

TECHNICAL NOTE

Electrolytic production of magnesium: effect of current density

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The effect of current density on current efficiency for the electrolytic production of magnesium metal and on the wetting of a steel cathode by magnesium has been studied in a proprietary sodium chloride-rich NaCl–MgCl₂ melt at $710 \pm 10^\circ\text{C}$. With the exception of the smallest applied current density, current reversal chronopotentiograms at a small steel electrode in an argon blanketed melt showed a linear increase of current efficiency with increasing current density up to 0.7 A cm^{-2} . The current efficiency then remained constant around 94% over a current range of $0.7\text{--}1.2\text{ A cm}^{-2}$. Further increase in the current density, however, produced a decline in the current efficiency. Interestingly, a linear increase in the current efficiency with current density even up to 1.2 A cm^{-2} , the highest applied current, was observed in a laboratory cell which simulated the production cell practice. The extent of the steel wetting by molten magnesium decreased with decrease in the cathodic current density, and the wetting was poor below 0.4 A cm^{-2} . This study suggests that magnesium cells can be run at higher current densities than $0.3\text{--}0.5\text{ A cm}^{-2}$, the average operating current density in commercial cells, to maximize the current efficiency, the production rate and the space time yield. Other variables in production cells may make higher current density operation difficult in practice.

1. Introduction

It is well known that the current efficiency of aluminium electrowinning from molten salts increases with an increase in the current density [1]. Although both magnesium and aluminum metals were electrolytically produced for the first time a century ago, there are only a few Russian studies [2] on the current density effect on the current efficiency of magnesium production in KCl-rich carnallite melts.

This work was, therefore, undertaken to study the effect of current density on the current efficiency for the electrolytic production of magnesium in a proprietary sodium chloride-rich NaCl–MgCl₂ melt at $710 \pm 10^\circ\text{C}$. In addition, the influence of current density on the wetting by magnesium of the steel was studied because higher current efficiencies have usually been achieved on well-wetted steel surfaces.

2. Experimental details

A conventional, high-temperature controlled Argon atmosphere furnace, as described pre-

viously [3], was adapted for the chromopotentiometric measurements. The Vycor viewport (2.5 cm in diameter) at the top brass flange was protected against salt attack and fogging by a moveable shutter. Additionally, the inner vertical wall of the Inconel chamber was protected against salt attack with a Grafoil liner. To avoid the development of excessive stress inside the furnace due to pressure, temperature and power differentials, a nozzle attachment with a graphite rupture disc was installed on the Inconel chamber at about one-third the distance from the top. A full description of this furnace will be presented in a separate paper [4].

Sodium chloride-rich NaCl–MgCl₂ melt, a proprietary bath of The Dow Chemical Company, was used in all experiments; CaCl₂ and KCl were also present as other components in this melt. All chemicals used were anhydrous and Analar grade. As an extra precaution these chemicals were further dried individually under vacuum at 200°C . A salt mixture for the proprietary bath was prepared in a dry box. About 100–150 g of this mixture was weighed into a glassy carbon crucible and transferred quickly

from the dry box into the furnace. The cell was assembled as soon as possible and then evacuated while gradually raising the temperature to 200°C. After overnight drying at 200°C the salt mixture was melted under an argon atmosphere. The molten bath thus prepared was studied at $710 \pm 10^\circ\text{C}$ only after a pre-electrolysis purification to remove residual water, hydroxide, oxide and other metallic impurities. The electrodeposition and dissolution of magnesium were studied at a steel cathode (of immersed area $\sim 0.35\text{ cm}^2$) with a glassy carbon crucible counter electrode and a silver-silver ion (0.01 M) reference electrode in a pear-shaped quartz bulb with a very thin end. The steel cathode was mechanically polished, hydrochloric acid etched, washed with deionized water and dried prior to the measurements. Current reversal chronopotentiometric measurements were carried out using a PAR 175 potentiostat with a type 173 programmer and the potentiograms were recorded on a Houston Omnigraph X-Y recorder.

For laboratory cell experiments which simulated the production cell, the cell description, melt preparation and other experimental parameters were presented in an earlier paper [5]. The steel cathode and graphite anode were, however, arranged in a parallel-plate configuration. Nevertheless, the cell top was unprotected against air other than by existing chlorine gas. Unlike in the controlled atmosphere experiments, hydrous feed from Dow was used as a source of magnesium chloride. Moreover, pre-drying of chemicals at 200°C and weighing all chemicals in a dry box were omitted. To enhance the cohesion of magnesium balls [5], about 1% fluorspar was maintained in these baths. Also, the cell was fed continuously during electrolysis with the hydrous feed to keep the magnesium chloride concentration at the optimum level. Electrolytically produced magnesium was removed at a pre-determined interval, washed quickly with plenty of water to remove adhered salts, washed with alcohol, air-dried and weighed. This weight and the total amount of charge consumed to produce this amount of magnesium was used to calculate the current efficiency of magnesium.

3. Results and discussion

3.1. Current reversal chronopotentiometry

Current reversal chronopotentiograms were obtained on the steel electrodes at constant current densities between 0.1 and 3 A cm^{-2} . Although a nucleation effect due to the deposition of magnesium on steel was seen at lower current densities and at shorter times, well-defined deposition plateaus were normally observed except at very high current densities. Typical chronopotentiograms for the applied current densities of 0.3–1.4 A cm^{-2} are presented in Fig. 1.

Interestingly, a linear relationship was found between the deposition potential (at 2.5 s from the deposition plateau, Fig. 1) and the applied cathodic density which suggests an ohmic-type current-potential relationship. Such a relation may postulate for the rate-determining step a volume diffusion of the magnesium species rather than an interface kinetic process for the magnesium ion reduction. The absence of a diffusion-limited current for the magnesium ion reduction can possibly be explained by the suggestion that succeeding sodium ion reduction reaction is likely to obscure such a plateau, particularly at high current densities and in a sodium-rich melt such as is used here.

Even though well-defined dissolution plateaus were seen at all applied current densities (Fig. 1), the length of these plateaus showed a strong dependence on the applied cathodic current density and the plateaus were longest between 250 and 400 mA currents (Fig. 1). Since both deposition and dissolution of magnesium were carried out at a constant current, a ratio of the dissolution to the deposition time gives the current efficiency for magnesium production at a given applied current. The current efficiencies thus calculated at the various applied currents are presented in Fig. 2. With the exception of the first data point, the current efficiency increased almost linearly up to 250 mA and then remained fairly constant at about 94% between 250 and 400 mA. However, the current efficiency decreased with a further increase in current. The loss in current efficiency at both extremes

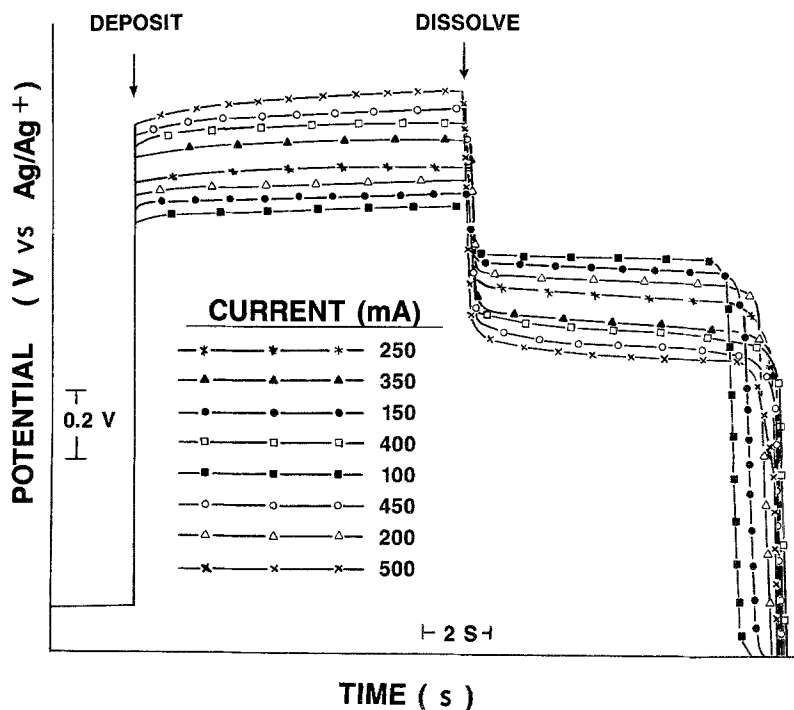


Fig. 1. Potential-time plots for the deposition and dissolution of magnesium at various currents. Area of steel cathode = 0.35 cm².

of the applied currents can be attributed to other undesirable electrochemical reactions, i.e. the reduction of impurities such as water, hydroxides, metal hydroxides and metal ions at low currents, and the reduction of sodium ion at high currents.

3.2. Current efficiency in the laboratory cell

Since the controlled argon atmosphere transient measurements, as described in the preceding section, indicated that the current efficiencies either

increased or remained highest as the current densities increased to 1.2 A cm⁻², it was decided to employ current densities up to 1.2 A cm⁻² in the laboratory cell experiments whose operating conditions closely resembled those of production cells.

In the first series of runs the apparent area of the cathode was approximately 86 cm²; this area is about one-half that of the anode. The metal was dipped after the passage of a 200 A h charge. The effect of the current density on the current efficiency is shown in Fig. 3. As anticipated,

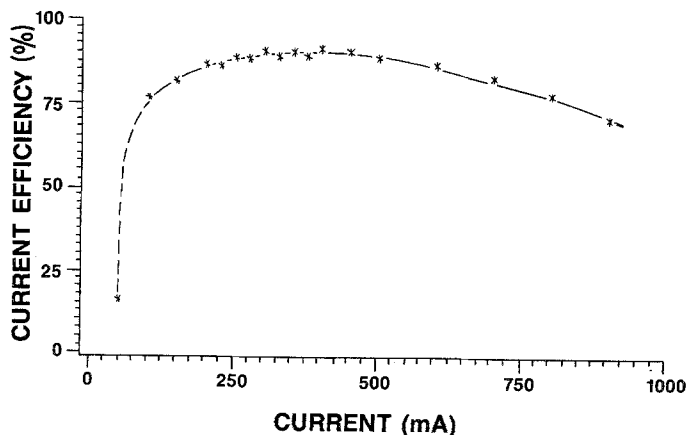


Fig. 2. Plot showing the effect of current on the magnesium current efficiency. Area of the steel cathode = 0.35 cm².

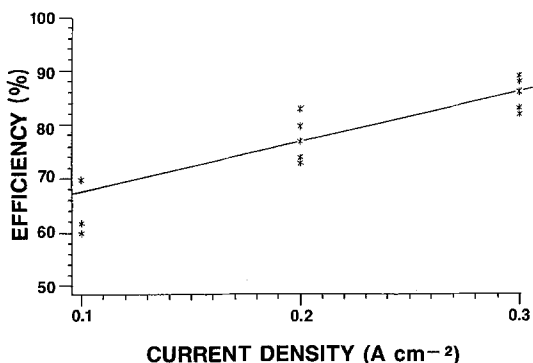


Fig. 3. Plot showing the dependence of current efficiency on the cathodic current density. Total Ah = 200; anode area = 140 cm²; cathode area = 86 cm².

an approximately linear increase of the current efficiency with the cathodic current density was found although there were considerable scatter of the data. In order to increase the cathodic current densities, and due to limitation of our rectifier output, smaller cathodes of area approximately 25 cm² were used in the second series of runs. Consequently, the cathode to anode ratio was reduced to about one-fourth. The results showed an increase in the current efficiency with increasing cathodic current density, a similar observation as in the first series. However, the current efficiency at a given current was apparently the same for the first and the second series even though the cathodic current density was higher for the latter because of the smaller cathode. This indicates the importance of anodic chlorine evolution on the current efficiency, which probably influences the circulation

of the electrolyte and, hence, the rechlorination of the electrolytically produced magnesium.

The anode area was also reduced in the next two series of runs such that a ratio of cathode to anode area of about one-half, as in the first series, was established. The applied cathodic current densities were in the range 0.2–1.2 A cm⁻². In the third series, electrolysis was terminated after passing a 100 Ah charge and the results are shown in Fig. 4. In agreement with the earlier series, the current efficiency increased with increase in the cathodic current density. It is important to note that the experiments, in general, were at high currents during the day and at lower currents during the night; during the later runs the cells were unattended. For a comparison, 8 h daytime experiments at different cathodic current densities were performed in the fourth series. Unfortunately, one of the experiments at 1 A cm⁻² (174 Ah) gave a slightly lower current efficiency than the anticipated value due to a short-circuit condition which existed for about an hour. In spite of this, Fig. 5 clearly supports the current efficiency dependence on the applied current density as found in the earlier series.

Thus, the increase in the current efficiency with the increase in the current density, as observed in the laboratory cell measurements, is in agreement with the data from the chronopotentiograms described in the preceding section and with the reported data for magnesium in KCl-rich carnallite melt [2] and for aluminum in cryolite [1].

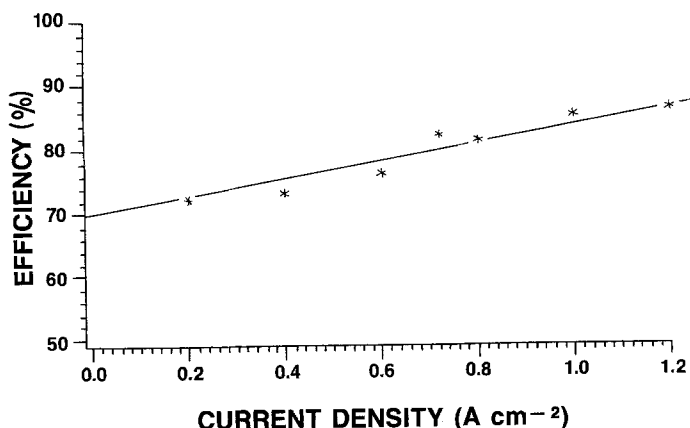


Fig. 4. Plot showing the dependence of current efficiency on the cathodic current density. Total Ah = 100; anode area = 50 cm²; cathode area = 25 cm².

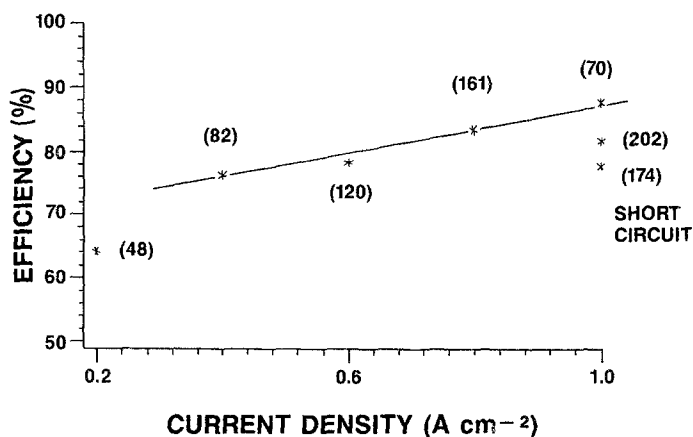


Fig. 5. Plot showing the dependence of current efficiency on the cathode current density after 8 h electrolysis; the number shown in the parenthesis is the total Ah passed. Anode area = 50 cm²; cathode area = 25 cm².

3.3. Wetting

Just prior to metal dipping, in the experiments as described in the preceding section, the steel cathode was slowly lifted above the melt, viewed for magnesium wetting and photographed. Typical photographs for the electrolysis at two cathodic current densities are shown in Fig. 6. Interestingly, cathode wetting by magnesium at 1 A cm⁻² or above was superior (Fig. 6a), so that films of magnesium a few millimetres thick or isolated magnesium balls adhered well on to both sides of the cathode. However, the extent of cathode wetting appeared to decrease with decrease in cathodic current density. The non-wetted areas at a given lower cathodic current density were always greater on the side not facing the anode compared with the side facing the anode; this is obviously due to the shorter current path to the former side than the latter. Moreover, the wetting was poor below 0.4 A cm⁻² even on the side facing the anode (Fig. 6b).

Super-wetting by magnesium and the higher current efficiencies for magnesium electrodeposition clearly suggest that the well-wetted substrate facilitates the growth of the electrodeposited magnesium to form bigger balls prior to detachment from the cathode substrate. A poorly-wetted surface, i.e. at lower cathodic current densities, is a likely source of fine magnesium spheres which chlorinate readily in the cell bath and give a low magnesium yield.

4. Conclusions

The data presented in this paper indicate a clear and marked effect of current density on the current efficiency for the electrolytic production of magnesium, and on the wetting of the steel by magnesium in a Dow proprietary sodium chloride-rich NaCl-MgCl₂ melt. Both the efficiency and the extent of wetting increased with an increase in cathodic current densities up to 1.2 A cm⁻². Thus, this study suggests that

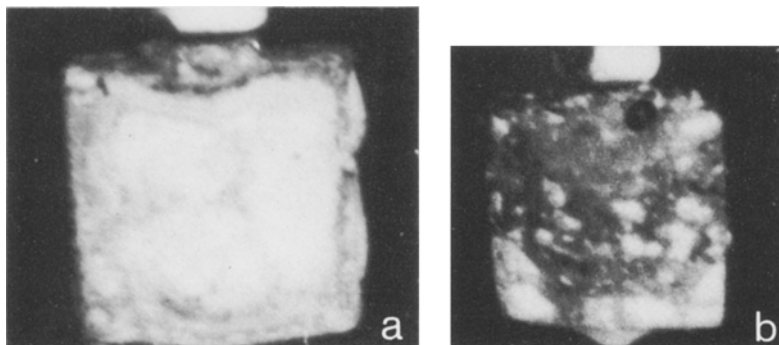


Fig. 6. Photographs showing the wetting by magnesium on the steel cathode surface facing the anode (conditions as in Fig. 5). a, 1 A cm⁻²; b, 0.2 A cm⁻².

operating current densities greater than 0.3–0.5 A cm⁻², the average operating current densities in commercial cells [2, 6–10], can increase the current efficiency and, hence, the production rate and the space–time yield. Certainly, sodium metal deposition can set the theoretical limit for the maximum operating current. Equally, the influence of the anodic current density on the efficiency is also evident from this work; the rate of chlorine evolution and the size of chlorine bubbles, which depend on the anodic current density, change the mass transfer conditions within the electrode gap. Furthermore, heat balance at high current densities would unfortunately be a problem. Therefore, more work in commercial cells or cells that simulate the hydrodynamic conditions of the commercial cells is needed to further optimize the maximum current density for magnesium cells.

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