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Electrochemical Investigations of the System Li/UO_2F_2

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Uranyl fluoride, UO_2F_2, and a lithiated uranyl fluoride, $Li_2UO_2F_2$, have been studied as the electrochemically active materials in nonaqueous lithium batteries. Both open circuit and discharge potentials have been measured as a function of utilization. The reversibility of the couple has been demonstrated. It is concluded that the phase $Li_2UO_2F_2$ is an end member of a nonstoichiometric homogeneity range of generalized composition $Li_xUO_2F_2$ where x varies from 0 to 2.

Introduction

Materials assuming layered solid state structures have recently been exploited for electrochemical applications. Certain transition metal dichalcogenides having this structure have been thoroughly explored (*1*). A compound which is structurally related to these dichalcogenides is uranyl fluoride, UO_2F_2 (*2*). Besides forming a layered lattice, uranyl fluoride also contains a metal ion in its highest oxidation state. The accessibility of lower oxidation states of uranium suggests that uranyl fluoride could be considered for similar battery applications.

n-Butyl lithium has been employed as an effective screening agent for the identification and evaluation of materials for battery cathode applications (*3*). It has recently been observed that uranyl fluoride, UO_2F_2, undergoes a two-electron reduction when subjected to treatment with this reagent (*4*). The product of this reduction has been identified as $Li_2UO_2F_2$ and details of its structure as it relates to the layered structure of UO_2F_2 are forthcoming (*5*).

The reduction of UO_2F_2 by *n*-butyl lithium has been qualitatively observed to be both highly exothermic and quite rapid. The high heat of reaction in combination with a moderate formula weight per lithium (154/Li) can be related to a potentially high energy density for a nonaqueous electrochemical cell having lithium as an anode and uranyl fluoride as a cathode. Likewise, a rapid reaction rate suggests the ability of such a cell to be discharged at relatively high current levels.

This paper describes the basic characteristics of this couple under reasonable battery test conditions.

Experimental

UO_2F_2 was obtained from Gallard–Schlesinger Chemical Manufacturing Corp., and $Li_2UO_2F_2$ was prepared by adding hexane solutions of *n*-butyl lithium to suspensions of anhydrous UO_2F_2 in hexane. Chemical analyses of both the excess *n*-butyl lithium and the isolated solid product indicated that 2 moles of lithium per mole of U had reacted and also that these two equivalents of Li had been included in the product phase giving the empirical formulation $Li_2UO_2F_2$.

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The electrolyte employed in the present study consisted of lithium perchlorate dissolved in a 2:1 (v/v) solution of tetrahydrofuran and propylene carbonate. Tetrahydrofuran (THF) (Matheson, Coleman, and Bell) and propylene carbonate (PC) (Eastman Kodak Company. bp = 121–123°C at 17 mm) were dried with molecular sieves (Linde 4A) in an argon dry box for a period of more than 24 hr before they were used. Reagent-grade anhydrous lithium perchlorate (ROC/RIC) was dried under high vacuum (10^{-4} mm) at 230°C for a period of several days before it was used.

Both UO_2F_2 and $Li_2UO_2F_2$ were found to be poor electrical conductors, with conductivities of 10^{-5}–$10^{-6}\ \Omega^{-1}\ cm^{-1}$ at room temperature. To increase the conductivity of electrodes fabricated with either UO_2F_2 or $Li_2UO_2F_2$, graphite (Union Carbide, SP-1) was intimately mixed with the particular compound. The electrodes were prepared by mulling the test material, graphite, and powdered polytetrafluoroethylene binder in an inert organic solvent. This mull was pressed onto a nickel screen and the organic solvent was evaporated at room temperature under vacuum to yield the electrode ready for testing.

The lithium electrode was prepared in an argon dry box by pressing commercial lithium ribbon (ROC/RIC) onto a nickel screen. The test cell was assembled by sandwiching the test electrode between two lithium electrodes. Layers of glass-fiber filter paper (GF/A Whatman) were used as separators between the electrodes. All electrodes and filter paper were rigidly positioned on Teflon supports. The electrode assembly was then placed inside a Teflon cell containing electrolyte solution. Electrical connection to the appropriate monitoring and control circuitry was then made to the electrodes by means of nickel leads which had been previously spot welded on the nickel screens.

Cell discharges and charges were carried out in an argon atmosphere at constant currents with a Model 173 potentiostat/galvanostate in conjunction with a Model 179 digital coulometer and a Model 178 electrometer probe, all of which were manufactured by EG&G Princeton Applied Research. Only the potential difference between the test electrode and the lithium reference electrode (one of the two lithium electrodes) was measured during the galvanostatic discharge and charge. At various stages of discharges and charges of the test cells, lithium electrodes were interchanged and no detectable difference in the measured voltage was measured.

Results

The first electrochemical experiment was performed on a $Li/LiClO_4$ $(THF/PC)/UO_2F_2$ battery. An initial open circuit potential of 3.14 V was observed for this cell. The discharge voltage at a constant current rate of 0.1 mA/cm^2 is shown in Fig. 1. Large polarizations were observed soon after current draw was initiated, with a discharge potential of 1.5 V being observed at only 10% utilization based on an ultimate utilization of two lithiums per uranium. Dis-

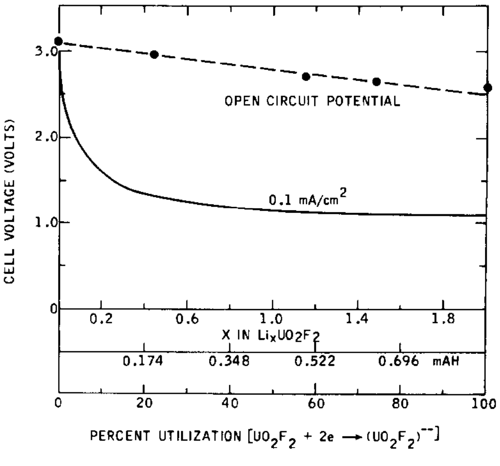

FIG. 1. Discharge characteristics of UO_2F_2 cell.

charge was allowed to proceed to a potential of 1.06 V where the possibility of electrolyte degradation could lead to ambiguous interpretations of potential values. The possible electrolyte participation in the measured voltage was further evidenced by an observed cell potential of 1.06 V at more than 20% beyond the theoretical capacity of the electronegative material. Attempts to discharge this cell at higher current densities resulted in completely unacceptable polarizations, with the 1.06-V cutoff being observed early in the discharge.

Periodically throughout the discharge of the cell, the open circuit potential was measured. This was found to vary smoothly from the initial 3.14 V to approximately 2.50 V at the end of the discharge. During the course of the discharge, the length of time required to return to a constant open circuit potential from the discharge potential increased dramatically. The final open circuit potential stabilized only after a period of several hours following current interruption.

A second type of electrode was prepared containing presynthesized $Li_2UO_2F_2$ which could not be discharged without an initial charging cycle. The behavior of the battery couple during this charging step is shown in Fig. 2. The initial open circuit potential observed was approximately 2.4 V, which matches well with that observed for UO_2F_2 at the theoretical end of its discharge. Charging was carried out at 0.1 mA/cm^2 with periodic interruptions to determine the open circuit potential. This open circuit potential closely followed the observed open circuit potential values noted during the discharge of UO_2F_2. Likewise, the final open circuit potential observed at the culmination of the charging step was just over 3 V, again very similar to UO_2F_2 itself.

After this initial charging step, the same cell was discharged at a constant current rate of 0.1 mA/cm^2. This is shown in Fig. 3. A discharge curve was observed which was similar to that observed for the UO_2F_2 cell. However, in this case, where the cell had undergone an initial charging step, less polarization and a higher discharge potential as a function of utilization were observed. After this first discharge, the cell was recharged a second time and then returned to the discharging mode. The discharge potential of this second discharge closely mimicked that of the first discharge of this cell. A slight decrease in polarization during the initial stages of this second discharge was noted. The final discharge potential was approximately 1.53 V in each case, and after the

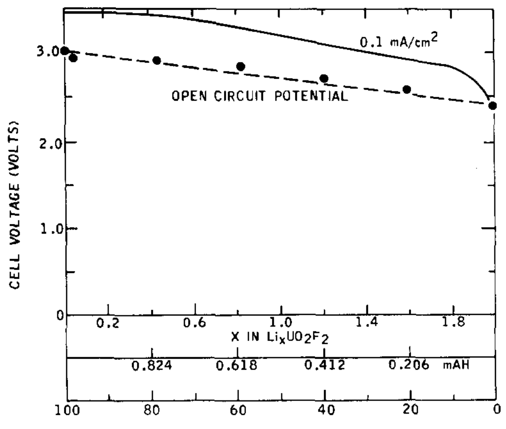

FIG. 2. Initial charging of $Li_2UO_2F_2$.

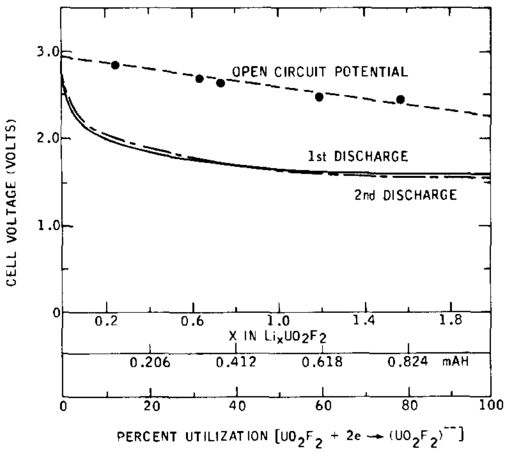

FIG. 3. First and second discharges of $Li_2UO_2F_2$ cell.

theoretical end of discharge of the electrochemically active species, a drop in discharge potential to values which could be interpreted as indicative of solvent degradation was noted.

Discussion

We have demonstrated that uranyl fluoride, UO_2F_2, can be utilized as the cathodically active material in a nonaqueous lithium battery. Presumably this activity is not limited to lithium anodes and is undoubtedly applicable to other anode materials. Thus, this technique could be utilized to synthesize other compounds of the type $M_xUO_2F_2$ which are not accessible by other techniques due to the lack of a convenient source of other metals as *n*-butyl lithium is for lithium.

While the open circuit potentials observed in this study are impressive, the use of UO_2F_2 as a battery cathode is not without drawbacks. The low electrical conductivity of UO_2F_2 and of the product of lithiation, $Li_2UO_2F_2$, necessitates the addition of a conductive material such as graphite in order to fabricate a usable electrode.

The cells tested exhibited large polarizations when current was drawn. These polarizations possibly have their origin in relatively low lithium ion mobility in the lattice. This is consistent with our inability to prepare phases of composition $Li_xUO_2F_2$, where $0 < x < 2$, by reactions of UO_2F_2 with stoichiometrically controlled amounts of *n*-butyl lithium. The products isolated from these reactions consisted of fully lithiated $Li_2UO_2F_2$ with completely unreacted UO_2F_2 as indicated by powder X-ray diffractometry. The observed results from controlled stoichiometric reactions could then be interpreted as arising from a crystallite of UO_2F_2 reacting with *n*-butyl lithium on the surface, yielding a smaller crystallite of UO_2F_2 covered with a homogeneous layer of $Li_2UO_2F_2$.

This interpretation of our observed results implies that thermodynamic equilibrium has not been attained in the reactions in which the overall Li/U stoichiometry has been limited to values of less than two. This is not unreasonable considering the heterogeneous nature of the reaction which effectively increases the ratio of *n*-butyl lithium to uranium at the surface of the solid uranyl fluoride crystallites. While heterogeneous reactions of this type often reach thermodynamic equilibrium rapidly, this system's inability to do so can be rationalized considering mechanistic aspects associated with the reduction of U^{6+} and the diffusion of Li^+ through the lattice. Logically in such a heterogeneous reaction, the reduction proceeds from the surface of a uranyl fluoride crystallite toward its center. There are two possibilities for the migration of the reductant toward the interior of the solid particle.

Either the reacted layer is loosened and detached from the crystallite to expose fresh surface to be reduced or the reductant must proceed diffusionally through the crystallite. Both possibilities lead to the same conclusion. To elaborate, if the former mechanism were invoked, a fragment of a crystallite of UO_2F_2 after some, possibly low, degree of reduction would be detached from the uranyl fluoride crystallite to provide fresh surface on the initial crystallite to be reduced. At the same time, however, the detached fragment, now partially lithiated, and still insoluble in the reaction solvent, would have a much larger percentage of its mass subjected to the local surface excess of reducing reagent, producing a particle with a higher degree of lithiation and decreasing the amount of *n*-butyl lithium available for reaction with the remaining UO_2F_2.

The alternative reaction pathway, that invoking retention of crystallite integrity coupled with diffusion of the reductant to the interior of the crystallite, could also result in kinetically preferential production of a nonequilibrium heterogeneous product. For diffusion to be efficient in a solid, facile diffusion mechanisms for the diffusing species must be available. Considering this system, pathways for a lithium cation with its separated electron must be identified. The migration of an electron through the UO_2F_2 lattice is an unfavorable process, at best, since the material is an insulator. Likewise, the migration of a positively charged lithium ion into regions of close proximity to highly charged ionic species (U^{6+}) in the lattice would hinder equilibration of the Li^+. These two impediments would make migration of the reducing agent into the internal regions of the uranyl fluoride crystallites slow and allow for more extensive treatment of a partially lithiated surface with more lithiating reagent in the solution.

Considering the insulating nature of the uranyl fluoride lattice, it is conceivable that the reduction involves a multistep process. That is, the initial insertion of some small amount of lithium ions into a surface, together with the accompanying reduction of the local lattice, serves to separate the uranyl fluoride layers and "props" them apart. This can then dramatically lower the kinetic barrier for the incorporation of the remaining lithiums into that specific microscopic region resulting in the production of portions of the product being completely lithiated to form $Li_2UO_2F_2$ while leaving much of the UO_2F_2 unaffected.

While in our heterogeneous reactions with *n*-butyl lithium, we have not reached thermodynamic equilibrium at intermediate compositions under the conditions employed, it is to be expected that it could be achieved if sufficient time were allowed and appropriate conditions were imposed to allow equilibration of the lithium with all of the solid uranyl fluoride employed. One would expect a closer approach to equilibrium to be attained during an electrochemical insertion of these lithiums where the reduction of the lattice is rigorously controlled.

It was observed that after charging a battery initially containing $Li_2UO_2F_2$, the discharge potential exhibited less polarization. This improvement is attributed to the charging process itself. The charging step forces all of the lithium out of the lattice and, in this process (carried out at relatively high chemical potentials), forms microscopic pathways for the lithium to subsequently reenter the crystallite lattice upon discharge. Likewise, the second discharge of the $Li_2UO_2F_2$ battery showed less polarization during the early stages of utilization. Perhaps even more polarization could be eliminated by a long series of charge/discharge cycles to further break up the UO_2F_2 crystallites to facilitate lithium migration into the lattice.

The open circuit potentials noted during charging and discharging cycles of UO_2F_2 electrochemical cells give some insight into the nature of the phase $Li_xUO_2F_2$, where $0 \leq x \leq 2$. If intermediate compositions ($0 < x < 2$) were not stable, one would expect to see a constant open circuit potential until utilization of the electroactive material was complete. The smooth decrease in open circuit potential with utilization, however, indicates that the ability of the UO_2F_2 lattice to incorporate lithium ions changes smoothly over the entire compositional range. This is to be expected if a nonstoichiometric homogeneity range exists in this system. While open circuit potentials in cells which exhibit large polarizations can be misleading, we believe that our experimentally observed values are reasonably close to those rigidly imposed on the system by thermodynamics. This is supported by the observed open circuit potential of presynthesized $Li_2UO_2F_2$ versus metallic lithium of approximately 2.4 V. This value is in good agreement with the final open circuit potential observed after a two-equivalent discharge of a cell initially containing UO_2F_2 as the cathodically active material. Likewise, no indications of "stage" compounds, often observed for other layered systems (*6*), were obtained. A step-type behavior of the open circuit potential in the compositional region of the stable stage compound would be expected. No such behavior was observed in any discharge.

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