Journal of Fluorine Chemistry, 57 (1992) 93–99

A novel carbon electrode impregnated by molten metal fluoride for the production of fluorine

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Abstract

The catalytic ability of solid LiF or AlF_3 to decrease anode overvoltage and the anode behavior of a carbon electrode impregnated with molten LiF–NaF or AlF_3–NaF in KH_2F_3 were investigated When the graphite-sheet electrode was electrolyzed in a bath containing 2% by weight LiF or AlF_3, the anode effect did not occur, but fluorine–graphite intercalation compounds were formed by catalytic reaction of these solid metal fluorides Under these conditions, the dispersion term of the surface energy of the electrode was nearly the same as that of the control electrode, however the polar term of the electrode increased 30 times over that of the control electrode The carbon electrode impregnated with molten LiF–NaF or AlF_3–NaF was operated with a high current density (*e g* 20 A dm^{-2}) for 40 days without the occurrence of the anode effect, contamination of CF_4 in the F_2 was as low as 2 ppm

Introduction

The anode reaction for the production of elementary fluorine is shown in eqn. (1). The side reactions are formation of graphite fluoride $(CF)_n$ and the decomposition of $(CF)_n$ as shown in eqns. (2) and (3), respectively.

$$HF_2^-(l) \longrightarrow 1/2F_2(g) + HF(l) + e^- \tag{1}$$

$$2nC(s) + nF_2(g) \longrightarrow 2(CF)_n(s) \tag{2}$$

$$4(CF)_n(s) \longrightarrow 3nC(s) + nCF_4(g) \tag{3}$$

The electrolyte cannot come into contact with that part of the electrode which is covered with $(CF)_n$ because of its extremely low surface energy. The large polarization of the carbon anode in KH_2F_3 is caused by this phenomenon, because the active surface area of the electrode for reaction (1) decreases with the increase in $(CF)_n$ which is decided by the rates of reactions (2) and (3). In a well-dehydrated bath, the formation of fluorine–graphite intercalation compounds as shown in eqns. (4) and (5) proceeds competitively with the formation of $(CF)_n$ to suppress the occurrence of the anode effect [1, 2].

$$xC(s) + F^-(l) \xrightarrow{LiF} C_x{}^+F^-(s) + e^- \tag{4}$$

$$xC(s) + HF_2^-(l) \longrightarrow C_x{}^+HF_2^-(s) + e^- \tag{5}$$

0022-1139/92/$5 00

LiF or AlF_3 are catalysts for the formation of the fluorine–graphite intercalation compound and formation of this compound ensures the wettability of the anode surface by the electrolyte, so lowering the anode overvoltage [1]. A new carbon electrode impregnated with LiF or AlF_3 was developed by the authors [3–5] for the production of fluorine. In the present study, the anode overvoltage of the electrode in a KH_2F_3 bath which contained 2% by weight of LiF or AlF_3 was investigated from the viewpoint of the change in surface energy of the electrode with the formation of fluorine–graphite intercalation compounds.

The carbon electrode impregnated with molten LiF–NaF or AlF_3–NaF was operated for long periods to evaluate the persistence of the catalytic action of these metal fluorides and the behavior of the anode.

Experimental

An appropriate mixture of metal fluorides LiF and NaF or AlF_3 and NaF at a molar ratio of 2:3 was placed with carbon (Toyo Tanso, Co.; FE-5) in a graphite crucible, then put into an autoclave. The crucible was heated to the melting point of each eutectic mixture (melting point of LiF–NaF is 650 °C and that of AlF_3–NaF is 850 °C with the above molar ratios [6]) under an atmosphere of nitrogen. The pressure in the autoclave was increased up to 50 kg cm^{-2} by introducing nitrogen at the same temperature, and these conditions were maintained for 30 min. The size of the carbon electrode was 210 mm × 80 mm × 20 mm. The cathode was nickel plate and the reference electrodes were Pt wires located near the anode and the cathode. A trace amount of water in the KH_2F_3 bath was carefully eliminated by electrolysis with carbon electrodes prior to the electrolysis with the impregnated electrodes. These impregnated electrodes were operated in 40 l of a KH_2F_3 melt at 90 °C for 40 days.

The electrolytic cell was made of poly(tetrafluoroethylene); a copolymer of tetrafluoroethylene–perfluoroalkylvinyl ether was prepared for the contact angle measurements. The working electrode and counter electrode were a graphite sheet (40 mm × 5 mm × 1 mm) and a nickel plate (20 mm × 30 mm × 1 mm), respectively. LiF or AlF_3 were dried at 200 °C under vacuum for 48 h prior to electrolysis. A trace amount of water in the bath was eliminated by electrolysis with carbon electrodes, and then 2% by weight of dried LiF or AlF_3 was added to the bath. The galvanostatic electrolysis was continued at 3.3 mA cm^{-2} for a given duration, then the graphite-sheet electrode was taken out of the electrolytic bath. The electrode was analyzed by X-ray diffraction and contact angle measurements. The contact angle was measured with water and methylene iodide at 25 °C.

Results and discussion

The physical properties of the control carbon and the carbon impregnated with molten LiF–NaF (2:3) or AlF_3–NaF (2:3) are shown in Table 1. The density of the impregnated carbon increased by 0.22 g cm^{-3} compared to that of the control carbon, and the pores of the carbon were impregnated with metal fluorides. The flexural strength of the impregnated carbon is nearly the same as that of the control carbon. The steady-state anode polarization curves using three types of electrodes are shown in Fig. 1. The anode effect was observed in the control carbon at 30 A dm^{-2}, but was not observed even at 60 A dm^{-2} with the carbon electrode impregnated with metal fluorides; another advantage of the impregnated electrode is the very small overvoltage in high current density.

The anode voltage of the electrode impregnated with LiF–NaF (2:3) was the lowest among the three types of electrodes. Figure 2 shows the

TABLE 1

Physical properties of raw carbon and impregnated carbon

Sample	Density (g cm^{-3})	Porosity (vol%)	Flexural strength (MPa)
Raw carbon,	1.69	11.7	103
impregnated[a]	1.91	0	106

[a] Carbon material impregnated with an eutectic mixture of LiF–NaF (2:3) and AlF_3–NaF (2:3).

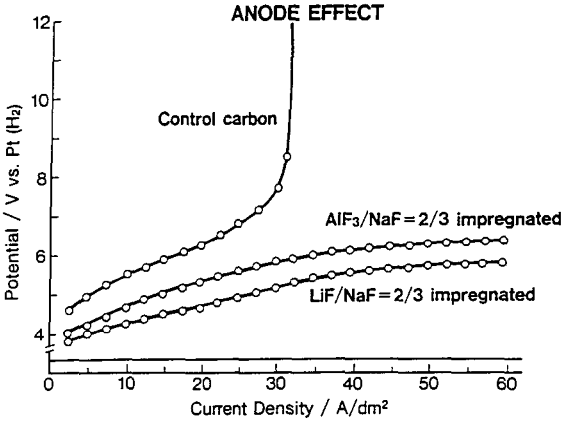

Fig. 1. Galvanostatic polarization curves for metal-fluoride-impregnated carbon in a fluorine cell at 90 °C.

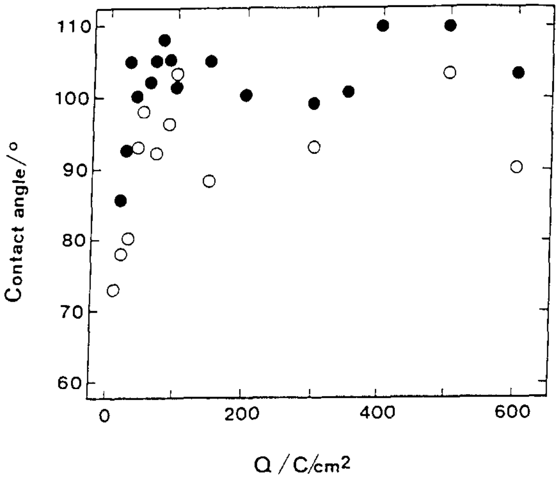

Fig. 2. Variation of the contact angle of a water drop on the electrode as a function of the quantity of electricity passed: (●) 2% by weight AlF_3, (○) 2% by weight LiF, added to the bath.

variation in the contact angle of a water drop measured for the graphite sheet anode polarized in KH_2F_3 with 2% by weight LiF or 2% by weight AlF_3 at 90 °C. The anode effect was observed in the well-dried KH_2F_3 free of these metal fluorides at 400 C cm^{-2}. The contact angle of a water drop was then 120°, while the contact angle of a water drop was maintained at about 95° and 105° without occurrence of the anode effect in the melt containing 2% by weight LiF or AlF_3, respectively. The fluorine–graphite intercalation compounds were stable during these measurements.

Three new lines are observed at $2\theta = 16°$, 22° and 27° on the X-ray diffraction patterns of these electrodes. These lines are assigned to (003), (004) and (005) of the stage IV fluorine–graphite intercalation compound [1]. The relationship between the contact angle and surface energy can be derived from the Young–Dupré and Fowkes equations given by eqn. (6):

$$1 + \cos\theta = 2/\gamma_L(\sqrt{\gamma_S{}^D\gamma_L{}^D} + \sqrt{\gamma_S{}^P\gamma_L{}^P}) \qquad (6)$$

where θ is the contact angle; γ_L, is the surface energy of the liquid–gas interface; $\gamma_S{}^D$ and $\gamma_S{}^P$ are dispersion and polar terms, respectively, of the surface energy for a solid–gas interface; $\gamma_L{}^D$ or $\gamma_L{}^P$ are those of the surface energy for a liquid–gas interface [7].

By measuring the contact angle on the polarized electrode with two kinds of polar and non-polar solvent whose γ_L, $\gamma_L{}^D$ and $\gamma_L{}^P$ are known, two simultaneous equations can be obtained and solved for the two unknowns $\gamma_S{}^D$ and $\gamma_S{}^P$. In this case, water and methylene iodide were used to measure the contact angle. The polar and dispersion terms of the surface energy of fluorine–graphite intercalation compounds formed on the electrode are

TABLE 2

Polar and dispersion terms for surface energy on a fluorine–graphite intercalation compound formed on an electrode

Q ($C\ cm^{-2}$)	Surface energy for graphite sheet with 2% LiF added to bath ($erg\ cm^{-2}$)			Surface energy for graphite sheet with 2% AlF_3 added to bath ($erg\ cm^{-2}$)		
	Polar term	Dispersion term	Total surface energy	Polar term	Dispersion term	Total surface energy
0	0.2	43.0	43.2	0.2	43.0	42.3
10	6.0	40.0	46.0	0.6	32.1	32.7
100	3.6	30.0	33.6	0.1	27.1	27.2
600	2.4	30.0	32.4	0.4	37.7	38.1

summarized in Table 2. A slight decrease in the total surface energy due to partially formed $(CF)_n$ on the electrode was observed during the electrolysis. The dispersion term for the surface energy did not change much, but the polar term increased drastically for the electrode polarized in the melt containing 2% by weight LiF. The increase in polarity due to the formation of fluorine–graphite intercalation compounds by the catalytic reaction of solid LiF ensures the wettability of the electrode with an ionic melt such as KH_2F_3. This might be the main reason for the lowering of the anode overvoltage in the presence of solid LiF. When the fraction α per unit area of the electrode is defined as the effective part for the reaction (1), the relationship between α and the contact angle θ of the water drop is given by eqn. (7):

$$\alpha = 1/2(1 + \cos\theta) \qquad (7)$$

The true curernty density i_t is given by eqn. (8), where i is the applied current density.

$$i_t = i/\alpha \qquad (8)$$

For a bath containing 2% by weight of LiF or AlF_3, the value of i_t was calculated by eqn (8) in the course of electrolysis at $i = 3.3\ A\ dm^{-2}$. The relationship between i_t and the corresponding anode potential are plotted in Fig. 3. The potential difference between the data obtained from the electrode polarized in the melt containing 2% by weight LiF and that in the melt containing 2% by weight AlF_3 at the current density of 7 to $8\ A\ dm^{-2}$ was about 0.7 V. This value coincides with that obtained from $i-V$ curves for LiF–NaF or AlF_3–NaF impregnated electrodes, as shown in Fig. 1.

Operational data for a 50-A cell for the carbon electrode impregnated with LiF–NaF (2:3) or AlF_3–NaF (2:3) in KH_2F_3 are shown in Fig. 4. The stage IV fluorine–graphite intercalation compound was formed on the

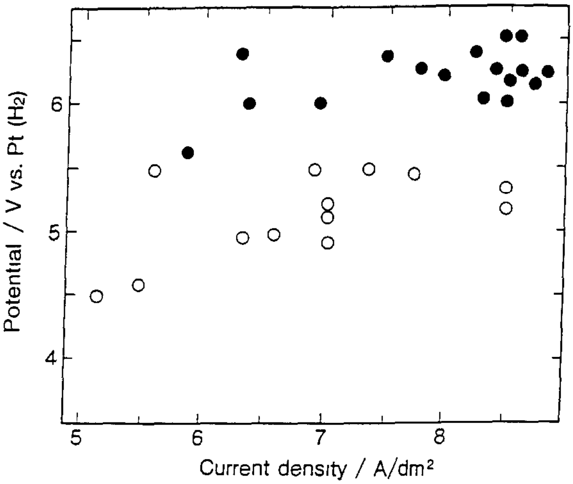

Fig 3 Relationships between the true current density and anode potential for a graphite-sheet electrode (●) 2% by weight AlF_3, (○) 2% by weight LiF, added to the bath

carbon electrode impregnated with metal fluorides during the first 4 days with a low current density, such as 5 A dm^{-2}. The cell voltage remained constant in both impregnated electrodes with a high current density such as 20 A dm^{-2}. The cell voltage of the carbon electrode impregnated with LiF–NaF (2:3) was lower than that of the carbon electrode impregnated with AlF_3–NaF (2:3) by 1 V at 20 A dm^{-2}.

The concentration of CF_4 was as low as 2 ppm during electrolysis with both metal-fluoride-impregnated electrodes, and was independent of the value of the applied current density. The high mechanical strength of

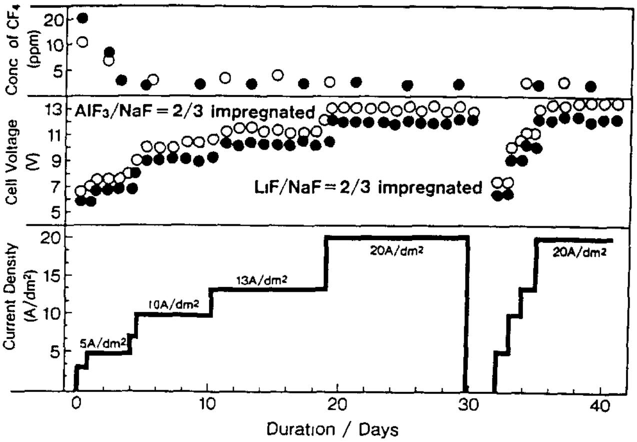

Fig 4 Operational data for a 50-A fluorine cell for the carbon electrode impregnated with LiF–NaF or AlF_3–NaF.

the carbon and the metal fluorides inserted into the pores of the carbon decrease the formation of CF_4 by reaction between the disintegrated powdery carbon and the fluorine. The lower amount of $(CF)_n$ generated by the low-polarized electrode produces a smaller amount of CF_4 by reaction (3).

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