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New solid-state electrochemical source of pure fluorine

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Abstract

A new source of elemental fluorine is described, based on the electrochemical decomposition of a solid F^- conducting electrolyte. The use of a chemically and thermally stable solid electrolyte provides the possibility of pure fluorine production over a wide temperature range and also under high vacuum conditions. Fluorine evolution was investigated by volumetric and mass-spectrometric methods.

Keywords: Elemental fluorine; Solid conducting electrolyte; Electrochemical decomposition; Mass spectrometry

1. Introduction

The production of pure elemental fluorine for various experimental purposes still causes certain difficulties due to its strong reactivity [1]. Although elemental fluorine has been known for more than 100 years, it is still produced by Moissan's original method: the electrolysis of anhydrous HF/alkali fluoride solutions. The significant vapour pressure of HF over these solutions leads to contamination of the evolving fluorine and additional purification is needed.

Only three alternative routes for fluorine preparation have been reported to date. Two of them are based on the thermal decomposition of the complex fluorides K_2NiF_6 [2] and $CaNiF_6$ [3]. The temperature ranges for the decomposition of these compounds are 350–450 °C and 120–220 °C, respectively. It should be mentioned that K_2NiF_6 and $CaNiF_6$ are unstable in moist air and that for the production of $CaNiF_6$ a stronger oxidant (KrF_2) than elemental fluorine is needed. A very interesting photoelectrochemical process for fluorine preparation has been described by Wang et al. [4]. Elemental fluorine was evolved at an n-type $TiO_{2-x}F_x$ positive electrode in an electrochemical cell with an HF/NaF solution as the electrolyte. Using band-gap illumination (365 nm) of the positive electrode, the gaseous F_2 was obtained with a sizable photovoltage as well as with high power and current efficiencies. However, the use of an NaF/HF electrolyte leads to inevitable contamination due to autogenous HF pressure.

There is another possibility which has not been considered to date. This is connected with the use of a number of fluorides (LaF_3, PbF_2, SnF_2, BiF_3 and related composites) as solid F^- conducting electrolytes. These compounds are characterised by a high F^- ionic conductivity ($\sigma \sim 10^{-3}$ to 10^{-5} Ω^{-1} cm^{-1}), low vapour pressures and high melting temperatures as well as by stability in moist air. Such properties make their use attractive for the production of elemental fluorine [5].

The present work is the first to describe a new electrochemical source of pure elemental fluorine based on the effect of neutralising mobile F^- ions on the surface of a solid electrolyte with subsequent evolution of elemental fluorine into the gas phase. Due to the unique combination of properties of the materials used as well as to the simplicity of controlling the gas evolution process, such a method has a potential for a wide diversity of procedures.

2. Experimental details

The source was a solid electrochemical cell consisting of F^- conducting electrolyte in the form of a tablet and two electrodes [Fig. 1(a)]. A solid solution of LaF_3 with the addition of 3–10 mol% of BaF_2 was used as the electrolyte. Its ionic conductivity σ was equal to $(4–8) \times 10^{-5}$ Ω^{-1} cm^{-1} at 20 °C.

The solid solution was produced by melting the LaF_3 and BaF_2 mixture in an inert atmosphere. The electrolyte tablets in the form of disks of 1–3 mm thickness and 5–20 mm diameter were cut out of the melted material ($\rho \doteq 5.85$ g cm^{-3}) or pressed out of powdered electrolyte ($\rho = 5$ g cm^{-3}) with subsequent sintering in a dry argon atmosphere. Both types of material had similar experimental characteristics

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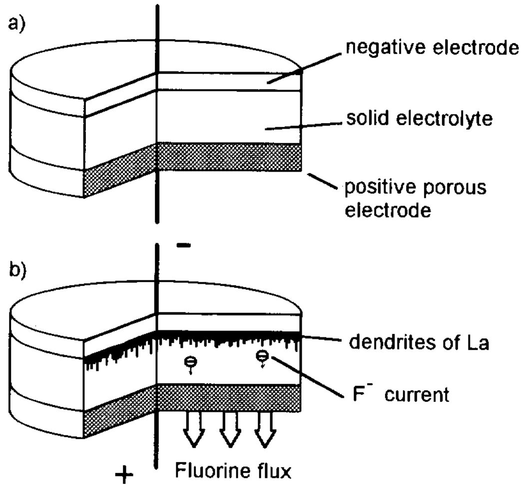

Fig. 1. (a) Internal structure of solid cell and (b) its operation as a fluorine electrolyser.

despite the fact that the sintered tablets had a considerable porosity.

The negative electrodes of the electrochemical cells were produced by vacuum evaporation of Bi, Cu and Ni, or by graphite rubbing.

The porous positive electrode was also produced by graphite rubbing or by vacuum evaporation of an Ni layer of 0.2–0.5 μ thickness.

To study the rate of gas evolution from the solid electrolyte, the assembled cell was mounted inside a hermetic measuring chamber (~ 45 cm^3 volume). Before the measurements were undertaken, the chamber was passivated by XeF_2 or F_2 and then evacuated to 1.3 Pa pressure. During the experiments a pressure variation occurred in the chamber depending on the current passing through the cell. The pressure in the chamber was registered by means of a membrane pressure transducer (DP-5, Russia) with an accuracy of 1.3 Pa, and the current through the cell was controlled by means of an electrochemical interface (EI-1286 Solartron). The collection, storage and preliminary treatment of the data concerning the electric parameters of the cell (current, voltage) and pressure were carried out using an HP-85B computer.

The composition of the gas evolved from the porous electrode was determined by means of a mass spectrometer. The cells used in this procedure were composed either of monocrystalline or melted samples of $LaF_3(BaF_2)$ with a diameter of 6, 15 and 20 mm fitted with positive and negative electrodes made from graphite. The cells were placed at 10 mm distance from the inlet diaphragm of the ioniser of an APDM-1 quadruple mass spectrometer. The gas molecules evolved when the current passed through the electrolyte were ionised by electron impact, and the positive ions were analysed with resolution $M/\Delta M > 60$ in the range 0–400 a.u. The background pressure in the mass spectrometer chamber was maintained at $\sim 10^{-3}$ Pa.

3. Results and discussion

On passing a current through the solid electrochemical cell located in the measuring chamber, an increase in pressure was noted. The typical form of the signal from the pressure transducer for the thoroughly passivated chamber is shown in Fig. 2(c). The voltage across the cell (b) and the cell current (a) are also shown in the same figure. The voltage applied to the electrodes causes the diffusion of F^- ions in the electrolyte and results in the electrochemical decomposition of the electrolyte at the interface between the solid electrolyte and the negative electrode [6]. The dendrite structure of the reduced metallic phase was observed microscopically. The appearance of such a structure can be understood qualitatively by taking the considerable difference in conductivities between the reduced metallic phase and the solid electrolyte into account. Chemical and ESCA analysis showed that this phase consists of La and Ba. It was also found that the Ba/La ratio in the dendrites corresponded to that in the electrolyte.

Thus the electrochemical decomposition of the LaF_3 solid electrolyte leads to the creation of a metallic phase of lanthanum in the form of dendrites [Fig. 1(b)] at the negative electrode via the following process:

$$LaF_3 + 3e^- \longrightarrow La + 3F^-$$

This process occurs independent of the choice of negative electrode material.

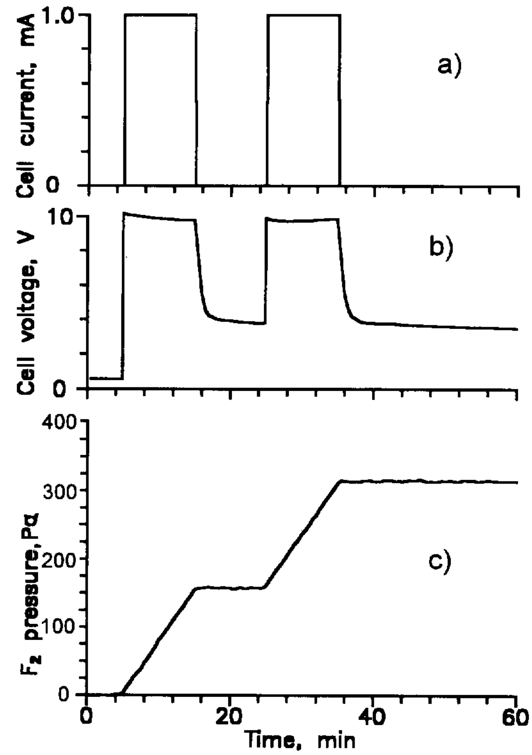

Fig. 2. Evolution of F_2 (c) in the closed chamber and the cell voltage (b) on passing a direct current (a) through the solid cell (electrolyte area, 3 cm^2; electrode material, graphite; temp., 20 °C).

The evolution of elemental fluorine is caused by processes occurring at the positive electrode to which the F^- ions diffuse under the influence of the electric field. The main processes are suggested to be the following.

1. Recombination of a fluorine ion and a hole:

$$F^- + h^+ \longrightarrow F^0$$

2. Recombination of fluorine atoms causing the evolution of elemental fluorine:

$$2F^0 \longrightarrow F_2$$

3. Fluorination of the material of the positive electrode:

$$Me + nF \longrightarrow MeF_n \qquad (1)$$

It should be noted that if the electrolyte contains components possessing fluorides which are not in their highest oxidation state, atomic fluorine can further oxidise them at the interface with the positive electrode. This can give rise to passivation of the electrochemical cell and result in an increase in its internal resistance. Under these conditions gas evolution may not occur at all. Such effects were found when electrolyte layers based on PbF_2, SnF_2 and BiF_3 were used in the cells. Hence the experiments were mainly conducted using the $LaF_3(BaF_2)$ electrolyte.

The possibility of reaction (1) occurring depends on the choice of material for the positive electrode. It is traditional [1] to use graphite or nickel in fluorine electrolysers. Nickel has no volatile fluorides which could contaminate the evolving elemental fluorine, and its use is preferable. However, we did not obtain measurement reproducibility using positive Ni electrodes, probably because of the formation of nickel fluorides on the metal surface. These fluorides have a high resistance and cause an increase in voltage across the electrodes of the solid electrolyser by up to 20 to 50 V.

In our experiments, a positive graphite electrode gave the lowest voltage and a high reproducibility of results (Figs. 2 and 3) over a wide range of current densities from 5 to 1000 $\mu A\ cm^{-2}$. The results show a linear dependence of the rate of gas evolution on the current (Fig. 3). This dependence can be described by the following equation:

$$dP/dt = (I/nF) \times (RT/V)$$

where dP/dt = the rate of increase in pressure, I = current through the electrolyser, F = Faraday's constant, R = gas constant, T = absolute temperature, V = volume of the measuring chamber and n = number of fluorine atoms per gas molecule. The value of n determines the chemical composition of the gas released from the electrolyser. The value obtained in our experiment over a range of currents from 0.1 to 3 mA was equal to 1.9 ± 0.15, corresponding to the formula for elemental F_2. This conclusion was corroborated by traditional chemical reaction of the evolved gas with KI and mercury.

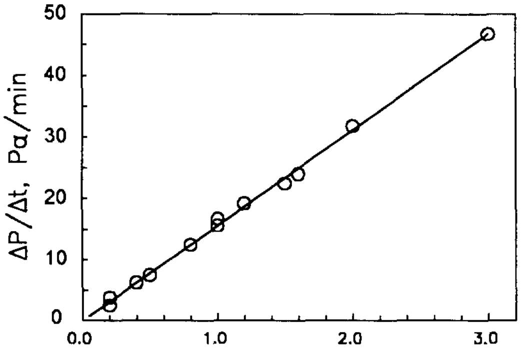

Fig. 3. The rate of fluorine evolution versus the electric current through the cell (electrolyte area, 3 cm^2; electrode material, graphite).

To obtain more information about the content of the gas evolved from the electrolyser, the solid electrochemical cell was mounted in the vacuum chamber of a mass spectrometer. Typical mass spectra obtained for the melted sample of the solid electrolyte at room temperature are shown in Fig. 4. The mass spectrometer had a high constant background [Fig. 4(a)]. Nevertheless, as a result of the passage of the current, new peaks can be seen quite well [Fig. 4(b)]. These peaks correspond to masses of 19, 20 and 38 a.u. and were identified as F, HF and F_2.

Both the HF peak and some growth of the 44 a.u. peak corresponding to CO_2 were apparently caused by chemical interaction of the fluorine with traces of H_2O and oil on the walls of and within the vacuum chamber. Although our construction did not allow heat application, it might to be possible to decrease these effects by preheating the vacuum chamber with the sample.

It was also found that the spectra contained no components of 88 a.u. This value corresponds to the CF_4 molecule which

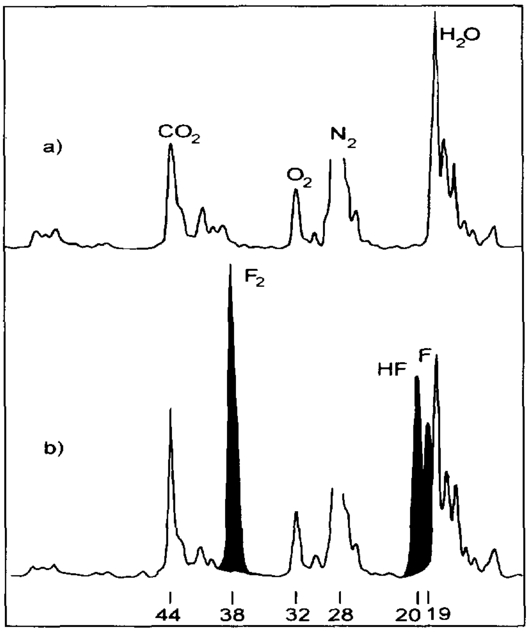

Fig. 4. Mass spectra of (a) the residual gas in the vacuum chamber (current through cell I=0 mA) and (b) the gas evolved from a polycrystalline electrolyte cell. The filled peaks result from a cell current I = 0.6 mA (electrolyte area, 1.2 cm^2; electrode material, graphite; temp. 20 °C).

is the most likely volatile product of the interaction of atomic fluorine and the graphite electrodes. Thus the use of graphite as the positive electrode material makes no contribution to the contamination of the fluorine evolved.

The current density in the solid cell can be varied from a few microamperes per square centimeter to 1 mA cm^{-2}. The lower limit is defined by the sensitivity of the pressure transducer, whereas the upper one is defined by the operating range of the current controller. The productivity of the solid fluorine source can be varied from 10^{-8} to 10^{-3} mol h^{-1} corresponding to an operating current range from 1 μA to 50 mA. The lower productivity limit was achieved with one electrolyser tablet, while the upper limit was observed with an electrolyser containing from 15 to 20 tablets operating at 1 mA cm^{-2}. To achieve precise control of the F_2 flow, it is important to remember that elemental fluorine can react chemically with metal dendrites at the negative electrode. A vacuum-tight deposition of the negative electrode layer and vacuum-tight tablets of solid electrolyte must be used to prevent this reaction.

A solid electrolyser cell of 20 mm in diameter and ~ 1 mm thickness (~ 1.5 g of LaF_3) contains about 0.01 mol of bound F_2. However, the electrochemical process at room temperature yields only from 0.2% to 0.6% of this amount at current densities from 1 mA cm^{-2} to 100 μA cm^{-2}, respectively. Passing a current through the cell results in a deviation from the proportionality between the current and the rate of gas evolution, and in the appearance of random, noisy voltage drops across the cell electrodes. This fact is explained by dendrite growth through the solid electrolyte thereby short-circuiting the electrodes. The problem of increasing the electrolyser yield may be solved in two ways. The first is as follows. At elevated temperature the ionic conductivity of the solid electrolyte increases rapidly ($\sigma \sim 10^{-2}\ \Omega^{-1}\ cm^{-1}$ at 200 °C), the dendrite conductivity decreases slightly and dendrite growth is moderated. At 200 °C the yield is equal to 5% at a current density up to 10 mA cm^{-2}. The second way may be concerned with the production of an additional protecting layer in the cell, which would prevent electrode shorting by dendrites. It seems to be probable that in this case the electrochemical process would release up to 50%–90% of bound F_2. This corresponds to an absolute specific yield of the electrolyser described of several tens of litres of F_2 per kilogram. The realisation of such an approach is in progress.

4. Conclusions

1. A new type of source of pure elemental fluorine on the basis of solid F^- conducting electrolytes is described. The evolution of elemental fluorine arises as a result of the electrochemical decomposition of a solid electrolyte which contains metal–fluorine compounds, and does not contain HF or other volatile fluorides. This approach has potential for producing pure F_2 without additions connected with the source itself.
2. The solid source of fluorine can have a productivity from 10^{-8} to 10^{-3} mol h^{-1} over the current range from 1 μA to 50 mA. The lower limit of the productivity is achieved with one tablet of electrolyser while the upper limit can be reached with an electrolyser containing from 15 to 20 tablets operated at 1 mA cm^{-2} (20 °C).
3. Fluorine emission can be varied over a wide range by varying the current through the cell.
4. The solid electrolyser has a current efficiency close to 100%. The power efficiency of the electrolyser depends upon the working regime. At current densities up to 1 mA cm^{-2} the electrolyser potential does not exceed 10–13 V. Assuming the equilibrium potential for the decomposition of LaF_3 is 5.811 V [7], one can obtain a power efficiency for the solid electrolyser of about 50%.
5. Because of dendrite growth, the F_2 yield at room temperature is as low as 0.2%–0.6% of bound F_2 at current densities from 1 mA cm^{-2} to 100 μA cm^{-2}, respectively. There are two ways to increase the electrolyser yield. The first is to raise the temperatures to that the ionic conductivity of the solid electrolyte increases and dendrite growth is moderated. At 200 °C the yield is 5% at current densities up to 10 mA cm^{-2}. The second method may be concerned with the production of an additional protecting layer in the cell which would prevent electrode shorting by dendrites. It would be expected that in this case the absolute specific yield of the electrolysers described could reach several tens of litres of F_2 per kilogram.

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