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Influence of Substrates on the Electrochemical Deposition and Dissolution of Aluminum in NaAlCl₄ Melts

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ABSTRACT

The deposition and dissolution of aluminum in NaAlCl₄ melts saturated with NaCl have been investigated by voltammetry and potentiometry for different electrode materials at 175°C. The tungsten and glassy carbon electrodes are shown to be electrochemically inert in the melts, whereas copper is electrochemically active; it dissolves into the melts at a low anodic potential. On a nickel substrate, nickel dichloride will be formed at a potential of ca. 1.0 V vs. an aluminum reference electrode. The reversibility (of deposition and dissolution of aluminum) is found to be strongly affected by current density and the coulombic charges used for glassy carbon electrodes, mainly because of poor adhesion of the deposits to the substrate. The reversibility is noticeably affected by the magnitude of deposition current density for the tungsten electrodes, while it remains high on the nickel electrode under all conditions investigated. Nickel and, to some extent, tungsten electrodes proved to be appropriate as working anodes in the Al/NaCl-AlCl₃/Ni battery system.

Electrodeposition of aluminum in chloroaluminate melts has been extensively studied. It has been shown that the electrode substrates used have a predominant influence on the electrode processes. In early studies on a new aluminum refining technique at rather low temperatures in NaCl-AlCl₃ melts, Midorikawa (1-3) found that a lead plate was the most favorable material for the formation of compact, smooth, and adherent aluminum deposits, followed by zinc, copper, iron, silver, aluminum, magnesium, and carbon in that order. Aluminum deposits on a carbon plate were never adherent but were powdery (1).

Later, several investigations dealing with aluminum electroplating were performed (4-9). Iron, copper, and various types of steel were usually used as the substrates. Nayak and Misra (4) and Paučírová and Matiašovský (6) found that a copper cathode was better than iron for aluminum plating. Also, for a mild steel substrate, pretreatment by electropolishing in the melt itself proved to be very helpful (5).

The kinetics of aluminum electrodeposition have been studied mainly for aluminum electrodes (10-14). Glassy carbon, platinum, and tungsten electrodes have also been used in the investigations of electrochemical reduction of aluminum in MCl-AlCl₃ melts, where MCl is an alkali metal chloride (15) or an organic chloride, e.g., N-butylpyridinium chloride (16-18) or 1-methyl-3-ethylimidazolium chloride (19). It was found that the tungsten and platinum electrodes allowed for underpotential deposition and that an Al-Pt alloy was formed on the platinum electrode.

In connection with our development of high energy density batteries with aluminum anodes (20, 21), studies on both deposition and dissolution of aluminum in chloroaluminate melts have been performed by using glassy carbon electrodes (22-25). It was found that the deposition of aluminum on carbon takes place via a progressive nucleation and growth mechanism (24). Current reversal chronopotentiometry (CRC) measurements showed that coulombic ratios of dissolution to deposition depended significantly on the nature of the substrates (25).

On the other hand, in batteries with aluminum anodes, aluminum deposited during charging cannot be completely reused in the following discharging process. Some deposited aluminum was probably lost by falling off, and thus the aluminum base was consumed instead. This resulted in the deterioration of aluminum anodes after prolonged cycling (26). This problem can be resolved by using an inert anode such as tungsten or nickel, which can be completely and quantitatively stripped for aluminum to obtain a reproducible surface for the next cycling. A successful attempt was made using nickel felt as an electrode substrate in an Al/NaCl₍ₛ₎-AlCl₃/Ni battery (27). However, the cathodic formation of nickel chloride occurred in this system or nickel chalcogenide in melts containing chalcogens like sulfur or selenium.

The present paper examines the aluminum deposition and dissolution processes as a function of substrates.

Experimental

The distillation of aluminum chloride and the drying of NaCl have been described previously (23). NaAlCl₄ prepared from an equimolar mixture of AlCl₃ and NaCl was further purified by zone refining (24). All handling of chemicals was performed in a dry-air-filled glove box (dew point < - 50°C).

Glassy carbon (V10, Le Carbone Lorraine, France), tungsten (99.94%, Wolfram-Industrie, Germany), copper (> 99.99%, ECU), nickel (99.99%, Johnson Matthey Chemical, Limited, England) as well as aluminum (99.999%, Vereinigte Aluminium-Worke AG, Erftwerk, Germany) were used as electrodes. Three millimeter diameter rods of various materials were sealed under vacuum into Pyrex tubing, which were then cut and polished to a mirror-like finish. In the case of the aluminum electrode, a Teflon tube was used instead of Pyrex as the insulating material. The glassy carbon rods were treated at 900°C under vacuum before sealing. Aluminum electrodes were used as the counter and reference electrodes in all cases.

The test cells were made of a square Pyrex tube as described previously (23). All measurements were performed in a see-through oven of our own construction (24).

Voltammograms were obtained using an electrochemical system built in this laboratory. Current reversal chronopotentiometry (CRC) was performed by using a Keithley 224 Programmable Current Source. A Keithley 199 System DMM/Scanner was used to monitor the potential. All measurements were controlled by a battery test program developed in this laboratory and were executed on an IBM compatible computer with IEEE-4988 interface.

Results and Discussion

Voltammograms.—Figure 1 shows voltammograms obtained for NaAlCl₄ saturated with NaCl at 175°C using glassy carbon, tungsten, nickel, aluminum, and copper substrates.

For glassy carbon and tungsten electrodes, a small difference in the cathodic branches of the voltammograms was seen. On the tungsten electrode, a small cathodic current appeared and increased continuously before solvent reduction started at −65 mV. This may suggest underpotential deposition taking place on the tungsten electrode. During the anodic potential sweep, electrochemical windows of 2200 mV (from 50 to 2250 mV vs. Al) and 2050 mV (from 50 to 2100 mV vs. Al) were observed on glassy carbon and tungsten electrodes, respectively. Only 3 and 5 μA, respectively, of residual currents occurred in the windows, showing that the melts used were virtually pure. Chlorine gas was observed evolving on the electrodes at potentials corresponding to the decomposition of the solvents. It has been shown by Uchida and co-workers (28, 29) that evolution of chlorine from chloroaluminate

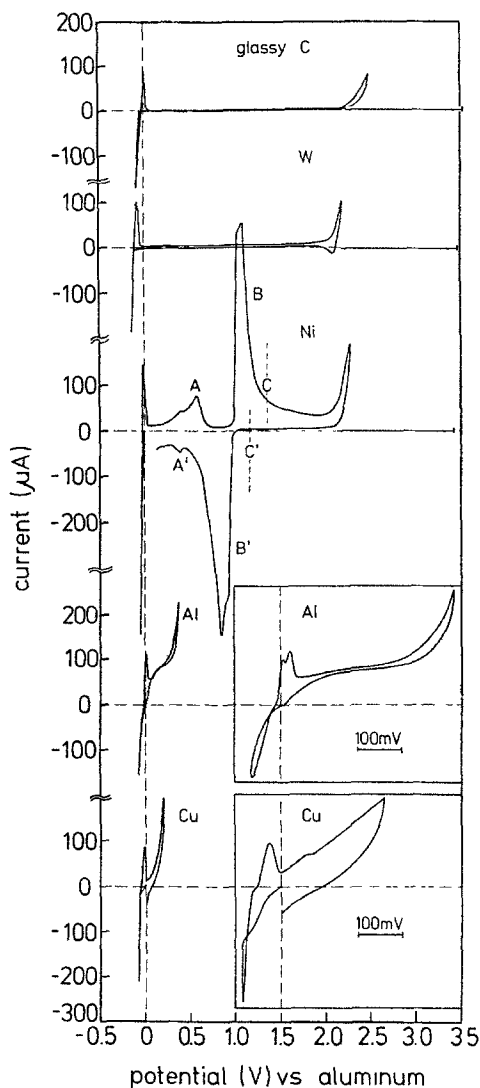* Electrochemical Society Active Member.

Fig. 1. Voltammograms obtained in NaAlCl₄ saturated with NaCl at 175°C. Sweep rate, 4 mV/s. Electrode area, 0.07 cm². Substrates: glassy carbon, tungsten, nickel, aluminum, and copper. The locations of C and C' found in Ref. (30) are indicated with short dashed lines.

eign substrates. By anodic potential sweeping, a stripping peak is observed immediately after scan reversal followed by a relatively constant anodization current until the electrode potential is >200 mV. At this point, stripping from the bulk electrode phase appears to become very important. This behavior may result from a porous, but insoluble oxide film on the electrode surface.

The voltammetric behavior of the copper electrode was very similar to the aluminum electrode. Copper dissolves continuously into the melt starting at a slightly anodic potential *vs.* the aluminum reference. No passivation phenomenon was observed. After numerous measurements had been performed, the melt still appeared fairly colorless. The possible products from the copper dissolution, readily soluble in the melt, were univalent copper ions, as found in NaCl-KCl-AlCl₃ (31) and other alkali chloride-AlCl₃ (32) melts.

Current reversal chronopotentiometry.—Figure 2 shows a set of chronopotentiograms obtained for NaAlCl₄ melts saturated with NaCl at 175°C. In agreement with the voltammetric measurements, completion of dissolution of the deposited aluminum was very definite for glassy carbon, tungsten, and nickel electrodes, but indefinite for aluminum and copper substrates. In the latter case, no transition data could be obtained from the chronopotentiograms. For glassy carbon, tungsten, and nickel electrodes, the transition time was determined from the potential-time curves by extrapolation of the maximum slope at the completion of aluminum dissolution (followed by the chlorine evolution). The coulombic efficiency (ratio of charge in reoxidation to charge in deposition) was then calculated.

Figures 3-7 show the results of the coulombic efficiencies as functions of deposition current density or stripping current density as well as coulombic charge. Each point in these figures was the average value for three cycles. The vertical bars indicate the ranges of standard deviations.

It can be seen that in some cases, especially for the glassy carbon electrode, the standard deviations are significant (*ca.* 10%). This lower reproducibility was the result of the poor adhesion of aluminum deposits to the glassy carbon substrate. As mentioned previously (25), it can be observed through a microscope that some forms of small aluminum pieces fell off into the melt during reoxidation and that small aluminum particles remained on the electrode surface during chlorine gas evolution, apparently adhering poorly to the electrode.

In order to examine the definite effect of deposition current density on the coulombic efficiency, an arbitrary cur-
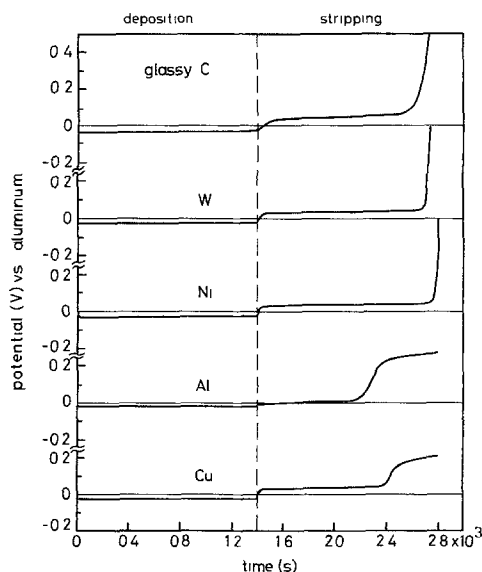
melts was dependent on the types of substrate used. That may explain the difference in the electrochemical windows observed for carbon and tungsten electrodes.

On the nickel electrode, cathodic deposition of aluminum was identical to that on a tungsten electrode. Upon sweeping toward the positive potential side, two couples of current peaks appeared and were marked with A, A', and B, B', respectively. In the voltammetric measurements on nickel in NaCl-KCl-AlCl₃ melts by Prepostffy (30), a similar B and B' current peak couple was observed, followed by an indistinct couple, C and C'. Potentiometric measurements (27) in the Al/NaCl-AlCl₃/Ni system have shown that nickel dichloride was formed at *ca.* 1.0 V *vs.* an aluminum reference. This corresponds to the couple of sharp current peaks, B and B', *i.e.*

$$Ni + 2Cl^- \leftrightarrow NiCl_2 + 2e^-$$

The reactions corresponding to the couple A and A' are unknown, though there is more evidence on their existence (27). The couple C and C' found in Ref. (30) and confirmed by potentiometry (27), however, was ambiguous in the present measurement. At potentials ranging between 1.3 and 2.1 V *vs.* the aluminum reference, a small anodic current was observed at the nickel electrode. Above this range, chlorine evolved due to solvent decomposition.

For the aluminum substrate, aluminum deposition occurred starting at zero potential *vs.* aluminum. As shown previously in cathodic polarization measurements (25), aluminum is easier to deposit on itself than on some for-

Fig. 2. Chronopotentiograms obtained in NaAlCl₄ saturated with NaCl at 175°C. Current densities for both deposition and dissolution, 0.7 mA/cm². Total charges for both deposition and dissolution, 1 C/cm². The vertical dashed line indicates current reversal. Substrates: Glassy carbon, tungsten, nickel, aluminum, and copper.
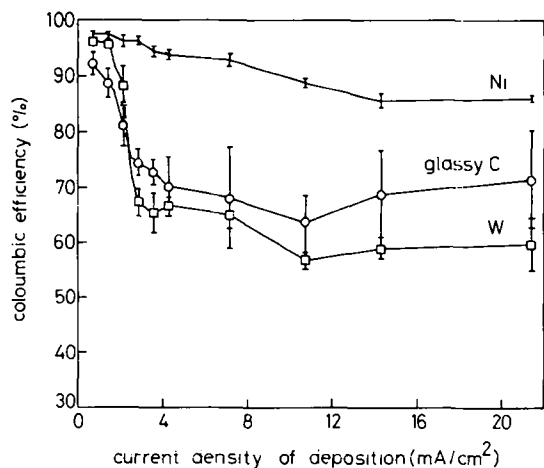
Fig. 3. Coulombic efficiency of aluminum deposition and dissolution as a function of deposition current density in $NaAlCl_4$ saturated with NaCl at 175°C. Dissolution current density, 0.7 mA/cm². Substrates: nickel, glassy carbon, and tungsten.

Fig. 5. Coulombic efficiency of aluminum deposition and dissolution as a function of current density in $NaAlCl_4$ saturated with NaCl at 175°C. Same current densities were used for both deposition and dissolution. Substrates: nickel, glassy carbon, and tungsten.

rent density of 0.7 mA/cm² was used for the dissolution of aluminum deposited at different current densities (Fig. 3). Similarly, 0.7 mA/cm² of current density was used for deposition, followed by dissolution at different current densities (Fig. 4). In both cases, a total charge of 1 C/cm² was used for each run of deposition or dissolution. It can be seen from Fig. 3 that the deposition current density had a strong effect on the coulombic efficiency, especially for carbon and tungsten substrates. Coulombic efficiencies of more than 90% were obtained on carbon and tungsten electrodes only, at current densities below ca. 2 mA/cm². At higher current densities, coulombic efficiencies went down to around 60%. For the nickel electrode, however, the influence of deposition current density was not so strong, and coulombic efficiencies not far from 90% were obtained in the whole range of investigated current densities.

The dissolution current densities, however, generally had a smaller effect on the coulombic efficiency for the electrodes (see Fig. 4). Remarkably high coulombic efficiencies (more than 95%, highest value 98.5%) were achieved throughout the current range investigated for the nickel electrode. For tungsten and glassy carbon electrodes, the effect of varying the dissolution current density alone was also smaller than that of varying the deposition current density alone. Furthermore, the relative positions of glassy carbon and tungsten were exchanged.

Figure 5 shows the results gained from measurements using the same varying current densities for both deposi-
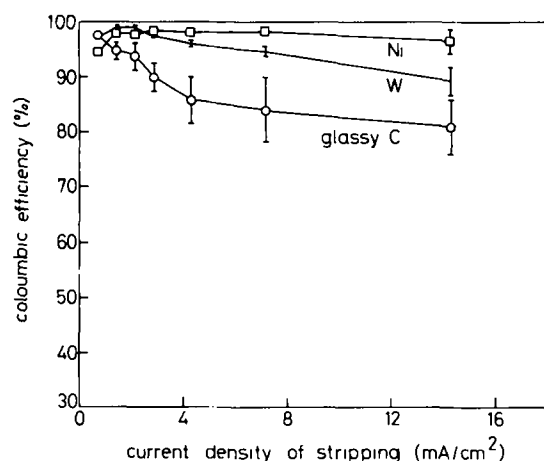
tion and dissolution. Also in this case, a total charge of 1 C/cm² was used in each run of deposition or dissolution. As seen in Fig. 3 and 4, the variation of both deposition and stripping current densities was seen to have a rather small consequence in the coulombic efficiencies for the nickel electrode. Furthermore, for this electrode there was no clear indication, as seen from Fig. 5, of an additive effect by varying both deposition and dissolution in the same experiment. However, for the glassy carbon and the tungsten electrode (where generally a more pronounced decrease was found) a comparison between Fig. 3, 4, and 5 showed that the sum of the decreases seen in Fig. 3 and 4 for a given current density was not far from the decrease seen in Fig. 5 at the same current density.

As can be seen from Fig. 6 and Fig. 7, the overall coulombic charges used for deposition or dissolution processes in each cycle affected the coulombic efficiency only for glassy carbon electrodes. With nickel or tungsten electrodes, coulombic efficiencies around 95% were normally obtained throughout the range of coulomb charge used (from 1 to 20 C/cm²) at both 0.7 and 1.4 mA/cm² current densities.

Conclusions

The influence of substrates on the deposition and dissolution of aluminum in $NaAlCl_4$ melts saturated with NaCl has been investigated by voltammetry and chronopotentiometry. Tungsten and glassy carbon electrodes were shown to be electrochemically inert in the melts. Copper dissolved electrochemically into the melts at low positive

Fig. 4. Coulombic efficiency of aluminum deposition and dissolution as a function of dissolution current density in $NaAlCl_4$ saturated with NaCl at 175°C. Deposition current density, 0.7 mA/cm². Substrates: nickel, tungsten, and glassy carbon.
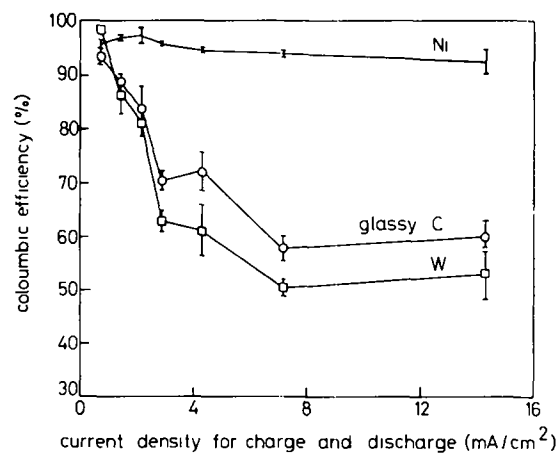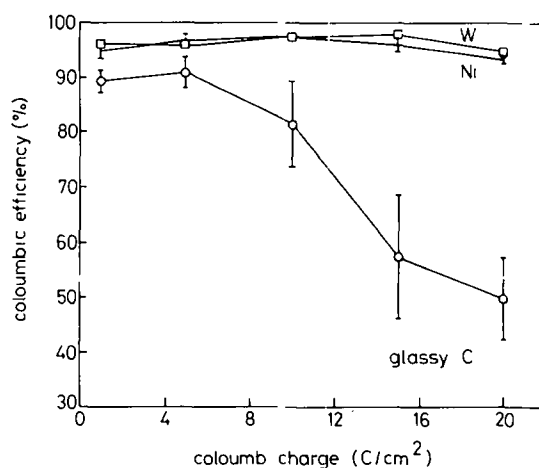

Fig. 6. Coulombic efficiency of aluminum deposition and dissolution as a function of coulombic charge in $NaAlCl_4$ saturated with NaCl at 175°C. Current density of 0.7 mA/cm² was used for both deposition and dissolution. Substrates: tungsten, nickel, and glassy carbon.
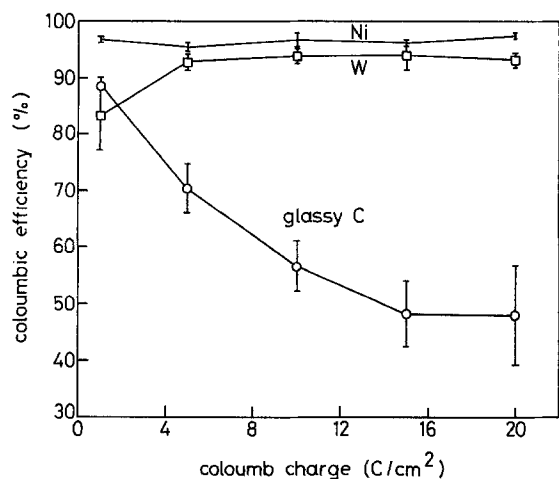
Fig. 7. Coulombic efficiency of aluminum deposition and dissolution as a function of coulombic charge in $NaAlCl_4$ saturated with $NaCl$ at 175°C. A current density of 1.4 mA/cm² was used for both deposition and dissolution. Substrates: nickel, tungsten, and glassy carbon.

potentials. On nickel electrodes, nickel dichloride was formed at a potential of *ca.* 1.0 V *vs.* an aluminum reference. The reversibility of deposition and dissolution of aluminum was found to be strongly affected by current density and coulombic charges used on a glassy carbon electrode, mainly because of the poor adhesion of the deposits to the substrate. The reversibility of aluminum was found to be noticeably affected by the deposition current density on tungsten electrodes, while it remains high on nickel electrodes under all conditions investigated. The nickel and tungsten electrode proved to be applicable as working anodes in the Al/NaCl-AlCl₃/Ni battery system. The nickel electrode is, however, relatively easy to oxidize and this could be a potential problem for battery use.

Acknowledgment

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