6. "Kirk-Othmer Encyclopedia of Chemical Technology," Vol. 9, p. 881, John Wiley & Sons, Inc., New York (1980).
7. A. Broese van Groenov, P. E. Bongers, and A. L. Stuijts, *Mater. Sci. Eng.*, **3**, 317 (1968-1969).
8. S. Kawado, *Jpn. J. Appl. Phys.*, **9**, 24 (1970).
9. M. Uemura, T. Hyono, M. Umeno, and H. Kawabe, *J. Mater. Sci.*, **21**, 1341 (1986).
10. M. J. N. Pourbaix, "Atlas of Electrochemical Equilibria in Aqueous Solutions," Oxford University Press, New York (1966).
11. H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids," 2nd ed., pp. 11 and 89, Oxford University Press, New York (1959).
12. *ibid.*, p. 358.
13. "Handbook of Chemistry and Physics," 63rd ed., p. E-10, (CRC Press Inc., Boca Raton, FL (1982-1983).
14. L. T. Romankiw, M. H. Gelchinski, R. E. Acosta, and R. J. von Gutfeld in "Electroplating Engineering and Waste Recycle, New Developments and Trends," (PV 83-12) D. D. Snyder, U. Landau, and R. Sard, Editors, p. 66, The Electrochemical Society Softbound Proceedings Series, Pennington, NJ (1982).
15. D. J. Sanders, *Appl. Opt.*, **23**, 30 (1984).
16. G. Egbert, IBM Corporation, Rochester, MN, Private communication.
17. Y. Suzaki and A. Tachibana, *Appl. Opt.*, **14**, 2809 (1975).

Production of Fluorine by the Electrolysis of Calcium Fluoride-Containing Tetrafluoroborate Melts

Gleb Mamantov* and T. M. Laher

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996-1600

ABSTRACT

Tetrafluoroborate melts have been shown to be viable electrolytes for the electrochemical production of fluorine from dissolved CaF_2. The anode reaction at pyrolytic graphite electrodes apparently involves the oxidation of BF_4^- and/or F^- to yield BF_3 and F_2. LiF may be used to trap BF_3; the resulting $LiBF_4$ may be reused in the bath. Observed anode current efficiencies are generally on the order of 50-60% at an optimum anode current density of 40 mA/cm^2. The cathode reaction at tin and/or zinc cathodes involves the reduction of Ca^{2+} to the metal along with the reduction of alkali metal ions to the respective metals. The presence of zinc in the cathode pool appears to favor the deposition of calcium over that of alkali metals.

Fluorine is currently produced by the electrolysis of KF-HF (50/50 mole percent [m/o]) melts at temperatures of *ca.* 150°C (1). These materials are produced from naturally occurring minerals containing CaF_2, most notably fluorspar (CaF_2). It would be more desirable to produce fluorine directly from CaF_2. Due to the reactivity of fluorine, especially at elevated temperatures, it is necessary to carry out the electrolysis for the production of fluorine using relatively low liquidus temperature electrolytes in which CaF_2 is at least partially soluble. This requirement narrows the field of prospective electrolytes to relatively low melting alkali fluoride mixtures such as the LiF-NaF-KF eutectic and various melts containing tetrafluoroborate, all of which have liquidus temperatures below 500°C (2, 3). No reports could be found in the literature for the electrolytic production of fluorine from melts containing CaF_2. In the mid-1960s, Mastrangelo reported an electrolytic method for the production of fluorine from molten $NaBF_4$ (4). In this method, carbon or gold anodes were used to produce F_2 by the oxidation of BF_4^-, and Na^+ was reduced at a lead cathode pool to give a Na-Pb alloy which could be used in the production of tetraethyl lead. Some problems were encountered with the tetrafluoroborate melts, especially with melts containing $LiBF_4$, in that BF_3 is evolved during electrolysis and it is necessary to trap BF_3, preferentially by a method which recycles BF_3 back into the electrolyte (4). $LiBF_4$ is known to undergo spontaneous decomposition to LiF and BF_3 at 325°C (5). In this paper we discuss a method for the electrolytic production of fluorine from tetrafluoroborate melts containing CaF_2 at temperatures of 315°-375°C.

Experimental Section

Electrochemical cell.—The electrochemical cell (Fig. 1) consisted of a nickel cell body containing an alumina crucible (Coors AD 998, 36 mm id). The crucible which contained the electrolyte was separated from the cell body by means of a larger alumina crucible of slightly smaller diameter than the inside of the nickel cell body. The purpose of the second crucible was to protect the heated portion of the cell body from attack by hot fluorine gas. The top flange of the cell body was fitted with a center port equipped with a Swagelok fitting for introduction of the anode or an addition tube through which the cathode metal pool was added, and with four ports equipped with Cajon ultra-torr fittings for introduction of the gas en-

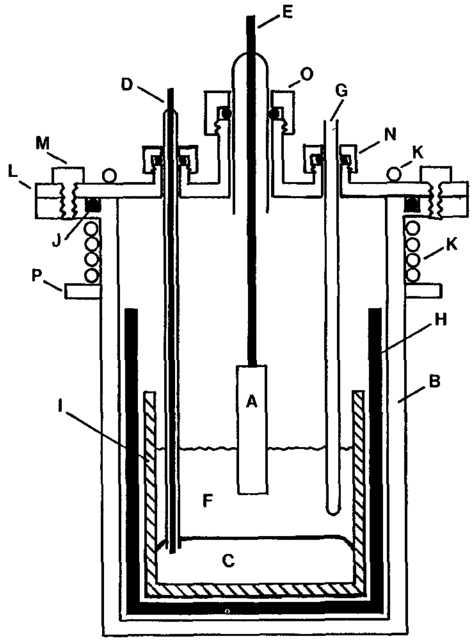

Fig. 1. Electrochemical cell used for electrolysis of tetrafluoroborate melts containing CaF_2. The parts of the cell are listed: (A) anode substrate, (B) Ni cell body, (C) cathode metal pool, (D) Ni cathode contact lead, (E) Ni anode contact lead, (F) tetrafluoroborate melt, (G) thermocouple well (alumina tube), (H) alumina insert, (I) alumina crucible containing melt, (J) Viton O-ring, (K) cooling coils, (L) Ni top flange, (M) bolt, (N) Cajon fitting, (O) specially adapted Swagelok fitting, and (P) Ni support ring. Dimensions are not to scale.

---

* Electrochemical Society Active Member.

trance/exit lines, the cathode lead contact, and a thermocouple well. Both the upper portion of the cell body and the top flange were water-cooled in order to enable sealing of the cell via a Viton O-ring. The electrochemical cell was assembled inside a dry box to maintain an inert atmosphere within the cell.

Anode and cathode preparation.—The anode material used was primarily pyrolytic graphite (Union Carbide), with one exception when glassy carbon (Tokai) was used. Pyrolytic graphite plate was machined into rectangular pieces and baked out under vacuum at 500°C (the degassed material was found to be less subject to cracking while immersed in the melt than the raw material). After degassing, the pyrolytic graphite piece was connected to a nickel contact rod, which was electrically isolated from the cell body by means of an alumina sleeve.

Tin, zinc, and a Sn-Zn (80-20 m/o) alloy were used as materials for the cathode metal pool. Tin and zinc were purified by washing each successively with 1*M* HCl, distilled water, and ethanol and then dried under vacuum. Each metal was melted in an alumina crucible under a blanket of argon, refrozen and cut into the desired size pieces for introduction into the electrochemical cell. Sn-Zn (80-20 m/o) alloy was prepared by melting the corresponding amounts of purified zinc and tin together in a ceramic crucible, recooling, and then cutting the alloy into the desired shape. Electrical contact with the cathode metal pool was achieved using a nickel contact rod sheathed with an alumina sleeve to prevent electrical contact with the cell body; only the lower 5 mm of the rod was exposed to permit contact with the cathode metal pool only. Analyses of the used cathodes after electrolysis of the melts were performed using atomic absorption by IT Analytical Services, Knoxville, Tennessee.

Chemicals.—Anhydrous KF (Aldrich, 99%), NaF (Aldrich, 99%), LiF (Alfa Products, 99%), $NaBF_4$ (Alfa Products, 99%), and $LiBF_4$ (Aldrich, 98%) were prepurified by heating under vacuum at 200°C for three days to remove as much water and HF as possible before introduction into the cell. CaF_2 (Cerac, 99.99% anhydrous) was used without further purification.

Cell operating procedures.—A diagram of the entire system used for the electrolytic production of fluorine is shown in Fig. 2. The cell was placed within a Lindberg Model 56622 furnace equipped with a Lindberg Model 59344 temperature controller and was heated under an argon stream until the electrolyte was molten. At this point, an alumina bubbler tube was inserted into the cell below the level of the melt, and a mixture F_2/He (5/95 volume percent [v/o]) was bubbled through the system. This process was done to remove remaining melt impurities and to ensure passivation of the cell parts (with the exception of the anode and the cathode) at the operating temperature of the cell during electrolysis. During this process the exit gases were vented through an activated alumina trap to remove excess F_2. Afterward the cell was flushed with argon for 4h to remove residual F_2 (checked with a KI solution). At this point the bubbler tube was replaced with an alumina tube through which the cathode material was added to the cell under fast argon purge. Once the cathode material was molten, the anode and the cathode leads were introduced into the cell. The gas stream was then switched to pass argon along with any effluent gases produced by the electrolysis of the melt, through a BF_3 trap (containing anhydrous CaF_2 or LiF) and then into a 3*M* KI solution trap (to detect any F_2 produced). The KI trap was protected from slow oxidation by air by means of a silicone oil bubbler trap. A PAR Model 173 potentiostat/galvanostat served as a constant current source. Cell voltages were measured with a Keithley Model 616 multimeter 30s after applying the current.

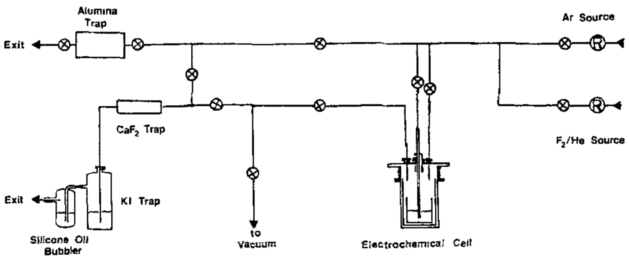

Fig. 2. The experimental setup for the electrolysis of tetrafluoroborate melts containing CaF_2. In the center port of the electrochemical cell is a 1/4 in. OD alumina tube immersed in the melt through which F_2/He is passed during the passivation step. All other lines are made of copper. ⊗ = regulating valve. ® = two stage regulator.

IR spectroscopic analysis of anode gases.—To obtain an IR spectrum of the product gases produced during electrolysis, the BF_3 and KI traps and the silicone oil bubbler were replaced by an IR cell. This cell was made from a Cajon ultratorr tee union fitting; it was equipped with silver chloride windows. Prior to electrolysis, the IR cell was evacuated and closed off to the rest of the system. Electrolysis was then conducted inside the electrochemical cell (filled with 1 atm of argon) with the IR cell inlet and outlet closed. Sampling of the gases inside the electrochemical cell after electrolysis was done by opening the IR cell to the electrochemical cell and obtaining a representative sample of the gases inside the electrochemical cell. IR spectra (background corrected) of the product gases were obtained using a Digilab Model FTS20 FTIR spectrometer.

Results and Discussion

Solubility of CaF_2 in tetrafluoroborate melts.—Before conducting electrochemical experiments using melts containing tetrafluoroborate, it was necessary to determine the approximate solubility of CaF_2 in the various tetrafluoroborate melts used. A series of solubility measurements was performed for CaF_2-saturated solutions of the following melts at the temperatures listed for each: $NaBF_4$-KF (90/10 m/o), 375°C; $LiBF_4$-LiF (90/10 m/o), 315°C; and $LiBF_4$-$NaBF_4$ (50-50 m/o), 340°C. In each case the melt was loaded into an alumina crucible which was placed into a quartz tube through which argon could be passed to maintain an inert atmosphere. The mixtures were brought to the desired temperature and left overnight to ensure complete saturation of the melts with CaF_2. The undissolved CaF_2 settled to the bottom permitting separation of the melt containing dissolved CaF_2 from the undissolved CaF_2. Each melt sample was analyzed for Ca^{2+} using standard EDTA titration methods. The solubility of CaF_2 in these melts containing tetrafluoroborate was found to be *ca.* 1-2 m/o, which is sufficient to permit electrolysis of CaF_2 in these melts.

Electrolysis of tetrafluoroborate melts containing CaF_2.—In an initial experiment 150g of a $NaBF_4$-KF-CaF_2 (89.1/9.9/1.0 m/o) melt was electrolyzed at 375°C between either a pyrolytic graphite or a glassy carbon anode (10 cm^2 area) and a Sn-Zn (80/20 m/o, 200g) cathode of approximately similar area at current densities (based on the geometric area of the anode) of 200, 80, 40, and 20 mA/cm^2. For the initial experiments conducted at anode current densities (ACDs) of 200 and 80 mA/cm^2, there was no BF_3 trap in the exit gas line. In all other experiments, a BF_3 trap was placed in the exit gas line. Upon initiation of the electrolysis, in each case the KI solution in the trap began to turn yellow and eventually reached a brownish-red color after the passage of 8000C of charge. This coloration of the KI solution indicates the reaction of an oxidizing material in the exit gases (most likely fluorine) with the KI solution to give iodine. Anode current efficiencies (ACEs), calculated for the production of fluorine by electrolysis based on the analysis for iodine in the KI solution by spectrophotometry (6) as a function of ACD for this melt system and for other melt systems studied, are listed in Table I. ACEs were also measured by monitoring the amount of F^- produced as a result of the reaction between F_2 and KI using a F^- ion selective electrode. The fact that both methods give ACEs within 1% of each other is further evidence that fluorine is produced as a result of the electrolysis of the melts studied. An IR spectrum of the anode gases had intense bands at 1504, 1452, 721, 693, and 480 cm^{-1} which may be assigned to the ν_2, ν_3, and ν_4 vibrational modes for BF_3 (7).

Table I. Anode current efficiency data for the electrolysis of tetrafluoroborate melts at carbon electrodes

Melt system	t (°C)	Anode type	Anode current density (mA/cm^2)	Anode current efficiency	Cell voltage (uncorrected) (V)
$NaBF_4$-KF-CaF_2 (89.1/9.9/1.0 m/o)	375	glassy carbon	200	12.2%	16.3
$NaBF_4$-KF-CaF_2 (89.1/9.9/1.0 m/o)	375	pyrolytic graphite	80	23.1%	8.6
$NaBF_4$-KF-CaF_2 (89.1/9.9/1.0 m/o)	375	pyrolytic graphite	40	29.5%	5.0
$NaBF_4$-KF-CaF_2 (89.1/9.9/1.0 m/o)	375	pyrolytic graphite	20	16.4%	2.8
$LiBF_4$-LiF (90-10 m/o sat'd with CaF_2)	315	pyrolytic graphite	70	37.3%	7.7
$LiBF_4$-LiF (90-10 m/o sat'd with CaF_2)	315	pyrolytic graphite	60	47.7%	7.2
$LiBF_4$-LiF (90/10 m/o sat'd with CaF_2)	315	pyrolytic graphite	50	67.2%	6.6
$LiBF_4$-LiF (90/10 m/o sat'd with CaF_2)	315	pyrolytic graphite	40	70.1%	5.8
$LiBF_4$-LiF (90/10 m/o sat'd with CaF_2)	315	pyrolytic graphite	30	29.9%	3.5
$LiBF_4$-$NaBF_4$ (50/50 m/o sat'd with CaF_2)	340	pyrolytic graphite	70	30.1%	7.7
$LiBF_4$-$NaBF_4$ (50/50 m/o sat'd with CaF_2)	340	pyrolytic graphite	60	39.9%	7.1
$LiBF_4$-$NaBF_4$ (50/50 m/o sat'd with CaF_2)	340	pyrolytic graphite	50	57.9%	6.7
$LiBF_4$-$NaBF_4$ (50/50 m/o sat'd with CaF_2)	340	pyrolytic graphite	40	53.4%	5.7
$LiBF_4$-$NaBF_4$ (50/50 m/o sat'd with CaF_2)	340	pyrolytic graphite	30	12.6%	3.6

The low-intensity bands that were observed at 1283 and 1361 cm^{-1} can be attributed to the C-F stretch in CF_4 and a C-C stretching mode, respectively, which indicates the presence of CF_4 and possibly higher order fluorocarbons in the anode gas (7). However, the relative intensities of these bands compared with those for the BF_3 bands indicate that the amount of any fluorocarbons is insignificant when compared with that of the major products. There are other weak bands at higher frequencies (between 1900 and 3050 cm^{-1}) which are difficult to assign; they may be due to CO_2 and COF_2 (7), but they may also be assigned to various combination modes for BF_3 (8). The above evidence concerning the nature of the anode products for the electrolysis of $NaBF_4$-KF-CaF_2 indicates that the anode process most likely involves the oxidation of BF_4^- and/or F^- to yield BF_3 and F_2.

In a parallel series of electrolysis experiments $LiBF_4$-LiF (90/10 m/o saturated with CaF_2, 315°C, Sn cathode) and $LiBF_4$-$NaBF_4$ (50/50 m/o saturated with CaF_2, 340°C, Sn-Zn [80/20 m/o] cathode) were electrolyzed at pyrolytic graphite anodes (10 cm^2 area) employing ACDs of 30, 40, 50, 60, and 70 mA/cm^2. The analysis of the anode gases in both cases indicated that F_2 and BF_3 were the major anode products as found in the case of the $NaBF_4$-KF-CaF_2 melt system. It should be noted (Table I) that for all three melt systems studied, the maximum ACE is attained at an ACD of 40-50 mA/cm^2. It can also be seen that the maximum ACE is lowest for $NaBF_4$-KF-CaF_2 (t = 375°C) and the highest for $LiBF_4$-LiF (saturated with CaF_2) (t = 315°C). A reasonable explanation for this observation is that at the higher temperature fluorine is more reactive and is lost from the effluent gases by reaction with various heated cell parts. Another reason for losses in ACE is the possibility of reaction of F_2 produced with the cathode products (*vide infra*). While the ACE is the highest in the case of the $LiBF_4$-LiF (saturated with CaF_2) system, $LiBF_4$ underwent a significant amount of thermal decomposition at 315°C such that the melt became rich in LiF and solidified after three days. The $LiBF_4$-$NaBF_4$ (saturated with CaF_2) system, however, appeared to be stable to thermal decomposition at 340°C for a period of at least 3 weeks (2). The ACE observed for this system (57.9 percent at an ACD of 50 mA/cm^2), although lower than that for $LiBF_4$-LiF (saturated with CaF_2), is still reasonably high. For all three systems an average cell voltage of *ca.* 3.5V (extrapolated to zero ACD) was observed.

Cathode product analysis.—In a study to determine the nature of the cathode reaction for the melt systems studied, 150g of $NaBF_4$-KF-CaF_2 (89.1/9.9/1.0 m/o, 375°C), $LiBF_4$-LiF (90/10 m/o saturated with CaF_2, 315°C), and $LiBF_3$-$NaBF_4$ (50/50 m/o saturated with CaF_2, 340°C) were electrolyzed between a pyrolytic graphite anode and a Sn-Zn (80-20 m/o, 200g) cathode at an ACD of 40 mA/cm^2. (It was necessary to use a Sn cathode in the case of $LiBF_4$-LiF due to melting point considerations.) After the passage of 12,000C of charge in each case, the melts were frozen and the cathode was separated from the bulk of the melt in the dry box. The solidified cathode was washed with distilled water to remove adhering melt and was analyzed for Li, Na, K, and Ca. Cathode current efficiencies (CCE's), based on the amount of each element found *vs.* the maximum amount possible for the amount of charge passed, are shown in Table II. In each case there is a considerable codeposition of Ca with the alkali metals, particularly Li. In the case of $NaBF_4$-KF-CaF_2 it was observed that potassium produced during electrolysis floated on the surface of the melt [possibly because potassium does not form compounds readily with either tin or zinc (9)]. This may in part explain why the ACE is so low for this system as F_2 produced during the electrolysis will react with potassium floating on the surface of the melt. It is interesting that phase diagram studies of the Ca-Zn, Li-Zn, and Na-Zn systems indicate that only Ca alloys appreciably with Zn, which was added to the cathode metal pool in hope of favoring only the deposition of Ca at the cathode (9, 10).

The effect of current density on the ratio of cathode products was studied by electrolyzing two $LiBF_4$-$NaBF_4$ (50/50 m/o saturated with CaF_2, 340°C) melts using Sn-Zn (80/20 m/o) cathodes at ACDs of 30 and 50 mA/cm^2. For the run made at 50 mA/cm^2, the ratio of Li, Ca, and Na CCEs (Table II) was found to be *ca.* 28:4:1; for the electrolysis at 30 mA/cm^2, this ratio was *ca.* 1:4:1. While the ratio of Ca to Na remains nearly constant, the change observed in the Ca to Li ratio indicates that Ca deposition is preferred over Li deposition at lower current densities. In order to examine the effect of adding zinc to the cathode substrate, a $NaBF_4$ melt saturated with CaF_2 was electrolyzed at 425°C at an ACD of 40 mA/cm^2 using a zinc pool cathode. The analysis of the cathode gave a Ca-to-Na ratio of 40:1, indicating that at least at a pure zinc cathode the deposition of calcium is preferred over that of sodium (and perhaps also lithium) as previously thought (9, 10). However, the ACE was found to be only *ca.* 8% at this ACD.

Trapping of BF_3.—For the electrolysis of tetrafluoroborate melts for the production of fluorine to be industrially significant, the problems encountered with coproduction of BF_3 need to be eliminated or at least minimized. Mastrangelo (4) used dry NaF heated to 400°-500°C to collect BF_3 produced during the electrolysis of $NaBF_4$. In the present case it was more desirable to recycle BF_3 in the

Table II. Cathode current efficiency data for the electrolysis of tetrafluoroborate melts

Melt system	t (°C)	Cathode type	Anode current density (mA/cm^2)	Cathode current efficiency (%)			
				Li	Na	Ca	Total
NaBF$_4$-KF-CaF$_2$ (89.1/9.9/1.0 m/o)	375	Sn-Zn (80/20 m/o)	40	—	3.7 (some K is produced)	16.4	20.1
LiBF$_4$-LiF (90/10 m/o sat'd with CaF$_2$)	315	Sn	40	43.6	—	24.1	67.7
LiBF$_4$-NaBF$_4$ (50/50 m/o sat'd with CaF$_2$)	340	Sn-Zn (80/20 m/o)	50	48.7	1.6	7.0	57.3
LiBF$_4$-NaBF$_4$ (50/50 m/o sat'd with CaF$_2$)	340	Sn-Zn (80/20 m/o)	40	30.0	4.1	18.8	52.9
LiBF$_4$-NaBF$_4$ (50/50 m/o sat'd with CaF$_2$)	340	Sn-Zn (80/20 m/o)	30	2.0	2.0	8.4	12.4
NaBF$_4$ sat'd with CaF$_2$	425	Zn	40	—	0.2	7.9	8.1

form of Ca(BF$_4$)$_2$ or LiBF$_4$ using CaF$_2$ or LiF, respectively (primarily due to cost factors). In two parallel experiments, LiBF$_4$-NaBF$_4$ (50/50 m/o saturated with CaF$_2$, 340°C) melts were electrolyzed at an ACD of 40 mA/cm^2, and a trap (15 × 2 cm id tube equipped with coarse Ni frits at both ends) in each case containing 0.25M of either dry CaF$_2$ or LiF (both 200 mesh and somewhat loosely packed), respectively, heated to 250°C was placed in the gas stream before the KI solution trap to collect the BF$_3$ produced during electrolysis. The trap was considered to have maximum conversion of the fluoride to its corresponding tetrafluoroborate before the first sign of fog formation above the KI solution is observed (this fog formation occurs immediately upon initiating the electrolysis in the absence of any BF$_3$ trap). Based on the ACE previously determined and the stoichiometry for the conversion of each fluoride to its corresponding tetrafluoroborate, the BF$_3$ trapping efficiencies for CaF$_2$ and LiF were found to be *ca.* 33% and 70%, respectively. These results are supported by the x-ray powder diffraction patterns observed for the two trapping agents after electrolysis. For the CaF$_2$ trap, strong lines indicative of CaF$_2$ were found in the x-ray diffraction pattern along with some very weak lines of an unknown substance (possibly due to Ca(BF$_4$)$_2$, since no report in the literature could be found for the x-ray diffraction pattern for this substance). On the other hand, the x-ray powder diffraction analysis of the LiF trap revealed strong lines due to LiBF$_4$ and somewhat weaker lines for LiF. Thus, it appears that LiF is the better trapping agent for BF$_3$.

Conclusions

Tetrafluoroborate melts appear to be viable electrolytes for the electrolytic production of F$_2$ from CaF$_2$ using carbon anodes. The anode reaction appears to involve the oxidation of BF$_4^-$ and/or F$^-$ to BF$_3$ and F$_2$. With the present cell design, the average anode current efficiency is on the order of 50%. The fact that there is little formation of fluorocarbons indicates that the loss in anode current efficiency is most probably due to reaction of F$_2$ with the cathode and/or cathode products (which is reflected in the observation that the total ACE and CCE are roughly the same) or reaction of hot F$_2$ with the various cell components. For the cathode reaction, the reduction process of Ca^{2+} to the metal is accompanied by the reduction of alkali metal ions present in the melt, particularly Na$^+$ and Li$^+$. Some of the problems encountered with codeposition of Ca with the alkali metals (especially Li) can be solved by using lower current densities, but only at a sacrifice in the anode current efficiency. Also, it appears that the presence of Zn in the cathode may help favor the deposition of Ca over that of the alkali metals. In fact, phase diagram studies indicate that the cathode substrate should have the highest Zn content possible for a given operating temperature (10). The overall electrolysis was found to proceed with higher current efficiency at lower temperature. An optimum anode current density of *ca.* 40 mA/cm^2 should be employed.

There are some problems encountered with this method for producing fluorine. The major problem appears to be that the oxidation of BF$_4^-$ to yield F$_2$ also involves the production of BF$_3$, which must be separated from the F$_2$ in the gas stream and returned to the melt if the process is to be cost effective. In this regard, LiF seems to be a good material for trapping BF$_3$ since the LiBF$_4$ produced can be recycled back into the electrolyte. There still remains the problem of codeposition of Ca with various alkali metals at the cathode, but there is enough difference in the boiling points (and hence vapor pressures) of the various metals in the cathode that it may be possible to distill the various metals and thus be able to recycle the cathode substrate materials. In addition, some thought should be given to improving the cell design (perhaps using a separator between the anode and cathode) in order to improve the anode current efficiency.

Acknowledgments

The authors wish to acknowledge support from the E. I. du Pont de Nemours Company and useful discussions with Dr. Ernst Tomic, du Pont.

Manuscript submitted Feb. 1, 1988; revised manuscript received June 23, 1988.

The University of Tennessee assisted in meeting the publication costs of this article.

REFERENCES

1. R. E. Banks, D. W. A. Sharp, and J. C. Tatlow, in "Fluorine—The First Hundred Years (1886-1986)," Elsevier Publishing Company, New York (1986).
2. H. Ohno and K. Furukawa, *J. Nucl. Mat.*, **64,** 37 (1977).
3. C. J. Barton, L. O. Gilpatrick, J. A. Bornmann, H. H. Stone, T. N. McVay and H. Insley, *J. Inorg. Nucl. Chem.*, **33,** 337 (1971).
4. S. V. R. Mastrangelo, U.S. Pat. 3,196,090 (1965).
5. Alfa Products, Thiokol/Ventron Division, Product Safety Data Sheet no. 44150, "Lithium Tetrafluoroborate—Safety and Handling Procedures" (January, 1981).
6. L. Meites, "Handbook of Analytical Chemistry," and references therein, pp. 6-36, McGraw-Hill, Inc., New York (1963).
7. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed., pp. 77-148, Wiley Interscience, New York (1970).
8. J. Vanderryn, *J. Chem. Phys.*, **30,** 331 (1959).
9. E. E. Stansbury, Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN, Private communication.
10. "Metals Handbook," Vol. 8, 8th ed., American Society for Metals, Metals Park, OH (1973).