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# **Preparation and Purification of Flinak**

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PREPARATION AND PURIFICATION OF FLINAK

By  
G. L. Green  
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R. A. Sutula

23 FEBRUARY 1973

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NAVAL ORDNANCE LABORATORY, WHITE OAK, SILVER SPRING, MARYLAND

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**PREPARATION AND PURIFICATION OF FLINAK**

This report describes the apparatus and techniques used in the preparation and purification of the fluoride salt eutectic of LiF, NaF, and KF (Flinak). This eutectic has been proposed for use as the electrolyte in high-energy-density thermal batteries.

This work was conducted in the Electrochemistry Division, Chemistry Research Department, under Task No. MAT 03L-000/ZR00-001-010, Prob 175, Fused Salt Electrochemistry.

The identification of commercial materials or apparatus implies no criticism or endorsement by the Naval Ordnance Laboratory.

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## INTRODUCTION

A high-energy-density thermal battery system has been proposed employing a high oxidation state transition metal as the cathode and the eutectic of lithium fluoride-sodium fluoride-potassium fluoride (LiF-NaF-KF, referred to as Flinak) as the electrolyte (Reference 1). The substitution of Flinak for the commonly employed thermal battery electrolyte, LiCl-KCl, is based on the higher potential span of the Flinak. This higher potential span eliminates the problem of oxidation of the electrolyte by the high oxidation state cathode materials which had been encountered when molten LiCl-KCl was used as the electrolyte. However, Flinak suffers from the disadvantage that it is difficult to prepare in a highly purified form. Water and its hydrolysis products ( $\text{OH}^-$ ,  $\text{O}^{2-}$ ) constitute the impurities of greatest concern since such wet melts are highly corrosive due to the formation of HF. In thermal battery applications, these impurities are oxidized by reaction with the high oxidation state cathode materials (such as potassium hexafluorocuprate), thereby reducing the coulombic efficiency of the cathode.

The objective of this investigation was to determine a method of preparing pure, dry melts of Flinak. This report describes the development of a purification technique and then compares the impurity level obtained using this method to that obtained by other techniques currently in use.

## PREPARATION AND ANALYSIS OF FLINAK

## Materials

Fisher Reagent Grade LiF, J. T. Baker Reagent Grade NaF, and Baker and Adamson Reagent Grade anhydrous KF were used to prepare the Flinak. Since the KF is extremely hygroscopic, this fluoride salt was carefully ground, screened through a 60 mesh sieve and stored in a dry box to prevent lumping. The liquid bromine pentafluoride (Technical Grade -- 98.0%) was obtained from Air Products and Chemicals, Inc. Fluorine (98.0%) gas was obtained from Matheson Gas Products. Prior to use the fluorine was passed through a NaF trap to remove HF. The high purity vitreous carbon crucibles were obtained from the Carbone Corporation. A Teflon vessel and cap, machined in cylindrical form, were used as the collection-reaction vessel. Karl Fischer reagent and standard water in methanol solutions were obtained from Fisher Scientific Company.

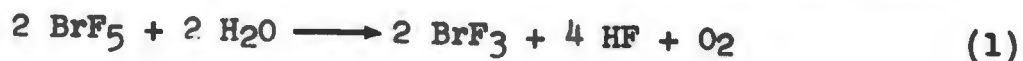
Purification with  $\text{BrF}_5$ 

The proper ratio of the fluoride salts for the preparation of a 10g Flinak sample (42.0 mole %KF, 46.5 mole %LiF, 11.5 mole %NaF) was weighed out and carefully mixed. The Flinak was then placed in the Teflon vessel, the cap secured and the vessel attached to the apparatus as illustrated in Figure 1. With the  $\text{BrF}_5$  tank valve closed the system was evacuated to  $5 \times 10^{-3}$  mm Hg in order to remove atmospheric

contaminants. During the evacuation process, the BrF<sub>5</sub> tank and stainless steel tubing were heated to 35°C to insure condensation of the BrF<sub>5</sub> only in the Teflon reaction vessel. Under vacuum, the Teflon vessel was chilled to approximately -72°C by means of a dry ice-ethanol slush in a Dewar flask. After the Teflon vessel had reached temperature equilibrium with its surroundings (15 to 20 minutes), the BrF<sub>5</sub> tank valve was opened and approximately 15 ml of BrF<sub>5</sub> was vacuum distilled into the vessel. The BrF<sub>5</sub> tank valve was closed and the Teflon vessel was allowed to remain in contact with the dry ice-ethanol slush for 15 minutes in order to insure that all of the BrF<sub>5</sub> in the stainless steel tubing had condensed into the Teflon vessel. By so doing, the possible safety hazard of the collection of BrF<sub>5</sub> in other parts of the system was minimized.

After the Dewar filled with dry ice-ethanol slush was removed, the system was vented by unscrewing the cap from one of the unused sample tees. The contents of the Teflon vessel were then transferred to a vitreous carbon crucible which in turn was placed in the Al<sub>2</sub>O<sub>3</sub> tube as illustrated in Figure 2. A flow of fluorine gas (approximately 30 cc/min.) was begun and maintained over the sample while the furnace temperature was slowly raised to 400°C. This temperature was maintained for one hour to remove bromine trifluoride formed (b.p. 127°C) and excess bromine pentafluoride (b.p. 40.5°C). Under a fluorine flow, the Flinak was cooled to room temperature and then transferred to a vacuum desiccator.

The use of bromine pentafluoride as the active agent in the purification of Flinak involves the following probable reactions:



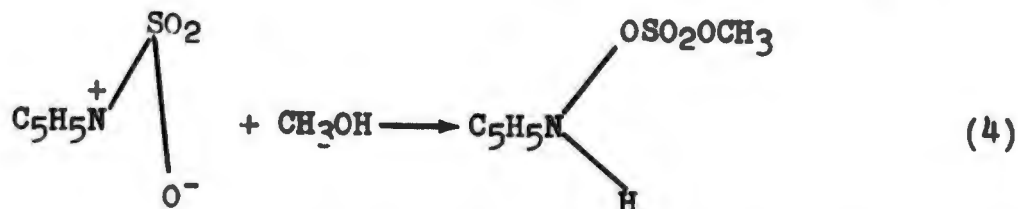
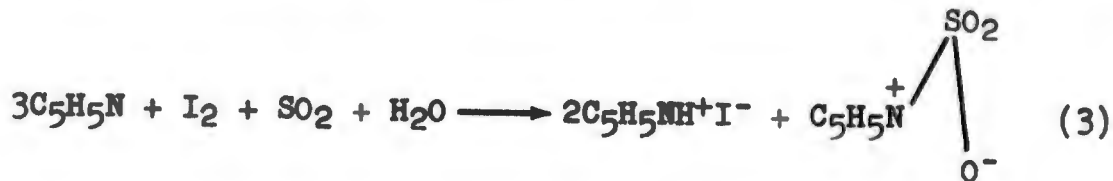
with similar reactions between the other oxygen-containing impurities and BrF<sub>5</sub>. As is noted in Reaction (1), initial reaction of the water with BrF<sub>5</sub> leads to the formation of BrF<sub>3</sub> which in turn also reacts with the water.

#### Purification by Vacuum Drying

This method involves the use of high temperature drying under reduced pressure for long periods of time (References 2 and 3). The proper ratio of the fluoride salts was mixed and placed above the frit in a Pyrex apparatus as illustrated in Figure 3. A temperature of 200°C and a vacuum of  $1 \times 10^{-3}$  mm Hg were maintained for 24 to 48 hours. Still under vacuum, the Flinak was heated to 500°C and held in the molten state for one hour (the melting point of the eutectic is 454°C). The vacuum was replaced with a slight, positive pressure of ultrapure argon, and the molten Flinak was forced through the frit into the Pyrex receiving tube. The receiving tube was then evacuated and sealed off to be reopened just prior to use.

Analysis by Karl Fischer Titration

Analysis for the total water plus oxide impurities was performed using Karl Fischer titrations (Reference 4). In order to increase the precision of the end-point determination, a potentiometric system was utilized. A constant current of 1.5 microamperes was imposed across the platinum electrodes in the titration vessel. The potential drop across the electrodes was monitored by a Fairchild digital multimeter. The reactions of the Karl Fischer reagent with water in a methanol solution are:



It is seen from Equation (3) that at the first excess of Karl Fischer reagent there will be free iodine in the solution. Thus, the resistivity of the solution will greatly decrease, effectively reducing the potential across the electrodes to zero. For back titrations with a standard water in methanol solution, the potential across the electrodes will increase dramatically from zero when the last trace of free iodine has been consumed.

In order to exclude atmospheric contamination of the Karl Fischer reagent during titration, the titration vessel, burettes, and burette reservoirs were constructed so as to form a single closed system. Communication to the vessel, a five-neck, flat-bottomed flask, was accomplished through ground glass joints. In addition, each burette was connected to a two-liter reservoir which allowed for refilling the burettes without opening the system to the atmosphere. Thus, the vessel could be sealed after the introduction of the Flinak sample to be opened again only after the titration was complete. As an additional precaution to reduce surface contamination of the Flinak during the grinding process and subsequent transfer to the reaction vessel, the entire process, including titration, was carried out in a glove box under a helium atmosphere.

RESULTS AND DISCUSSION

When Flinak samples, prepared by vacuum drying, were analyzed by Karl Fischer titrations, they were found to contain 800 to 3000 ppm

water plus hydrolysis products (hereafter simply referred to as impurities). This level of impurities is in close agreement with the impurity content of Flinak samples reported by Pizinni, et al., in their use of the technique of vacuum drying (Reference 5). In striking contrast with these results are the impurity levels for samples of the eutectic prepared using  $\text{BrF}_5$ . Using Karl Fischer titrations, such samples were found to have an impurity level of 30 to 35 ppm. Excepting the addition of an active metal or a silver halide (Reference 6) (since this is, in general, undesirable in electrochemical studies), the use of  $\text{BrF}_5$  produces Flinak with a substantially lower impurity level than the other currently employed purification techniques (References 5 and 7).

Since one segment of our studies has been concerned with the use of Flinak as a solvent in high temperature spectrophotometric studies of certain high oxidation state transition metals, the purity of the solvent has been of basic concern (Reference 3). A typical spectrum of a sample of Flinak, prepared by vacuum drying, is given in Figure 4 by the top line. As is noted, the strong end-absorption of such a melt would tend to obscure any fine structure of the sample being studied in the 300 to 400 nm region. The greatly reduced end-absorption of the  $\text{BrF}_5$  purified melt is revealed by its spectrum (Figure 4 -- middle line). The slight end-absorption, about 0.3 absorption units, still present in the  $\text{BrF}_5$  purified melt spectrum, is due to characteristic absorption by the diamond windows. The bottom line (Figure 4) shows the spectrum of the graphite-diamond cell.

In conclusion, it should be reemphasized that the primary interest in our research is the application of Flinak as the electrolyte in high-energy-density thermal batteries. In the thermal battery systems currently under study, the proposed cathode materials are fluoride complexes of high oxidation state transition metals (such as  $\text{K}_3\text{CuF}_6$  or  $\text{KAgF}_4$ ). In these systems the presence of water or oxygen in the Flinak electrolyte (usually present in the form of oxides at the molten eutectic temperature --  $454^\circ\text{C}$ ) is particularly detrimental since such impurities are oxidized by reaction with the cathode material. This reaction, typified by the following reaction (Equation 5) of the  $\text{Cu(III)}$  species from  $\text{K}_3\text{CuF}_6$  with oxide impurities



results in a lower oxidation state for the cathode material ( $\text{Cu(III)} \rightarrow \text{Cu(II)}$ ) which reduces the coulombic efficiency of the cathode. As previously discussed, treatment of the Flinak eutectic with bromine pentafluoride serves to reduce the impurity level of the melt by at least two orders of magnitude and, therefore, greatly increases the stability of the cathode material. This increase in stability of cathode materials was observed spectrophotometrically during studies of  $\text{K}_3\text{CuF}_6$  in  $\text{BrF}_5$  purified melts.

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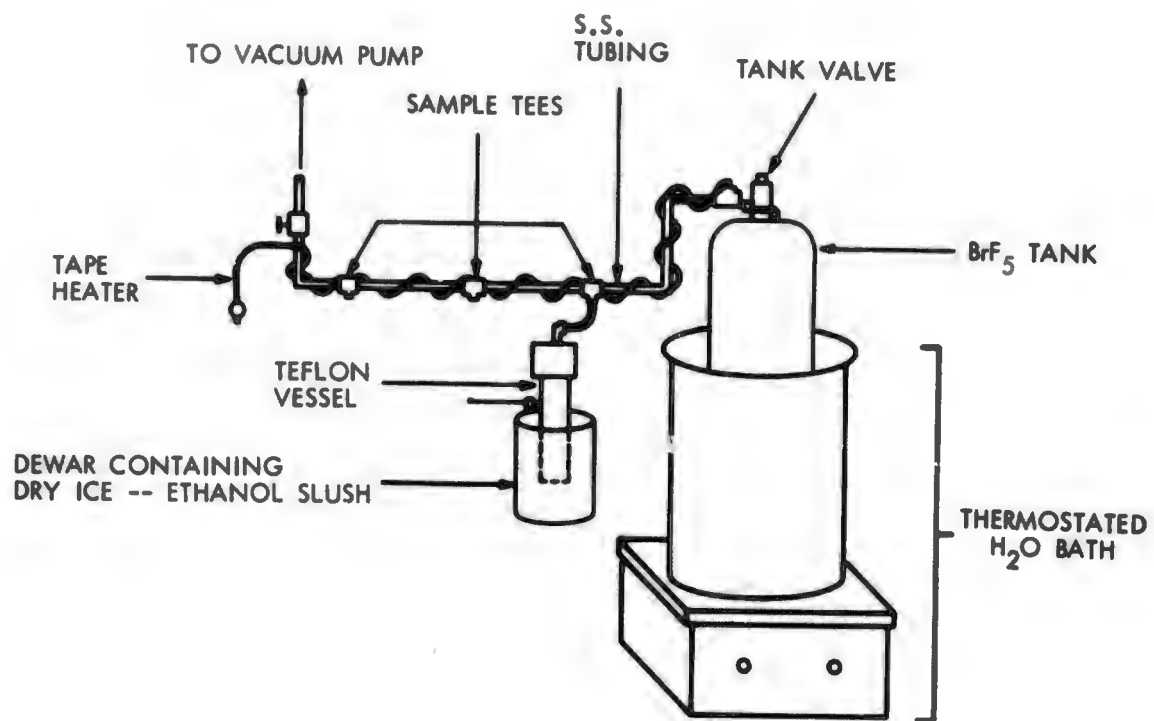


FIG. 1 BrF<sub>5</sub> TRANSFER APPARATUS

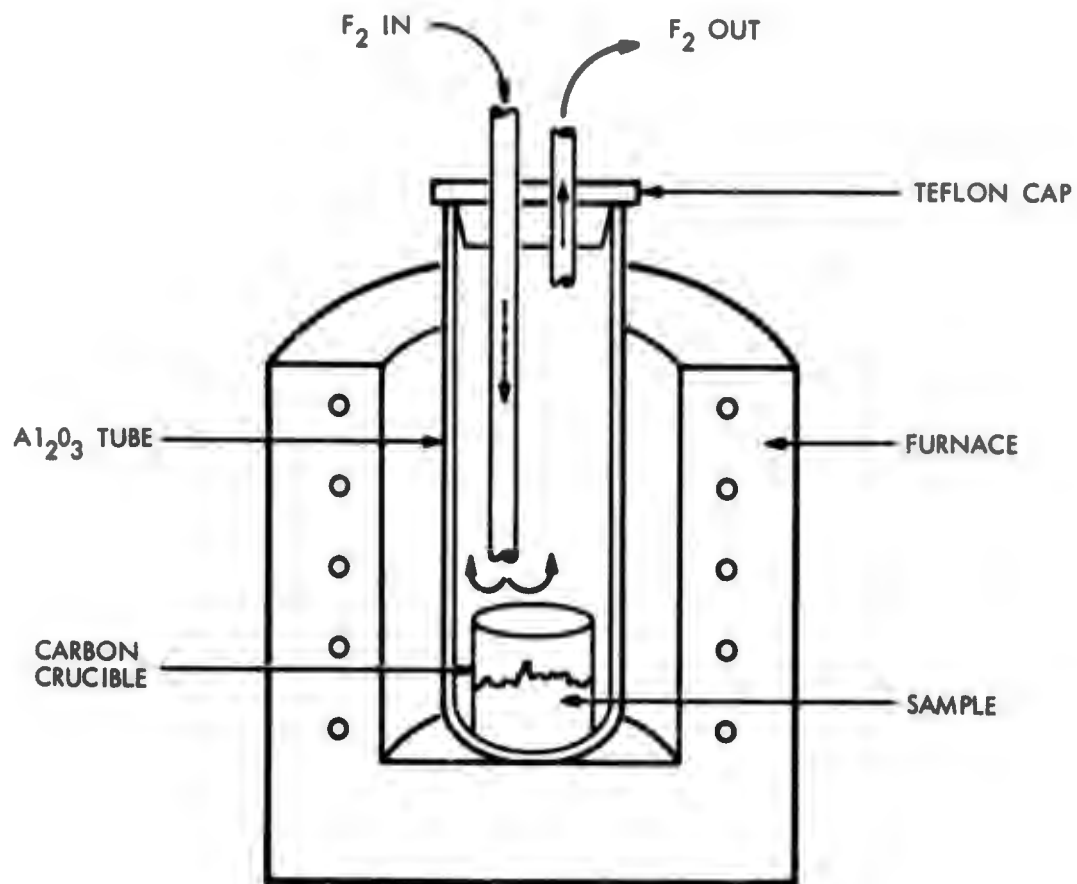


FIG. 2 FLUORINATION APPARATUS

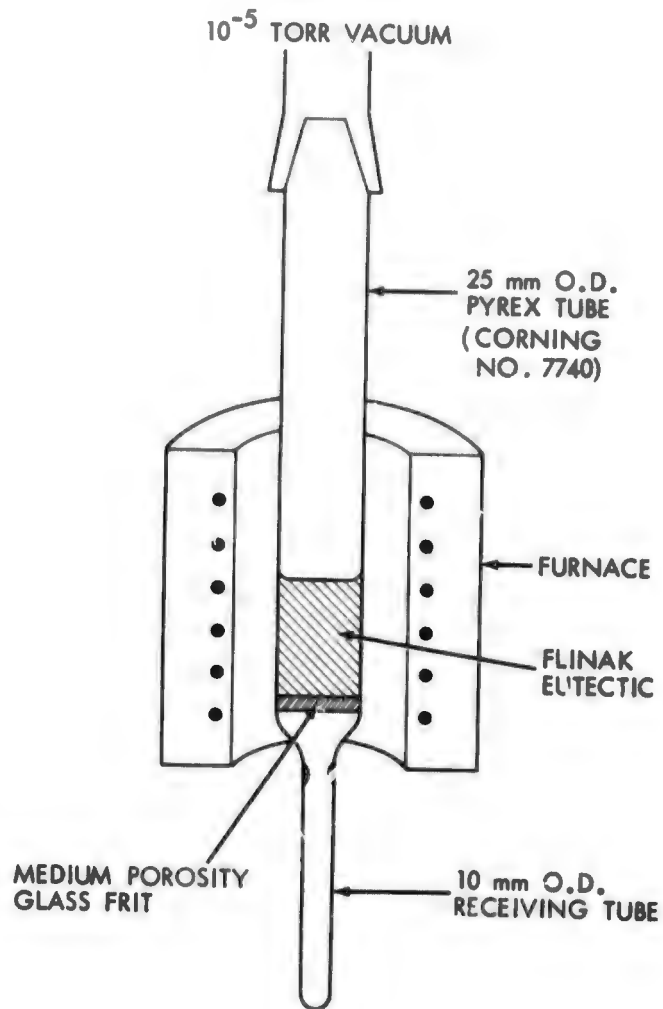


FIG. 3 VACUUM DRYING APPARATUS

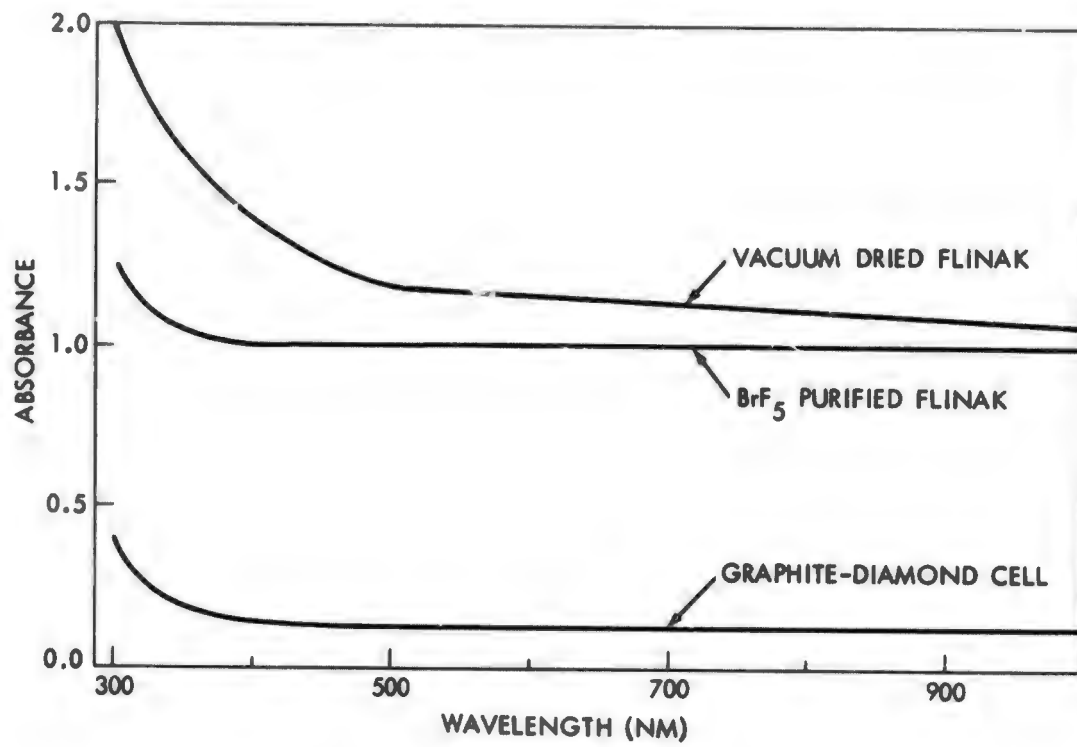


FIG. 4 SPECTRA OF FLINAK AND GRAPHITE-DIAMOND CELL