Towards Elimination of the Anode Effect and Perfluorocarbon Emissions from Hall-Héroult Cells

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In the primary production of aluminum metal by the Hall-Héroult process, a cell malfunction known as the anode effect 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: (i) measurements of PFC emissions from industrial smelters (4), and (ii) basic research into the attendant electrochemistry. The substance of the latter is reported herein. On the strength of the study of the fundamental electrochemistry the authors propose an operational procedure for total elimination of the anode effect and PFC emissions.

Previous work in this laboratory had shown that, in conformity with industrial data, PFCs are generated only when the cell goes on anode effect (5). Time-resolved data taken by Kimmerle et al. on industrial cells (6) and by Nissen and Sadoway on laboratory-scale cells (5) confirm that by far the highest PFC levels are attained during the first several minutes after the cell goes on anode effect. Further work in this laboratory on the mechanisms of electrode reactions on stationary carbon anodes revealed that when the voltage 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. Again, 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.

The cell design, instrumentation, and experimental procedures are described elsewhere (5,8). The melts under investigation contained 1 wt % alumina dissolved in 84 wt % Na_3AlF_6 - 11 wt % AlF_3 - 5 wt % CaF_2.

The study of a graphite anode rotating at rates as high as 600 r.p.m. polarized at a sweep rate of 100 mV s^{-1} showed that the current-voltage characteristic is unaffected by mass transport conditions. This indicates that the pronounced decrease in current through the anode at potentials exceeding ~3.5 V is 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.

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). No CF_4 was detected in the anode off-gas at potentials below 3 V which is reasonable given that the value of E^o for CF_4 is 2.54 V and activation overvoltages for the formation of polyatomic gas molecules on carbon are ~100s mV. CF_4 levels rose up to a maximum at ~3.5 V. Between 3.5 and 4.5 V CF_4 levels fell, which we believe to be indicative of the formation of the resistive surface film. 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. Thus, controlling anode potential is the key to avoiding upset conditions. In an industrial setting this requires some ingenuity as Hall cells operate under conditions of fixed current, not fixed voltage. We judged that we could regulate voltage by varying cell current. Specifically, it was our contention that stepping down cell 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. 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 ~10 min of electrolysis the anode was consumed to the point that the anode potential had risen beyond 3.0 V *vs* Al/Al^{3+}. When the anode potential reached 3.1 V the current was stepped from 800 to 750 mA. The potential on the anode abruptly decreased from 3.1 to 2.8 V. It took more than 4 min for the anode potential to rise again to 3.1 V at which time the current was dropped to 700 mA. Then, more than 6 min passed before the anode potential reached 3.1 V. In both cases anode effect was averted by dropping the current by only ~6%. This, we believe, is a strategy that is transferable to industrial cells.

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