THE ELECTRODE KINETICS OF PERFLUOROCARBON (PFC) GENERATION

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Abstract

The kinetics of perfluorocarbon (PFC) generation in the NaF-AlF_3-Al_2O_3 system have been studied by a variety of electroanalytical techniques, including voltammetry, chronoamperometry and chronopotentiometry. Anode gases have been analyzed by gas chromatography on-line during controlled-potential electrolysis in a laboratory-scale aluminum reduction cell. Based upon preliminary results, the following hypothesis is offered in explanation of the mechanism of the anodic process of PFC generation:

(1) fluoride ion discharges at potentials exceeding 3.0 V and forms a "CF" film which, in turn, inhibits the electrode process until the potential reaches 6.0 V;

(2) CF_4 and C_2F_6 evolution occurs at potentials exceeding 6.0 V. The results of the present study do not indicate that COF_2 is formed during the initial stages of the anode effect.

Introduction

One of the undesirable consequences of the anode effect is the generation of perfluorocarbons (PFCs), most notably CF_4 and C_2F_6 [1]. These gases have been implicated in climate change owing to their high global warming potentials [2]. It is estimated that in the U.S., aluminum production represents the number one point source of fluorocarbon emissions. In response, the U.S. Environmental Protection Agency and the domestic primary aluminum producers have established the Voluntary Aluminum Industrial Partnership (VAIP) with the goal of reducing annual emissions of PFCs from aluminum smelters by 45% by the year 2000 from 1990 levels [3].

Considerable research has been conducted on industrial and laboratory cells in response to the growing recognition of the environmental impact of PFC emission. The behavior of industrial cells has been reported by Kimmerle and Potvin [4], Marks [5], and Leber *et al*. [6]. The common result of all these studies is that PFCs are emitted from Hall-Héroult cells only when they are on anode effect. Nissen and Sadoway [7] studied the generation of PFCs in a laboratory-scale electrolysis cell. They, too, found that in Hall bath of industrial composition PFCs were generated only when the cell went on anode effect. In addition they derived a functional relationship between the intensity of PFC generation and anodic overvoltage. Dorren et al. monitored anode gases produced during the transition from normal operation to anode effect [8]. They claim that just before the cell is about to go on anode effect they detect the presence of certain COF-type compounds in the anode gas.

In spite of the fact that over the years many investigations have been conducted, neither the mechanism of the initiation of the anode effect nor the mechanisms of the reactions occurring during the anode effect have been clearly established [9]. Perhaps an understanding of the underlying kinetics of the anode effect could point the way to an understanding of PFC generation. This, in turn, would provide the rational basis on which to formulate a plan for reducing emissions. This article reports the results of a set of experiments focused on electrode kinetics. The work is nontrivial for a number of reasons. First, the high temperatures and the chemically aggressive nature of the molten fluoride electrolyte combined with the severely limited number of compatible materials contribute to poor reproducibility in the results. Secondly, in this instance, gas evolution is a highly complex process involving three phases (gas, liquid, and solid) and multiple competing reactions (simultaneous discharge of oxygen-bearing and fluorine-bearing species).

In the past, anodic reactions in alumina-cryolite melts have been studied by various electroanalytical procedures including chronoamperometry [10], chronopotentiometry [11-13], cyclic voltammetry [14 - 16] and impedance spectroscopy [17 - 19]. However, among published results there is no general agreement on an explanation of the observed behavior. This may in part be a consequence of poor reproducibility. Furthermore, almost all the previous work involved simultaneous oxygen discharge to CO and CO_2. To help bring forth the electrode reactions involving PFC generation, for some of our studies we adopted a surrogate electrolyte that was free of solute oxide, *i.e.*, the electrolyte was alumina-free. Results of these experiments were compared to those made in “normal” Hall bath.

Previous work on the electrode kinetics of PFC generation includes the following. Calandra *et al.* [16] studied the electrode reactions that take place at carbon anodes in cryolite-alumina melts at alumina concentrations between 0.05 and 1.5 wt %. Using various sweep rates in the range of 0.04 – 600 mV s^{-1} they observed four current peaks at 1.1, 1.75, 2.38, and 3.6V. Three of the four peaks were attributed to the formation of CO_2, COF_2, and CF_4, respectively, while the fourth peak at 3.6 V was not discussed. Jarek and Thonstad [15, 20] performed very fast cyclic voltammetry on graphite in molten cryolite with alumina additions in the range 0.25 - 5 wt %. At a sweep rate of 10 V s^{-1} and an alumina concentration of 0.5 wt % they observed five current peaks at 1.1, 1.98, 2.57, 3.24, and 4.73 V. The first peak was attributed to absorption of discharged oxide species, forming carbon -oxygen surface compounds, while the second, third, fourth, and fifth peaks were attributed to highly irreversible reactions involving the formation of CO_2, COF_2, CF_4, and F_2, respectively. Djokic and Conway [14] attributed a voltammetric peak at 1.95 V to the formation and evolution of COF_2. Most of these assignments must remain speculative in the absence of experiments involving controlled-potential electrolysis combined with analysis of anode gas.

Experimental

Figure 1 shows the apparatus. The cell design was largely identical to that used previously in this laboratory [7, 21].

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,

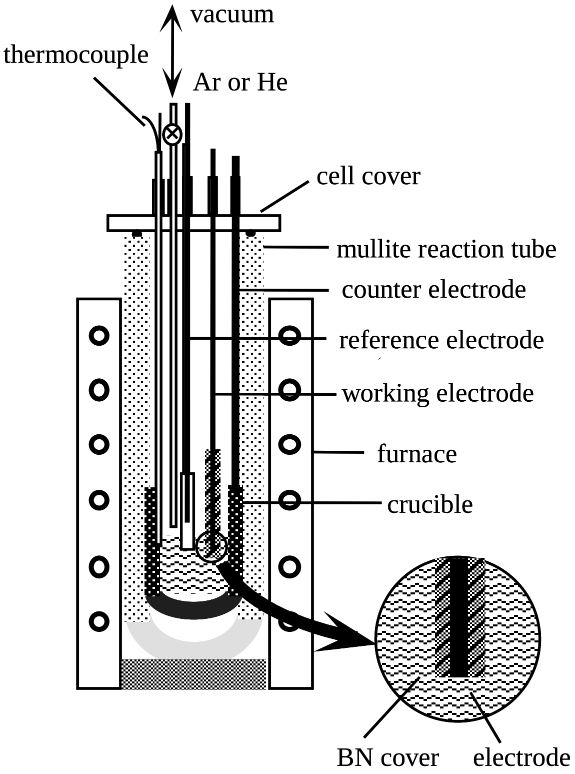

Fig. 1 Schematic diagram of experimental apparatus for electrochemical measurements.

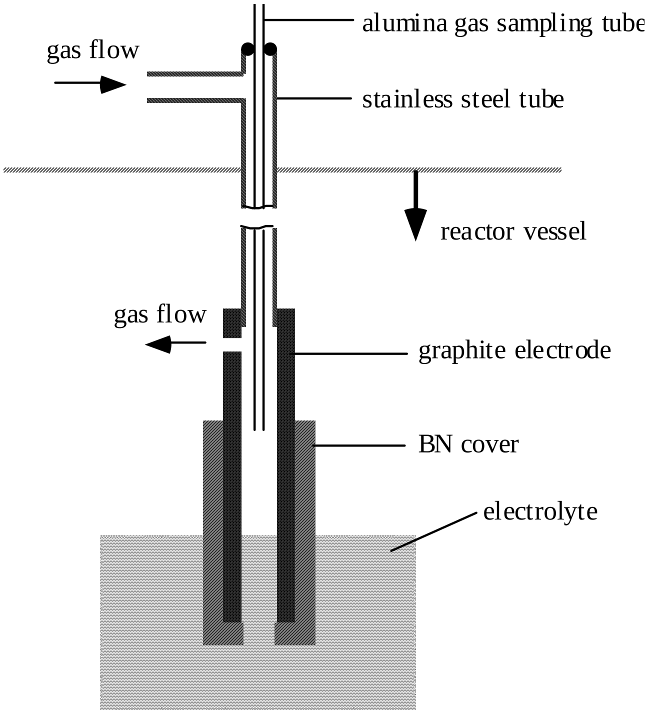

Fig.2 Tubular type electrode for anode gas analysis

about 1 to 2 mm in diameter, and shrouded by BN so that only the bottom surface was exposed to the melt and electrochemically active. The crucible (nickel or graphite) served as the counter electrode. The reference electrode was Al/AlF_3 based upon the design patented by Sadoway [21]. Anode gas was sampled during controlled-potential electrolysis and analyzed by gas chromatograph (Model M200 Dual Gas Analyzer, MTI Analytical Instruments, Fremont, CA). To separate PFCs from other constituents the anode gas was passed through Porapack-Q and molecular sieve columns. CF_4, C_2F_6, CO, CO_2, and O_2 were monitored on line. With the aid of gas standards the threshold of detection of this instrument was determined to be less than 1 ppm for PFCs. New for this study is a tubular anode shown in Figure 2. The outer vertical surface is insulated with BN; hence, only the inside walls (8 mm in dia., 10 mm height) contact the electrolyte. The anode gas was sampled through an alumina tube from the chamber formed above the melt "inside" the electrode. The electrolyte was prepared from reagent grade chemicals of NaF (99%), AlF_3 (98%), Na_3AlF_6 (97%) and Al_2O_3, and dried at 500°C under Ar flow for about 12 hours before being introduced into the cell.

Results and Discussion

Cyclic Voltammetry

The initial measurements were performed mainly in the alumina-free NaF-AlF_3 melt to focus on the reactions that generate PFCs without the complications presented by the simultaneous generation of CO and CO_2. To reduce the influence of oxide impurities in the melt, a preliminary electrolysis was carried out at a set potential of 2.0 V for 24 hours. The voltammograms of Figures 3 - 5 show that on glassy carbon and graphite electrodes the anodic current rises noticeably at potentials exceeding 1.7 V which is not extreme enough to support the discharge of fluoride (The lowest potential for PFC evolution is 2.54 V.). The wave at 1.7 V is reproducible on the anodic sweep and thought to be related to the adsorption of discharged oxide species forming carbon-oxygen surface compounds. On the reverse scan nothing measurable in the way of a cathodic current was found indicating that the electrode process is highly irreversible. At potentials greater than 6 V there was a substantial jump in current on the anodic sweep.

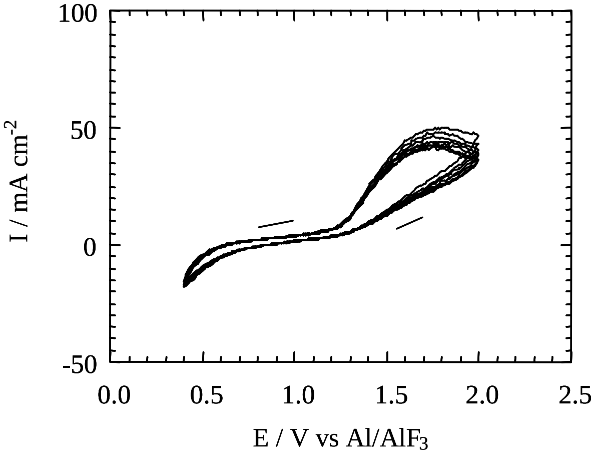

Fig. 3 Cyclic voltammogram of NaF - 13.3% AlF_3 melt at 1173 K. Glassy carbon electrode, v = 100 mV s^{-1}

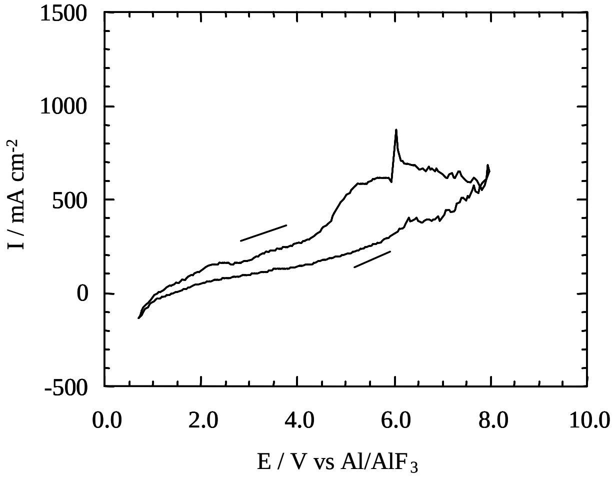

Fig. 4 Cyclic voltammogram of NaF - 13.3 % AlF_3 melt at 1173 K. Graphite electrode, v = 100 mV s^{-1}.

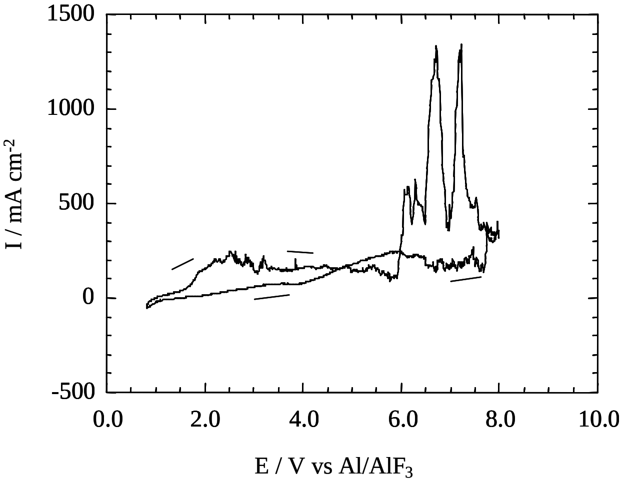

Fig. 5 Cyclic voltammogram of NaF - 13.3% AlF_3 melt at 1173 K. Glassy carbon electrode, v = 100 mV s^{-1}.

Since the evolution of CO and CO_2 occurs at potentials below 1.5 V, we suspect that reactions at higher potentials involve electron transfer with fluoride. It seems, however, that below 6.0 V the rate of gas evolution is low. Perhaps the wave at intermediate potentials is associated with the formation of a "CF" film on the electrode surface. As proposed by Imoto *et al.* [22] and Bai *et al.* [23] in molten KF-HF, the formation of the "CF" film will inhibit the electrode process and contribute to anode effect. This is consistent with our voltammetry, namely, that at intermediate potentials, *i.e.*, < 3 V, we see fluoride ion discharge resulting in the formation of "CF", and at extreme potentials, *i.e.*, > 6 V, PFC gas evolution occurs.

Chronopotentiometry and Chronoamperometry

Figure 6 shows chronopotentiometric traces for AlF_3 - NaF taken at various currents. The first wave at 2 V seems invariant with the magnitude of the applied current. However, the second wave changes dramatically with the applied current. As current increases, the transition time decreases, and the height of the voltage plateau increases. It should be noted that the second wave occurs on top of the first wave at 2 V which is suspected to involve the formation of a resistive film on the electrode.

Figures 7 and 8 show the current response at different potential steps. Spikes are found at potentials exceeding 1.6 V *vs.* Al/AlF_3. Up to 2.1 V (Fig. 7) the period of the spikes as well as the value of the current increases with applied potential. At these values of potential the only gases evolving on the anode are CO and CO_2. At high anode potentials (Fig. 8) the current is somewhat reduced which is consistent with the formation of a resistive film.

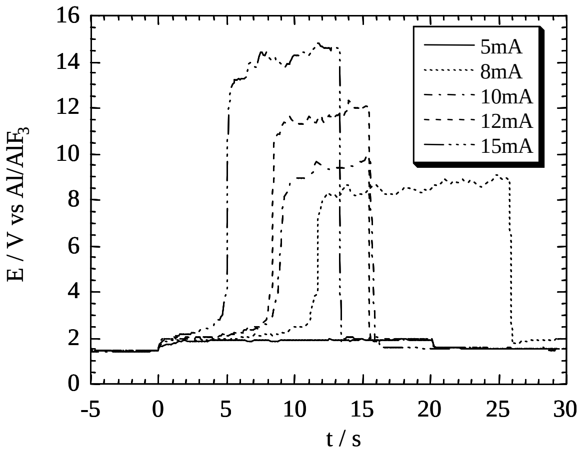

Fig. 6 Chronopotentiongram of NaF - 25% AlF_3 melt at 1323 K. Graphite electrode, s = 0.08 cm^2.

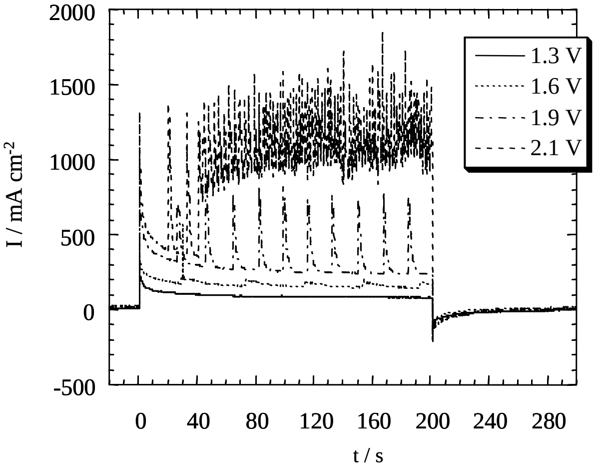

Fig. 7 Current response of potential step in NaF - 25% AlF_3 melt at 1323 K. Graphite electrode. Potentials are referenced against Al/AlF_3.

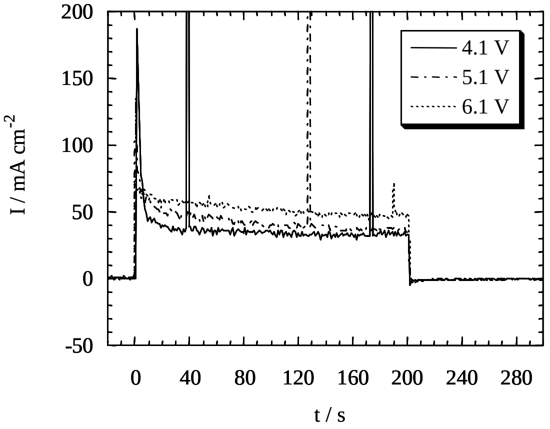

Fig. 8 Current response of potential step in NaF - 25% AlF_3 melt at 1323 K. Graphite electrode. Potentials are referenced against Al/AlF_3.

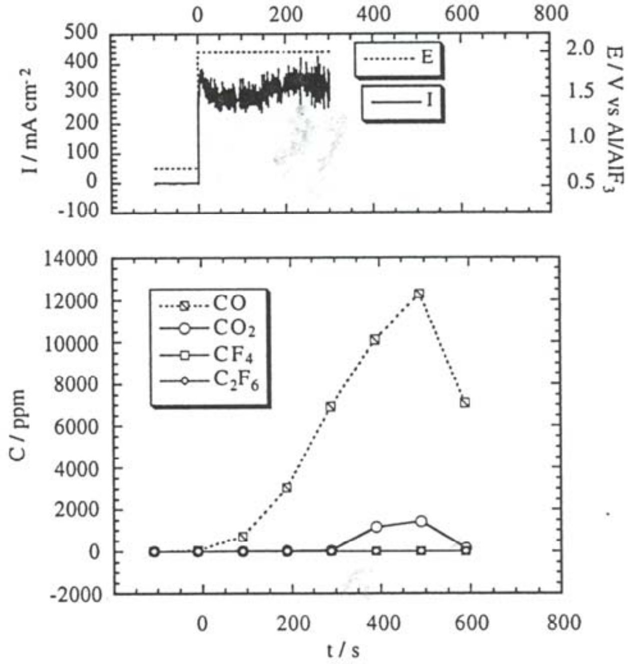

Fig. 9 Gas concentration in anode chamber during potential-step electrolysis of NaF - 13.3 % AlF_3 at 1173 K. Potential step = 2.0 V vs Al/AlF_3 .

Gas Analysis During Controlled-Potential Electrolysis

To help reveal the nature of the anodic reaction, controlled-potential electrolysis was performed. At the same time, the anode gas was analyzed before, during, and after application of the potential. Figures 9, 10, and 11 display the data for potential steps of 2.0, 5.0, and 6.0 V, respectively. In each figure the upper plot shows the potential step and the current response, while the lower plot shows how the concentration of CO_2, CF_4, and C_2F_6 varied with time in the anode chamber. It is evident that at an applied potential of 2.0 V the cell is well

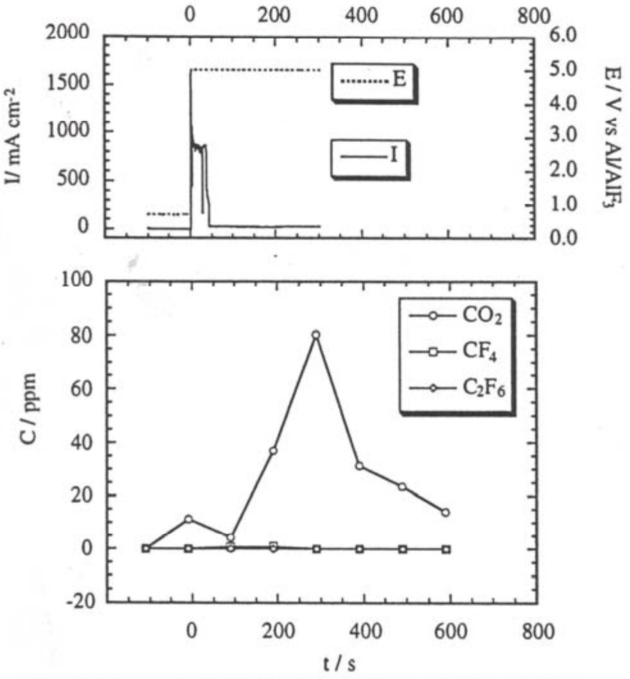

Fig. 10 Gas concentration in anode chamber during potential-step electrolysis of NaF - 13.3 % AlF_3 at 1173 K.
Potential step = 5.0 V vs Al/AlF_3 .

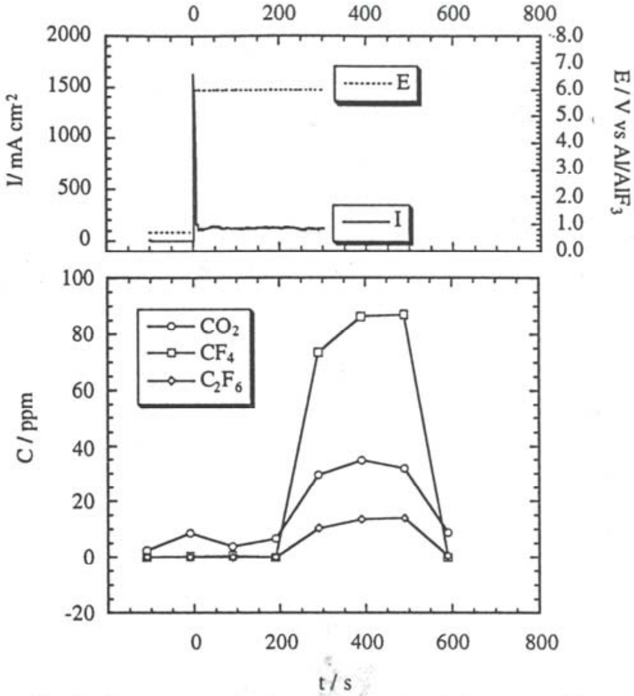

Fig. 11 Gas concentration in anode chamber during potential-step electrolysis of NaF - 13.3 % AlF_3 at 1173 K.
Potential step = 6.0 V vs Al/AlF_3 .

behaved (Fig. 9). Only CO and CO_2 are detected in the anode gas. In contrast, at potentials of 5.0 and 6.0 V the cell quickly goes on anode effect (Figs. 10 & 11). In all three experiments the CO_2 concentration rises after 100 seconds. This delay represents the time it takes for the gas generated at the anode surface to be detected by the gas chromatograph. The CO_2 concentration is much lower at high potentials (5.0 V and 6.0 V) than it is at 2.0 V. At 6.0 V strong signals for both CF_4 and C_2F_6 were measured. At potentials lower than 6.0 V no PFCs were detected which means that if they were present their concentration was below 1 ppm. Also, in all experiments no peak other than those of N_2, O_2, Ar, CO, CO_2, CF_4 and C_2F_6 was detected. In another words, nothing that could be associated with the presence of COF_2 or F_2 was found.

Based upon these preliminary results, we offer the following hypothesis to explain the mechanism of the anodic process of PFC generation:

1) fluoride ion discharges at potentials exceeding 3.0 V and forms a “CF” film which, in turn, inhibits the electrode process and is stable up 6.0 V.
2) CF_4 and C_2F_6 evolution occurs at potentials exceeding 6.0 V.

Our present results do not indicate that COF_2 is formed during the initial stages of the anode effect. Research continues.

Acknowledgments

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