PERFLUOROCARBON (PFC) GENERATION IN LABORATORY-SCALE ALUMINUM REDUCTION CELLS

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Abstract

The generation of the perfluorocarbons (PFCs), CF_4 and C_2F_6, was studied in a laboratory-scale aluminum reduction cell. During electrolysis in well behaved cells and in cells on anode effect, anode gases were analyzed by gas chromatography (GC) on-line. Process parameters were systematically varied to determine how PFC generation depends upon anode material (industrial pre-bake and Søderberg), bath ratio (1.45, 1.15 and 0.56), LiF concentration (0 and 2.3%), current density (0.7 A/cm² and higher), and temperature (970 and 800°C). Measurements agree with those reported for industrial cells with respect to total PFC level as well as the ratio of CF_4 to C_2F_6. There is a strong correlation between PFC concentration in the off gas and the overvoltage on the anode. The functional relationship between the rate of PFC generation and anodic overvoltage was derived from the current-overpotential equation. Experiments with low-ratio bath (BR = 0.56) indicated steady production of both CF_4 and C_2F_6 at *normal* voltage, *i.e.*, in a cell not on anode effect.

Introduction

It is well established that during anode effect the Hall cell emits 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 (see Table 1 below).[1] 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].

Table I: Global Warming Potentials [2].

compound	lifetime (years)	Global warming potential (referenced against CO_2)		
		time horizon (years)		
		20	100	500
CO_2	200	1	1	1
CF_4	50,000	4,100	6,300	9,800
C_2F_6	10,000	8,200	12,500	19,100

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[1] The global warming potential (GWP) of a substance is a combined measure of its expected lifetime in the atmosphere and its infrared absorbing capacity.

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. Perhaps if we understood how the anode effect works we could then understand how PFCs are generated. Ultimately we might then be able to move forward with a plan for reducing emissions. The role of this laboratory has been to conduct laboratory scale investigations of the elementary processes that control the generation of PFCs in the Hall cell. In concert we are studying origin and nature of the anode effect as it is commonly believed that PFCs are generated only when the cell is malfunctioning. The thrust of this stage of the work is to characterize the behavior of our laboratory cell under various operating conditions in preparation for the more basic electrochemical studies to follow. This article reports the results of the first set of electrolysis experiments and presents a new functional relationship between the rate of PFC generation and process conditions in the cell.

The Chemistry and Electrochemistry of PFCs in the Hall cell

Under normal operating conditions the electrochemistry at the anode is given by the two reactions

$$2\,Al_2O_3 + 3\,C = 4\,Al + 3\,CO_2 \qquad (1)$$

$$Al_2O_3 + 3\,C = 2\,Al + 3\,CO \qquad (2)$$
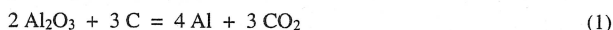
for which the standard potentials at 970°C are 1.18 V and 1.04 V, respectively. Under normal operating conditions, reaction 1 dominates owing to kinetic limitations. When the cell goes on anode effect, the production of CO is favored over CO_2, and fluorine is discharged. The result is the formation of PFCs according to

$$4\,Na_3AlF_6 + 3\,C = 4\,Al + 12\,NaF + 3\,CF_4 \qquad (3)$$

$$2\,Na_3AlF_6 + 2\,C = 2\,Al + 6\,NaF + C_2F_6 \qquad (4)$$
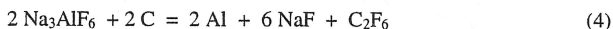
for which the standard potentials at 970°C are 2.55 V and 2.88 V, respectively. Figure 1 below shows a schematic representation of the *i-V* characteristic of the anode. Clearly, the diagram is highly idealized as it neglects various contributions to the cell voltage including the resistive drops across the electrolyte (roughly 1.5 V in industrial cells), down the anode (difficult to estimate, dependent upon grade of carbon), and across the busbar connections (small, depending on how the junction is fashioned), not to mention the overvoltage associated with gas evolution on the anode (not insignificant, may be as high as 0.6 V). The point of the figure is to illustrate that there is a rank order of reactions. Specifically, in theory there should be no generation of PFCs provided that the voltage on the anode does not exceed a critical value.

To estimate PFC emissions a number of empirical correlations have been reported. These are for the most part derived from regression analysis of plant data. The simplest is based upon Faraday's Law [1]:

$$\frac{kg\ PFC}{ton\ Al} = \frac{1.7 \times t \times f}{CE} \qquad (5)$$

where t is the time the cell is on anode effect in minutes per pot-day, f is the PFC fraction of the anode gas, and CE is current efficiency expressed as a fraction, *i.e.*, 92% CE is entered as 0.92.
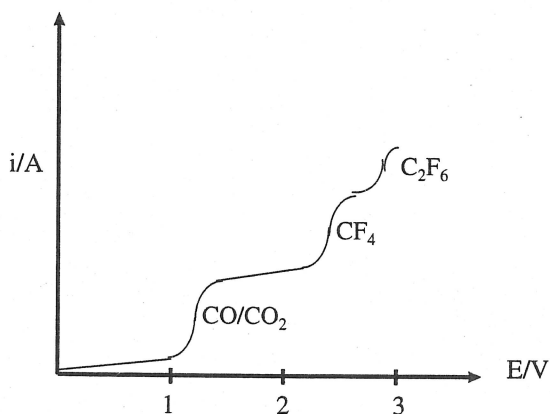

Figure 1. Idealized *i-V* Characteristic of Hall Cell Anode.

Another expression for PFC emissions is Tabereaux's empirical rule which is based upon observations of cells fitted with pre-baked anodes [3]:

$$f = \frac{16\,t\,\exp(4t+0.5)}{16 + t\,\exp(4t+0.5)} \tag{6}$$

where f is the percentage of CF_4 in the anode gas and t is the duration of the anode effect in minutes. Finally, Bouzat, Carraz, and Meyer at Pechiney have observed that the intensity of PFC emissions is related to average potline overvoltage as measured over a 24-hour period [4].

In a departure from the empirical, we suggest a model based on the underlying kinetics of electrode processes. We recognize that the reactions involved in the anode effect are rather more complicated than the prototypical reaction for simple charge-transfer controlled kinetics, but our purpose here is simply to bring forth the important process variables that play a role in determining the rate of PFC generation. Under these circumstances, we feel that the mathematical formalism of elementary electrochemical reactions will suffice. Justification can be found in the fact that the proposed model accounts for the overall PFC emission rate as well as the ratio between CF_4 and C_2F_6. The basis of the model is the recognition that the rate of generation of PFCs is directly proportional to the rate of reaction at the anode, r, which is given by

$$r = k_f\,C_i^n \tag{7}$$

where k_f is the specific heterogeneous rate constant, C_i is the concentration of species i at the electrode/electrolyte interface, and n is the order of reaction. The rate constant, k_f, is a function of voltage through the relationship

$$k_f = k^o \exp\left\{-\frac{\alpha z F(E - E^o)}{RT}\right\} \tag{8}$$

where k^o is the standard rate constant, α is the transfer coefficient, z is the number of electrons transferred in the rate determining step of the electrochemical reaction, F is the Faraday constant, R is the gas constant. Given the extremely high voltages observed in industrial cells on anode effect, we can approximate the quantity, $E - E^o$, in equation 8 by the overvoltage, η, recognizing that the pre-exponential term, k^{o*}, must be altered accordingly

$$k_f = k^{o*} \exp\left\{-\frac{\alpha z F \eta}{RT}\right\} \tag{9}$$

In the instant use of equation 9 the overvoltage is defined somewhat arbitrarily as the difference between cell voltage and steady state voltage under normal operating conditions. Thus, the rate of reaction can be related to the instant value of overvoltage on the electrode as

$$r = k^{o*} \exp\left\{-\frac{\alpha z F \eta}{RT}\right\} C_i^n \tag{10}$$

Finally, the total amount of PFC emitted is simply the integral of the instant rates

$$total\ emissions = f_{CF_4} \int r_{CF_4}\,dt + f_{C_2F_6} \int r_{C_2F_6}\,dt \tag{11}$$

where f_i is the scale factor associated with species i. This relationship can be tested by comparing measured emissions with the voltage history of the cell.

Experimental

Electrolysis Testing

Figure 2 shows the apparatus for measuring PFC emissions. The cell design was to a large extent identical to that used previously in this laboratory [5]. Modifications were made to enable gas sampling from the vicinity of the anode. During electrolysis, a constant flow of inert gas (argon or helium) established a flush rate of 500 to 600 mℓ/min at STP (The cell volume is estimated to be 2 ℓ, while to volume of the gas shroud is estimated to be 200 mℓ.). Data were taken with an eight-channel scanner (Keithley, Model 199, Cleveland, OH) connected to a personal computer through a GPIB board. Gas samples were analyzed on line by a gas chromatograph (Model M200 Dual Gas Analyzer, MTI Analytical Instruments, Fremont, CA). To separate PFCs from other constituents of the anode gas, it was passed over a Porapack-Q column and a molecular sieve column. With the aid of gas standards (Scott Specialty Gases, Plumsteadville, PA) the threshold of detection of this instrument was determined to be less than 10 ppm – Tabereaux *et al.* [6] report it to be 1 ppm, a value too low for verification in our study. The cell was also fitted with an aluminum reference electrode [7] which enabled the measurement of electrode potentials on the anode and the cathode, each independently and with respect to a thermodynamically meaningful reference potential: the equilibrium between Al and Al^{3+}. Made of hot-pressed boron nitride, the reference electrode contains a solution of Hall bath from main cell compartment and 30% BaF_2. Molten aluminum will float on the reference melt and can thus be directly contacted by a refractory-metal leadwire. This arrangement completely avoids the possibility of shorting between the reference melt and the leadwire, a condition that gives rise to mixed potentials. The reference electrode was found to be highly reliable, *i.e.*, immune to drift and fluctuation. The open circuit potential measured between the reference electrode and the aluminum cathode was typically on the order of 30 mV.

Cylindrical anodes, 2 cm in dia. × 6 cm tall, were machined from various carbons: prebake (supplied by Eastalco), Søderberg (supplied by Reynolds), and high-purity graphite (Beaumac, Epson, NH). In two experiments the cell was operated with an inert anode made of refractory metal treated so as to form an oxidized reaction layer on its surface. The electrolyte consisted of salt drawn from industrial pots on anode effect. For some experiments LiF was added. The electrolyte with the very low bath ratio (BR = 0.56) was prepared in the laboratory from the basic constituents: AlF_3, CaF_2 (3.7%) and Al_2O_3 (1.9%) were added to pure Greenland cryolite. The mixture was then baked at 300°C in a box furnace for about 24 hours in order to get rid of moisture. The test matrix above shows the range of process parameters investigated.

Bath Ratio (NaF-AlF$_3$ ratio)	Anode Material			
	Prebake	H.P. Graphite	Søderberg	Inert Anode
Bath Ratio = 1.15 (T=970°C)	0 % LiF	0 % LiF	0 % LiF	0 % LiF
Bath Ratio = 1.40 (T=970°C)	0 %, 2.7 % LiF	0 %, 2.7 % LiF	0 %, 2.7 % LiF	-
Bath Ratio = 0.56 (T=800°C)	0 % LiF	-	-	0 % LiF

The cell was operated at fixed current furnished by a power supply with a rated capacity of 40 V and 25 A (Model SRL 40-25, Sorensen Company, Hudson, NH). During an experiment we measured cell current, cell voltage, the voltage between the reference electrode and the cathode, the voltage between the reference electrode and the anode, temperature, and the composition of the anode gas. To provoke an anode effect, the current density was stepped from a normal value of 0.7 A/cm^2 to an arbitrarily high value in excess of 1 A/cm^2.

Results and Discussion

Figure 3 displays data from a typical experiment. It is evident that when the current density is stepped to a value exceeding 1 A/cm^2 the voltage rises sharply to values indicating that the cell is on anode effect, i.e., approximately 20 V. This is somewhat lower than voltages measured in industrial cells and is attributed to the different geometry of the laboratory cell — by this we refer, among other things, to the aspect ratio of the anode and its relative depth of immersion into the electrolyte. Within 2 minutes from the moment the current is increased, PFCs are detected in the anode gas. The two-minute delay represents the time it takes for the gas generated at the anode to flow to the detector (approximately one minute) plus the one minute it takes for the gas chromatograph to make the analysis. Typical PFC concentrations lie between 3 and 15% for CF$_4$ and 0 to 3% for C$_2$F$_6$. In some experiments peak levels of CF$_4$ were detected as high as 24%. CF$_4$/C$_2$F$_6$ ratios ranged from 5 to 40, values common to those measured in plant studies. It can also be seen in Figure 3 that if the cell is on anode effect and the power supply is capable of maintaining constant current, the PFC level stays pretty much constant. Industrial cells exhibit this behavior if the metal pad remains stable. Figure 3 also shows that when the current is interrupted, within 2 minutes the PFC signal drops to zero. The two-minute delay in the measured change in the PFC signal is an experimental artifact — see above for the explanation of the time delay between the onset of PFC generation and the detection of PFCs by the gas chromatograph. Clearly, the cell cannot be producing PFCs when no current is flowing. Figure 3 also shows that when the current is interrupted, within 2 minutes the PFC signal drops to zero. These results are in good agreement with those of other studies conducted in the plant and in the laboratory [6,8,9].

Among the industrial carbons we could detect in the level of PFC emissions no difference that could be correlated to type of carbon. We interpret this to mean that differences in performance in industrial cells may be more attributable to cell design and operator practice than to carbon composition. Indeed, recently published data taken at industrial smelters confirm this [10]. Specifically, there is ample evidence of cells fitted with Søderberg anodes achieving emission rate comparable to those from cells fitted with pre-baked anodes. For comparison we also tested high purity graphite and found that it would sustain higher current densities than any of the industrial carbons before going on anode effect.

Over the entire range of bath chemistries tested (see Table II above) we found no pattern in the level of PFC emissions among compositions representative of those used in industry. The exception was the low-ratio bath (BR = 0.56), a composition that has attracted interest among researchers but to our knowledge is not used in contemporary industrial cells. In this melt we measured low levels of CF$_4$ even at *normal* voltage, i.e., in a cell not on anode effect. To confirm that this observation was not simply an experimental artifact, we conducted electrolysis in a carbon-free cell (MgO crucible instead of graphite) fitted with a metal anode made of anodized hafnium [5]. In this experiment the bath ratio was 0.56

and the alumina concentration was 2.3%. There was positively no signal representing either CF$_4$ or C$_2$F$_6$. After an hour the hafnium anode was replaced with a prebake carbon anode and the experiment continued. Within minutes, both CF$_4$ and C$_2$F$_6$ were observed in the off gas, along with CO and CO$_2$. We searched for a threshold current density below which PFC generation would not be supported. The PFC level scaled with current density over the entire range of interest, but even at 0.25 A/cm^2 we detected continuous PFC evolution. In view of the attendant environmental consequences of this finding, the use of low-ratio bath would almost certainly require carbon-free anodes. The generation of PFCs at *normal* operating voltage in this bath can be rationalized by the fact that the fluoride activity is so much higher than in conventional industrial baths.

The relationship put forth earlier between process variables, PFC emissions, and ratio between CF$_4$ and C$_2$F$_6$ has been confirmed in the following manner. In our test cell a series of experiments was conducted in which we stepped the current from its normal value, i.e., 0.7 A/cm^2, to progressively higher and higher values, up to about 2.5 A/cm^2. At each current, the steady-state potential on the anode was measured along with the instant concentrations of CF$_4$ and C$_2$F$_6$ in the off gas. Equation 12 reports the regression analysis of one such set of experiments (not the same data set shown in Figure 3):

$$CF_4 \ emission \ rate \quad = \quad 0.1264 \exp\left\{0.3306 \left(E - E_{norm}\right)\right\} \quad (12)$$

where E_{norm} is the potential on the anode when the cell is operating "normally." Equation 12 is clearly of the same mathematical form as equation 10. The time integral of equation 12 gives the value of total CF$_4$ emissions.

Equation 12, then, is the theoretical basis for observations such as those at Pechiney where it was found on prebaked pots that total PFC emissions are related to the average "excess" overvoltage, *AEO*, over the duration of the anode effect in the following manner [4]:

$$\frac{kg \ CF_4}{ton \ Al} = \frac{1.9 \times AEO}{CE} \quad (13)$$

where average excess overvoltage, *AEO*, is defined somewhat arbitrarily as that amount of cell voltage in excess of 8 V, and *CE* is expressed as a fraction.

The overvoltage model proposed here can also explain why from a given cell significantly different levels of PFC emissions can be measured from anode effects with nearly identical average voltage. The key to understanding this phenomenon is to look at different voltage - time histories. Because the emission rate varies **exponentially** with overvoltage, anode effects with identical average voltages but with different instant variations in voltage will generate PFCs in different amounts. In other words, when there is a substantial difference between the average overvoltage, i.e., $\int \eta \, dt / \int dt$, and the average of the exponential of the overvoltage, i.e., $\int \exp \eta \, dt / \int dt$, one can expect that the PFC levels will differ. Mathematically, for two different anode effects designated 1 and 2, it is possible for $\int \eta_1 \, dt / \int dt = \int \eta_2 \, dt / \int dt$ but $\int \exp \eta_1 \, dt / \int dt \neq \int \exp \eta_2 \, dt / \int dt$. The smaller the values of overvoltage on anode effect, the better the average overvoltage correlates with the PFC emission intensity. Our model also speaks to the relative concentrations of CF$_4$ and C$_2$F$_6$ in the off gas. Since the standard

potentials for CF_4 and C_2F_6 differ, at any given anode potential the overvoltage is more severe for CF_4. Furthermore, we should expect that the values of α and z are different in equations 3 and 4. In the extreme, *i.e.*, at very high cell voltages, α and z may prove to be functions of potential. Hence, it should come as no surprise that we measure higher levels of CF_4 than C_2F_6 and that we observe more rapid attenuation of the C_2F_6 signal with time as the anodic potential decreases.

Conclusions and Recommendations

The concentration of PFCs in the off gas is strongly correlated with the overvoltage on the anode. A functional relationship between PFC concentration and anodic overvoltage has been derived from first principles and is based upon the current-overpotential equation. Tests have shown this relationship to be valid in laboratory cells.

It would be interesting to track instant voltage readings taken on individual anodes in industrial cells. By expressing the data in the form of the integral of equation 12 we might find a superior correlation to an accurate measure of PFC emissions. In contrast to some current approaches that assess PFC emission levels solely on the basis of type of anode technology employed, the metric proposed in this article has the capability to recognize and reward good operating practice.

Finally, in the light of the finding that a cell containing low-ratio bath produces PFCs continuously under *normal* operating conditions, *i.e.*, not just on anode effect, it might make sense to re-examine efforts to develop commercial technology based on this melt. Clearly, there is a tradeoff between the expected energy savings associated with operating a cell at 800°C and the attendant environmental effects of sustained PFC emission. As for new research, perhaps a fresh look at nonconsumable anodes is warranted. Fitted with metal anodes, our cells were totally incapable of generating PFCs under any circumstances.

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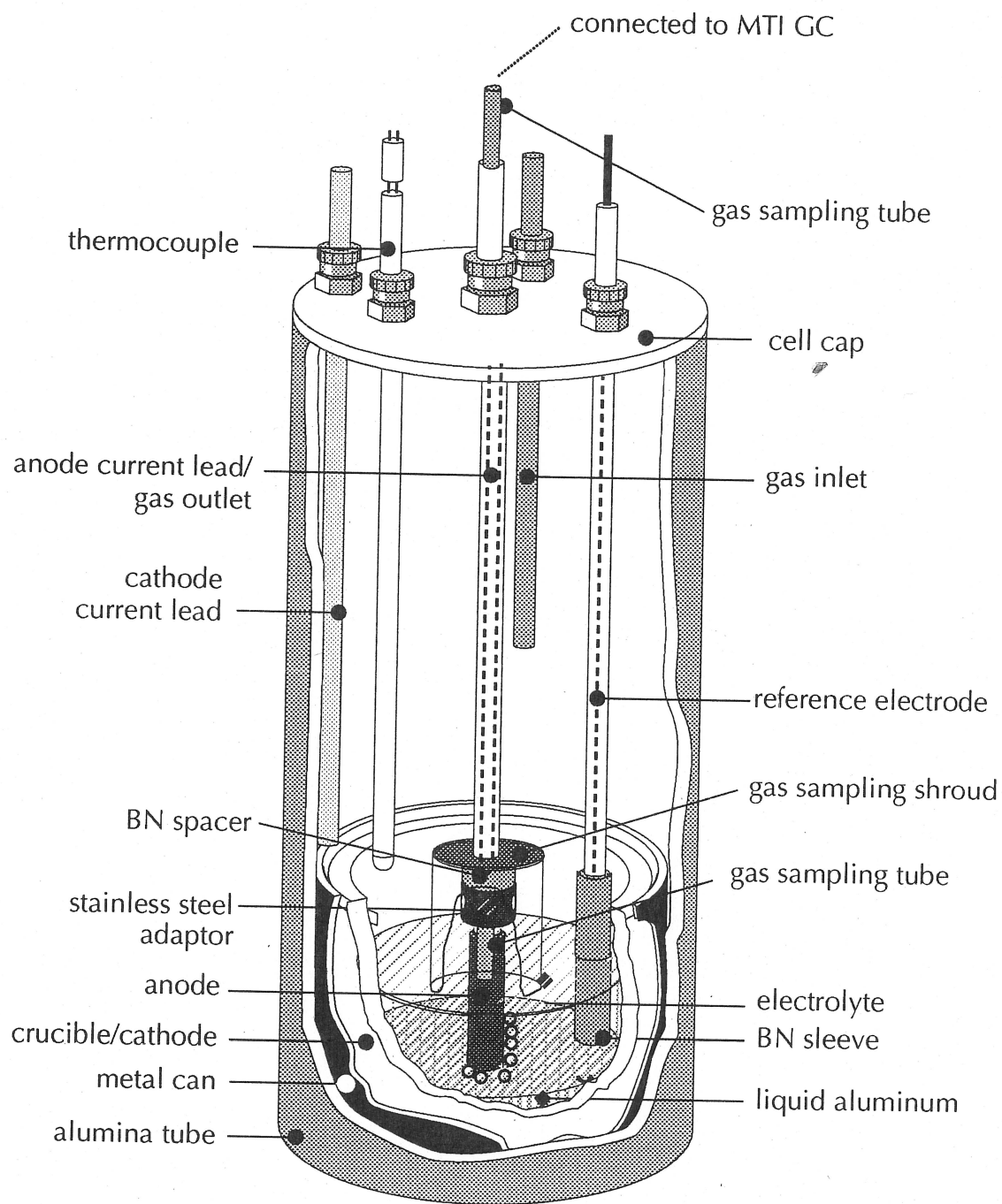
connected to MTI GC

gas sampling tube

thermocouple

cell cap

anode current lead/
gas outlet

gas inlet

cathode
current lead

reference electrode

gas sampling shroud

BN spacer

gas sampling tube

stainless steel
adaptor

anode

electrolyte

crucible/cathode

BN sleeve

metal can

liquid aluminum

alumina tube

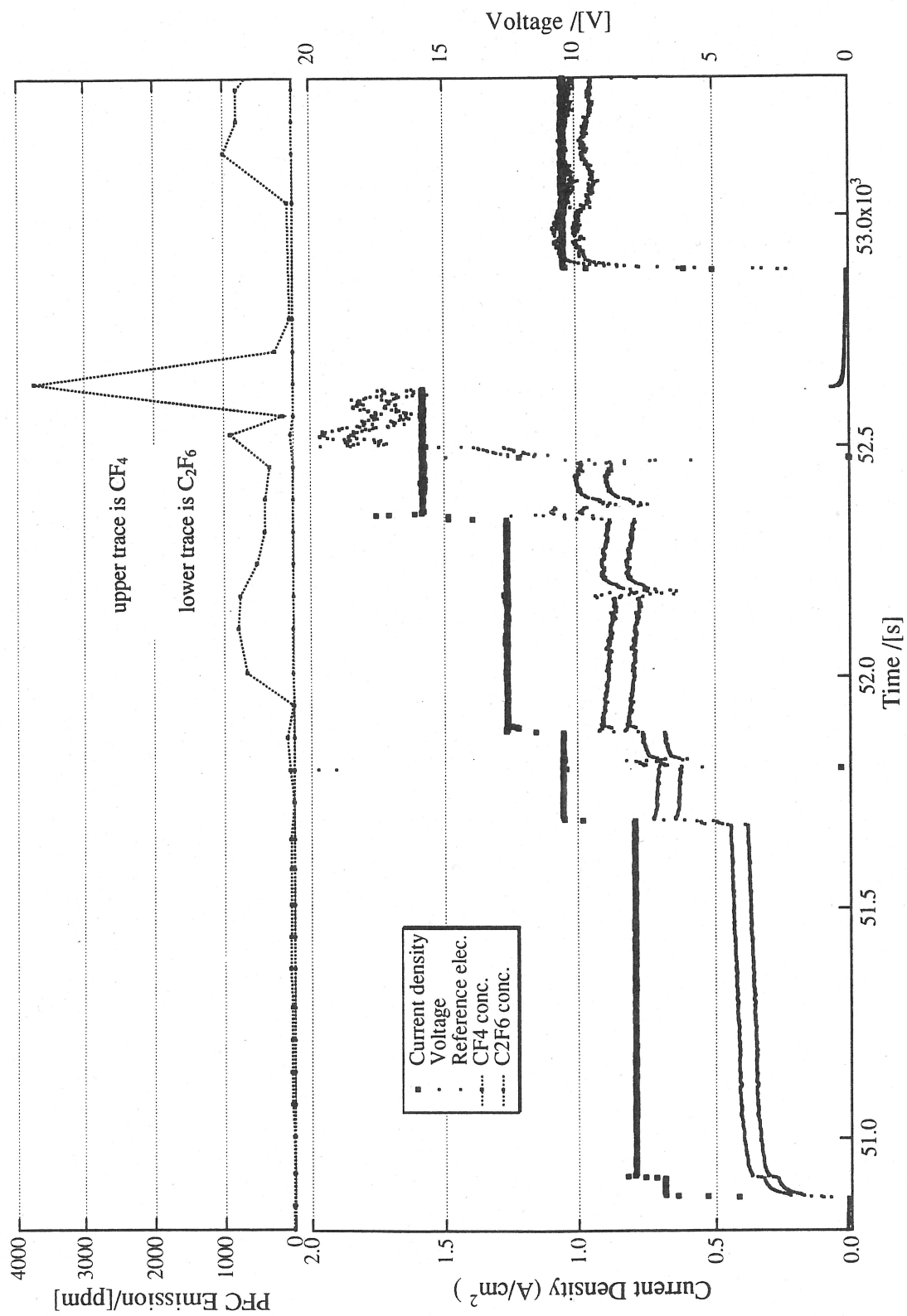Figure 2: Laboratory-scale Aluminum Reduction Cell for Measuring PFC Emissions.

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Figure 3: Data from an Electrolysis Experiment with Pre-baked Carbon Anode, BR= 1.15, no LiF, T = 970°C