



Fluoride-Conducting Solid Electrolytes in Galvanic Cells

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ABSTRACT

Concentrated fluoride-excess solid solutions based on the alkaline earth fluorides and with CeF_3 and UF_4 as dopants are suitable solid electrolytes for application in thin film galvanic cells. Galvanic cells were fabricated using Pb or Ca as the anode, the concentrated solid solutions as electrolytes, and either BiF_3 or $\text{BiO}_{0.1}\text{F}_{2.8}$ as the cathode. Discharge characteristics were studied in air from 300° to 540°K. The cells are rechargeable. The electrical properties of BiF_3 were studied and compared with data reported for $\text{BiO}_{0.1}\text{F}_{2.8}$. Partly discharged cells contain anode passivation layers which consist mainly of Pb_2OF_2 when Pb is the anode, and of nominally pure CaF_2 in which fluoride interstitials carry the current if Ca is the anode

Fluoride ion conductors with fluorite structure have been explored as solid electrolytes in solid-state galvanic cells. Notably, undoped lead fluoride has been employed in vacuum-evaporated thin-film galvanic cells Pb-CuF_2 (1), Pb-BiF_3 (2), and Pb-AgF (1, 2), while AgF -doped $\beta\text{-PbF}_2$ has been used as a solid electrolyte in the cell $\text{Pb|BiO}_{0.1}\text{F}_{2.8}$ (3). In the fabrication of the latter cell, solid electrolyte-ethyl acetate and cathode-ethyl acetate mixtures are used. The rapid evaporation of ethyl acetate at room temperature allows an easy and fast way to construct reliable all-solid cells (3).

Concentrated solid solutions $\text{Pb}_{1-x}\text{Bi}_x\text{F}_{2+x}$ exhibit unusually high ionic conductivities (4). Attempts to decrease the d-c resistance of the cells Pb-BiF_3 by replacing evaporated PbF_2 -electrolyte films by $\text{Pb}_{0.75}\text{Bi}_{0.25}\text{F}_{2.25}$ -electrolyte films failed to improve the cell performance. This was ascribed to difficulties in obtaining films of the solid solution by coevaporation techniques (2).

It has been shown recently that concentrated fluoride-excess solid solutions based on the alkaline earth fluorides exhibit interesting solid electrolyte properties at low and moderate temperatures (4-6). The room temperature ionic conductivity of a solid solution based on BaF_2 with 26.5 mole percent (m/o) of excess fluoride increases by a factor of about 10^9 with respect to undoped BaF_2 (6).

The easy-to-fabricate solid-state galvanic cells $\text{Pb|solid electrolyte|BiO}_{0.1}\text{F}_{2.8}\text{|Bi}$ (3) are suitable to test the applicability of solid solutions as solid electrolytes. In the present study the solid solutions $\text{M}_{1-x-y}\text{U}_x\text{Ce}_y\text{F}_{2+2x+y}$ ($\text{M} = \text{Ca, Sr, Ba}$ and $0.0267 \leq 2x + y < 0.266$) are employed as the solid electrolytes. The electrical properties of these solid solutions (6), and of the tysonite-related cathode material $\text{BiO}_{0.1}\text{F}_{2.8}$ (3, 7) have been published before. In addition, the present paper includes a comparison between the electrical properties of the cathode materials $\text{BiO}_{0.1}\text{F}_{2.8}$ and BiF_3 , and those of the possible anode discharge products $\alpha\text{-PbF}_2$ and Pb_2OF_2 .

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Key words: solid electrolytes, alkalines, galvanic cells.

Experimental Aspects

The melt-growth and crystallographic data of the solid solutions $\text{M}_{1-x-y}\text{U}_x\text{Ce}_y\text{F}_{2+2x+y}$ ($\text{M} = \text{Ca, Sr, Ba}$ and $0.0267 \leq 2x + y < 0.266$) have been reported by Catalano and Wrenn (8). The solid solutions used in the present study have a fluoride excess ($2x + y$) of 2.67 and 18.80 m/o for solid solutions based on CaF_2 , 20.83 m/o for an SrF_2 -based solid solution, and 9.5, 20.07, 20.89, 23.15, and 26.58 m/o for those based on BaF_2 (6).

The preparation of the cathode material $\text{BiO}_{0.1}\text{F}_{2.8}$ has been published elsewhere (3). The cathode material BiF_3 was prepared from Bi_2O_3 (Baker) and excess NH_4F (Baker A. R.) (9). A heat-treatment at 575°K for 30 min yielded a mixture of cubic BiF_3 and NH_4F . The excess NH_4F was removed upon a subsequent heat-treatment at 475°K in dried, oxygen-free nitrogen. Doping with PbF_2 or KF was achieved by adding the dopants to the starting $\text{Bi}_2\text{O}_3\text{-NH}_4\text{F}$ mixtures.

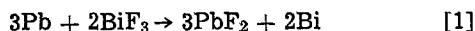
We have synthesized Pb_2OF_2 by melting equimolecular amounts of PbO and $\beta\text{-PbF}_2$ at about 1025°K in an aluminum oxide crucible. The reaction was not quantitative, since in addition to the Pb_2OF_2 diffraction peaks, small peaks showed up which could be attributed to the binary constituents. A detailed description of the fabrication of the solid-state galvanic cells from dispersions of the solids in ethyl acetate has been published before (3). In this study $6.65 \times 10^{-5} \text{ m}^2$ area cells were fabricated by painting a flat disk of the anode metal with a dispersion that contains the solid electrolyte and a Bi-disk with a dispersion that contains the cathode, and by springloading the (dried) disks in the appropriate sequence between two flat Pt electrodes of a conventional conductivity cell. Each cell contained about $1 \times 10^{-5} \text{ kg}$ of the solid electrolyte and about $1 \times 10^{-5} \text{ kg}$ of the cathode material. In several experiments the Pb anode was replaced by Ca (Merck), and the $\text{BiO}_{0.1}\text{F}_{2.8}$ cathode by BiF_3 . Galvanic cells with Ca as the anode were assembled and tested in an N_2 -atmosphere glove box. All other cells were fabricated and tested in air.

Electrical measurements were made from 300°–550°K. Open-circuit voltages (OCV) were measured with a Keithley Model 616 digital electrometer. Short-circuit currents were measured with a Keithley Model 445 digital picoammeter. Current-voltage characteristics of the polarization cells (–)Bi|BiF₃|Pt, or Ag(+), were studied as reported before (10).

Alternating current conductivities of undoped and doped BiF₃ and of Pb₂O₇F₂ were measured with impedance bridges and a Frequency Response Analyser (Solartron 1172), details of which have been published elsewhere (11).

Experimental Results

Galvanic cells.—The galvanic cells Pb–BiO_{0.1}F_{2.8} and Pb–BiF₃ with the solid solutions M_{1–x–y}U_xCe_yF_{2+2x+y} (M = Ca, Sr, Ba and 0.0267 ≤ 2x + y < 0.266) as solid electrolytes all exhibited OCV's of 0.33V. This is concordant with the cell reaction



The tysonite-related cathode material BiO_{0.1}F_{2.8} can be considered as oxide-doped BiF₃. The galvanic cell Ca–BiO_{0.1}F_{2.8} has a theoretical OCV of 3.10V according to a similar reaction as shown in Eq. [1]. In the temperature region 330°–430°K the experimentally observed OCV's of cells with Ba_{0.882}U_{0.113}Ce_{0.005}F_{2.231} as solid electrolyte were time and temperature dependent. Right after assembling, the cell OCV's increased from 2.42 to 3.00V in the temperature region involved. Although storage at constant temperature improved the OCV, it did not exceed 3.00V. In the temperature region 430°–520°K OCV's between 3.00 and 3.08V were readily attained.

It has been shown in a recent paper (6) that the ionic conductivity of the alkaline earth fluoride-based solid solutions increased more rapidly than linearly with dopant content. For a more detailed study of the performance characteristics of this type of galvanic cell we therefore utilized the most concentrated solid solutions. Figure 1 presents normalized load-circuit voltages (LCV/OCV) vs. current densities at different temperatures for the initial discharge of Pb–BiO_{0.1}F_{2.8} and Pb–BiF₃ cells with the BaF₂-based solid solution as solid electrolyte. These cells behave when placed under load and current drawn as the cell Pb–BiO_{0.1}F_{2.8} with β–PbF₂:AgF as the solid electrolyte (3), of which data (6.65 × 10⁻⁵ m² area) have been included for comparison. Similar results were obtained with the other alkaline earth fluoride-based solid solutions. The data indicate that polarization is of minor importance. The d-c resistances of the cells were calculated using the expression

$$R_{dc} = \frac{\text{OCV} - \text{LCV}}{\text{LCV}} R_L \quad [2]$$

where R_L denotes the load resistance. Further performance characteristics are presented in Table I.

Figure 2 presents the temperature dependence of R_{dc}⁻¹ for partly discharged Pb–BiO_{0.1}F_{2.8} and Pb–BiF₃ cells with Ba_{0.882}U_{0.113}Ce_{0.005}F_{2.231} as solid electrolyte. These data, and data for cells which have other solid solutions as solid electrolytes, lead to activation enthalpies ΔH which are presented in Table II. This table

Table I. Composition, d-c resistance, current density for R_{dc} = R_L, and short-circuit currents, I_{sc}, of 6.65 × 10⁻⁵ m² area galvanic cells

Anode	Solid electrolyte	Cathode	T (°K)	R _{dc} (Ω)	I (R _{dc} = R _L) (A/m ²)	I _{sc} (A/m ²)
Pb	β-PbF ₂ :AgF (0.5 m/o)	BiO _{0.1} F _{2.8}	483	7.30 × 10 ²	3.40	6.50
Pb	Ba _{0.882} U _{0.113} Ce _{0.005} F _{2.231}	BiO _{0.1} F _{2.8}	512	4.60 × 10 ²	5.40	10.75
Pb	Sr _{0.894} U _{0.102} Ce _{0.004} F _{2.208}	BiO _{0.1} F _{2.8}	522	1.55 × 10 ³	1.60	3.20
Pb	Ca _{0.903} U _{0.0915} Ce _{0.0035} F _{2.188}	BiO _{0.1} F _{2.8}	512	1.44 × 10 ³	1.72	3.46
Pb	Ba _{0.882} U _{0.113} Ce _{0.005} F _{2.231}	BiF ₃	517	4.00 × 10 ²	11.00	22.80
Ca	Ba _{0.882} U _{0.113} Ce _{0.005} F _{2.231}	BiO _{0.1} F _{2.8}	513	1.53 × 10 ⁴	1.52	3.24

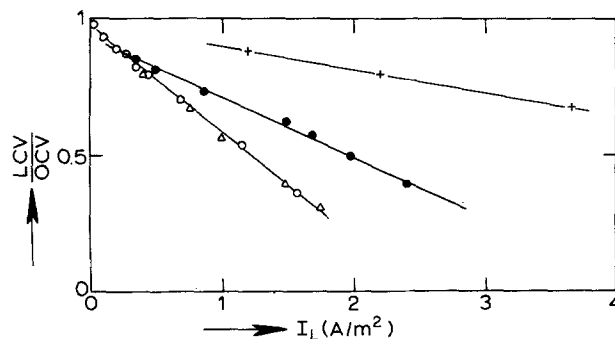


Fig. 1. Normalized load-circuit voltages (LCV/OCV) vs. load-current densities. (I_L) for 6.65 × 10⁻⁵ m² area cells; ΔΔ, Pb–BiO_{0.1}F_{2.8}, T = 466°K, Ba_{0.882}U_{0.113}Ce_{0.005}F_{2.231}, R_{dc} = 2.03 × 10³Ω; ○○, Pb–BiF₃, T = 454°K, Ba_{0.882}U_{0.113}Ce_{0.005}F_{2.231}, R_{dc} = 2.03 × 10³Ω; ●●, Pb–BiO_{0.1}F_{2.8}, T = 433°K, β–PbF₂:AgF (0.5 m/o), R_{dc} = 1.26 × 10³Ω; ++, Pb–BiO_{0.1}F_{2.8}, T = 512°K, Ba_{0.882}U_{0.113}Ce_{0.005}F_{2.231}, R_{dc} = 4.60 × 10²Ω.

also includes the migration enthalpies of the mobile point defects in the employed solid electrolytes. For the partly discharged cell Ca–BiO_{0.1}F_{2.8} with Ba_{0.882}U_{0.113}Ce_{0.005}F_{2.231} as the solid electrolyte the temperature dependence of R_{dc}⁻¹ leads to an activation enthalpy of 0.88 eV.

The cycling behavior was investigated for a cell Pb–BiO_{0.1}F_{2.8} with Ba_{0.882}U_{0.113}Ce_{0.005}F_{2.231} as the solid electrolyte. The cell was discharged for 70 hr at 313°K over a 50 kΩ load. A capacity of 0.44C was calculated from the discharge curve. Then the cell was charged at 10⁻⁵A for 17 hr: passed charge 0.61C. Before the discharge experiment and after charging the cell the same load-circuit voltage vs. load current density curves were obtained. Subsequently the cell was discharged for 7 days at 506°K over a 15 kΩ load. A capacity of 1.9C was calculated. During discharge R_{dc} increased from 14 to 50 kΩ. After charging the cell at 10⁻⁵A for 64 hr (2.3C) the value of R_{dc} dropped to its original value. Thereafter, the cell was discharged for 22 days at 493°K over a 50 kΩ load. A capacity of 2.03C was obtained.

Bismuthtrifluoride.—Bismuthtrifluoride is currently employed as the cathode. Its electrical properties have not been reported previously. In Fig. 3 we have plotted the temperature dependence of the ionic conductivity

Table II. Activation enthalpies, ΔH, for R_{dc}⁻¹ of the galvanic cells Pb | solid electrolyte | BiO_{0.1}F_{2.8} | Bi, and the conductivity activation enthalpies, ΔH_m, for the solid electrolytes

Solid electrolyte	Temperature range (°K)	ΔH (eV)	ΔH _m * (ref.) (eV)
β-PbF ₂ :AgF (0.5 m/o)	300-340	0.35	0.20 (ex. V _F) (3)
	340-540	0.64	0.65 (in. V _F) (3)
Ca _{0.903} U _{0.0915} Ce _{0.0035} F _{2.188}	345-520	0.64	0.78 (ex. F _i) (6)
Sr _{0.894} U _{0.102} Ce _{0.004} F _{2.208}	410-520	0.72	0.59 (ex. F _i) (6)
Ba _{0.882} U _{0.113} Ce _{0.005} F _{2.231}	330-525	0.63	0.50 (ex. F _i) (6)

* ex. denotes extrinsic conductivity via
in. denotes intrinsic conductivity via

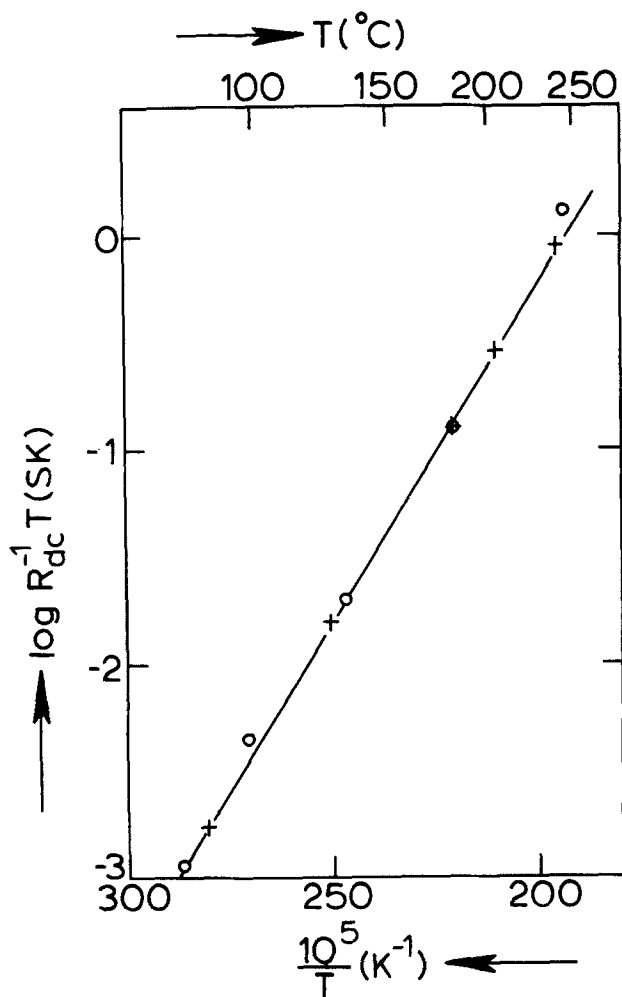


Fig. 2. The temperature dependence of R_{dc} of galvanic cells discharged in air with $Ba_{0.882}U_{0.113}Ce_{0.005}F_{2.231}$ as solid electrolyte, plotted as $\log R_{dc}^{-1} T$ vs. $10^5/T$. ++, Pb-BiO_{0.1}F_{2.8}; ○○, Pb-BiF₃.

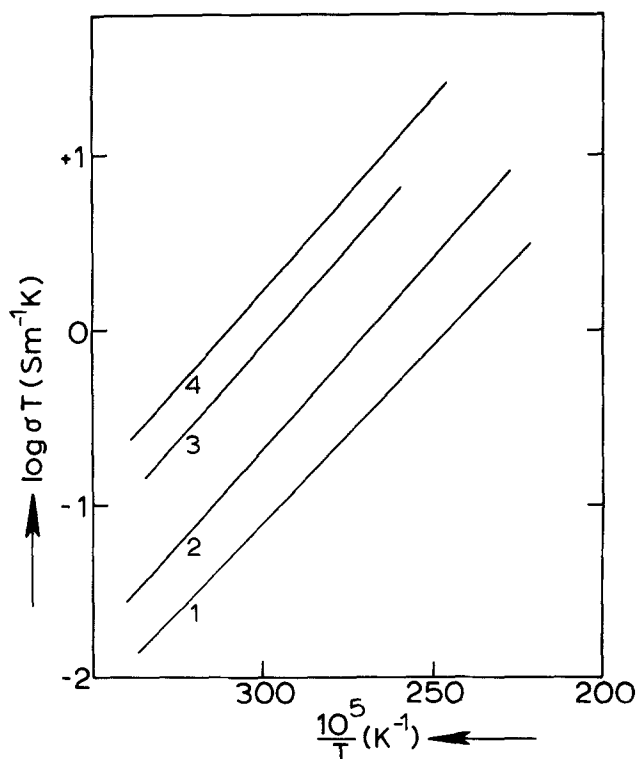


Fig. 3. The temperature dependence of the ionic conductivity of undoped and doped BiF₃. 1, BiO_{0.1}F_{2.8} (7); 2, undoped BiF₃; 3, BiF₃:PbF₂ (260 ppm); 4, BiF₃:KF (~60 ppm).

of undoped BiF₃, BiF₃:PbF₂, and BiF₃:KF. Complex plane analyses (11) of admittance data recorded in the range 0.1 Hz-50 kHz were employed to obtain bulk conductivity data. The low frequency data pass through the origin in the complex plane plot, indicating negligible electronic conductivity. For comparison, the data for the cathode material BiO_{0.1}F_{2.8} have been included (7). The ionic conductivity of the undoped cubic BiF₃ is of the same order of magnitude as that of tysonite-related BiO_{0.1}F_{2.8}, in which fluoride ion vacancies constitute the mobile species. The difference between the conductivity activation enthalpies is also small, i.e., 0.44 eV for undoped and doped BiF₃ and 0.41 eV for BiO_{0.1}F_{2.8}. The incorporation of PbF₂ and KF into BiF₃ both leads to an increase of the ionic conductivity.

In the polarization cells (-)Bi|BiF₃|Pt, or Ag(+) similar current instabilities occurred as observed by Van der Meulen and Kröger (12) in their study of the electronic conductivity of silver halides. Above 350°K these instabilities were not observed for Ag anodes. Although these current instabilities interfered with determining steady-state currents, voltage-independent steady-state currents of the order of 5×10^{-10} A were measured up to 1.5V at 313°K for the cell (-)Bi|BiF₃|Pt(+). Figure 4 presents a current-voltage characteristic of the cell (-)Bi|BiF₃:KF|Ag(+) at 373°K.

Anode discharge products.—The anode reaction



leads to the formation of orthorhombic α -PbF₂ (13, 14). In air the deposits on a lead anode even consist of mixtures of α -PbF₂ and Pb₂OF₂ (13, 15). Conductivity data for α -PbF₂ are available in the literature (13, 16). Data for Pb₂OF₂ are not available. In Fig. 5 we have plotted the temperature dependence of the ionic conductivity of Pb₂OF₂ contaminated with small amounts of the binary constituents. The data reveal a conductivity activation enthalpy of 0.66 eV.

Discussion

Galvanic cells.—It is apparent from this study that the present concentrated anion-excess solid solutions based on the alkaline earth fluorides can be used as solid electrolytes in thin film galvanic cells. Powders of these electrolytes are, when dispersed in ethyl acetate, suitable in the fabrication of the cells. However, this fabrication technique does not ensure films of uniform

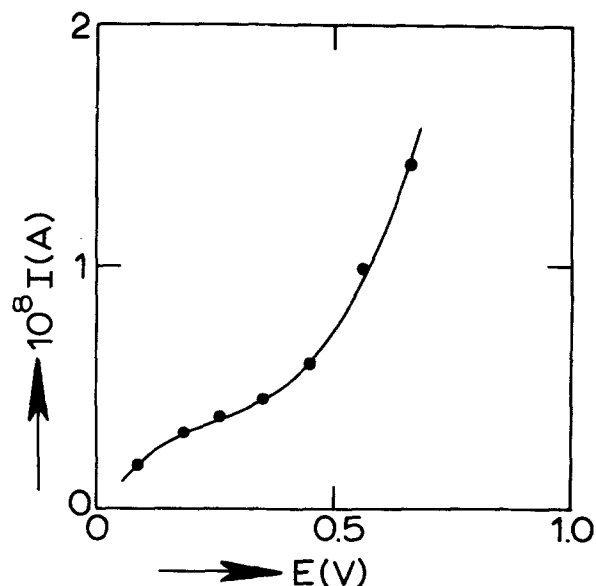


Fig. 4. Current-voltage characteristic of the cell (-)Bi | BiF₃:KF | Ag(+) at 373°K in nitrogen. Cell constant 10 m⁻¹.

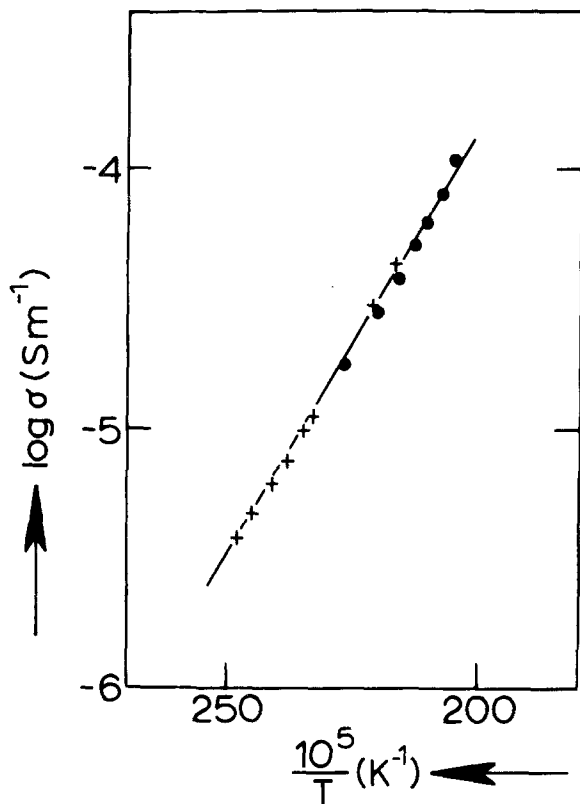


Fig. 5. The temperature dependence of the ionic conductivity of $\text{Pb}_2\text{O}_2\text{F}_2$ containing small amounts of PbO and $\beta\text{-PbF}_2$. $\bullet\bullet$, heating; $++$, cooling.

thicknesses, and does not provide reproducible film thicknesses. This precludes a quantitative comparison between the different galvanic cells. Nevertheless, it is obvious that galvanic cells with these alkaline earth fluoride-based solid solutions have performance characteristics that are comparable to those of cells in which AgF -doped $\beta\text{-PbF}_2$ is employed as the solid electrolyte (3).

Of the present solid solutions, those based on BaF_2 have the highest ionic conductivity (6), typically 10^{-1} sec m^{-1} at 473°K . In addition, the ionic conductivity of undoped cubic BiF_3 exceeds that of tysonite-related $\text{BiO}_{0.1}\text{F}_{2.8}$. That $I(R_{\text{dc}} = R_{\text{L}})$ and I_{sc} (Table I) of freshly prepared cells with the BaF_2 -based solid solution as solid electrolyte and either $\text{BiO}_{0.1}\text{F}_{2.8}$ or BiF_3 as cathode are large in comparison to the other cells is then to be expected, although the aforementioned comment on film thicknesses must be kept in mind.

The application of $\text{BiO}_{0.1}\text{F}_{2.8}$ as the cathode originated from the observation that tysonite-related metal fluorides exhibit at low and moderate temperatures high ionic conductivities (3, 7). The present data reveal that $\text{BiO}_{0.1}\text{F}_{2.8}$ can be replaced by cubic BiF_3 as the cathode material.

It has been emphasized (3) that in the region $300^\circ\text{--}370^\circ\text{K}$ the temperature dependence of R_{dc} [$\Delta H = 0.41$ eV (3)] of the partly discharged cells $\text{Pb}|\beta\text{-PbF}_2:\text{AgF}|\text{BiO}_{0.1}\text{F}_{2.8}|\text{Bi}$ indicates that the cathode material is involved in the rate-determining step in the cell reaction. Inspection of Table II shows that this cannot be true for the present galvanic cells for $T > 340^\circ\text{K}$. The solid electrolytes lead to comparable ΔH values, except for higher value of the SrF_2 -based solid solution. That, for instance, $\Delta H_{\text{m}}(\text{Ca}_{0.9035}\text{U}_{0.0915}\text{Ce}_{0.005}\text{F}_{2.188}) > \Delta H$, and $\Delta H_{\text{m}}(\text{Ba}_{0.882}\text{U}_{0.113}\text{Ce}_{0.005}\text{F}_{2.231}) < \Delta H$ then indicates anode passivation to be the predominant contribution to R_{dc} . Since the ionic conductivity of $\beta\text{-PbF}_2:\text{AgF}$ exceeds that of the alkaline earth fluoride-based solid solutions in the temperature region involved, anode passivation is also predominant in this cell,

despite the observation that ΔH of this cell equals $\Delta H_{\text{m}}(\beta\text{-PbF}_2:\text{AgF})$ for $T > 340^\circ\text{K}$.

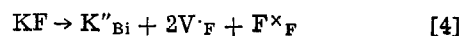
During discharge low conducting $\alpha\text{-PbF}_2$ (13) is formed. Although $\alpha\text{-PbF}_2$ converts irreversibly to $\beta\text{-PbF}_2$ at elevated temperatures, the α to β conversion starts at temperatures greater than 600°K (13), i.e., beyond the temperature range employed in this study. The conductivity activation enthalpy for undoped $\alpha\text{-PbF}_2$ is found in the range $0.51\text{--}0.56$ eV (13, 16), i.e., values that are lower than the observed ΔH values. Therefore, anode passivation is not caused by $\alpha\text{-PbF}_2$. The cell-discharge experiments were all performed in air. Under these conditions mixtures of $\alpha\text{-PbF}_2$ and $\text{Pb}_2\text{O}_2\text{F}_2$ can be formed at the anode (13-15). The conductivity of the nominally pure $\text{Pb}_2\text{O}_2\text{F}_2$ is well below that of the metal fluorides in the cells. The conductivity activation enthalpy of 0.66 eV is in agreement with the observed ΔH values. Therefore, we propose that the anode passivation layers in the present cells consist mainly of $\text{Pb}_2\text{O}_2\text{F}_2$.

The present cells are rechargeable with decomposition of $\text{Pb}_2\text{O}_2\text{F}_2$ as is indicated by the R_{dc} values. They increase on discharge and decrease to their initial value on charging. Cyclic voltammograms of the asymmetric cells $\text{Pb}|\beta\text{-PbF}_2|\text{C}$ in air confirm that the presence of $\text{Pb}_2\text{O}_2\text{F}_2$ does not affect the rechargeability of the present galvanic cells (14).

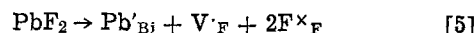
The use of Ca as the anode leads to the formation of CaF_2 during discharge in N_2 . The conductivity of nominally pure CaF_2 is so low that it leads to anode passivation. For the cell $\text{Ca-BiO}_{0.1}\text{F}_{2.8}$ ΔH has the value 0.88 eV. This value is close to the activation enthalpy of the mobility of fluoride interstitials in CaF_2 , i.e., 0.92 eV (17). In comparison to the cells with Pb as anode, this cell has a rather high value for R_{dc} .

The present study reveals that at about 500°K capacities of 2C can easily be obtained with cells utilizing Pb as the anode, despite the formation of the described anode passivation layers.

Bismuthtrifluoride.— BiF_3 is an ionic conductor with fluoride ion vacancies as the mobile species. The aliovalent dopants KF and PbF_2 increase the fluoride ion vacancy concentration according to



and



respectively. In view of the preparation technique the extrinsic conductivity of our undoped BiF_3 is probably governed by the presence of oxide ions, i.e., $[\text{O}'_{\text{F}}] = [\text{V}'_{\text{F}}]$. The conductivity data lead to a concentration of about 30 ppm. In addition, the conductivity data were used to calculate the temperature dependence of the mobility of the fluoride ion vacancies. We obtained

$$\mu(\text{V}'_{\text{F}}) = \frac{14.6}{T} \exp\left(-\frac{0.44 \text{ eV}}{kT}\right) \frac{\text{m}^2}{\text{Vs}} \quad [6]$$

The total electronic current I through the polarization cell $(-)\text{Bi}|\text{BiF}_3:\text{KF}|\text{Ag}(+)$ can be expressed by (18)

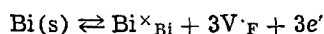
$$I = \frac{kT}{qL} \left\{ \sigma_{\text{n}}^0 \left[1 - \exp\left(-\frac{qE}{kT}\right) \right] + \sigma_{\text{p}}^0 \left[\exp\left(\frac{qE}{kT}\right) - 1 \right] \right\} \quad [7]$$

L denotes the cell constant, σ_{n}^0 , and σ_{p}^0 are the specific electron and electron hole conductivity for $\text{BiF}_3(\text{:KF})$ in contact with Bi . E denotes the applied d-c voltage, whereas q , k , and T have their usual meaning. For $\sigma_{\text{n}}^0 \gg \sigma_{\text{p}}^0$ the current-voltage curve will show a saturation current at low voltages

$$I = \frac{kT}{qL} \sigma_{\text{n}}^0 \quad [8]$$

which depends on the extrinsic region of the conductivity on the purity of the ionic conductor. The data in Fig. 4 do not reveal a distinct saturation current, but as has recently been shown by Fang and Rapp (19) such data clearly indicate n-type conductivity. The present data lead to a value of about 9.3×10^{-5} sec m^{-1} for the specific electron conductivity in $BiF_3:KF$ (~ 60 ppm) at $373^\circ K$. At that temperature the bulk ionic conductivity reads 1.12×10^{-2} sec m^{-1} , thus confirming that $BiF_3:KF$ is a predominate ionic conductor.

The equilibrium between BiF_3 and metallic Bi can be represented by



with

$$K = [V_F]^3 [e']^3 \quad [9]$$

For $BiF_3:KF$ the electroneutrality condition reads

$$n + 2[K''_{Bi}] = [V_F] \quad [10]$$

For the electron concentration n we obtain from Eq. [9] and [10]

$$n = -[K''_{Bi}] + ([K''_{Bi}]^2 - K^{1/3})^{1/2} \quad [11]$$

This relation predicts that n decreases upon doping with aliovalent dopants that increase the fluoride ion vacancy concentration. This result is independent of whether Schottky- or anti-Frenkel disorder governs the thermal generation of the ionic point defects in BiF_3 . Tysonite-related $BiO_{0.1}F_{2.8}$ behaves like oxide-doped BiF_3 in the galvanic cells. The concentration of fluoride ion vacancies in this material is much larger than in the employed $BiF_3:KF$, which revealed n-type conductivity. Electron currents could not be measured in $BiO_{0.1}F_{2.8}$ in contact with Bi. Instead electron hole currents were observed (3). This is in line with $BiO_{0.1}F_{2.8}$ behaving as oxide-doped BiF_3 .

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An Electrochemically Regenerative Hydrogen-Chlorine Energy Storage System

A Study of Mass and Heat Balances

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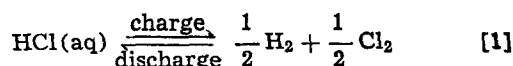
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ABSTRACT

A study has been made to characterize the operating conditions of an electrochemically regenerative hydrogen-chlorine energy storage system. A non-steady-state mass and heat balance was used to determine the changes in the electrolyte concentration, temperature, cell voltage, and flow rate requirements during charge and discharge. The over-all electric-to-electric efficiency was calculated for various operating overvoltages. A simple thermal analysis is also presented for estimating temperature excursions and system performances.

An electrochemically regenerative hydrogen-chlorine cell has recently been considered for electric utility

load leveling applications (1-3). The over-all reaction is



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