INERT ANODE MATERIALS FOR HALL CELLS

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As part of an investigation of candidate inert anode materials for Hall cells, fundamental property data are being measured. As well, performance in laboratory-scale Hall cells operating at current densities up to 3 A/cm² is being assessed. The first generation of materials is selected from the NiO-Fe₂O₃ and CoO-Fe₂O₃ systems. Monocrystalline and grain oriented polycrystalline specimens have been produced by laser processing. The use of a current interrupter in conjunction with an aluminum reference electrode has facilitated overvoltage measurements for oxygen evolution as a function of current density.

Introduction

To improve the energy utilization of the Hall-Héroult cell requires increasing the current efficiency and decreasing the cell voltage. The largest component of the cell voltage is the ohmic drop across the electrolyte, about 1.8 V, which depends upon the electrical conductivity of the melt and electrode separation. Replacing the carbon electrodes with a wettable cathode and a nonconsumable anode would permit significant reduction in electrode separation. However, there would be an increase in cell voltage resulting from a change in cell reaction to:

\[ \text{Al}_2\text{O}_3 \text{ (in cryolite)} = 2\text{Al} \text{ (liquid)} + \frac{3}{2} \text{O}_2 \text{ (gas)} \]

for which the standard potential at 960°C is 2.20 V in contrast to the value of 1.18 V for the present cell reaction.

Despite intensive research efforts, no fully satisfactory inert anode material has been found (1). Such a material must meet the following requirements: resistance to chemical and electrochemical attack by the highly corrosive cryolite-based electrolyte, stability with respect to the evolution of pure oxygen gas at 1 atm pressure, and high electrical conductivity. Such a material must also be affordable, easy to fabricate, and facilitate low-resistance electrical connections.

Metals such as platinum and gold, which can serve as anodes in laboratory-scale cells, are not economical on an industrial scale. Other metals such as nickel or copper, which as metals alone cannot be used as electrodes, have found use in multiphase cermet materials where the ceramic phase is typically an oxide that exhibits low chemical solubility in the melt. These cermet anodes are formulated with the goal of maximizing electrical conductivity and achieving adequate mechanical stability without increasing their solubility in cryolite melts. The metal phase improves the electrical conductivity and provides ductility. The ceramic phase acts as a sparingly soluble monolith. However, neither oxides nor cermet have proved to be completely successful as anodes.

The present research is an attempt to address the issue as a problem in materials science. Through careful control of composition and microstructure it is possible to alter the properties of candidate materials. This combined with newly designed test methods establishes a paradigm for materials selection and formulation.

The most successful compositions so far have been based upon Fe₃O₄ and SnO₂. Compositions from the NiO-Fe₂O₃ and CoO-Fe₂O₃ systems have been chosen for initial examination in this research. Work is underway in three areas: sample preparation, measurement of electrical conductivity, and testing of anode behavior. Sample preparation consists of the growth, wherever possible, of single crystals of the desired compositions. The elimination of other phases, porosity, and grain boundaries enables the study of the intrinsic properties and responses of the materials. Samples are prepared by the floating-zone melting technique described elsewhere (2). Most of the prior studies of the electrical conductivity of ferrites have been performed for electromagnetic applications where the goal is to decrease conductivity. As well, the temperature range of interest in these studies generally was lower than that encountered in Hall cells. As a result, the relevant data base is rather limited although much work has been done on ferrites. For this reason electrical resistivity
measurements of the systems of interest are being made at temperatures spanning Hall cell operating temperatures. Analysis of measurements made for various compositions and dopants may help in the formulation of predictive models for the conductivities in the regimes of interest. Bench-scale Hall cell testing completes the study and will be discussed in more detail.

Experimental

The bench-scale Hall cell is shown in figure 1. The ferrite crystal specimens have the shape of rods, 5 mm in diameter and several cm in length. A section of about 2 cm in length is cut from the crystal with a diamond saw. This section is mounted in an alumina tube with electrical connection provided by Pt paste and Pt foil. The mounting design minimizes the distance between the electrical connection and the electrolyte and insulates the sides of the sample from significant current flow. The mounted sample, attached to a stainless steel rod, is immersed only a few millimeters in the melt. Electrical connection to the molten Al pool cathode is provided by a molybdenum wire. The approximately 150 ml of electrolyte is contained in an alumina crucible which is covered with a BN cap to help minimize evaporation losses. The aluminum reference electrode is contained in a grade HB boron nitride tube which is immersed in the melt next to the test sample. Not shown are the thermocouple and gas inlet tubes which are held just above the melt. The whole system is contained in another alumina tube which allows maintenance of an inert atmosphere of argon. Heating is done by an electrical resistance furnace. The top fitting is designed to permit rapid removal and replacement of anodes.

To resemble industrial compositions, the electrolyte was formulated to contain 5\% CaF$_2$, 7\% Al$_2$O$_3$, and have a bath ratio (BR) of 1.18. Greenland cryolite and reagent grade CaF$_2$ and Al$_2$O$_3$ were used. The AlF$_3$ was supplied by ALCLOA. Impurity levels were taken into account in the formulation. After electrolysis the melt was analyzed for \%Al$_2$O$_3$ and BR using the AlCl$_3$ and pyrotritiation methods, respectively. The Al$_2$O$_3$ content increased to the saturation value of 11\% while the BR stayed at 1.11 ± 0.02. On the basis of these measurements it was decided that AlF$_3$ and Al$_2$O$_3$ additions need not be made during this set of experiments.

Once the electrolyte was molten and temperature was stable at 960°C pre-electrolysis was conducted using a Pt anode. At an applied voltage of 3.00 V a current density of about 1 A/cm$^2$ was observed. Electrolyte purity was measured by applying voltage sweeps at a rate of 20 mV/sec to determine the residual current, defined as the current density at a voltage slightly less than that required for Al$_2$O$_3$ reduction. A clean melt would show a residual current density of less than 20 mA/cm$^2$. Generally pre-electrolysis took less than 3 hr.

Test anodes were immersed into the melt after pre-electrolysis. As of this writing, measurements are made during slow voltage sweeps, at steady state, and during electrolysis. Conversion to computer control and measurement will facilitate the application of current pulses and faster voltage sweeps. The overvoltage was calculated by subtracting the IR drop and the current to the reference electrode of the IR drop in this case refers to the portion of the ohmic drop across the electrolyte that is included in the anode-to-reference potential and is measured with a current interrupter (ESC Model 810-02- modified, The Electrolysis Co., Inc., E. Amherst, N.Y.). The zero current emf was obtained from the extrapolation of the anode-to-reference voltage to open circuit, i.e., i = 0, and usually measured 2.16 V. This voltage contains a component of magnitude 0.06 V, the result of membrane and thermal emf's. This component can be assessed by measuring the potential between the Al pool cathode and the aluminum reference electrode while the cell is at rest, i.e. not passing current.

After the completion of testing, the solidified melt and metal were analyzed for Ni, Co and Fe. The oxide samples were mounted and examined by optical and scanning electron microscopy. The chemical compositions of these mounted samples were determined by electron microprobe analysis.

Results

Carbon, Pt, and Au anodes as well as nickel ferrite and cobalt ferrite samples have been tested in the apparatus described above. To date the most consistent results have been obtained for Pt. Since it is expected that oxygen will also be evolved on ferrite samples it is important that the behavior of the melt with a known inert oxygen evolving anode be characterized. For
Figure 2 - Plot of cell voltage vs. current density for Pt, Au, and cobalt ferrite (25 w/o CoO in Fe₂O₃) anodes. Electrolyte composition: \( \text{BR} = 1.11, 5\% \text{CaF}_2, 11\% \text{Al}_2\text{O}_3 \), in Greenland cryolite. \( T = 960^\circ\text{C} \).

Figure 3 - Plot of overvoltage vs. current density for Pt, Au, and cobalt ferrite (25 w/o CoO in Fe₂O₃) anodes. Electrolyte composition: \( \text{BR} = 1.11, 5\% \text{CaF}_2, 11\% \text{Al}_2\text{O}_3 \), in Greenland cryolite. \( T = 960^\circ\text{C} \). The results of J. Thonstad (3) are for an electrolyte consisting of Greenland cryolite saturated with \( \text{Al}_2\text{O}_3 \). \( T = 1000^\circ\text{C} \). These measurements were made under steady state current conditions in a melt containing 5\% \( \text{CaF}_2, 11\% \text{Al}_2\text{O}_3 \), at a bath ratio of 1.11 at 960°C. At least 20 sec elapsed between each measurement. These results are obtained from experiments conducted in three identically formulated electrolytes. The degree of correspondence between data sets is satisfactory. Figure 3 also contains the results of J. Thonstad (3), whose results were obtained at 1000°C in a melt of Greenland cryolite saturated with \( \text{Al}_2\text{O}_3 \).

Figure 4 - Scanning electron micrographs of the cobalt ferrite sample of figures 2 and 3 after electrolysis at a voltage of 3.0 V. Electrolyte composition: \( \text{BR} = 1.11, 5\% \text{CaF}_2, 11\% \text{Al}_2\text{O}_3 \), in Greenland cryolite. \( T = 960^\circ\text{C} \). (a) 100X, (b) 1000X

The chemical analyses indicate that the concentrations of Fe, Ni, and Co in the electrolyte are not significantly increased by the use of a ferrite anode. However, the Fe concentration in the aluminum metal shows a slight increase, while Ni and Co concentrations stay about the same when a ferrite anode is used. These results are reasonable given that the immersion time of the ferrite anodes is presently limited to about 2 hr.

The micrographs shown in figures 4 and 5 are for two cobalt ferrite samples of similar composition tested as anodes in two different experiments. The data shown in figures 2 and 3 are for the sample in figure 4. This sample was electrolyzed for 1 hr at a voltage of 3.1 V and a current density of about 1 A/cm² in a melt containing 5\% \( \text{CaF}_2, 11\% \text{Al}_2\text{O}_3 \) and a \( \text{BR} \) of 1.11 at 960°C. The sample in figure 5 was electrolyzed at 2.00 V for 1 hr in an electrolyte of the same composition.
The current density changed from 0.20 to 0.29 A/cm² during electrolysis. The lower area in all micrographs is the sample, the upper area being electrolyte with shrinkage voids.

The electrolyte in fig. 4a shows mainly cryolite with Al₂O₃ crystals. Fig. 4b shows the micro-roughness that evolves on the sample surface. The white spheres just inside the electrolyte consist of a sulphide of Na, Al, and Co. The source of S is probably the Al₂F₆. The intermediate region between the electrolyte and the sample consists mainly of the elements Al, O, F with some Co and Fe. The sample side of the interface differs very little from the bulk of the sample. As of this writing the chemical analysis technique employed is incapable of distinguishing between O and F.

Figure 5 shows that the effects of cell exposure extend to a much greater depth than observed in the sample in figure 4. In fact, in the region of the sample in contact with the electrolyte about 10% Na by weight was found. In contrast, no Na was found in the anode in figure 4. The appearance of at least two other phases in the affected region is also noted. These have yet to be identified. Possibly the greater rate of oxygen evolution on the anode of figure 4, as compared to that on the anode in figure 5, afforded some measure of protection to the former.

Discussion

The three curves shown in figure 2 extrapolate to a zero current emf of about 2.2 V, as expected for an alumina reduction cell in which oxygen evolution is the anodic reaction. Variations in operating cell voltage at a given cell current are due to variations in geometry caused by differences in sample dimensions. Uncertainties in the measurement of the actual anode surface area also lead to uncertainties in the reported current densities. The line for the cobalt ferrite sample also shows a higher residual current of 100 mA/cm² as compared to a value of less than 40 mA/cm² for the Pt and Au anodes. While the higher residual current could be due to a recontamination of the melt occurring while electrodes are being changed, it is more likely that the residual current is the result of some anode dissolution. This point requires further study.

The Tafel plot shown in figure 3 also confirms that oxygen evolution is the anodic reaction at the anodes studied. The measurement accuracy of the overpotential is about ± 10 mV at lower potentials and ± 20 mV at higher potentials, where electrical noise caused by gas evolution is significant. The
mechanism of oxygen evolution suggested by Thonstad (3) predicts a slope of RT/F at high current densities and RT/3F at low current densities. All three samples exhibit this behavior. The deviation at current densities above about 2 A/cm² is thought by Thonstad to be due to Pt dissolution or a slow oxygen desorption step. The effect of surface roughness of the anode was also noted by Thonstad. Higher overvoltages were observed on smoother surfaces. In this experiment the Pt anode was heavily etched, having been used in several previous experiments, while the Au anode was new. The surface of the ferrite anode was also expected to be rough as a result of the sectioning done with the diamond saw. The surface of the ferrite could be polished for a subsequent experiment in order to confirm this.

These preliminary results demonstrate that the experimental apparatus and method are capable of producing reliable data. The investigation continues with other ferrite samples.

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