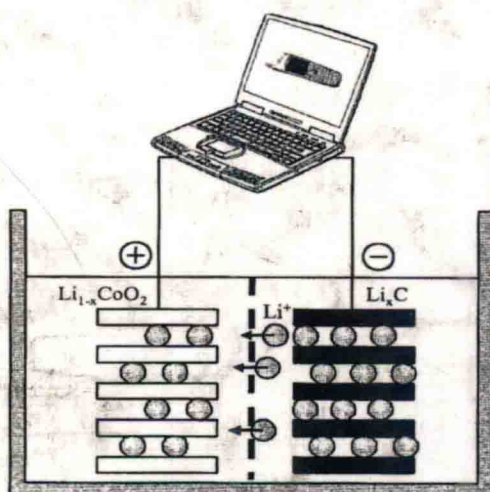




Fluorinated Materials for Energy Conversion

Tsuyoshi Nakajima & Henri Groult



Fluorinated Materials for Energy Conversion

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Fluorinated Materials for Energy Conversion

Preface

Since the discovery of fluorine by Henri Moissan at the end of the 19th century, fluorine chemistry has developed many applications in energy conversion, medicine, biology, agriculture, telecommunication and so on. However, fluorine chemistry is not widely spread probably because of the difficulty in the fluorination techniques and handling of fluorinating reagents and fluorides. Elemental fluorine is a typical fluorinating gas with high reactivity arising from its small dissociation energy. Efficient production of elemental fluorine by molten salt electrolysis is still one of the important research subjects in fluorine chemistry notably because of industrial applications in nuclear energy field. A new and promising aspect in fluorine chemistry is the applications of fluorination reactions and various fluorides to energy conversion materials for lithium batteries, fuel cells, solar cells etc. Many examples regarding the introduction of fluorine into lithium battery materials, that is, fluorination of carbonaceous anodes and oxide cathodes, synthesis of new fluorine containing electrolytes, fluorination of organic solvents and so on, were recently reported and revealed the importance of fluorine chemistry in this field. It was also shown that the fluorinated materials had important roles in fuel cells and solar cells. This summarizes the recent advances on these topics. All authors are specialists actively working in fluorine chemistry, electrochemistry, polymer chemistry and solid state chemistry. We hope that the book offers new aspects of fluorine chemistry to readers in the various fields.

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Chapter 1

Experimental and theoretical aspects of the fluorine evolution reaction on carbon anodes in molten KF–2HF

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1. PROPERTIES AND INDUSTRIAL USES OF FLUORINE GAS

Fluorine gas is a yellowish, poisonous and highly corrosive gas which reacts with practically all organic and inorganic substances [1–6]; it reacts with all elements except helium, neon and argon to form ionic or covalent fluorides. Until World War II, there was no commercial production of elemental fluorine. However, due to the development of the atomic bomb and nuclear energy applications, the production of large amounts of elemental fluorine became necessary. Now, F_2 gas can be considered as a necessary intermediate in uranium isotopic enrichment: separation of the isotopes of natural uranium is carried out by a diffusion process involving gaseous UF_6 . Uranium tetrafluoride (UF_4) is first produced by the reduction of the oxide H_2 or NH_3 and fluorination by HF at 400–600°C according to



UF_6 is then prepared by the reaction of fluorine gas and UF_4 at a high temperature ($> 1000^\circ\text{C}$) according to



Uranium enrichment performed by gaseous diffusion or ultracentrifugation consists of increasing the content of natural uranium's in isotope 235 to levels up to 3–5%. About 90% of the nuclear reactors currently in operation use this type of enriched uranium.

In the coming decades, energy consumption is expected to rise significantly, due to dramatic increases in world population, coupled with the industrialisation of developing countries, notably in Asia and Latin America. Since the beginning of the 20th century, the emission of greenhouse gases has risen drastically because of the use of fossil fuels in industry and transportation. This emission is expected to increase considerably in the near future. Thus, to respect the climatic and environmental equilibrium, intense research programmes are being devoted to the development of renewable energies (solar, wind, etc.); however, the latter have, at the present time, a limited potential. Therefore, nuclear power, which could be considered as an environmentally safe form of energy since it does not produce harmful gases contributing to the greenhouse effect, should play an important role in the production not only of electricity, but also of other energy sources (hydrogen, etc.). For example, it generates 110 times less CO_2 than natural gas and close to 240 times less CO_2 than coal for electricity production. In the European Union, nuclear energy accounts for 35% of electricity production, thereby avoiding the emission of 300 million tonnes of CO_2 . In 2001, the installed capacity of all types of nuclear power plants in the world amounted to 358,000 MW, about a quarter in the United States (over 100,000 MW) and about 17% in France (almost 60,000 MW). Thirty-two reactors are under construction worldwide: 22 in Asia and 10 in central and eastern Europe.

Fluorine gas is not only devoted to the synthesis of UF_6 , but is also widely used for the preparation of various fluorinated compounds involved in different industrial processes: WF_6 for depositing tungsten on insulating or conducting substrates by CVD, NF_3 for etching semiconductors, graphite fluorides (CF_x , $0.5 \leq x \leq 1.24$) for use as cathodes in primary lithium batteries and as lubricating agents, SF_6 as insulating gas in electric devices, ClF_3 to clean semiconductor fabrication vessels in the computer chip industry, CoF_3 as solid fluorine carriers and $\text{F}_2\text{-N}_2$ mixture to strengthen the surface properties of plastics (impermeability, chemical resistance, barrier effect, etc.) or to control the fluorination of molecules in organic chemistry.

Therefore, it seems to be of prime importance to study in detail the fluorine evolution reaction (FER) in order to optimise the process and to satisfy the increasing industrial requirement for this gas.

The purpose of this review paper is to provide a brief overview of both experimental and theoretical aspects of the FER on carbon anode in KF-2HF . The process has been analysed of by correlating results deduced from electrochemical tests in KF-2HF , *ex situ* surface characterisations, notably by AFM and STM, and numerical calculations. Owing to molecular dynamics simulations of molten KF-2HF , the constituents of KF-nHF melt have been identified, depending on the temperature and the HF content in KF-nHF . The origin of the strong adhesion of fluorine bubbles on the surface is also discussed. Finally, the particular shape of fluorine bubbles generated on horizontal carbon anodes in KF-2HF

is studied from a theoretical point of view taking into account capillary forces between the electrode surface and the gas–liquid interface.

2. ANALYSIS OF THE PREPARATION PROCESS

2.1. Generalities

In 1886, the French scientist Henri Moissan prepared, for the first time, fluorine by electrolysis of anhydrous hydrogen fluoride containing a small amount of potassium fluoride in an electrochemical cell with platinum–iridium electrodes. KF was used to render HF conducting. The description of industrial cells is widely reported in the literature [1,2,7]; briefly, the cells operate at 6 kA and contain molten KF–2HF (40.8 wt% HF) with about 24 plate carbon anodes and steel or iron cathodes. Carbon anodes are used to avoid dissolution occurring with most metals in parallel with the evolution of fluorine; in addition, graphite must be avoided since exfoliation takes place due to co-intercalation of ionic species and fluorine gas between the lamellar graphene sheets. Monel skirts are also required to separate the hydrogen and fluorine gases formed at the cathode and the anode, respectively, and to avoid their explosive recombination. The global reaction involves HF decomposition:



The two corresponding half-cell reactions are supposed to involve the HF_2^- electrochemical species:



at the anode, and



at the cathode.

First, molecular dynamic simulation of KF–*n*HF was investigated depending on the HF ratio and the temperature of the melt.

2.2. Molecular dynamics model for KF–*n*HF electrolytes

Within the framework of improvement of fluorine generation process, the model developed for KF–*n*HF electrolytes was intended to provide not only structural properties of the liquid (e.g. thermodynamical data, speciation, etc.) but also dynamical properties, especially transport coefficients such as self-diffusion coefficients, electrical conductivity and viscosity. This would make it possible, in principle, to address most of the previously cited problems on the microscopic scale.

Among the available simulation techniques, *ab initio* molecular dynamics (AIMD) was the only one previously used to study KF–2HF [8]. While it is accurate, it needs very few hypotheses, and is computationally extremely intensive, making it unsuitable for the long simulations needed for transport properties computation. Lighter techniques such as Monte-Carlo simulations or integral equations based methods were also rejected because they were unable to predict transport properties. The only theoretical method left to investigate KF–HF electrolytes was therefore *classical* molecular dynamics (MD) [9]. This statistical mechanics-based simulation method is fast and provides all the desired results as soon as the model used therein is adequately defined. Transport properties have been examined with the herein presented iono-molecular model [10], but we will focus only on the structural features of the liquid.

Molecular dynamics requires the description of the interaction forces between the liquid constituents. In pure molecular liquids, for example HF, this means defining the forces applied to each molecule by their surrounding molecular neighbours. In high-temperature molten salts, such as KF, this means defining the forces acting on each fluorine and potassium ion. But in KF–2HF, the microscopic nature of the constituents is still unknown: in electrochemistry, HF_2^- is often postulated, but there are no hints on how much HF are turned in that ionic form, how much in “neutral” HF. Oligomers are known to form in pure HF [11]. Polyfluorides, both centred $\text{F}(\text{HF})_n^-$ and chained $\text{H}_n\text{F}_{n+1}^-$, have also been revealed in several condensed phases [12–15]. In fact, the question is whether KF–2HF is a molecular liquid or an ionic liquid. Is KF–2HF closer to pure HF or to molten KF? The point of view adopted is crucial for acidity definition. Up to now, the only attempt was based on Brönsted acidity [16], but why not try with Lewis fluoroacidity pF? This only depends on the nature of the species on the microscopic scale, which is in general known from direct observation.

The paucity of available physical-chemistry data was an important obstacle to the definition of the model: to our knowledge, there are still no data on infrared, Raman spectroscopies, neutron scattering, and NMR spectroscopy (numerous corresponding data exist for the *solid*, but were not available for the *liquid* case). Therefore, the nature of the components was unknown, and *a fortiori* the forces acting between them.

The only direct information about the liquid structure was given by AIMD [8], showing essentially centred polyfluorides and transitionally chained ones. We therefore decided to build an iono-molecular model to retrieve these $\text{F}(\text{HF})_n^-$, and their proportions, as a function of n .

We denoted our model as iono-molecular since it describes, on the one hand HF molecules and K^+ and F^- ions on the other. For alkali halides, the models developed by Fumi and Tosi [17] are indeed well tested and used to describe accurately the solid phases, pure molten salts, their mixtures and even aqueous solutions of the salts. For KF, we used the interactions given in Table 1.

The centred polyfluorides essentially consist of a fluorine ion solvated by HF molecules. In these $F(HF)_n^-$ complexes, the fluoride-hydrogen distance d_{HF^-} ranges from 1.35 to 1.7 Å depending on n , and is very similar to an ordinary H-bond. For pure HF, several models have been developed. Only one of them explicitly describes the H-bond between HF molecules (H-bond is implicit in the others and results from Coulomb or dipole interactions): the HF3 model derived by Klein and McDonald [18] (see Table 2). We therefore decided to use this model for our HF molecules, and to apply the H-bonding Morse potential (V_{HF}) between HF molecules and fluoride. In addition to the attractive coulombic interaction between positively charged H and fluoride anions, this was intended to yield the right d_{HF^-} shorter than the H-bond in pure HF (1.8 Å).

The system was simulated at different temperatures ranging from 330 to 410 K (56.85 to 136.85°C). The initial simulation cell consisted of 384 atoms (64 times KF-2HF units) randomly arranged to get a density extrapolated, for each simulation temperature, from experimental data [19]. The coulombic forces were computed with an ordinary Ewald algorithm, the HF molecules were handled

Table 1
Interaction potential for K^+ and F^- ions

Parameter	++	+-	--
c_{ij}	1.25	1.00	0.75
σ_{ij} (Å)	2.926	2.642	2.358
C_{ij} (10^{-79} Jm ⁶)	24.3	19.5	18.6
D_{ij} (10^{-99} Jm ⁸)	24.0	21.0	22.0

Note: Analytical form is $V_{ij} = Z_i Z_j e^2 / r - bc_{ij} \exp[B(\sigma_{ij} - r)] - C_{ij} r^{-6} - D_{ij} r^{-8}$ with $b = 3.38 \times 10^{-19}$ J and $B = 2.96 \times 10^{-6}$ m⁻¹.

Table 2
Interaction potential for HF molecules

Pair	Potential
H-F	$2(\exp(-10.6(r-1.6)) - \exp(-5.6(r-1.6)))$
H-H	$600\exp(-3.34r)$
F-F	$2 \times 10^5 \exp(-4.25r) - V^{DISP}$

Note: Distances are in Å and energies in kcal mol⁻¹ with $V^{DISP} = f(r)(220v^6 + 400v^8 + 4500v^{10})$, where $f(r) = \exp(-(4.7/r-1)^2)$ if $r \leq 4.7$ and $f(r) = 1$ if $r > 4.7$.