**Fluoride Ion Conductive Polymer Electrolytes for All-solid-state Fluoride Shuttle Batteries**

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**Abstract**

To control the fluoride dissociation and conduction of polyether-based solid polymer electrolytes, an electrolyte system composed of a host polymer, metal salt, and anion acceptor was proposed. Appropriate choices of metal salt with low lattice enthalpy and anion acceptor concentration were important to obtain polymer electrolytes with high fluoride conductivity. The results of thermal and electrochemical measurements revealed that the optimal electrolyte system displayed a relatively high fluoride conductivity of ca. $1 \times 10^{-5}\text{ S cm}^{-1}$ at 303 K and fluoride transference number of over 0.8 (80%).

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**Keywords** : Fluoride Shuttle Battery, All-solid-state Battery, Solid Polymer Electrolyte, Transference Number

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1. Introduction

Continued performance improvements of secondary batteries are strongly desired to reach advanced energy storage targets for electric vehicles and unstable natural energy sources like wind and solar power. Lithium-ion batteries (LIBs) are now widely used as power sources with high energy density and long cycle life.1–3 However, the development of innovative battery systems is needed because of the materials limits of LIBs in terms of the energy density of lithium sources with high energy density and long cycle life.1

Recently, fluoride shuttle batteries (FSBs) have been attracting attention as alternative battery systems to conventional LIBs because of their higher energy density.3 Generally, FSBs contain a metal fluoride (MF$_x$) and metal element (M’) as positive and negative electrodes, respectively (M and M’ are different metal elements). The charge-discharge reactions in such an FSB can be expressed as follows,

\[
\text{(discharged state)} \quad \text{(charged state)}
\]

Positive electrode: $M + xF^- \leftrightarrow MF_x + xe^-$

Negative electrode: $M'F_x + xe^- \leftrightarrow M' + xF^-$

FSBs operate through the ionic conduction of fluoride ($F^-$) as a carrier species and stable redox reactions at the multivalent metal electrodes, and exhibit high-voltage multielectron transfer reactions during conversion-type charge-discharge operation. MF$_x$ compounds have high energy density as electrode active materials because of their low molecular weight. However, many fluoride compounds (salts) shows strong coulombic interaction, which inhibits their dissociation. Therefore, improvement of the ionic conductivity of $F^-$ is required. To overcome the issues limiting the ionic conduction of $F^-$, a sufficient concentration of MF salts in the electrolyte solution to realize high ionic conductivity is required.4,5 Generally, MF salts have quite high lattice enthalpy derived from their electronegativity, so they are difficult to dissolve in polar organic solvents irrespective of the dielectric constant, making it hard to realize desired $F^-$ concentrations.

To address this problem, MF salt-free inorganic solid electrolyte systems have been proposed for FSBs. For example, Reddy and Fichtner reported relatively high ionic conductivity of over $10^{-3}\text{ S cm}^{-1}$ and charge-discharge operation of various $[MF_x \mid Ce$ metal] cells at 423 K using La$_{1-x}$Ba$_x$F$_{3}$ electrolytes.8 Inorganic solid electrolytes have large resistance components derived from grain-boundary and interfacial resistance with electrodes and mechanical issues in the case of thin films, although such electrolytes exhibit suitable performance at present.9 Based on this background, recently, FSB liquid electrolytes containing an anion acceptor (AA) to dissociate the MF salt have been developed.10 Most AAs are tertiary boric compounds that can selectively trap $F^-$, which leads to sufficient dissolution of MF salt in the organic solvent. Although basic charge-discharge operations of FSBs with liquid electrolyte systems have been reported, the dissolution of electrode active materials and operation mechanisms need to be studied to allow their practical application.

Many researchers have investigated solid polymer electrolyte systems consisting of poly(ethylene)oxide (PEO) and metal salts.11,12 Either oxygen of PEO can coordinate with M+ by dipole interactions, and M+ are conducted by segmental motion of the flexible PEO chains above their glass transition temperature ($T_g$).11 An ideal polymer electrolyte system exhibits high flexibility, good mechanical properties, and easily forms suitable interfaces between solid-state electrodes, even in the thin-film state. To date, PEO-based electrolytes have been used as cationic (particularly Li+) conductors...
with a relative low transference number ($t_{Li^+} < 0.1$). If we can develop a polymer electrolyte system for FSBs, a high $F^–$ transference number ($t_F^–$) is expected. In this study, we investigate solid polymer electrolyte systems consisting of a PEO-based $F^–$-conductive polymer, MF salt, and AA. The effects of different MF salts (LiF and NaF) and AA concentration on the PEO matrix are precisely analyzed by thermal and electrochemical measurements.

### 2. Experimental

#### 2.1 Sample preparation

All procedures were conducted in an argon-filled glovebox ($O_2 < 10 ppm$, dewpoint $< 193 K$, Miwa Manufacturing Co., Ltd.)$^{11-13}$ The P(EO/$PO$)/MF (M = Li, Na)/AA (trimethoxyboroxine, C$_3$H$_9$B$_3$O$_6$) polymer electrolytes were prepared by photo-initiated radical polymerization using 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a photoinitiator. A cross-linked network polymer produced from a P(EO/$PO$) triacrylate macromonomer (number average molecular weight $M_n$ = 8,000, Dai-ichi Kogyo Seiyaku Co.) was used as the matrix of $F^–$-conductive polymer electrolytes. MF ([Li]/[O] = 0.02 and [Na]/[O] = 0.04 per mole of oxygen units of P(EO/$PO$), AA, and DMPA (0.1 wt% based on the macromonomer) were added to a mixture of the P(EO/$PO$) macromonomer to form a homogeneous solution. The AA concentration was defined as an MF:AA molar ratio of $1:x$. The solution was spread between two glass plates separated by poly(tetrafluoroethylene) spacers (Teflon, 0.5 mm thick) and irradiated with UV light to induce the cross-linking reaction of the macromonomers. Transparent and self-standing polymer electrolyte films were obtained in all cases.

**Figure 1.** DSC thermograms of P(EO/$PO$)/MF/AA polymer electrolytes with M of (a) Li and (b) Na (heating rate: 10 K min$^–1$). Glass transition temperature ($T_g$) was determined as a function of AA concentration (c).

#### 2.2 Measurements

The thermal properties of the prepared polymer electrolytes were evaluated by differential scanning calorimetry (DSC, Thermo plus EVO2/DSC, Rigaku) under N$_2$ atmosphere. The samples for DSC measurements were tightly sealed in Al pans in a dry argon-filled glovebox. Thermograms for the P(EO/$PO$)/MF/AA polymer electrolytes were recorded during a cooling scan from room temperature to 173 K followed by a heating scan from 173 K to 373 K at the same cooling and heating rate of 10 K min$^–1$. $T_g$s were determined as the onset temperature of the heat capacity change in the DSC thermograms during the programmed heating step. The ionic conductivity ($\sigma$) was measured in a hermetically sealed cell by AC impedance measurements from 353 K to each target temperature without any thermal treatment. The polymer electrolyte films were cut into disks with a diameter 12 mm and then sandwiched between mirror-finished stainless-steel blocking electrodes. The measurements were conducted at controlled temperatures with cooling (ESPEC, SU-262). A computer-controlled electrochemical measurement system (VSP, Bio-Logic, 200 kHz–50 mHz; applied voltage: 100 mV) was used for AC impedance measurements. The samples were thermally equilibrated at each temperature for at least 90 min prior to the impedance measurements.

The interfacial properties of the P(EO/$PO$)/MF/AA polymer electrolytes and metallic electrode were investigated in [metallic electrode] polymer electrolyte [metallic electrode] symmetric cells by the AC impedance method using the electrochemical measurement system (VSP, Bio-Logic). First, the dependence of interfacial resistance on storage time was monitored for the prepared cells at 333 K at 5 h intervals. After 200 h of stabilized the interfacial resistances, the apparent cationic transport number ($t_{cation^+}$) was determined by AC impedance measurements at an extremely low frequency range of 200 kHz to 10 µHz, applied voltage of 10 mV, and temperature of 333 K.

#### 3. Results and Discussion

##### 3.1 Thermal properties of $F^–$-conductive polymer electrolytes

Figure 1(a) and 1(b) show the DSC thermograms of the P(EO/$PO$)/MF/AA polymer electrolytes containing LiF and NaF, respectively. All electrolytes exhibited clear thermal transition (i.e., $T_g$) between glass and rubber states irrespective of their salt species and AA concentration. When the AA concentration was low ($x < 1$), obvious exothermic/endotherm peaks corresponding to recrystallization/melting processes were observed. Figure 1(c) shows $T_g$ of the P(EO/$PO$)/MF/AA polymer electrolytes, determined by DSC, as a function of AA concentration. Almost the same $T_g$ of ca. 210 K was observed in the case of the LiF-containing electrolytes regardless of AA concentration. Generally, metal cations in a polymer electrolyte with a PEO-based matrix form transient cross-linking points with ether oxygen through ion-dipole interactions. If dissociation of LiF was promoted by AA addition, $T_g$ should be elevated by the increase of the density of cross-linking points.
because of the increased number of Li–O interactions. However, no marked change of $T_g$ with AA concentration was observed. Therefore, AA addition was considered to have quite a small effect on the dissociation of LiF. For the electrolytes with NaF, $T_g$ increased with AA concentration. Thus, AA was considered to promote the dissociation of NaF by forming quasi cross-linking polymer electrolyte can be described as a coupling system, in which cooperative ionic conduction occurs by segmental motion of rubber-state polyether chains with continuous solvation and desolvation of NaF. This conduction mode should be governed by $T_g$, which was consistent with the increase of $T_g$ with AA content observed in Fig. 1.

### 3.3 Evaluation of anion transport number and effective conductivities for F⁻ conductive polymer electrolytes

Figure 3(a) and 3(b) shows impedance plots of the [Li | (EO/PO)/LiF/AA polymer electrolyte ($x = 10$)] and [Na | (EO/PO)/NaF/AA polymer electrolyte ($x = 10$)] symmetric cells at 333 K, respectively. Samples with relatively high $\sigma$ were used in the cells. Three semicircular arcs with highest, middle, and lowest frequencies of kHz, Hz, and µHz order, respectively, were observed in both impedance plots. The resistance components with high, intermediate, and low frequencies were assigned as electrolyte bulk resistance ($R_b$), electrolyte/metal electrode interfacial resistance ($R_{int}$), and resistance to M⁺ diffusion ($Z_{diff}$), respectively. The M⁺ transference number ($t_{M^+}$) of each polymer electrolyte was determined from AC impedance measurements using Eq. (2).

$$t_{M^+} = \frac{R_b}{(R_b + Z_{diff})}$$  \hspace{1cm} (2)

Calculated $t_{M^+}$ values were 0.13 for the (EO/PO)/LiF/AA polymer electrolyte ($x = 10$) and 0.20 for the (EO/PO)/NaF/AA polymer electrolyte ($x = 10$). In these cases, the mobile ionic species were only M⁺ and F⁻, so the F⁻ transference number ($t_{F^-}$) was given by Eq. (3),...
The obtained $t_{F^{-}}$ values were quite high at 0.87 for the P(EO/PO)/LiF/AA polymer electrolytes ($x = 10$) and 0.80 for the P(EO/PO)/NaF/AA polymer electrolytes ($x = 1$). This is the first insight regarding $t_{F^{-}}$ of F$^{-}$-conductive electrolytes.

Finally, assuming that $t_{F^{-}}$ did not change with temperature, the effective F$^{-}$ conductivities ($\sigma_{F^{-}}$) was calculated using Eq. (4),

$$\sigma_{F^{-}} = t_{F^{-}} \times \sigma$$

Figure 4 depicts the temperature dependence of $t_{F^{-}} \times \sigma$ for the P(EO/PO)/MF/AA polymer electrolytes (M = Li or Na; $x = 10$ for Li, $x = 1$ for Na) upon cooling.

4. Conclusions

We confirmed that inclusion of both an AA and MF salt with low lattice energy in a polyether-based host polymer provided an F$^{-}$-conductive polymer electrolyte for all-solid-state FSBs. AC impedance measurements revealed that the developed electrolyte system exhibited $\sigma_{F^{-}}$ of ca. $1 \times 10^{-6} \text{S cm}^{-1}$ at 303 K. These flexible solid electrolytes with relatively high $\sigma_{F^{-}}$ show promise to improve the performance of FSBs.

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