Electrochemistry of anodic fluorine gas evolution at carbon electrodes: Part III Characterization of activated carbon anodes following onset of the 'anode effect'

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The exceptional activity of carbon anodes for the fluorine evolution reaction (FER) in a KF · 2HF melt at 358 K that can be produced, based on a previously reported procedure for reactivation following onset of the 'anode effect', has been characterized. The activated carbon anodes that have been treated by applying the procedure exhibit unique, exceptionally active, polarization behaviour. This is manifested as a high exchange current-density, a low Tafel slope in the high current-density range, resistance to further anodic effects, facilitation of the detachment of F₂ gas bubbles and good electrode-life properties. At polarization current-densities of 0.1 and 0.2 A cm⁻², the anode potential is 1.5 and 2.5 V lower, respectively, for the activated than for a normal non-activated carbon electrode. The improvements of the activated carbon anodes are associated with facilitation of the detachment of the F₂ bubble/film. The F₂ bubble/film adherence effect is the main cause for the abnormally high polarization and anode effect for a normal, unactivated carbon anode, as concluded in our previous studies (Part I). It is shown that the facilitation of F₂ bubble/film detachment is due to two physical properties of the activated carbon electrode: a much smaller solid/gas/liquid contact angle and a much smoother surface. As determined by means of ESCA, it is shown that, compared with an unactivated carbon anode, the activated anodes have a smaller extent of surface fluorination corresponding to thinner 'CF' films. This may lead both to a favourable contact angle and a smaller barrier layer for activated electron tunnelling at the activated carbon anodes used for the FER, than at normal non-activated carbon electrodes.

1. Introduction

The origin of the unusually high Tafel slopes and so-called 'anode effect' which arises in the fluorine evolution reaction (FER) at carbon anodes in KF · 2HF melts was investigated in our previous studies, (Parts I and II of this series [1, 2]) and traced to two interdependent effects: barrier-layer 'CF' film formation; and resulting large fluorine gas bubble/KF · 2HF melt/carbon electrode contact angle leading to an unusual type of gas evolution through a gas film involving adherent lenticular bubbles. It was then demonstrated that rotation of the carbon cone electrodes used had strong effects on the current against voltage relation for the FER at carbon, due to facilitation of detachment of fluorine gas bubbles, and that polishing of the carbon electrodes improved the polarization behaviour, an effect that appears also due mainly to facilitation of fluorine gas bubble detachment. However, the rotating cone electrode technique is difficult, and also not economical, to be applied in the industrial fluorine production process.

In the light of the principal findings, as reported previously [1, 2], some attempts were made at investigating other materials as alternative anodes for fluorine gas production, in particular a RuO₂ DSA-type electrode of the kind successfully used for anodic chlorine generation. Exploratory experiments soon showed, however, that such an electrode was quite unstable under conditions of anodic fluorine gas evolution. Similarly, nickel and platinum are easily attacked. In other words, there are few alternatives to carbon as the substrate electrode material for fluorine gas production. Hence it is desirable to achieve a pre-treatment which can permanently improve the properties of the carbon electrode surface, e.g. by reducing the solid/gas/liquid contact angle and preventing onset of the well known 'anode effect', associated with a kind of passivation.

Rüdorff et al. reported [3], in 1948, that during electrolysis of an anhydrous KHF₂ melt at 523 K, using graphite or carbon as an anode, a film of carbon monofluoride (CF), was formed on the anode surface that leads to the apparent surface aging and the anode effect. It was indicated that this film can be anodically 'burned' off during the anode effect at \( i = 0.3 \sim 0.4 \text{ A cm}^{-2} \) with an electrode potential of 40–50 V; this produced a surface of the carbon anode
looking as if it had been polished with fine sandpaper to a mirror finish. The shiny smooth surfaces were, for further electrolysis, especially resistive towards further occurrences of the anode effect, and exhibited lower polarization as was stated in their paper [3].

In 1971, Childs and Ruchlen [4] patented a procedure in which the anode effect was deliberately induced at a carbon anode at which the FER and the electrochemical fluorination of organic materials were proceeding in KF·2HF and then the anode was subjected to an abnormally high polarization voltage (45–60 V) at $i = 0.2–0.3 \text{A cm}^{-2}$ for a period of time (0.1 to 10 min) sufficient to eliminate further anode effects. Later, Childs [5] improved the operation of one of several cells operating jointly in series without disturbing the operation of the remaining cells.

In the above publications [3–5] a similar procedure of deliberately inducing the anode effect to prevent occurrence of further anode effects at the same carbon anode was reported. However, characterization of the state and behaviour of such carbon electrodes that had been treated by induction of the anode effect has not hitherto been carried out. For example, the polarization behaviour, the mechanism of the improvement to the anode performance and the surface properties of the treated carbon electrodes have not been investigated.

In the present paper, carbon electrodes treated by the above procedure of deliberately inducing the anode effect (that will be referred to as ‘activated’ carbon electrodes in the following pages) are investigated by means of steady-state polarization, rotation (of carbon cone electrodes), SEM and ESCA techniques.

2. Experimental details

The essential details of the experimental procedures used were described in Part I of this series [1]. Briefly, a carbon rotating cone electrode (RCE), a Cu/CuF$_2$ reference electrode and a mild-steel counter electrode were used. The carbon for the RCE was cut from a block of porous carbon of the kind used in commercial fluorine gas production (supplied by Sers Savoie Carbone, France). The electrolyte was a melt of anyhydrous KF·2HF. The cylindrical plexiglass cell (volume 500 cm$^3$) was mounted in an air-heated oven, operating as a thermostat (± 0.5 K) controlled at 358 K. The steady-state polarization data were acquired by an on-line computer system as described previously [1]. The experimental conditions for ESCA measurements were described in [2].

The activated carbon electrodes that were characterized in the present work, were prepared, unless specified otherwise, by the following preparation and activation procedures involving inducing the anode effect and polarizing the carbon electrodes anodically at high current-density and correspondingly high electrode potential (cf. [3–5]) for a controlled period of time:

1. The surface of a carbon anode was first polished with 240–400–600 GRIT sandpapers, using distilled water as a lubricant.

2. The polished carbon anode was dried in an oven at 398–423 K overnight.

3. The carbon anode was then transferred from the oven into the KF·2HF melt and polarized galvanostatically at a current density $i = 10 \text{mA cm}^{-2}$ for 1 h.

4. The anodic current was then increased slowly until onset of the ‘anode effect’ was observed, which was indicated by a sudden jump of the anode potential to ~ 40–50 V with respect to CuF$_2$/Cu (in the melt).

5. The anode current was kept galvanostatically at 100 mA cm$^{-2}$ and ~ 40–50 V for 40 min.

6. The anode current density was then increased to 200 mA cm$^{-2}$ (the anode potential being still about 40–50 V) and the polarization maintained for another 20 min.

7. The activation procedure was then terminated by switching off the polarization current. In order to confirm if the activation procedure was successful, the polarization current was switched on again; the anodic potential should then be ~ 5.0 V (with respect to CuF$_2$/Cu) at $i = 200 \text{ mA cm}^{-2}$ if the activation of the anode had been successful.

8. The carbon electrode, thus activated, was kept in the melt overnight. Then the activated carbon anode is ready for use and is found, in most cases, to maintain its activity for extended periods of time at 200 mA cm$^{-2}$.

The activation effect can also be achieved at lower $i$ and $E$ values (for example, $i < 0.1 \text{A cm}^{-2}$, $E = 25–40 \text{V}$). for a short time (just a few minutes) when the above activation procedure is applied. However, this results in a smaller and less permanent activation effect than that generated by the general procedure described above. Especially, the activation time effect will be described and discussed in §3.1.3.

The purpose of pre-polishing the carbon surface in step 1 of the above procedure is to maximize the ‘electrolytic polishing effect’ that results in a mirror like smoothness of the carbon surface being generated, hence improving the facility of the fluorine gas bubble/film detachment (see later discussion). The drying procedure in step 2 was carried out in order to remove any traces of water in the porous carbon in order for the anode effect to be established at the carbon electrode in a much shorter time, as demonstrated previously [1].

The non-activated carbon samples for ESCA measurements were prepared by polarizing a polished carbon anode anodically in the melt at current density 0.1A cm$^{-2}$ (at ~ 5.5 V with respect to Cu/CuF$_2$) for 48 h.

3. Results and discussion

3.1. Steady-state polarization

3.1.1. Tafel plots. Figure 1 shows the Tafel plot for the FER at an activated carbon RCE under stationary conditions. Figure 2 shows the Tafel plots for the same data (O points) as in Fig. 1 together with data (* points) for the activated RCE but at a rotation rate