

Electrochemical Behavior of Carbon in the Electrolytic Evolution of Fluorine

P. T. Hough and D. M. Novak
Eldorado Resources Limited
Research Group

400-255 Albert St., Ottawa, Ontario, Canada. K1P 6A9

Introduction

A major application of elemental fluorine is in the production of uranium hexafluoride (UF_6), which is subsequently enriched in gaseous diffusion plants, and converted to UO_2 fuel for use in all light water power reactors (LWPR). Fluorine is produced in an electrochemical cell from a molten salt $\text{KF} \cdot 2\text{HF}$ using steel cathodes and non-graphitized carbon anodes. The technology used to generate fluorine was developed in the period 1942-1952 and has received very little study since. Reviews by Rudge¹, and Ring and Royston² provide excellent summaries of the technological aspects of commercial fluorine cells. In addition Arvia et al.³ and Watanabe et al.⁴ studied the kinetics of fluorine evolution at carbon, graphite and platinum anodes, while Novak and Hough⁵ have reported unusually high Tafel slopes over a much greater range of current densities than previously obtained.

Principal characteristics of the electrolytic generation of fluorine include very high overpotentials, especially at the carbon anodes, and a tendency for the carbon to exhibit passivation characteristics, thereby limiting the sustainable current density. This blockage phenomenon was originally interpreted by Watanabe⁶ to be due to the formation of a carbon fluoride film $(\text{CF}_n)_x$, and subsequent papers^{7,8} have supported this view.

In the work reported here, the effect of the carbon surface texture on the observed current-voltage behaviour is described.

Experimental

All experiments were conducted in a small size (1L) acrylic cell in which the gaseous products of the electrodes were kept separate by an acrylic

partition extending part way into the melt. The use of acrylic allowed visual observations to be made during a given experiment.

The carbon electrode materials used were obtained by cutting pieces from industrial anodes obtained from France (Sers Savoie Carbone) and from Canada (Union Carbide). Both materials are ungraphitized, relatively fine grained, carbon obtained by the usual processing of petroleum coke and pitch. Two different surface textures were prepared and assessed, the first being a standard carbon surface, the second being a modified surface. All electrodes were ultrasonically cleaned and dried prior to immersion in the $\text{KF} \cdot 2\text{HF}$ electrolyte.

Carbon steel was used as the counter electrode and $(\alpha + \beta)$ PdH was used as a reference electrode, to which all reported potentials are referred.

Experiments were carried out in both potentiodynamic and galvanostatic modes with "iR" corrections made to the galvanostatic data. A temperature of 354K was maintained using an electric immersion heater having a Monel sheath.

Results and Discussion

Potentiodynamic cyclic voltammetry measurements were conducted in the potential range 0 to 9.5V at various rates, but usually 50 mVs^{-1} . These experiments showed that the F_2 evolution reaction is an irreversible one with initiation of the reaction at 4.5V. Using the standard carbon electrodes, as the potential is changed to more positive values, the currents associated with the F_2 evolution initially increase but then drop markedly in the 6.0V-6.5V region. Increasing the potential to 9.5V does not result in any marked improvement in

the current. The initial sweep always results in much higher peak currents (at 6.0-6.5V) than subsequent repetitive sweeps. With continuous cycling the sweep becomes reproducible, still with a broad maximum in the 6.0-6.5V region. Reversing the sweep at potentials less than 6.0V results in i-E profiles for the forward and reverse direction that essentially overlap. These characteristics indicate that the process is an irreversible Faradaic one, which becomes inhibited, possibly through the fluorination of the carbon surface.

However, with the modified carbon electrodes in KF·2HF, the measured currents were very much greater, at all potentials, than those obtained with the standard carbon anodes, using identical geometrical configurations. The shape of the potentiodynamically obtained i-E curves, at the modified electrodes differed markedly from those obtained using the standard carbon electrodes in that passivation did not usually occur. Instead, the irreversible Faradaic process was the only apparent process to at least 8.5V. Discontinuous repeated cycling over a period of time of several weeks showed that this enhanced surface activity of the modified carbon was maintained. A measure of the relative activities of the modified vs the standard carbon electrodes was obtained by evaluating the maximum current densities at various increasing anodic end potentials, obtained at constant sweep rate and experimental conditions. A steady and reproducible complete i-E profile was always obtained following each of the potential cutting experiments, in order to always start with a surface having the same electrochemical treatment. The dependence of i_{\max} reached at various end potentials up to 8.0V is a measure of the overall electrode performance; the greater the slope of these linear relationships, the greater the electrochemical activity of the electrode. Slopes obtained with the standard carbon electrodes were in the range 1 to 6 $\text{mAcm}^{-2}\text{V}^{-1}$ while those obtained with the modified electrodes were in the range 75 to 130 $\text{mAcm}^{-2}\text{V}^{-1}$.

Log (current)-potential relations were also obtained galvanostatically, resulting in Tafel plots over at least 5 decades of current. The slopes of all these plots were remarkably high, with the standard carbon electrodes having slopes in the 0.4 to 0.5V/decade range,

while the modified carbon electrodes exhibited slopes in the 0.2 to 0.3 V/decade range. Extrapolation of the linear portion of the Tafel plot to the potential axis provided estimates of the reversible potential for F_2 evolution: 2.8V in the case of the standard carbon, vs 2.3 to 2.6V for modified carbon electrodes.

Visual observation of the carbon surfaces consistently shows the following distinctions between the standard and modified carbon electrodes; at the standard electrode surface bubbles form in the 4.0 to 4.5V region and then coalesce into a vein like film covering much of the surface; at modified electrodes bubbles form in the same potential region but these tend to disengage easily rather than forming a coherent gas film. While enhanced reversibility has been reported previously using carbon electrodes with modified surfaces⁹, the authors are not yet aware of reports of similar enhanced i-E behaviour at carbon having similarly modified surfaces.

References

1. A. J. Rudge, in *Industrial Electrochemical Processes*, A. Kuhn (ed.), Elsevier (1971).
2. R. J. Ring and D. Royston, Australian Atomic Energy Commission, Report AAEC-E281, (1973).
3. A. J. Arvia, and J. Bebczuk de Cuminsky, *Trans. Faraday Soc.* **58**, 1019, (1962).
4. N. Watanabe, M. Inoue, and S. Yoshizawa, *J. Electrochem. Soc. Jpn.* **31**, 168, (1963).
5. D. M. Novak and P. T. Hough, *J. Electroanal. Chem.* **144**, 121, (1983).
6. M. Nishimura, A. Tasaka, K. Nakanishi, and N. Watanabe, *Denki Kagaku* **38**, 294, (1970).
7. H. Imoto, T. Nakajima, and N. Watanabe, *Bull. Chem. Soc. Japan* **48**, 1633, (1975).
8. D. Devilliers, F. Lantelme, and M. Chemla, *J. de chimie physique*, **80**, 267, (1983).
9. R. Mark Wightman, M. R. Deakin, P. M. Kovach, W. G. Kuhr, and K. J. Stutts, *J. Electrochem. Soc.* **131**, 1578, (1984).