

SHORT COMMUNICATIONS

THE REMOVAL OF DISSOLVED IRON CHLORIDES FROM MOLTEN CHLORIDE MIXTURES

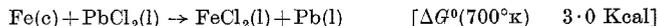
By J. IWANEC* and B. J. WELCH*

[Manuscript received March 4, 1969]

The presence of small amounts of ferric chloride¹ has been found to adversely affect current efficiencies during electrodeposition of metals from molten chlorides. Suggestions are that this is due to the anodic oxidation of Fe²⁺ and cathodic reduction of Fe³⁺ dissolved in the melts. Ferrous compounds could also be oxidized by anodically evolved chlorine which dissolves in chloride melts.² Besides influencing current efficiencies small amounts of iron co-deposited have been found to have adverse effects on the nature of the co-deposit.³ Iron compounds are often present in bulk quantities of chloride due to the method of manufacture and are difficult to remove by normal laboratory purification methods.^{4,5} In this work co-deposition was found to be unsatisfactory; however, oxidation by bubbling oxygen through the melt quantitatively removed all iron from the solution.

Experimental

All experiments were carried out at 400°C. The melt used was enclosed in a Pyrex apparatus that enabled the atmosphere to be controlled. The relative concentration of iron(II) chloride in the melt was measured by recording a voltammogram between the molybdenum working and the platinum comparison electrodes when the potential of the working electrode was increased at the rate of 200 mV/min. This technique was also used to follow the course of purification. The working electrode (cathodic) was a 0.05-in. diameter molybdenum wire protruding 1 cm below the glass seal of the Pyrex insulating sheath. The counter electrode was a 0.25-in. diameter spectroscopically pure graphite rod and the indicator or comparison electrode was simply a platinum wire sealed into a glass tube. The experiments were carried out in a purified^{4,5} LiCl-KCl eutectic to which was added 4.5 mole % lead(II) chloride. Iron(II) chloride was introduced to the melt by immersing a cleaned iron rod into the melt which reacted according to the equation



The two approaches used in our attempt to remove iron(II) chloride from the melt were controlled potential electrolysis and oxidation. The former was electrolysis with recovery of cathode product and periodic measurement of the iron(II) chloride concentration by a voltammo-

* School of Chemical Technology, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033.

¹ Appelberg, A., *Z. anorg. Chem.*, 1903, **36**, 36.

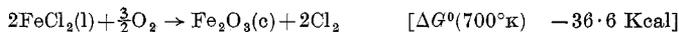
² Swinkels, D. A. J., *J. electrochem. Soc.*, 1966, **113**, 6.

³ Iwanec, J., M.Sc. Thesis, University of New South Wales, 1969.

⁴ Laitinen, H. A., Osteryoung, R. A., and Ferguson, W. S., *J. electrochem. Soc.*, 1957, **104**, 516.

⁵ Maricle, D. L., and Hume, D. N., *J. electrochem. Soc.*, 1960, **107**, 354.

gram. The oxidation was attempted because of the general insolubility of oxides in molten chlorides and the general ease with which ferrous compounds can be oxidized. The following reaction is thermodynamically favourable, and formed the basis of our attempts, viz.



Purified oxygen was bubbled through the melt as a means of bringing about this reaction.

Electrolysis

During the controlled potential electrolysis the concentration of iron(II) chloride was reduced by iron and lead co-depositing as a fine magnetic powder. When low concentrations of iron(II) chloride (about 0.7 mole %) were reached removal of iron was negligible. Two explanations are forwarded to interpret this phenomenon:

(a) The electrodeposit is of such fine particle size that the bubbling nitrogen and evolving chlorine transports it freely through the melt where recombination of the iron with chlorine occurs.

(b) The evolved chlorine provides a mechanism for oxidation of the iron(II) chloride according to the equation



Oxidation of all the iron(II) chloride will result because of the solubility of chlorine in LiCl-KCl melts.² The cathodic reactions could then include a reduction of iron from Fe^{3+} to Fe^{2+} (both soluble species) as proposed by Appellberg.¹

Oxidation

During the progress of the reaction the intensity of the colour of the melt steadily diminished while a black insoluble material accumulated on the surface of the melt. On completion of the oxidation the melt had a colourless water-like appearance except for the scum on the top. The insoluble material could be readily separated by normal techniques. This experiment was repeated using dried air, and similar results were obtained though the reaction took longer.

A sample of the insoluble residue was X-rayed to identify the reaction product and shown to be haematite (Fe_2O_3), as expected from the equation of change. Chemical analysis of the purified melt (after 300 min of oxidation) showed complete absence of iron oxides or chlorides within the accuracy limits of the analytic technique (i.e. less than 0.001 wt. %).

The oxidation technique was also found to be satisfactory for other chloride melt systems, e.g. LiCl-KCl-ZnCl₂.

The reaction mechanism for the oxidation appears to involve oxidation of ferrous ions to ferric ions as an intermediate step. This was indicated by the appearance of a new inflexion in the voltammograms.

Acknowledgments

We are indebted to Mr P. Gallen for analytical assistance. Some of the equipment used in this work was purchased from funds provided by the Australian Research Grants Committee.