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TOWARDS ELIMINATION OF ANODE EFFECT AND PFC EMISSIONS VIA CURRENT SHUNTING

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Abstract

Cyclic voltammetry, stepped-current chronopotentiometry, and stepped-potential chronoamperometry on stationary and rotating-disk carbon electrodes have shown that at potentials exceeding ~3.5 V *vs* Al/Al^{3+} in a laboratory cell the current drops off precipitously. Furthermore, if the potential on the anode falls below ~3.0 V *vs* Al/Al^{3+} the current is quickly restored to values it held previously. The mechanism at work is speculated to be a highly resistive surface film whose formation is strictly potential-dependent. To demonstrate the relevance of these findings to industrial operations, controlled-current electrolysis was conducted in a laboratory cell where it was found that the anode effect and, hence, PFC generation can be completely avoided by simply stepping down cell current in small increments, *i.e.*, by several per cent, whenever cell voltage reaches a critical value.

Introduction

In the primary production of aluminum by the Hall-Héroult process, a departure from normal cell operation known as the anode effect (AE) results in the generation of the perfluorocarbons (PFCs) CF_4 and C_2F_6 [1]. Owing to the high global warming potentials of these gases [2] and the fact that, in the U.S., aluminum smelting is the number one point source of PFC emissions, the Environmental Protection Agency and the primary aluminum producers have established the Voluntary Aluminum Industrial Partnership (VAIP) with the goal of substantially reducing PFC emissions [3]. To gain a better understanding of the mechanism of PFC generation, VAIP has undertaken two projects: (1) measurements of PFC emissions from industrial smelters [4], and (2) basic research into the attendant electrochemistry. The latter is the substance of the present article which reports the salient features of a two-year investigation that culminated in a proposed operational procedure for total elimination of AE and PFC emissions.

While, in the main, PFC emissions are associated with AE, recent measurements made on industrial cells indicate that trace levels of CF_4 are present in the anode off-gas during periods of normal operation [5]; accordingly, AE-free emissions make a very slight contribution to the total quantity of PFCs generated in the production of primary aluminum. Time-resolved data taken by Kimmerle *et al*. on industrial cells [6] show that by far the highest PFC levels are attained during the first minute or so after the cell goes on anode effect. Previous work in this laboratory on the mechanisms of electrode reactions on stationary carbon anodes showed that when the potential exceeds a critical value (about 3 V *vs* Al/Al^{3+}) the cell current drops precipitously [7]. This was attributed to the formation of a highly resistive film on the surface of the anode. The existence of this putative film was shown to be strictly potential-dependent which means that the film can be formed and removed at will by regulation of applied potential. In harmony with this first finding, the rate of PFC generation was found to vary with the magnitude of the anodic overpotential. A PFC reduction strategy that takes into account the design of the power supply was proposed [7]. In the present study we repeated our earlier measurements of the kinetics of anodic reactions, but this time with a rotating-disk electrode. Now, with substantially different flow conditions, we found the same potential dependence as before. Recognizing that it is impractical to operate industrial cells at fixed voltage, we sought to devise another way to exploit the potential dependency of the putative film and propose a scheme involving stepwise reduction of cell current.

Experimental

The cell design was largely identical to that used previously in this laboratory [8,9]. The main difference in the present study was the additional capability to rotate the working electrode. Electrochemical measurements were made with a potentiostat (Solartron Electrochemical Interface, model 1287, Allentown, PA) controlled by a personal computer running Corrware (Scribner Associates, Southern Pines, NC). The working electrode was made of either a graphite or a glassy carbon rod, about 2 to 3 mm in diameter, shrouded by BN, so that about 10 mm in length was exposed to the melt and electrochemically active. The molybdenum crucible served as the counter electrode. The reference electrode was Al/AlF_3 based upon the design patented

by Sadoway [10,11].

For the analysis of anode gas during the electrolysis, a tubular anode was used [8]. The outer vertical surface is insulated with BN; hence, only the inside walls (8 mm in dia., 10 mm height) contact the electrolyte. Anode gas was drawn through an alumina tube from the chamber formed above the melt "inside" the electrode. Gas analysis was performed by gas chromatograph (Model M200 Dual Gas Analyzer, MTI Analytical Instruments, Fremont, CA). The electrolyte was prepared from reagent-grade chemicals: AlF_3 (98%), CaF_2 (99%) and Na_3AlF_6 (97%) dried at 500°C under Ar flow for about 12 hours and pre-melted before being introduced into the reduction cell. Prior to cell testing, melts were subjected to pre-electrolysis to rid them of impurities. All experiments were conducted at a temperature of 975°C.

Results and Discussion

Cyclic Voltammetry

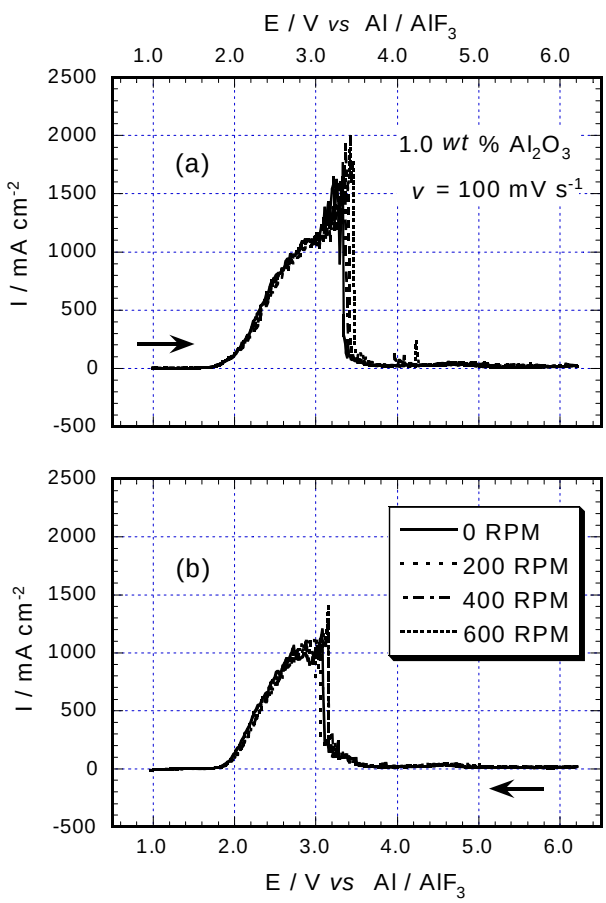

Fig. 1. Cyclic voltammetry of 1 wt % Al_2O_3 melt. Rotating-disk electrode made of graphite. Voltage sweep rate, v, set at 100 mV s^{-1}.

To determine whether the existence of the putative film on the anode was an artifact of the instant flow conditions, the set of experiments described in our previous publication was repeated, but this time with a rotating-disk electrode. The melts under investigation contained 1 wt % alumina dissolved in 84 wt % Na_3AlF_6 - 11 wt % AlF_3 - 5 wt % CaF_2.

Figure 1 shows the behavior of a graphite anode rotating at rates as high as 600 r.p.m. The voltage sweep rate was held constant at 100 mV s^{-1}. For clarity, the forward and reverse sweeps are separated: Fig. 1(a) shows the forwards sweeps, and Fig. 1(b) shows the reverse sweeps. It is clear from the figure that there is no significant difference in behavior between a stationary anode and a rotating-disk anode. This indicates that the pronounced decrease in current through the anode at potentials exceeding ~3.5 V cannot be attributed to poor mass transport. At the same time these data are consistent with the hypothesis that a resistive film forms on the anode strictly in response to the instant value of potential. Likewise, the rapid restoration of cell current on the reverse sweep at potentials below ~3.0 V appears also not to be affected by the flow conditions on the anode.

The seeming lack of dependence of the relationship between current and potential on flow conditions at the anode was seen in our previous work on stationary electrodes where identical voltammograms were obtained by linear sweep voltametry, stepped-potential chronoamperometry, and stepped-current chronopotentiometry [7].

Gas Analysis During Controlled-Potential Electrolysis

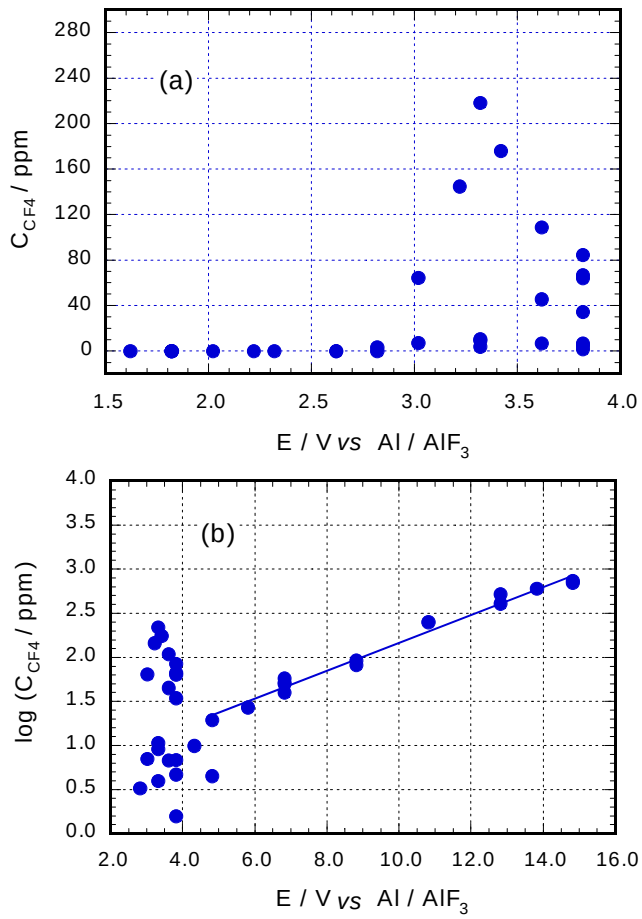

Fig. 2. Steady-state CF_4 concentrations during controlled-potential electrolysis.

To examine the relationship between anode potential and PFC emission rate, we performed controlled-potential electrolysis in a

cell fitted with a tubular anode which facilitated gas collection and analysis [8].

Figure 2 displays steady-state values of the concentration of CF_4 in the anode off-gas as a function of anode potential. For clarity, the data are presented in two segments. Fig. 2(a) shows values of CF_4 concentration measured at potentials up to 4 V. No CF_4 is detected at potentials below 3 V which is reasonable given that the value of E^o, the standard potential, for CF_4 is 2.54 V and activation overvoltages for the formation of polyatomic gas molecules on carbon are typically on the order of several hundred millivolts. At potentials above 3 V, CF_4 levels rise and reach a local maximum at a potential of ~3.5 V. Between 3.5 and 4.5 V CF_4 levels fall, which we believe to be indicative of the formation of the resistive surface film. Fig. 2(b) shows that at voltages exceeding 4.5 V CF_4 levels rise according to the expression

$$\ln c = \alpha + \beta E$$

where c is the concentration of CF_4 in the anode off-gas and E is the potential on the anode measured against an Al/Al^{3+} reference electrode; α and β are constants. This relationship is consistent with an equation derived by Sadoway on the assumption that the rate of formation of CF_4 is limited by chemical reaction kinetics at the electrode-electrolyte interface [9].

So from the data in Fig. 2 it seems clear that CF_4 emission rates track with potential. In addition, the data in Fig. 1 show that at potentials exceeding ~3.5 V there is a sharp rise in resistance to current flow. We speculate that a resistive film forms on the surface of the anode but have no direct evidence of same. Importantly, the increased resistance quickly disappears when the potential drops below ~3.0 V. Since high voltages are necessary to generate PFCs, and the presence of the putative resistive film forces cell voltage to rise, preventing the formation of this film should prevent PFC generation. Accordingly, controlling anode potential is the key to avoiding upset conditions. While industrial cells operate galvanostatically (in controlled-current mode), it should still be possible to exercise control over anode potential. One such indirect approach has been demonstrated in our laboratory cell and is described in the next section.

Elimination of Anode Effect and PFC Generation

It is evident from the previous section that the anode effect can be averted by preventing the potential on the anode from exceeding a critical value which we estimate to be ~3.5 V *vs* Al/Al^{3+}. To control this in an industrial setting requires some ingenuity as Hall cells operate under conditions of fixed current, not fixed voltage. We reasoned that we could regulate voltage by varying current. Specifically, it was our contention that stepping down current as voltage rose to near-critical intensity would delay the onset of the anode effect long enough to permit physical intervention. Such a strategy was tested in a laboratory cell with success.

Figure 3 shows the results from a cell operated so as to illustrate the point. The cell was fitted with a graphite rod anode, active area 0.58 cm^2, and current was set at a value of 800 mA which meant a current density of 1.38 A/cm^2 initially. After about 10 minutes of electrolysis the anode was consumed to the point that its potential had risen beyond 3.0 V *vs* Al/Al^{3+}. When the anode potential reached 3.1 V the current was stepped down from 800 to 750 mA. In response, the potential on the anode abruptly decreased from 3.1 to 2.8 V. It took more than 4 minutes for the anode potential to rise again to 3.1 V at which time the current was stepped down to 700 mA. It took more than 6 minutes for the anode potential again to reach 3.1 V. Anode effect was averted both times following a decrease in cell current ***by only ~6%***. This, we believe, is a strategy that is transferable to industrial cells.

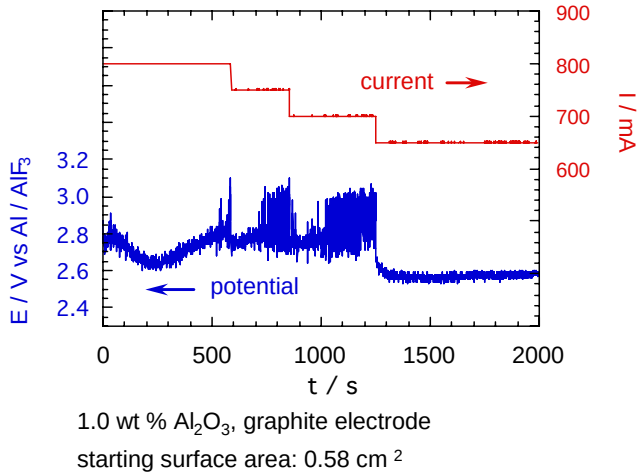

Fig. 3. Anode Potential as a Function of Cell Current in a Laboratory Cell.

Of course, some adaptation is necessary. We recognize that, it is not feasible to have a reference electrode reliably function for long periods of time in a Hall cell. Fortunately, the presence of a large pool of molten aluminum on the bottom of the cell and the fact that the overvoltage for the deposition of aluminum onto molten aluminum is negligibly small allows the cathode pool in a Hall cell to act as a pseudo reference electrode against which anode potential can be measured. Thus, what we report as anode potential *vs* Al/Al^{3+} in our laboratory cell can be broadly interpreted as being equivalent to cell voltage for an industrial-scale Hall cell.

The important finding of our study of laboratory cells is that it is not necessary to divert or shunt the entire cell current in order to avert the onset of AE; rather, with a reduction in cell current of only 6% the onset of AE could be delayed for several minutes. In an industrial cell operating at 300 kA, this would mean shunting less than 20 kA. Heavy-duty electrical equipment capable of switching such currents is readily available as it is used in the electric power industry. Importantly, current stepping can be repeated to delay further the onset of AE and allow time for physical intervention. We advocate testing this approach in an industrial smelter. What is required is the relevant electrical engineering to develop the necessary voltage sensors. If successful, this approach would result in total elimination of anode effect and PFC emissions.

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