electrochemically formed Hg<sub>2</sub>Cl<sub>2</sub> dissolves and diffuses in the solvent creating an appreciable concentration around the electrode which is

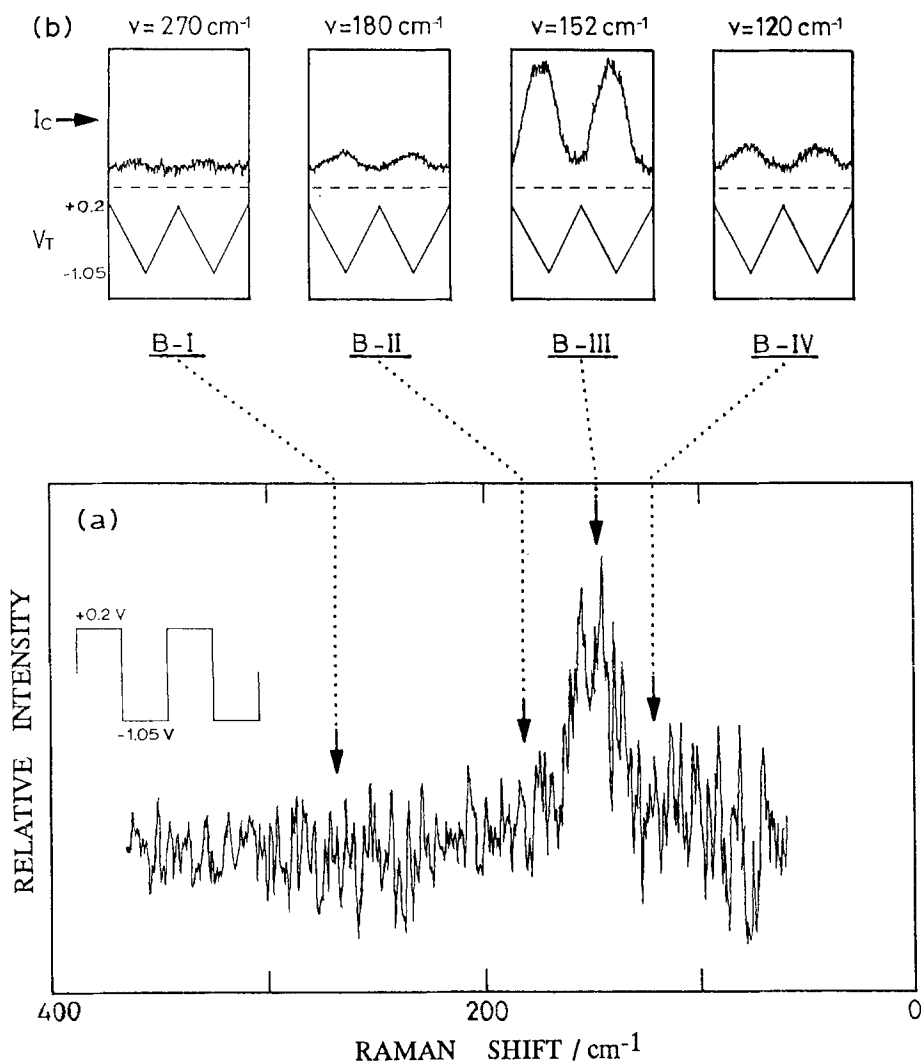


Fig. 3. (a) Modulation Raman spectrum from amorphous carbon electrodes in LiCl-KCl eutectic-HgCl<sub>2</sub> solution at 370°C. Modulation frequency: 1 Hz; square wave amplitude: 0.2—1.05 V; lock-in amplifier:  $\tau = 1$  s;  $\lambda_0 = 514.5$  nm;  $SSW = 8.5$  cm<sup>-1</sup>;  $SR = 0.35$  cm<sup>-1</sup> s<sup>-1</sup>. (b) Trigonal wave-constant wavenumber spectra. Trigonal wave frequency: 0.03 Hz amplitude -1.05 to +0.2 V. Set wavenumber of monochromator B-I: 270 cm<sup>-1</sup> (peak of HgCl<sub>4</sub><sup>2-</sup>), B-II: 180 cm<sup>-1</sup>, B-III: 152 cm<sup>-1</sup> (peak of Hg<sub>2</sub>Cl<sub>2</sub>) and B-IV: 120 cm<sup>-1</sup>. In insert figures B-I to B-IV are parallel plots of the Raman scattered intensity  $I_C$  at the specified wavenumber and the applied trigonal  $V_T$  potential.  $\lambda_0 = 514.5$  nm;  $SSW = 8.5$  cm<sup>-1</sup>; rate meter system:  $\tau = 0.1$  s and  $R = 1 \times 10^3$ . The recorder chart speed (RSC) was common for recording both  $I_C$  and  $V_T$  ( $RCS = 6$  cm<sup>-1</sup> min<sup>-1</sup>).

capable of giving a measurable Raman intensity. The melt volume covered by the focussed "line" of the laser beam on the electrode has a variable Hg<sub>2</sub>Cl<sub>2</sub> concentration which depends both on the duration of the applied potential and the decomposition Reaction 1. Finally it should be noted that the stability of the Hg<sub>2</sub>Cl<sub>2</sub> species as well as its high scattering Raman intensity were two favourable factors for the identification of this species by the described methods. These factors are important and should be considered before making similar measurements in other molten salt systems.

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