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 F_2 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 F_2 bubble/film. The F_2 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 F_2 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 investi-

gating other materials as alternative anodes for fluorine gas production, in particular a RuO_2 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 KHF_2 melt at 523 K, using graphite or carbon as an anode, a film of carbon monofluoride $(CF)_x$ 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 $i = 0.3 \sim 0.4$ 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 $i = 0.2$–$0.3\,\mathrm{A\,cm^{-2}}$ 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 $\mathrm{Cu/CuF_2}$ 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 anyhdrous 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 $i = 10\,\mathrm{mA\,cm^{-2}}$ 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 $\mathrm{CuF_2/Cu}$ in the melt).

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

6. The anode current density was then increased to $200\,\mathrm{mA\,cm^{-2}}$ (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 $\mathrm{CuF_2/Cu}$) at $\sim i = 200\,\mathrm{mA\,cm^{-2}}$ 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 $200\,\mathrm{mA\,cm^{-2}}$.

The activation effect can also be achieved at lower i and E values (for example, $i < 0.1\,\mathrm{A\,cm^{-2}}$, $E = 25$–40 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 $0.1\,\mathrm{A\,cm^{-2}}$ (at ~ 5.5 V with respect to $\mathrm{Cu/CuF_2}$) 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
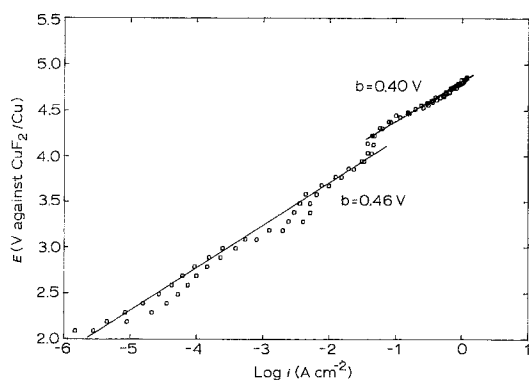
Fig. 1. Tafel plot for the FER in KF · 2HF melt at an activated RCE under stationary conditions (0 r.p.m.).

of 2500 r.p.m. For comparison, in Fig. 2, the behaviour of a normal polished *non*-activated carbon RCE (0 r.p.m., stationary) is also illustrated (× points) (*cf.* Part I). For the activated anode, the current density is as high as $1.2 \, A \, cm^{-2}$ at as low a polarization as 4.9 V with respect to CuF_2/Cu, (iR corrected data, electrolyte resistance $R = 0.8 \, \Omega$). Under stationary conditions, at $i = 0.1 \, A \, cm^{-2}$, the polarization potential is 1.5 V lower for the activated than the non-activated RCE, as shown in Fig. 2, while at $i = 0.2 \, A \, cm^{-2}$, the potential is 2.5 V lower for the activated than the non-activated carbon RCE.

There are three characteristics of the polarization behaviour of the FER at the activated compared with the non-activated carbon electrodes, that are different. The first is that the Tafel relation becomes shifted almost parallel by 2 decades in *i* towards the higher current density direction as shown in Fig. 2. This behaviour indicates that the activated carbon electrodes have about 100 times more 'active sites' per unit area for fluorine gas generation than a non-activated one. This may imply that a much smaller coverage by adherent fluorine gas bubble/film exists on the activated carbon electrodes. The second difference is that the Tafel relation for the activated carbon RCE does not bend upwards and tend to reach a limiting current $\sim i = 0.2 \, A \, cm^{-2}$; instead, in the high *i* range from 0.08 up to $1.2 \, A \, cm^{-2}$ as shown in Figs 1 and 2, it becomes a straight line with a slope $b = 0.40 \, V$. The slopes of the Tafel lines for activated carbon RCE's
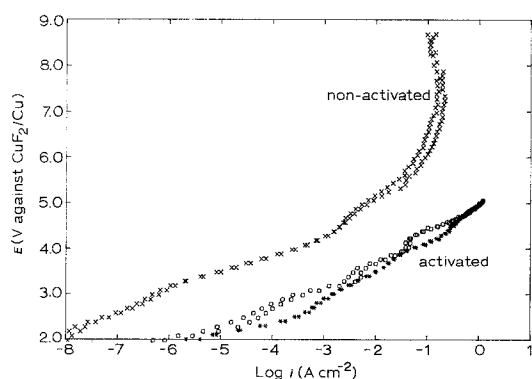

Fig. 2. Tafel plots for the FER in KF · 2HF melt at an activated carbon RCE under stationary conditions (O points) and rotated at 2500 r.p.m. (* points), and at normal, polished, non-activated carbon RCE (no rotation) (× points).

are even slightly smaller over the high *i* range than those for the lower *i* range (see Fig. 1). The much higher Tafel slope, $b = 0.88 \, V$ and the limiting maximum *i* in the higher *i* range for a non-activated carbon RCE (rotated at 2500 r.p.m.), reported in our previous study [1], was proved to be due mainly to the 'bubble polarization' effect, i.e. the difficulty of fluorine gas bubble detachment and the formation of the thin fluorine gas film. A similar low value of the slopes for the FER at an activated carbon RCE in both the low and high *i* ranges implies that the extra polarization due to fluorine gas bubble/film was eliminated or drastically diminished on the surface of the activated carbon electrodes!

The elimination of the 'bubble adherence effects' on the surface of the activated carbon electrodes is also related to the third characteristic, viz. that there is no rotation effect on the fluorine gas evolution polarization at the activated carbon RCE, especially over the high current region, as illustrated in Fig. 2. It was demonstrated in part I [1] of this series that the rotation of the carbon RCE has strong effects on the FER behaviour at a normal non-activated carbon RCE, due to facilitation of detachment of the fluorine gas bubbles. However, Fig. 2 shows that for an activated carbon RCE, the polarization behaviour under stationary conditions (no rotation) is virtually as good as when the electrode was rotated, especially over the high *i* region. This implies that bubble polarization effects are substantially changed, as is confirmed by visual observation of the bubble detachment (see the next section). This observation that, for activated electrodes, *no* rotation is required to diminish the bubble hyperpolarization effect is of practical significance since rotated electrodes could hardly be used in commercial cell operation although a vertically vibrated system is more conceivable. Activation by a special regime of anode high voltage polarization seems practically a much more feasible operation.

3.1.2. 12-Day polarization test. The galvanostatic polarization behaviour of the activated carbon anode (not rotated) over a 12-day period test, is illustrated in Fig. 3. This shows the plots of anode potential, *E* against time at a current density *i* of $0.2 \, A \, cm^{-2}$. Notice that the potential values in Fig. 3 include the *iR* drop ($R = 0.8 \, \Omega$, the electrolyte resistance between working and reference electrodes). During 12 days of continuous polarization at $0.2 \, A \, cm^{-2}$, it is seen that the anode potential even dropped slightly, from 5.06 to 4.97 V against Cu/CuF_2.

3.1.3. Effects of activation time and current density. The previously reported [3–5] carbon electrode activation procedure involves induction of the anode effect with polarization of the carbon electrodes anodically at ~ 40–50 V with $i \simeq 0.2$–$0.3 \, A \, cm^{-2}$ for about 3 min. A much longer time during the high voltage (40–50 V) polarization was used in the present work. This was found to result in much increased activity for the FER at the carbon electrodes thus treated.
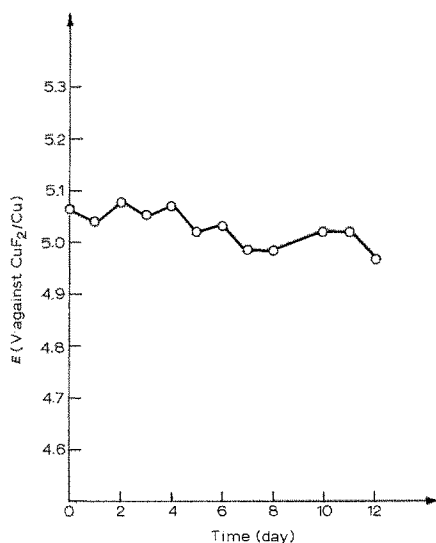
Fig. 3. The anode potential against time profile for an activated anode at a current density of $0.2\,A\,cm^{-2}$. The potential values in the figure include the iR drop ($R = 0.8\,\Omega$, the electrolyte resistance between working and reference electrodes).

Three activated carbon electrodes were prepared under different conditions. No. 1: $0.1\,A\,cm^{-2}$ for 1 min.; no. 2: $0.1\,A\,cm^{-2}$ for 45 min.; and no. 3: $0.2\,A\,cm^{-2}$ for 70 min. The anodic activation potential was about 38 to 40 V in all cases. The polarization behaviour, shown as linear E against i plots for the three carbon electrodes activated to different extents for the FER, is shown in Fig. 4 which clearly indicates that the carbon electrode subjected to activation for longer time (and higher i) has better polarization performance. The exceptionally active carbon electrode, no. 3, is produced by the longest activation (70 min) and at twice the i for nos. 1 and 2 ($0.2\,A\,cm^{-2}$). A short time of activation $0.1\,A\,cm^{-2}$ for 1 min., only results in a slightly improved carbon anode (no. 1 in Fig. 4).

The physical appearances of the surfaces of the three activated carbon electrodes are different. The surface of the most activated carbon electrode, no. 3, appears as if it had been polished with a fine sandpaper to a mirror finish like that of a metal surface, as also reported by Rüdorff et al. [3]. The surface of the least activated electrode (no. 1) has only a few spots which exhibit a shiny mirror-like surface. The intermediate
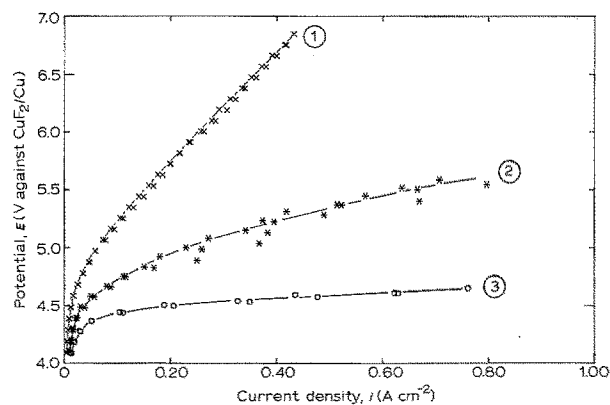
one, no. 2, has a surface exhibiting shiny mirror-like appearance on most of the visible area of the electrode.

It was previously demonstrated [1] that polishing of the carbon electrodes by sandpapers and abrasives [6, 7] improves the polarization behaviour, an effect that appears to be due mainly to facilitation of fluorine bubble detachment. The exceptionally improved activity of carbon anode, no. 3, must be attributed at least partly to an electrolytic-polishing effect associated with the induction of the anode effect which produces the mirror-like smooth surface. The smoothness of the carbon surfaces produced both by sandpapering and by electrolytic polishing procedures is illustrated in the SEM studies (§ 3.3).

Besides the greatly improved smoothness of the activated compared with the non-activated carbon electrode, a smaller extent of surface fluorination was found for the activated carbon electrodes by means of ESCA studies as will be described in § 3.4.

3.2. Bubble behaviour; photographic observation

It was found that, instead of formation of full-sized lenticular fluorine gas bubbles, as was observed on the normal non-activated carbon RCE's, shown in Fig. 5a, gaseous fluorine gas becomes evolved as many smaller bubbles that appear on the surface of the activated carbon RCE's, as shown in Fig. 5b. This is probably
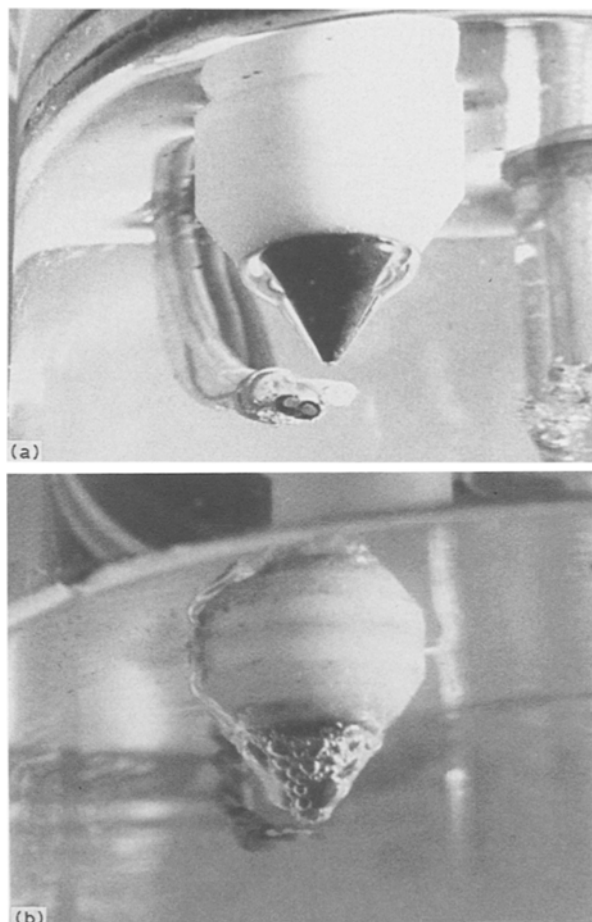

Fig. 4. Linear E against i plots for three differently activated carbon electrodes, curves correspond to no. 1, no. 2 and no. 3 in text.

Fig. 5. Photographs of the stationary RCE's in the cell for (a) a normal non-activated carbon RCE, polarized at $0.1\,A.cm^{-2}$ and (b) an activated carbon RCE, polarized at $0.4\,A\,cm^{-2}$.

one of the most important factors contributing to the high activity of the activated carbon electrodes.

The illustration in Fig. 5b is of an activated carbon RCE (0 r.p.m., stationary) polarized at $i = 0.4 \, A \, cm^{-2}$; a stream of fluorine gas leaving the electrode surface along the Teflon cylinder toward the melt surface can be seen. For a much lower i, the small-bubble pattern, as shown in Fig. 5b, was also observed on the activated carbon electrodes.

As indicated previously [1, 2], the 'CF' film on the carbon electrodes evidently gives rise to a very low surface energy and an unusually high solid/gas/liquid contact angle [8] which makes fluorine gas bubble formation on, and detachment from the electrode surface a serious problem. In fact, the abnormally high Tafel slope (0.88 V) in the high i range and the so-called anode effect appear to originate from the adherent fluorine bubble and/or fluorine gas film, i.e. a static bubble in another form on the carbon electrodes. It was concluded in work by Brown et al. [9] that, for most of the time, 99% of the surfaces of vitreous carbon or graphite anodes was blocked by a fluorine gas-bubble film.

The formation of much smaller bubbles on the activated carbon surface [Fig. 5b] implies that the contact angle at the solid/gas/liquid interface was significantly reduced, which may be associated with the change of the surface chemical compositions (see § 3.4.).

3.3. SEM examination of carbon electrodes

Figure 6 shows SEM photographs for (a) and (b): a non-activated carbon electrode polished by the procedure described in [6, 7], and polarized at 0.1 A cm^{-2} for 48 h; (c) and (d): an activated carbon electrode treated by the procedure described in § 2, at two magnifications. The photographs in Fig. 6 are typical SEM illustrations of the flat areas of the carbon electrode surfaces. Figures 6c and d show the shiny mirror-like surface areas of the activated carbon electrodes, which are obviously much smoother than the surfaces of non-activated, polished carbon electrodes [Figs 6a and b]. As mentioned earlier, in § 3.1.3., the smoothness of the mirror-like surface of the activated carbon electrodes is believed to be one of the factors that facilitate the fluorine gas bubble/film detachment and eliminate the abnormally high fluorine gas bubble/film polarization behaviour.

3.4. ESCA examination of 'CF' films

Figure 7 shows the ESCA spectra of the carbon 1s peaks of an activated carbon electrode surface. The experimental carbon 1s peaks (+ points) are resovable into four components which correspond to 'CC', 'CO', 'CF' and 'CF$_2$' states of carbon 1s at binding energies of 284.0, 285.5, 288.2 and 291.0 eV, the same as for a
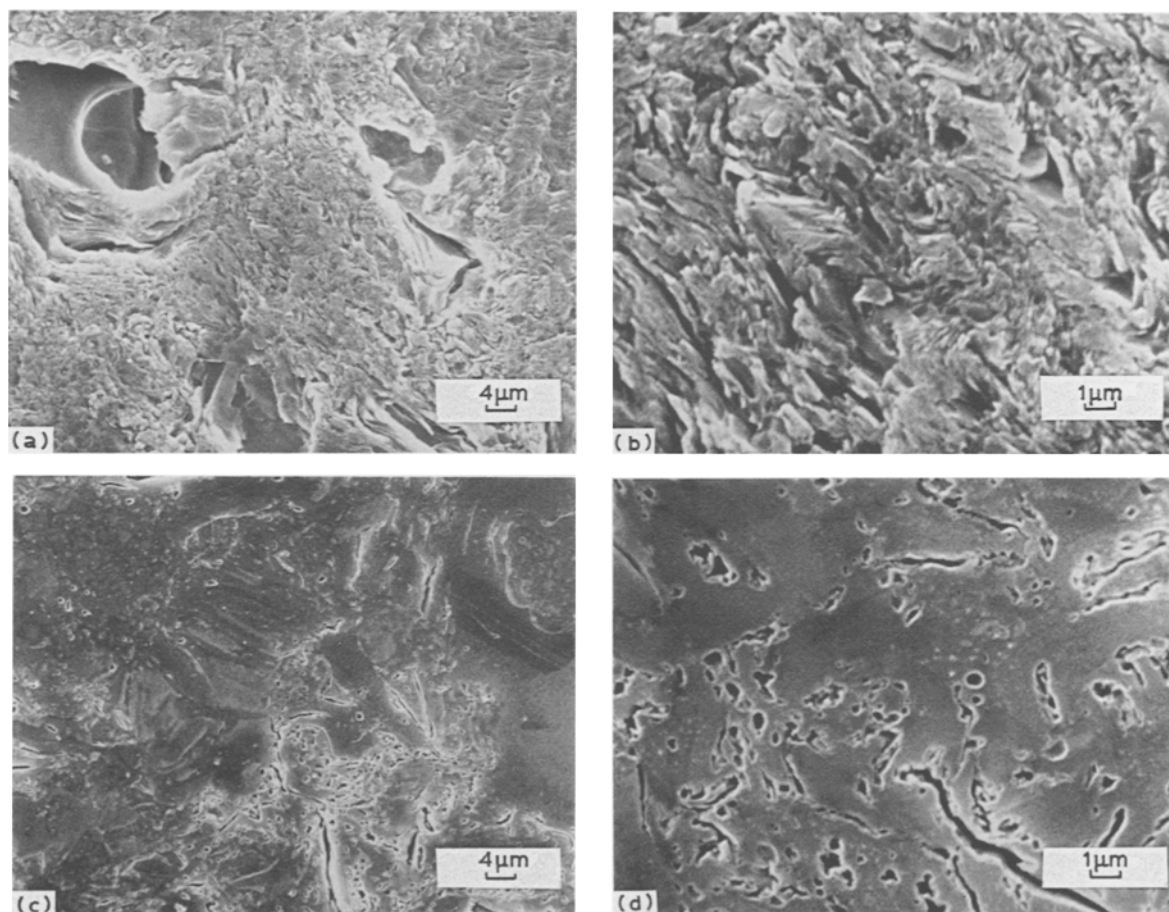

Fig. 6. SEM photographs, (a) and (b): for a non-activated polished carbon electrode; (c) and (d): for an activated carbon electrode at two indicated magnification scale factors. The non-activated carbon electrode was used for fluorine gas evolution at $i = 0.1 \, A \, cm^{-2}$ (5.5 V) over 48 h. The pictures are of the flat areas of the electrode surfaces for both cases.
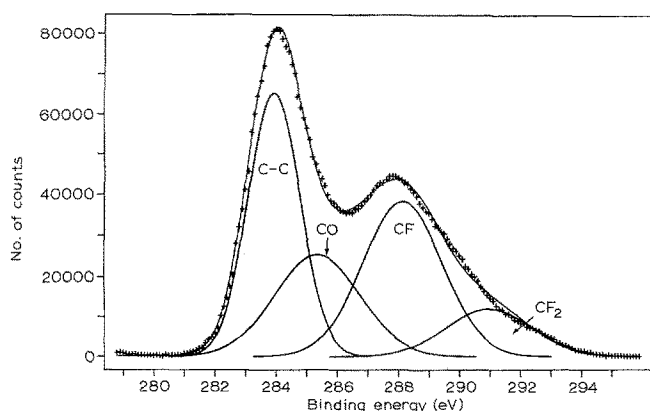
Fig. 7. The experimental points (+ + +) and computer-fitted and deconvoluted curves (——) for a detailed ESCA scan of the carbon 1s peaks for an activated carbon anode.

non-activated carbon electrode surface as reported previously [2]. However, the relative peak areas and heights of each component are different for the activated compared with the non-activated carbon electrodes. The peak area represents the 'composition' of each component of the overall carbon 1s peak. The percentage of each component associated with the carbon 1s profile in Fig. 7 for an activated carbon electrode, together with the results reported previously [2] for a non-activated one, calculated from the values of peak areas, are listed in Table 1.

The results recorded in this Table show that the non-activated carbon electrodes have a much higher surface percentage of the 'CF' and 'CF$_2$' components, the ratio of (CF + CF$_2$)/C–C being almost twice as high than that for the activated carbon electrodes.

Information on the thickness of the 'CF' films and the depth profiling of the sample surface is provided from ESCA ion-sputtering experiments, as discussed previously [2]. The derived thicknesses of the 'CF' films as a function of sputtering time for both activated and non-activated carbon samples are listed in Table 2. The data for a non-activated carbon sample are as reported previously [2].

The thickness of the 'CF' film on the anode surfaces is found to be twice as large for the non-activated as for the activated electrodes, this difference being well outside experimental error. Also, it was found that it takes much longer time to completely remove the 'CF' film from the surface of the non-activated than from the activated electrodes.

The depth profiling composition information, i.e.

Table 1. The surface percentage of the indicated component of the ESCA carbon 1s region for both activated and non-activated carbon electrodes

Percentage (%)	Peak	C–C	CO	CF	CF$_2$	$\dfrac{CF + CF_2}{C-C}$
	E_{max} (eV)	284.0	285.5	288.2	291.0	
Non-activated		28	11	47	14	2.2
Activated		35	22	32	11	1.2

Table 2. The thickness of 'CF' films against sputtering time for non-activated and activated carbon electrodes

Thickness of CF film (nm)	Sputtering time (s)							
	0	5	10	15	20	40	120	600
Non-activated	1.77	0.87	0.54	0.51	0.42	0.33	0.25	0
Activated	0.97	0.40	0.18	0.07	–	0	–	–

the atom fractions of 'CF' (as CF$_2$) and F plotted against sputtering time for the activated and non-activated carbon electrodes, is shown in Fig. 8.

From the above analysis, it may be concluded that the degree of fluorination of the carbon surface and the thickness of the 'CF' film are substantially higher on the non-activated than on the activated carbon anodes. This may be what leads to a more favourable contact angle of the carbon/F$_2$gas/melt interface and a smaller barrier for electron tunnelling for the case of activated carbon anodes used for the FER. Also the polarity, and hence lyophilicity, of the films at the two types of electrodes may be, in some way, different.

It is interesting to point out that the activation procedure is based on an induced anode effect, i.e. it is necessary that the activated carbon electrode be polarized anodically at ~40–50 V for a certain time. Surprisingly, the induced anode effect produces a much thinner 'CF' film with less extent of fluorination of the film on the activated than on the non-activated electrodes. These results support the qualitative explanation of Rüdorff *et al.* [3], proposed in 1948, that the CF film can be 'burnt off' during the electrolysis at higher voltages, especially during the anode effect (40–50 V). However, this is not entirely correct since a film of some kind of 'CF' film remains (and probably must remain) on the activated electrode but its state is evidently, in some significant ways, different from that at the non-activated electrodes.
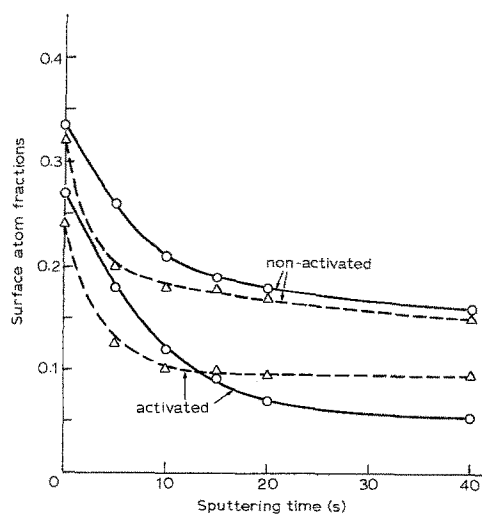

Fig. 8. The plots of the surface atom fractions of 'CF' (as CF$_2$) and of F against ion sputtering time for activated and non-activated carbon electrodes: (O——O) data for F 1s; (△– – –△) data for C 1s (as CF and CF$_2$, excluding CC).

4. Conclusions

1. Activated carbon electrodes that can be produced, based on a previously reported procedure of inducing the anode effect, have been characterized. It is found that the activated carbon electrode exhibits the following unique, exceptionally active, polarization behaviour compared with that of a normal non-activated carbon electrode for the FER in KF · 2HF melts at 358 K:

   (i) high i_0: the exchange current density becomes increased by 2 to 3 orders of magnitude, i.e. the Tafel relation becomes shifted 2-3 decades towards the high i side.

   (ii) low Tafel slope: in the high i range, from 0.08 to 1.2 A cm^{-2}, the Tafel slope (0.40 V) becomes reduced to less than half the value (0.88 V) for a non-activated electrode.

   (iii) resistance to further anode effects: the limiting maximum current density, at $\sim i$ = 0.2 A cm^{-2}, and the anode effect are virtually eliminated.

   (iv) absence of rotation effect: the polarization behaviour under stationary conditions (no rotation) is virtually as good as when the electrode is rotated at high rates (facilitation of the detachment of the fluorine gas bubbles).

   (v) good long-life properties: finally, but most important practically, the activity of the activated carbon anode *remains unchanged* during a 12-day galvanostatic polarization test at a current density of 0.2 A cm^{-2} (E = 5.0 V against Cu/CuF$_2$).

2. The improvements, listed above, of carbon anodes, due to activation, are believed to be associated mainly with facilitation of the detachment of the fluorine gas bubble/film which is the main reason for the abnormally high polarization and anodic effect observed at non-activated carbon anodes, as indicated in our previous studies on electrode rotation effects.

3. It was shown that the facilitation of the fluorine gas bubble/film detachment on activated carbon anodes is closely related to two physical properties of the activated carbon electrode surface: a much smaller solid/gas/liquid contact angle and a much smoother surface.

4. It was determined by means of ESCA that, compared with a non-activated carbon anode, the activated electrodes have a smaller extent of fluorination in the 'CF' film and a smaller thickness of this film. This may lead to a more favourable contact angle and a smaller barrier for electron tunnelling for the case of activated carbon anodes used for the FER.

5. Increasing the time for the activation process at high i and E values, i.e. the time of polarization involving the induction of the anode effect at high voltage (40-50 V) and high i (0.1-0.2 A cm^{-2}), results in much increased activity of the carbon electrodes for the FER than that given by previously reported procedures involving substantially shorter times.

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