

Metal production by electrolysis in molten salts

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Abstract: Modern electrolysis technologies can provide possibilities for developing sustainable processes in terms of energy and environment. Laboratory experiments were carried out to study electrodeposition of several metals and alloys including titanium, aluminium and high purity silicon from molten salts. Electrochemical techniques were used to study the electrochemical behaviour of dissolved species. Bulk electrolysis was carried out to deposit the pure metals. The influence of the formation of dissolved metals including so-called metal fog on the metal deposition process was investigated. The electrochemical nucleation was studied by potentiostatic current transients. Additional electrochemical experiments were performed to study anode processes in molten chloride and fluoride electrolytes containing dissolved oxides with the aim of improving the performance of the anode process during electrowinning. Calculations based on laboratory studies indicate that significant improvements in terms of reduced energy consumption and lower CO₂ emissions can be achieved by successful implementation of new technologies.

Key words: Electrolysis, molten salts, metal production

1. Introduction

Many important metals are being produced by electrolysis, in aqueous electrolytes (Cu, Ni, Co and others) and molten salts (Al, Na and other reactive metals). Also industrial electrorefining processes have been established in aqueous electrolytes (Cu) and molten salts (Al). Current efficiency for metal deposition, specific energy consumption and environmental issues are important topics for considering the success of such processes. A wide range of electrolytes including molten salts can be used to electrowin reactive metals. A new class of electrolytes, so called ionic liquids, being molten at room temperature may also be of future importance. Metal recycling is increasingly important, and it is believed that electrochemical routes in molten salts may be interesting due to the relative simplicity, low cost and high product purity usually associated with such processes.

Metal dissolution is a general phenomenon in molten salts, and dissolved metals are responsible for the major loss in current efficiency due to the reaction with the anode product. In some cases, especially for alkali systems, dissolved metals give rise to the existence of electronic conduction which may cause major losses in current efficiency. So-called metal fog is a visual phenomenon associated with metal deposition from molten salts. Results from experimental studies have shown that metal fog consists of small metal droplets formed by homogeneous nucleation from a supersaturated solution of dissolved metal [1]. The electrode kinetics for metal deposition reactions are known to be very fast. Therefore, limitations due to nucleation and diffusion are more important for the metal deposition process. Nucleation may be of significance both for solid and liquid metal products.

Drawbacks related to electrolysis are associated with high consumption of electrical energy and large plant footprint. However, recent developments may offer new and interesting prospects for the future use of electrolysis in terms of

sustainable development. The use of renewable electrical energy is of great importance to reduce the CO₂ emissions.

The anode product during electrowinning is a gas; usually Cl₂ or CO₂. The anode process forming a gaseous product is associated with a relatively high overvoltage, typically of several hundred millivolts at normal current densities of the order of ~0.5 A/cm². Inert anodes for oxygen evolution have not been implemented in industrial processes such as aluminium electrowinning, but significant research efforts have already provided for some commercially available oxygen evolving materials such as SnO₂ to be used at relatively low temperature.

A potential problem is the possible lower purity of future raw materials. Therefore it is important to develop new processes for taking care of impurities in raw materials and during the electrolysis process.

Fray et al. [2] proposed a new concept for electrowinning of metals and alloys from molten salts. Molten calcium chloride can dissolve large amounts of calcium oxide, while the solubility of other oxides may be low. By attaching a solid metal oxide to the cathode oxide ions dissolve in the electrolyte whereas the metal is reduced without going into solution. By using an inert oxygen evolving anode this concept is potentially very interesting for industrial use. The production of several metals has been demonstrated in laboratory and pilot plant experiments. Other researchers have also published experimental results from similar studies [3, 4]. Titanium seems to be the most promising metal in terms of future exploitation of these novel ideas. Electrolysis or electrorefining may also be of importance for the design of new processes for the production of advanced materials such as special alloys possessing unique properties. Electrodeposition of Al-Nb alloys [5] and Al-Sc alloys [6] has been proposed. In such cases electrolysis can be preferred over expensive techniques such as hot-dipping or physical vapour deposition. Other high value products such as solar grade silicon may also be obtained by molten salt electrolysis [7].

2. Experimental

Electrochemical techniques such as linear sweep cyclic voltammetry and potential step chronoamperometry were used to study electrode reactions in molten salts. Anhydrous salts of high purity were used. All handling of electrolyte components and cell materials took place in a glove-box under argon atmosphere. Experiments were carried out in standard laboratory furnaces with dry argon gas passing through and otherwise closed to the surrounding atmosphere. Electrodeposits were characterised by SEM/EDS and XRD.

3. Results

3.1 Recycling of waste by molten salt processing

With the introduction of plasma and LCD screens for computers and TV, the conventional Cathode Ray Tubes (CRT), which have been used for the past three decades are being phased out. These tubes pose a serious environmental problem as the lead content in these glasses are as high as 18 wt %. Today, there are no processes to recycle these CRT tubes. Thus, there is an urgent and acute need to develop a process to extract the lead values from these glasses. Dissolution of such waste in molten salts followed by electrodeposition of lead is a possible processing route.

The solubility of Pb in molten chlorides containing PbCl_2 is very low, i.e. below 0.01 mol% [8]. It is known that dissolved Pb exists as the subvalent ion Pb_2^{2+} [9]. Several studies of lead deposition from molten chlorides have been reported [10-12], and all reports have studied diffusion of Pb (II) species during electrodeposition of lead. Values in the range of $\sim 2 \cdot 10^{-5} \text{ cm}^2/\text{s}$ have been reported.

In dilute solutions of PbCl_2 in molten KCl-LiCl at 400°C the cathodic deposition of lead was found to be diffusion controlled with the influence of nucleation on substrates of glassy carbon, tungsten and molybdenum. Fig. 1 shows a typical cyclic voltammograms obtained at a glassy carbon electrode. A significant nucleation overpotential of $\sim 60 \text{ mV}$ was observed. By varying the sweep rate a linear relationship between the peak current density and the square root of the scan rate was obtained. The diffusion coefficient was calculated to be $2 \cdot 10^{-5} \text{ cm}^2/\text{s}$. Further voltammetry studies were carried out by extending the cathodic potential limit. At potentials in the range from $(-1.5) - (-2.0) \text{ V}$ two more cathodic and anodic current peaks were observed indicating the formation of Li containing alloys. Potential step chronoamperometry was carried out to study the electrochemical nucleation of lead. Fig. 2 shows current transients as a function of the cathodic potential. The characteristic current increase at short time is due to the formation and growth of nuclei on the cathode surface. A maximum current coincides with the situation where the whole cathode surface is covered by Pb. The subsequent current decrease is due to diffusion of Pb (II) species to continue the deposition of Pb.

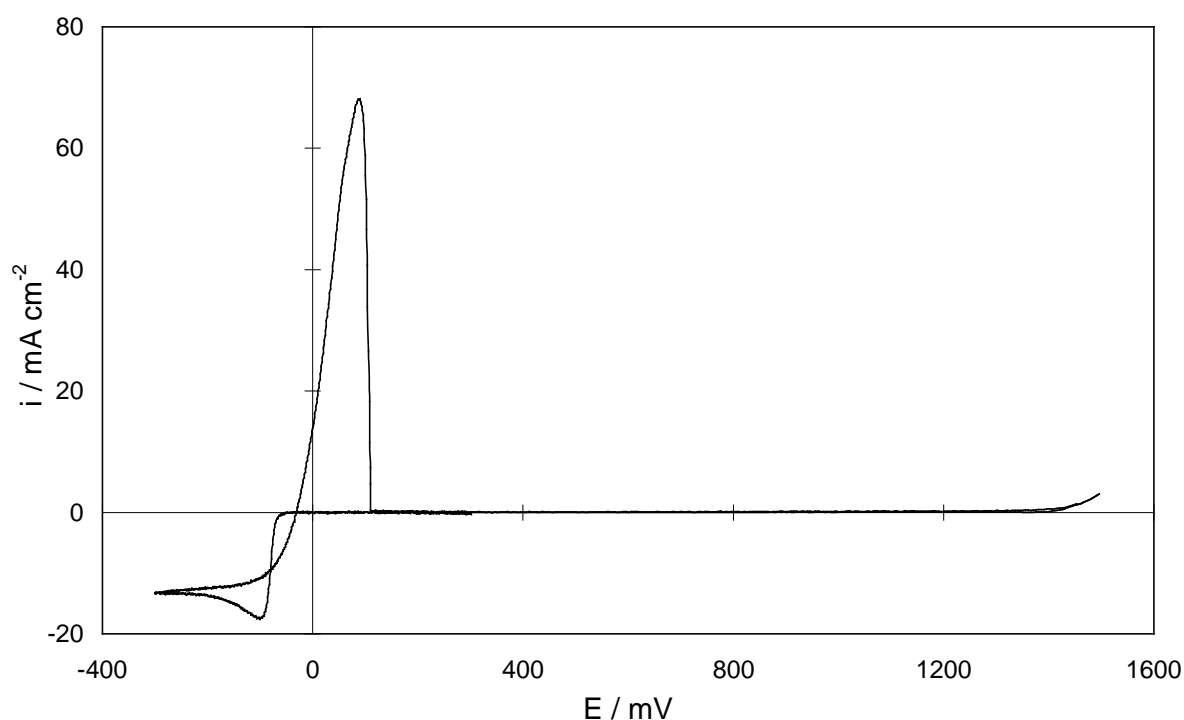


Fig. 1. Cyclic voltammogram (0.1 V/s) at a glassy carbon electrode in molten $\text{KCl-LiCl} + 0.1 \text{ mol \% PbCl}_2$ at 400°C .
Pb(II)/Pb reference electrode.

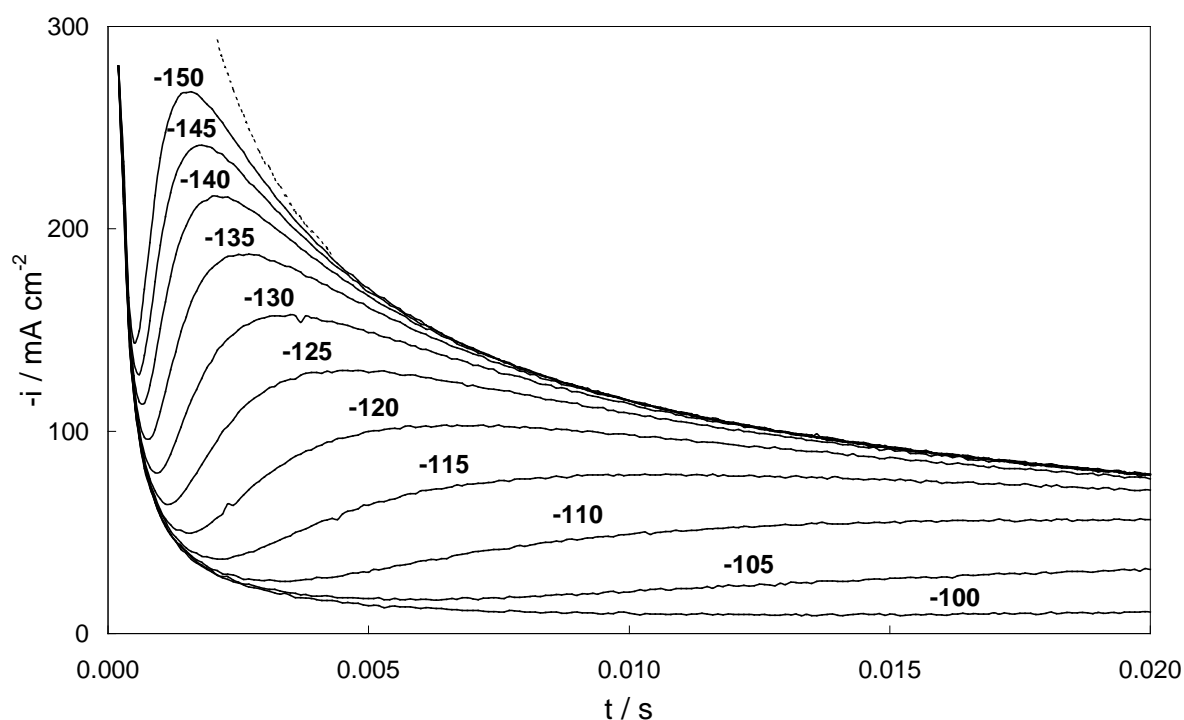


Fig. 2. Potentiostatic current transients at a glassy carbon electrode in molten KCl-LiCl + 0.1 mol % PbCl₂ at 400 °C. The numbers in the figure are overpotentials (mV). The broken curve represents the asymptotic behaviour at long times.

3.2 Electrodeposition of pure silicon

Therefore, molten salt electrolytes were considered. Many studies on electrodeposition of silicon have been published. The electrolytes were based on molten CaCl₂ with SiO₂ as the raw material, fluoride melts with K₂SiF₆ or cryolite (Na₃AlF₆) containing dissolved SiO₂ [13-14]. Based on literature reports most of the experimental studies were carried out in electrolytes based on molten CaCl₂ containing some NaCl and CaO at temperatures in the range from 800 - 900 °C. The presence of oxide is important for stabilising dissolved silicon containing complexes to avoid evaporation of silicon chlorides. It was found that silicon is electrochemically active and can be cathodically deposited and anodically oxidised in the CaCl₂ based electrolyte.

Characterisation and analyses of deposited silicon were carried out by SEM/EDS and XRD. Electrolysis at constant current density (300 mA/cm²) produced uniform deposits of high purity silicon, although the contents of boron and phosphorus were too high to meet the requirements for solar grade quality. Another problem was passivation of the silicon anode after relatively short time. Attempts to use pulsed current reduced the passivation significantly. A liquid alloy anode made up from metallurgical grade silicon and copper was used successfully. By constant current electrolysis at low current densities (~50 mA/cm²) it was possible to achieve promising electrorefining effects for key impurity elements such as titanium, phosphorus and boron.

More recently silicon electrodeposition from fluoride electrolytes was studied. Electrochemistry and electrolysis were

performed in molten LiF-KF containing dissolved K_2SiF_6 at temperatures from 550 - 800 °C at potentials well anodic of the deposition of potassium. The electrodeposition process was found to be diffusion controlled, and dissolved Si (IV) species were reduced to metallic Si in two steps via Si (II). High purity and adherent Si deposits were obtained on silver cathodes by galvanostatic electrolysis at 800 °C using moderate current densities ($\sim 40 \text{ mA/cm}^2$) and moderate contents of K_2SiF_6 ($\sim 5 \text{ mol\%}$). The best current efficiency for Si deposition was found to be $\sim 95 \%$. Fig. 3 shows results from cyclic voltammetry using a silver electrode. Silicon deposition takes place in one step, and the rate of the process is diffusion controlled. Square wave voltammetry indicated the intermediate presence of a Si (II) species.

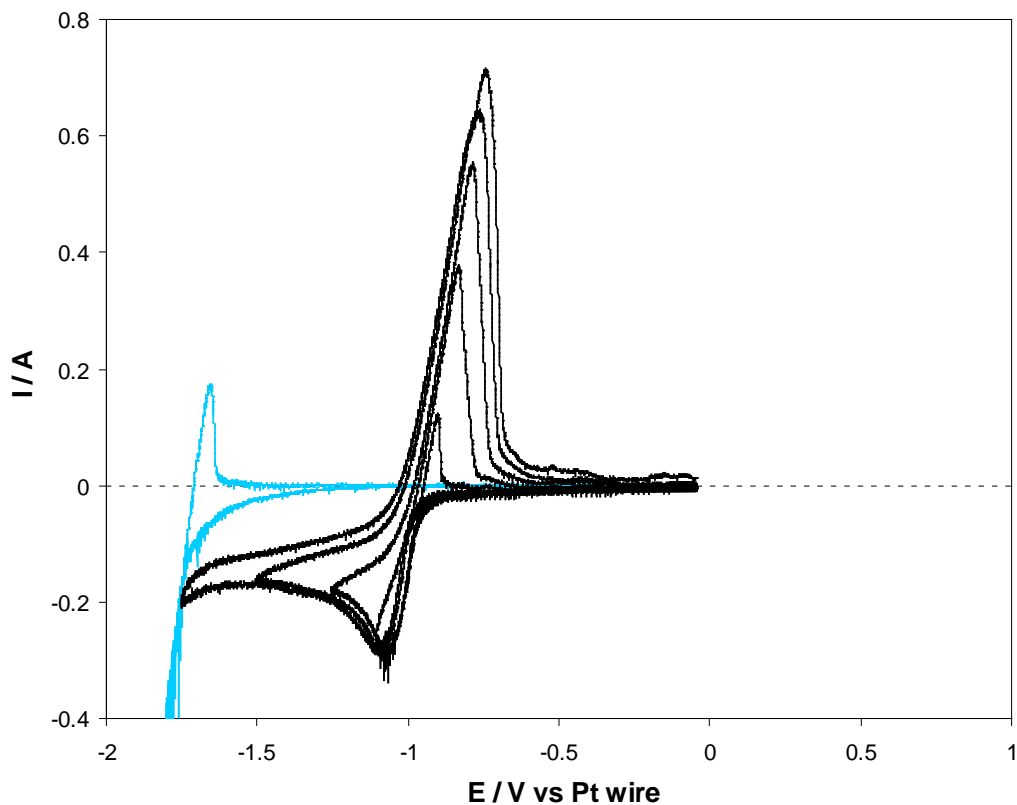


Fig. 3 Cyclic voltammetry (200 mV/s) at a silver working electrode at 800 °C in molten KF-LiF before and after addition of 5 mol% K_2SiF_6 .

3.3 Electrochemical production of titanium

Electrodeposition of titanium from molten chloride electrolyte by using a titanium oxycarbide anode prepared by sintering TiO_2 and carbon was studied in molten chloride electrolytes. This approach was studied in order to overcome problems related to carbon contamination and also possibly to reduce the influence of disproportionation reactions involving various oxidation states of titanium. Pure titanium has been obtained in electrolysis experiments, although contaminated by oxygen and carbon. Also the formation of Ti (III) species in the anode reaction is a challenge in developing this concept, and a main challenge is to achieve a uniform and well-adhering cathodic deposit.

Liquid metal cathodes of Bi, Sn and Zn were tested in preliminary experiments to improve the cathodic formation of

titanium. Alloys of Ti with Bi and Sn were obtained. Fig. 4 shows voltammetry using a liquid bismuth cathode. The results indicate that Ti (III) species are reduced to titanium metal in one step. Thus the use of liquid cathodes may eliminate the valency problems of dissolved titanium species. However, an extra processing step to separate titanium from the alloy is needed.

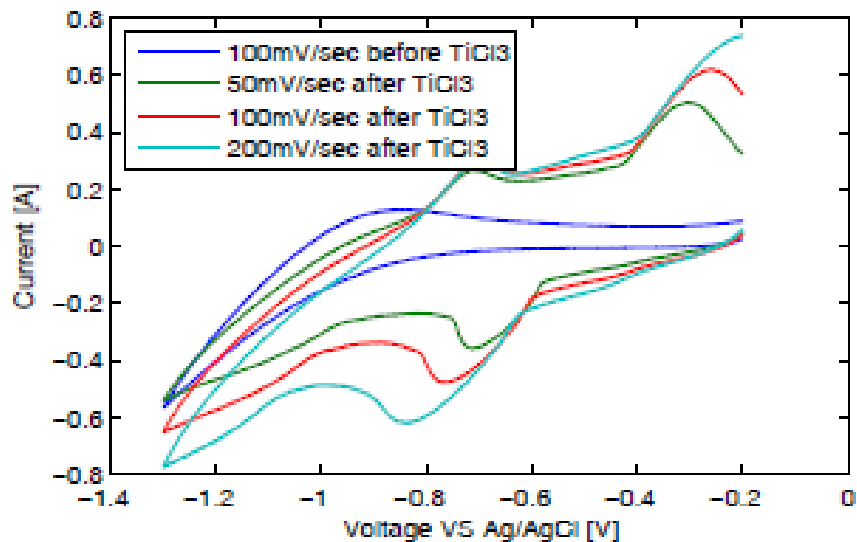


Fig. 4. Cyclic voltammograms at a liquid Bi electrode in molten NaCl-KCl before and after adding TiCl_3 at 800°C .

4. Conclusions

Experimental studies of metal deposition processes in molten salt electrolytes have shown that new and sustainable processes for the production of high value metals may be developed. These include electrodeposition of high purity silicon and titanium. Also the possibility to use molten salt electrochemical processing for handling of waste and isolating pure metals by electrodeposition is promising. Dissolution of metals and electrochemical nucleation are important features of metal deposition processes in molten salts.

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