ELECTRODEPOSITION OF LEAD FROM THE MOLTEN SALT MIXTURE $PbCl_2$–$ZnCl_2$–KCl

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We have proposed the eutectic melt $PbCl_2$ (18 mol %) – $ZnCl_2$ (30 mol %) – KCl (52 mol %), whose melting temperature is 326 °C, for the refining of lead and separation of lead-bismuth alloys; the melt is used in industry. The measured temperature dependence of the electrical conductivity of this melt is satisfactorily described by the equation $\lg\chi=\lg A–B/T$. χ at 450 °C is 0.63 $\Omega^{-1}cm^{-1}$, and the activation energy of electrical conductivity, U, calculated from its temperature dependence from the equation $\chi=A\cdot\exp(–U/RT)$, is 17.2 kJ/mol.

An electrochemical series for the metals in this eutectic melt: Pb/Pb^{2+}(0.000 V); Cu/Cu^{+}(0.181 V); Ag/Ag^{+}(0.357 V); Bi/Bi^{3+}(0.403 V) has been constructed by the results of e m f measurements of Jacobi–Daniell–type circuits. Here Cu, Ag, and Bi are the main impurities that are difficult to remove in lead refining.

The polarographic method was employed to investigate the cathodic process in the melt $ZnCl_2$ (36.5 mol %) – KCl (63.5 mol %) containing different $PbCl_2$ concentrations (0.08, 0.10, 0.27, 0.94, 1.35 mol %). When platinum electrodes are used, two waves are observed, whose half-height potentials are 0.96 V and 1.18 V. (Fig. 1).

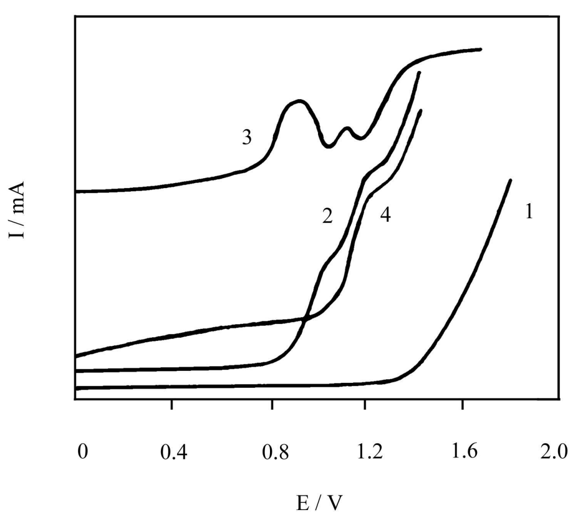

Fig. 1. Polarograms of lead ion reduction in the $ZnCl_2$–KCl melt as supporting electrolyte: (1) supporting electrolyte, (2) platinum cathode, (3) derivative polarogram at a Pt electrode, (4) molybdenum cathode.

With increasing $PbCl_2$ depolarizer concentration, the limiting-current magnitude of the second wave increases, and that of the first wave remains practically unchanged. The reduction waves of lead ions are described by the known Heyrovsky–Ilkovic equation. The before logarithms factors for the first and second waves are 0.072 and 0.074 respectively. The theoretical value of 2.3 RT/nF at 450 °C is 0.74 when n=2. The appearance of the first wave is accounted for by alloy formation (Pt_3Pb, PtPb), and the second wave reflects the lead deposition process on an intermetallide-coated platinum electrode. When a molybdenum or tungsten electrode is used instead of platinum indicator cathode, the polarogram exhibits only one wave, whose half-height potential is 1.18 V, and 2.3 RT/nF=0.078. Lead is known not to form intermetallic compounds with molybdenum or tungsten.

The parameters (exchange current, diffusion coefficient, rate constant of the electrochemical process) of the reaction in lead deposition from the salt melt $ZnCl_2$–KCl+$PbCl_2$ ($1.0\cdot10^{-5}$; $2.5\cdot10^{-5}$; $5.0\cdot10^{-5}$; $2.5\cdot10^{-4}$; $5.0\cdot10^{-4}$ mol/cm^3) have been determined using faradaic impedance method. (Fig. 2.).

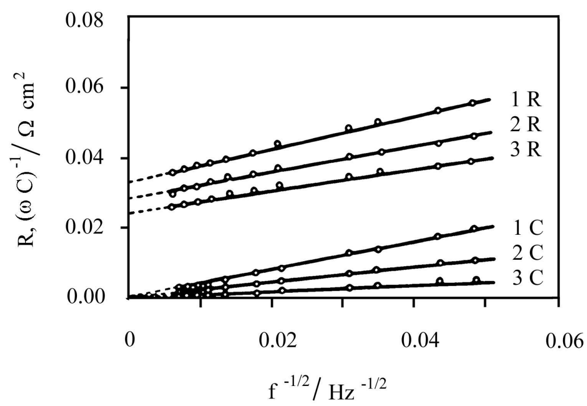

Fig. 2. Active (R) and capacitive (C) components of faradaic impedance of a lead electrode in the $ZnCl_2$–KCl melt containing $PbCl_2$ (mol/cm^3): (1) 2.5×10^{-5}, (2) 5.0×10^{-5}, (3) 2.5×10^{-4}.

The diffusion coefficient of lead ions calculated from the results of these measurments is $1.50\pm0.05\cdot10^{-5}$ cm^2/s and does not differ greatly from its value determined from cronopotentiometric measurements. The exchange current I_o increases from 0.71 to 2.08 A/cm^2 when the $PbCl_2$ concentration in the melt is increased from $1.0\cdot10^{-5}$ to $5\cdot10^{-4}$ mol/cm^3. The rate constant of the process calculated from experimental data is $1.14\cdot10^{-4}$ cm/s.

Current efficiencies for lead in the electrolysis of the eutectic melt $PbCl_2$–$ZnCl_2$–KCl have been measured over a wide range of current density and quantity of passed electricity. In all experiments, the cathodic and anodic current efficiency was close to 100%.