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Study of the electrochemical reduction of lead chloride on a liquid lead electrode in NaCl–KCl melt

M. E. DE ALMEIDI LIMA

Universidade Federal da Paraiba, Departemento de Quimica, 58050-João Pessoa Pb, Brasil

J. BOUTEILLON, J. P. DIARD

Centre de Recherche en Electrochimie Minérale et en Génie des procédés, ENSEEG, BP 75, 38402 Saint Martin d'Hères, France

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The electrochemical reduction of lead chloride on a liquid lead electrode of renewable surface was investigated in the NaCl–KCl eutectic melt at 700° C. Current oscillations were shown by voltammetric study. Under these circumstances the analysis of the experimental data was equivocal. Chronopotentiometric techniques similarly revealed potential perturbations. Nevertheless, it was possible to show that the lead chloride reduction occured in one reversible step involving a two electron transfer, according to the reaction

$$PbCl_2 + 2e^- \Longleftrightarrow Pb + 2Cl^-$$

The observed perturbations were ascribed to the electrode movements. Impedance measurements corroborated the results obtained by other methods: the electron transfer is fast and the electroactive species diffusion is the limiting step. The liquid electrode was considered similar to a rotating electrode whose Levich convective diffusion layer thickness and rotation speed were estimated.

1. Introduction

Most of the authors [1–10] who have investigated the kinetics of the lead chloride electrochemical reduction in fused chloride mixtures have concluded that it is controlled by the rate of mass transfer of the Pb(II) ions to the electrode surface and that the electronic exchange is reversible. Although in the NaCl–KCl equimolar mixture, Delimarskii *et al.* [11] and Stenberg *et al.* [12] have postulated that the Pb(II) reduction to the metal occured via the Pb(I) species formation, and Piron *et al.* [13] have observed that either an anodic or cathodic electrode passivation occurred when the lead chloride concentration was increased. The understanding of the double layer structure in molten salts has been studied with the liquid lead electrode and has also been the focus of attention (Russian school [14–16], Graves and Inman [8,17,18]). Graves and Inman have shown, in the LiCl–KCl eutectic mixtures, that in the domain where the capacitance varies sharply with the potential substantial charge transfer is taking place.

In a previous study of the NaCl–KCl–$PbCl_2$ mixtures we concluded that the lead chloride reduction on tungsten or molybdenum electrodes is reversible and the diffusion process was analysed over a large temperature range. Poor adherence of liquid lead formed in the reduction process to the electrode material was a problem, but we obtained evidence of the insolubility of lead in the electrolyte. So the use of a liquid lead electrode could be a better suited alternative for the kinetic study. Such an electrode was built in order to study the electrochemical reduction of lead chloride, by voltammetry, chronopotentiometry and electrochemical impedance spectroscopy (EIS) techniques.

Stationary or dropping liquid metal electrodes have already been used in fused salts, and it is well known that spontaneous surface convection appears under polarization [19–21], in some respects in very much the same way as the mercury electrode in aqueous solution [22]. These phenomena are responsible for characteristic features of voltammograms and chronopotentiograms distorted by signal irregularities. The application of EIS analysis could make it possible to take these perturbations into account, and moreover, by using an intermediate equivalent electrical circuit, to propose a mechanism. So it would be easier to separate the ohmic overpotential and to obtain values for the parameters of the electrode reaction.

2. Experimental details

The cell used for voltammetric and chronopotentiometric experiments has been described previously [23].

A special quartz cell was designed for impedance measurements. Its short length enabled the use of short electric cables, diminishing the self-inductive effects during the impedance measurements. A special intermediary chamber allowed us to collect electrolyte samples and to perform solute additions. The heating apparatus was a nickel–chromium furnace (Fig. 1)

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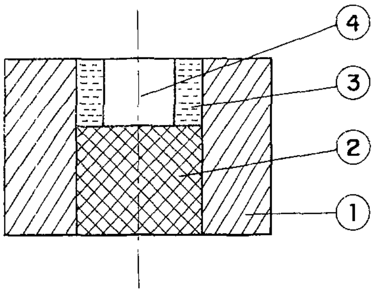

Fig. 1. Heating apparatus: (1) nickel-chrome furnace, (2) refractory basis, (3) potassium caloduc, (4) useful space.

assembled to a liquid potassium caloduc which kept the temperature constant inside the cell.

The solvent was prepared and purified as usual. Lead pellets were added in order to eliminate the metallic impurities which are more electropositive than lead by cementation (with liquid lead).

The working electrode (Fig. 2) was a liquid lead drop lying on the end of a U-shaped quartz tube. The current lead was a tungsten wire sealed in a Pyrex tube. The electrode shape was like a spheric calotte (radius: r; height: h) and its area was given by πrh. The height h was found from the parameters listed in Sugden's table [24]. For a liquid lead electrode of 0.4 cm diameter we found an area of 0.11 cm^2.

The reference electrode was the Ag–AgCl system, with a silver chloride concentration of 0.01 M in the reference solution. The auxiliary electrode was a graphite ring, to assure uniform current line distribution.

A PAR 173 potentiostat was used connected to a signal generator PAR 175 for chronopotentiometric and voltammetric experiments. A Nicollet 2090 digital storage oscilloscope recorded all the data obtained. Impedance measurements were performed using a Schlumberger-Solartron 1186 electrochemical interface. All calculations and data processing were performed by a HP 9826 computer.

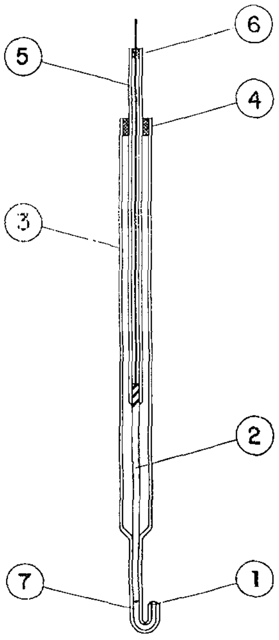

Fig. 2. Liquid lead electrode: (1) liquid lead drop, (2) tungsten wire, (3) quartz tube, (4) gyrolock, (5) pyrex tube, (6) araldite.

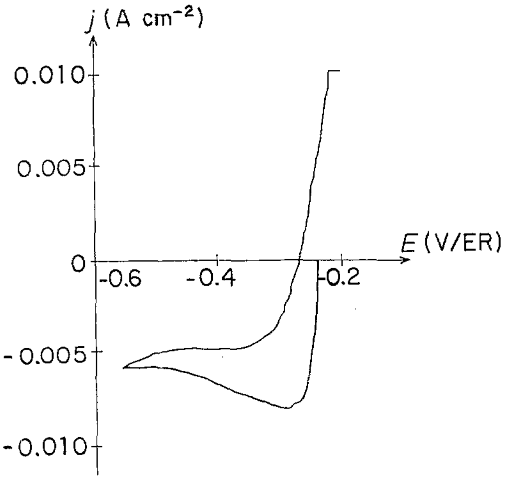

Fig. 3. Typical voltammogram in NaCl–KCl melt at 700° C, for the lead chloride reduction on a liquid lead electrode. Concentration: 0.009 M. Sweep rate: 0.5 V s^{-1}.

3. Results and discussion

3.1. *Voltammetric study*

The typical voltammogram of Fig. 3 was obtained on a liquid lead electrode immersed in a 0.009 M solution of lead chloride. A unique reduction peak was observed, but quantitative analysis was not reliable because of the current oscillations.

3.2. *Chronopotentiometric study*

Whatever the imposed current density, there was only one reduction plateau. Nevertheless, for transition times greater than 100 ms, potential perturbations, related to the current oscillations observed in the voltammograms, were observed.

The value of the product $j^*\tau^{1/2}$ as a function of the current density followed Sand's law only for transition times between 40 and 100 ms.

Polyakov *et al.* [21] have observed similar phenomena, and motions on the electrode surface, when they studied $PbCl_2$ reduction at the liquid lead electrode in NaCl–KCl equimolar mixtures, by using chronopotentiometric techniques. Their experiments were carried out in melts with 1 to 2 wt % of $PbCl_2$, in the 670–700° C temperature range, for current densities between 0.2 and 2 Acm^{-2}. On the other hand, Inman *et al.* [3], carrying out the same experiments in the LiCl–KCl eutectic at 400° C did not observe any potential fluctuation; however when the $PbCl_2$ concentration was raised to 0.0456 M Sand's relation was no longer verified.

The divergence from Sand's law could be assigned to a CE mechanism for the lead chloride reduction but it was attributed to the convection motion of the liquid electrode. Indeed, a similar discussion arose for the aluminum chloride [23] or the cadmium chloride [25] reduction mechanism on the corresponding liquid

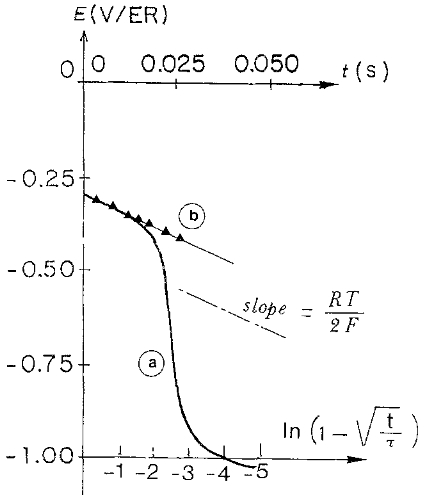

Fig. 4. Chronopotentiometric study of the lead chloride reduction on a liquid lead electrode in NaCl–KCl melt at 700° C. Concentration: 0.009 M. Curve (a): typical chronopotentiogram, and curve (b): logarithmic analysis according the insoluble hypothesis.

metal electrode, and it has been established that in both cases the liquid metal motion was responsible. It could therefore be postulated that the liquid motion was favoured when $PbCl_2$ concentration and temperature were increased, thus increasing the electron transfer rate.

The logarithmic analysis of the chronopotentiograms taken in the 40–100 ms transition time range showed the reversibility of the reduction, the potential variation as a function of $\ln (1 - t^{1/2}/\tau^{1/2})$ was linear (Fig. 4). The slope of the linear part was equal to 0,042 V per neperian logarithm unit which corresponds to the transfer of two electrons.

These results indicate that, even at 700° C, there was a narrow transition time domain range in which the convection effects induced by electrode motion could be neglected.

3.3 *Impedancemetry study*

The linearity domain of the system was determined by imposing excitation signals of amplitudes varying form 0.005 to 0.035 V. The modulus of the real part of the electrode impedance remained constant under 0.020 V (Fig. 5).

Figure 6a shows the Nyquist diagrams obtained at equilibrium for three concentrations of lead chloride. The three diagrams were taken in the same frequency range, and for the same number of logarithmic decades, with the same number of points per decade. Their shape was in good agreement with the one expected for a diffusion controlled reversible exchange, but we could not clearly see a circle in the high frequency range because the reaction was too fast. The slope of the linear part of the diagram was near unity, which proved this impedance could be related to the mass transport of an electroactive species. Moreover the shape of the Nyquist diagram in the high frequencies range corresponds to the theoretical one for diffusion process control when the double layer capacity is very high [28]; this agrees with the high values of the double layer capacity found by Graves *et al.* [18] for the lead electrode in the LiCl–KCl eutectic when reversible charge transfer is taking place.

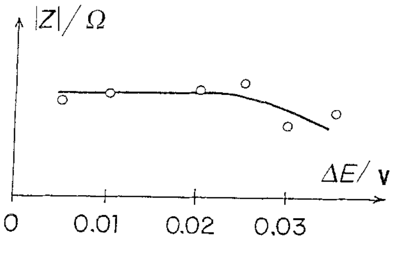

Fig. 5. Impedance analysis of the lead chloride reduction on a liquid lead electrode in NaCl–KCl melt at 700° C. Determination of the linearity domain of the system. Frequency: 30 Hz.

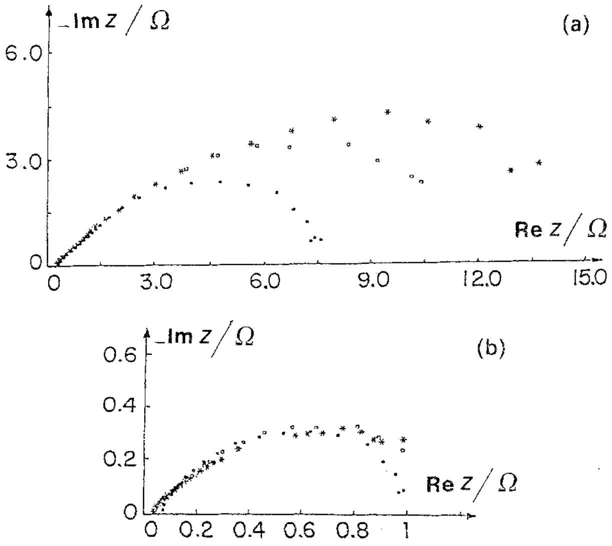

Fig. 6. Influence of lead chloride concentration on impedance diagrams of lead chloride reduction on a liquid lead electrode in NaCl–KCl melt at 700° C. Lead chloride concentration: (∗) 0.004, (○) 0.007, (●) 0.016 M. Frequency range: $0.05\,\text{Hz} < f < 60\,\text{kHz}$, for (a) experimental diagrams, and (b) reduced diagrams.

In order to clearly express the convective diffusion impedance, which was influenced by concentration, the real and the imaginary parts were divided by the maximum of the real part, taking the high frequency limit as the origin. The reduced diagrams thus obtained (Fig. 6b) virtually coincide.

The Nernst hypothesis is not thoroughly accurate for describing the diffusion layer when the convection regime is not well established. Moreover, Isaeva *et al.* [26] have observed that the diffusion layer width changes from the top to the edge of the liquid metal drop, in the case of a liquid lead electrode in a LiCL–KCl–$CaCl_2$ melt. The shape of the Nyquist diagrams, however, was in agreement with such a hypothesis.

Casidie [27] software permits simulation and calculus of electrochemical impedance and Nyquist-type diagrams of rotating disc electrodes, considering a rigourously uniform distribution of electroactive species concentration near the electrode and a finite diffusion layer thickness (Fig. 7). Similarity with the experimental diagrams can be explained supposing

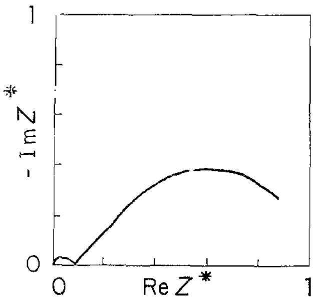

Fig. 7. Simulated impedance diagram for a fast redox system on a non polarized electrode, $A^- \Leftrightarrow A + e^-$, obtained with Casidie software. Oxidation rate: $K_0 = 0.01\,\mathrm{cm\,s^{-1}}$. Reduction rate: $K_r = 0.01\,\mathrm{cm\,s^{-1}}$. Diffusion coefficients D_A and $D_{A^-} = 4.4 \times 10^{-5}\,\mathrm{cm^2\,s^{-1}}$. Rotation speed = 1 rad s^{-1}.

that a diffusion layer of "mean" finite thickness may exist near the electrode.

The relation, $fc = 0.4\,D/\delta^2$, where fc is the characteristic frequency in the impedance diagram, D is the diffusion coefficient of the electroactive species and δ is the diffusion layer thickness is valid for a rotating disc electrode.

The diffusion coefficient D for the electroactive species, found in a previous study [10] was $4.5 \times 10^{-5}\,\mathrm{cm^2\,s^{-1}}$. The frequency fc corresponding to the maximum of the modulus of the imaginary part of the impedance diagrams is equal to 0.3 Hz. Hence, δ, the "mean" thickness of the diffusion layer can be estimated: $\delta = 7.7 \times 10^{-3}$ cm. This value corresponds to the Levich layer thickness on a rotating disc electrode, for a 750 r.p.m. speed.

4. Conclusion

The voltammetric and chronopotentiometric studies of the reduction of lead chloride on a liquid lead electrode in the NaCl–KCl equimolar mixture at 700° C showed current or potential oscillations on experimental curves. These features are ascribed to movements of the electrode coming from the hydrodynamical instability of the liquid metal under polarization and to mass transfer phenomena at the metal–molten salt interface. Under sharp experimental conditions one can verify that the Pb/Pb(II) exchange is fast and involves a two electron transfer with the formation of a product of unit activity:

$$PbCl_{2(l)} + 2e^- \Leftrightarrow Pb_{(l)} + 2Cl^-$$

Impedance diagrams obtained are typical of a high reaction rate, diffusion-controlled process. Convection interference can be inferred from the coalescence of the impedance diagram toward the low frequencies.

The diffusion layer is represented rather by the Levich model than by a Nernst one and a "mean" thickness of the Levich diffusion layer of an equivalent rotating disc electrode at 750 r.p.m., $\delta = 7.7 \times 10^{-3}$ cm was estimated.

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