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Author(s)	Konishi, Hiroaki; Minato, Taketoshi; Abe, Takeshi; Ogumi, Zempachi
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Triphenylboroxine and triphenylborane as anion acceptors for electrolyte in fluoride shuttle batteries

Hiroaki Konishi,*[1], Taketoshi Minato,*[2] Takeshi Abe,*[3] and Zempachi Ogumi,[1]
[1] *Office of Society-Academia Collaboration for Innovation, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan*
[2] *Office of Society-Academia Collaboration for Innovation, Kyoto University, Katsura, Nishikyo, Kyoto 615-8510, Japan*
[3] *Graduate School of Global Environmental Studies, Kyoto University, Katsura, Nishikyo, Kyoto 615-8510, Japan*
E-mail: hiroaki.konishi.yj@hitachi.com (H. Konishi), minato.taketoshi.5x@kyoto-u.ac.jp (T. Minato), abe@elech.kuic.kyoto-u.ac.jp (T. Abe)

For liquid-based fluoride shuttle batteries, electrolyte composed of organic solvent and supporting electrolyte salt is developed. To increase the solubility of supporting electrolyte salt in organic solvent, anion acceptors (triphenylboroxine or triphenylborane) are added. The addition of anion acceptor greatly increases the solubility of supporting electrolyte salt, and discharge-charge reaction of BiF_3 electrode is confirmed in the prepared electrolytes.

Keywords: Fluoride shuttle battery, Anion acceptor, Bismuth fluoride

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Currently, lithium ion batteries (LIBs) are widely used as power sources for electronic devices, and recent developments of devices have necessitated the improvement of energy density for batteries. [1–3] Therefore, many research institutions develop high-energy-density electrode materials for LIBs [4–6] and high-energy-density next-generation batteries.[7–10] Recently, new all-solid-based and liquid-based batteries employing metal fluoride as an active material have been proposed. [11–14] We have focused on liquid-based fluoride shuttle batteries (FSBs).[15] A schematic image of FSB is shown in Figure 1. For positive electrode, metal was formed ($MF_x + xe^- \rightarrow M + xF^-$) during the discharge process, and metal fluoride is formed ($M + xF^- \rightarrow MF_x + xe^-$) during the charge process. To facilitate the electrochemical reaction in a liquid-based electrolyte over a wide potential range, an electrolyte composed of an organic solvent and a supporting electrolyte salt such as a fluoride compound is used. However, fluoride compounds dissolved sparingly in the organic solvent.[15] It is reported that boron-based compounds are used as anion acceptors (AAs), and the addition of AAs in the organic solvent was effective in dissolving insoluble lithium salt for LIBs. [16–18] We previously found fluorobis(2,4,6-trimethylphenyl)borane (FBTMPhB) significantly increased the solubility of cesium fluoride (CsF) in bis[2-(2-methoxyethoxy)ethyl]ether (tetraglyme: G4) as an AA, and discharge and charge reactions of a BiF_3 electrode were progressed using the G4 containing CsF and FBTMPhB as an electrolyte. [15] In order to extend the usability of the FSB, the potential of other compounds as AA should be investigated for the electrolyte. In this work, two boron-containing compounds, triphenylboroxine (TPhBX) and triphenylborane (TPhB), were selected as potential AAs. The anion-accepting tendency of boron-containing compounds has been reported in the context of LIBs owing to the fact that the positively charged boron ions in the AA attract negatively charged fluoride ions, thus, increasing the solubility of fluoride compounds in organic solvents.[19–24] TPhBX contains a boroxine ring and three phenyl groups,[19, 20] whereas TPhB contains a boron atom bound to three phenyl groups.[21–24] Herein, the ability of TPhBX and TPhB to play the role of AAs for electrolytes in FSBs and the electrochemical performance of the BiF_3 electrode were investigated using prepared electrolytes.

The electrolytes for FSBs were prepared by dissolving 0.45 mol dm^{-3} CsF (Tokyo Chemical Industry Co., Ltd) and 0.5 mol dm^{-3} TPhBX (Tokyo Chemical Industry Co., Ltd) or 0.5 mol dm^{-3} TPhB (Tokyo Chemical Industry Co., Ltd) in G4 (KISHIDA CHEMICAL Co., Ltd). These electrolytes are denoted as CsF-TPhBX-G4 and CsF-TPhB-G4, respectively, in the following text. Cyclic voltammetry (CV) experiments were conducted to estimate the range of working potential of these electrolytes. The three-electrode electrochemical cell (EC FRONTIER CO., Ltd. VB7) setup of the CV experiment comprised a platinum foil as the working electrode, a platinum mesh as the counter electrode, and a silver rod immersed in acetonitrile containing 0.1 mol dm^{-3} silver nitrate and 0.1 mol dm^{-3} tetraethylammonium perchlorate as the reference electrode (0.587 V vs. standard hydrogen electrode).[25] CV experiments on the prepared electrolytes were performed at room temperature using a multipotentiostat (Biologic VMP-300) over a –4.0 to 2.0 V (vs. ref.) potential range at a sweep rate of 0.1 mV s^{-1}. BiF_3 (Fluorochem Ltd.) was used as the active material, and was mixed with acetylene black and and polyvinylidene difluoride (60:25:15 wt%) to prepare the electrode. The discharge and charge capacities of the prepared electrode were measured by using it as the working electrode in the three-electrode electrochemical cell with electrolytes CsF-TPhBX-G4 and CsF-TPhB-G4, separately. The whole setup containing the electrochemical cell was housed in an argon atmosphere in a glovebox maintained at room temperature. The charge-discharge measurements were performed using a multipotentiostat (Biologic VMP-300) at 0.025C (1C = 302 mA g^{-1}). The electronic state of Bi from each working electrode containing BiF_3 was analyzed via X-ray photoelectron spectroscopy (XPS; Ulvac Phi Quantera SXM™) using Al Kα X-ray radiation in ultra-high vacuum conditions. After discharging and charging the BiF_3

electrode, it was washed with G4, followed by dimethylcarbonate to remove any residual electrolyte. Next, the BiF_3 electrodes were transferred into an XPS chamber without air exposure using transfer vessels filled with high-purity argon. In the XPS chamber, the surface of the BiF_3 electrode was etched to an estimated depth of 12 nm by an Ar^+ beam to remove any potential contaminants adsorbed during the sample transfer. The binding energy of the obtained spectra was calibrated to that of the Bi $4f_{7/2}$ peak of Bi metal at 156.9 eV. The intensity of the spectra was normalized to the peak area of the Bi $4f_{5/2}$ peaks.

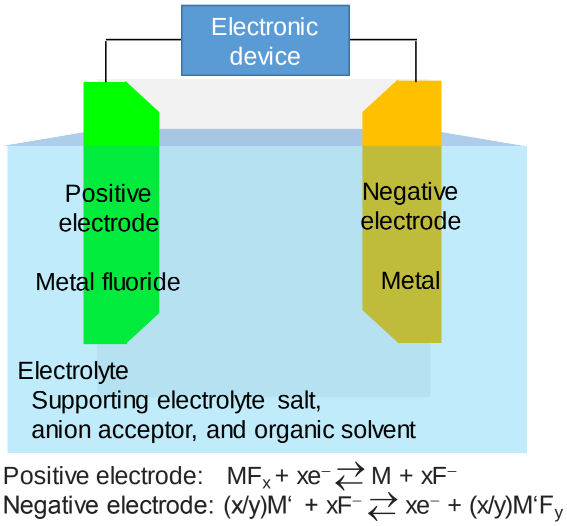

Figure 1. A schematic image of FSB.

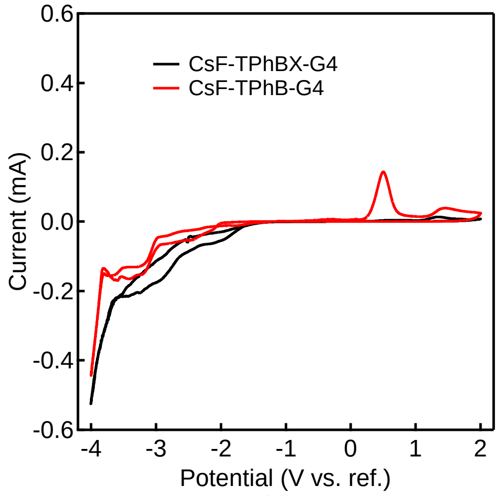

Figure 2. Cyclic voltammograms of a Pt electrode in CsF-TPhBX-G4 and CsF-TPhB-G4. Sweep rate: 0.1 mA s^{-1}. Sweep range: –4.0 - 2.0 V (vs. ref.).

The abilities of TPhBX and TPhB as AAs were investigated by observing the change in the solubility of CsF in G4. Previously, we reported that the solubility of CsF in the G4 is very low (2.6×10^{-5} mol dm^{-3}) without any AAs in the solution.[15] After adding 0.5 mol dm^{-3} TPhBX to G4, up to 0.45 mol dm^{-3} CsF dissolved in G4. This nearly four-order-of-magnitude increase in the solubility of CsF in G4 suggests strong interaction of TPhBX with fluoride ions in G4. Similar results were obtained for TPhB, suggesting the efficacy of both TPhBX and TPhB as AAs for G4.

The potential window of the prepared electrolytes was measured by CV (Figure 2). The reduction peaks in the CV appeared below –1.4 and –1.6 V for CsF-TPhBX-G4 and CsF-TPhB-G4, respectively. With CsF-TPhBX-G4 as the electrolyte, weak oxidation peak was observed due to the decomposition of the electrolyte above 1.0 V. With CsF-TPhB-G4 as the electrolyte, oxidation peaks were observed above 0.2 V. These results indicate that CsF-TPhBX-G4 and CsF-TPhB-G4 are stable between –1.4 and 1.0 V, and between –1.6 and 0.2 V, respectively.

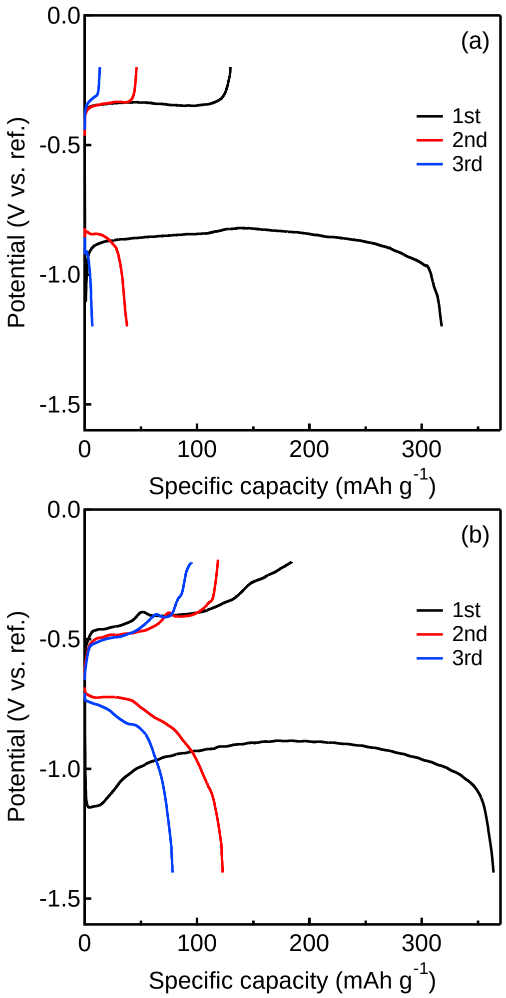

Figure 3. Discharge and charge curves of BiF_3 electrode with electrolyte (a) CsF-TPhBX-G4 within potential range from –1.2 to –0.2 V (vs. ref.) and (b) CsF-TPhB-G4 within potential range from –1.4 to –0.2 V (vs. ref.) in the first, second, and third cycle.

Based on the improved solubility of CsF in G4 by addition of TPhBX or TPhB and electrochemical window measurements, the discharge and charge capacities of BiF_3 were measured by using CsF-TPhBX-G4 and CsF-TPhB-G4 as the electrolytes. The discharge cut-off potential was limited to 0.2 V from the potential window (CsF-TPhBX-G4: –1.2 V and CsF-TPhB-G4: –1.4 V). The charge cut-off potential was limited to –0.2 V. Without AAs, the discharge capacity of the BiF_3 electrode is very low (2.0×10^{-5} mAh g^{-1}).[15] By using CsF-TPhBX-G4, clear improvements in the electrochemical performance were observed, as evident from the first discharge process in Figure 3(a). Here, a plateau at around –0.85 V was observed. The potential of the plateau is almost the same as that for the plateau observed in the electrolyte prepared by CsF, FBTMPhB, and G4 (CsF-FBTMPhB-G4).[15] In CsF-FBTMPhB-G4, the reduction of BiF_3 to Bi metal was observed in the discharge process.[15] This suggests that the reduction of BiF_3 can also proceed in CsF-TPhBX-G4. A discharge capacity of 318 mAh g^{-1} was observed in the first discharge process. The observed capacity is higher than the theoretical capacity (302 mAh g^{-1}) of the BiF_3 electrode, suggesting the reaction of the electrolyte with Bi metal, which forms during the discharge process. Similar behavior was also observed in CsF-FBTMPhB-G4.[15] In the next charge process, a capacity of 130 mAh g^{-1} was obtained. Although the charge capacity was lower than the discharge capacity, the charge capacity was clearly observed. By increasing the cycles, the observed discharge/charge capacities of BiF_3 in the CsF-TPhBX-G4 were changed to 318/130, 38/46, and 7/14 mAh g^{-1} in the first, second, and third cycles, respectively. The discharge and charge capacities decreased as the cycling progressed; however, the discharge and charge reactions progressed from the first to the third cycles. Figure 3(b) shows the discharge and charge curves of the BiF_3 electrode in CsF-TPhB-G4. The discharge/charge capacities of BiF_3 in CsF-TPhB-G4 were 364/184, 123/119, and 78/95 mAh g^{-1} in the first, second, and third cycles, respectively. The change of AA from TPhBX to TPhB improved the discharge and charge capacities and cycling performance. These results indicated that the discharge and charge reactions of the BiF_3 electrode progressed in the electrolyte containing TPhBX or TPhB, and the nature of AA affected the electrochemical performance of the BiF_3 electrode for the FSB.

To confirm the progress of discharge ($BiF_3 + 3e^- \rightarrow Bi + 3F^-$) and charge ($Bi + 3F^- \rightarrow BiF_3 + 3e^-$) reactions in the prepared electrolytes, the changes in the electronic state of Bi in the BiF_3 electrode during the discharge and charge processes were investigated by XPS. The Bi 4f spectra of the BiF_3 electrode in the pristine, fully discharged, and fully charged states prepared in the CsF-TPhBX-G4 and CsF-TPhB-G4 are shown in Figure 4. In Figure 4(a), in the pristine state, large peaks were observed at 160.5 and 165.8 eV, which are assigned to Bi $4f_{7/2}$ and $4f_{5/2}$ spectra for Bi^{3+} in BiF_3.[26, 27] Furthermore, peaks of smaller intensity were observed at 156.9 and 162.2 eV, which are assigned to the Bi $4f_{7/2}$ and $4f_{5/2}$ spectra of Bi metal, respectively.[26–28] This is due to the reduction of BiF_3 by the Ar^+ sputtering.

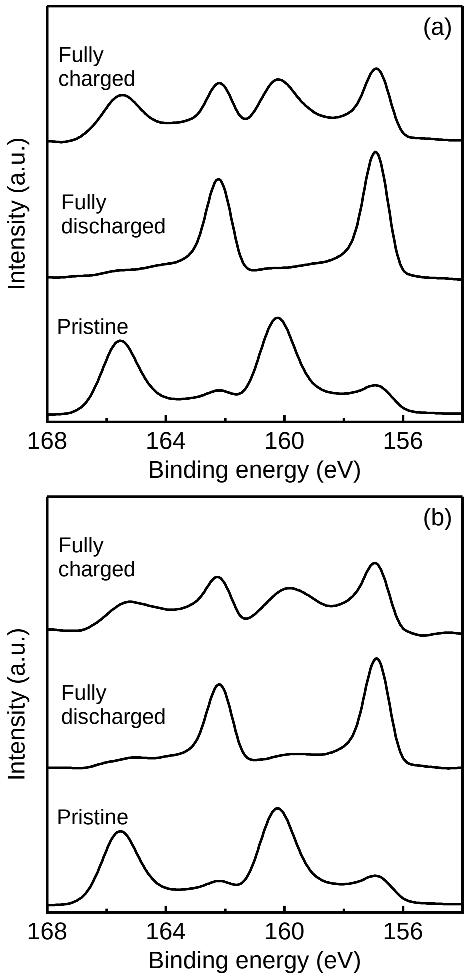

Figure 4. Bi 4f spectra of BiF_3 electrode during the discharge and charge processes in the first cycle [Electrolyte: (a) CsF-TPhBX-G4 and (b) CsF-TPhB-G4].

From the pristine to fully discharged state, the peaks assigned to Bi metal enlarged and the peaks assigned to Bi^{3+} diminished, indicating that Bi is reduced during discharging. From the fully discharged to fully charged states, the peaks assigned to Bi^{3+} appeared and the peaks assigned to Bi metal became smaller. This indicates that Bi is oxidized during charging. As shown in Figure 4(b), the changes in the spectra from the pristine to fully discharged, followed by fully charged state are similar for CsF-TPhB-G4 and CsF-TPhBX-G4 (Figure 4(a)). This indicates that Bi is reduced during discharging and oxidized during charging when using CsF-TPhB-G4. These results support the progress of discharge and charge reactions in both electrolytes.

In summary, the addition of TPhBX and TPhB greatly improved the solubility of CsF in G4. The discharge and charge reactions of the BiF_3 electrode can be progressed using an electrolyte containing TPhBX or TPhB. The cycling performance of the BiF_3 electrode in the electrolyte with TPhB was better than that with TPhBX. The boron-containing compounds can play the role of AAs, and the G4 containing these compounds can be used as electrolytes in

FSBs. The electrochemical performance of the BiF_3 electrode was affected by the nature of AA in the electrolyte. Future work will attempt to investigate the effect of AA nature on the electrochemical performance of the BiF_3 electrode and to improve the cycling performance of the BiF_3 electrode.

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References and Notes

1 Y. Nishi, J. *Power Sources* **2001**, *100*, 101.
2 Y. Wang, B. Liu, Q. Li, S. Cartmell, S. Ferrara, Z.D. Deng, J. Xiao, *J. Power Sources* **2015**, *286*, 330.
3 T. Minato, T. Abe, Prog. *Surf. Sci.* **2017**, *92*, 240.
4 Z. Lu, D.D. MacNeil, J.R. Dahn, Electrochem. *Solid State Lett.* **2001**, *4*, A191.
5 J.O. Besenhard, J. Yang, M. Winter, *J. Power Sources* **1997**, *68*, 87.
6 M.N. Obrovac, L. Christensen, *Electrochem. Solid State Lett.* **2004**, *7*, A93.
7 C. Delmas, J.J. Braconnier, C. Fouassier, P. Hagenmuller, *Solid State Ion.* **1981**, *3–4*, 165.
8 D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R. Turgeman, Y. Cohen, M. Moshkovich, E. Levi, *Nature* **2000**, *407*, 724.
9 A. Eftekhari, *J. Power Sources* **2004**, *126*, 221.
10 K.M. Abraham, Z. Jiang, *J. Electrochem. Soc.* **1996**, *143*, 1.
11 M. A. Reddy, M. Fichtner, *J. Mater. Chem.* **2011**, *21*, 17059.
12 C. Rongeat, M. A. Reddy, R. Witter, M. Fichtner, J. Phys. Chem. C **2013**, *117*, 4943.
13 A. Grenier, A.Porras-Gutierrez, H. Groult, K.A. Beyer, O.J. Borkiewicz, K.W. Chapman, D. Dambournet, *J. Mater. Chem. A* **2017**, *5*, 15700.
14 M.A. Nowroozi, K. Wissel, J. Rohrer, A.R. Munnangi, O. Clemens, *Chem. Mater.* **2017**, *29*, 3441.
15 H. Konishi, T. Minato, T. Abe, Z. Ogumi, *J. Electrochem. Soc.* **2017**, *164*, A3702.
16 H.S. Lee, X. Sun, X.Q. yang, J. McBreen, *J. Electrochem. Soc.* **2002**, *149*, A1460.
17 B. Xie, H.S. Lee, H. Li, X.Q. Yang, J. McBreen, L.Q. Chen, *Electrochem. Commun.* **2008**, *10*, 1195.
18 L.F. Li, H.S. Lee, H. Li, X.Q. Yang, K.W. Nam, W.S. Yoon, J. McBreen, X.J. Huang, *J. Power Sources* **2008**, *184*, 517.
19 V.P. Reddy, M. Blanco, R. Bugga, *J. Power Sources* **2014**, *247*, 813.
20 V.P. Reddy, E. Sinn, N. Hosmane, *J. Organometal. Chem.* **2015**, *798*, 5.
21 M. Marcinek, G.Z. Zukowska, W. Wieczorek, *Electrochim. Acta* **2005**, *50*, 3934.
22 G. Zukowska, M. Szczechura, M. Marcinek, A. Zubrowska, A. Adamczyk-Wozniak, A. Sporzynski, W. Wieczorek, *ECS Transactions* **2009**, *16*, 105.
23 M. Ciosek, M. Marcinek, G.Z. Zukowska, W. Wieczorek, *Electrochim. Acta* **2009**, *54*, 4487.
24 A. Adamczyk-Wozniak, M. Jakubczyk, A. Sporzynski, G. Zukowska, *Inorg. Chem. Commun.* **2011**, *14*, 1753.
25 V.V. Pavlishchuk, A.W. Addison, *Inorg. Chim. Acta* **2000**, *298*, 97.
26 W.E. Morgan, W.J. Stec, J.R.V. Wazer, *Inorg. Chem.* **1973**, *12*, 953.
27 A.J. Gmitter, A. Halajko, P.J. Sideris, S.G. Greenbaum, G.G. Amatucci, *Electrochim. Acta* **2013**, *88*, 735.
28 B. Hu, X. Wang, H. Shu, X. Yang, L. Liu, Y. Song, Q. Wei, H. Hu, H. Wu, L. Jiang, X. Liu, *Electrochim. Acta* **2013**, *102*, 8