

Electrochemical properties of boric ester electrolytes with high potential cathode for lithium ion batteries

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Introduction

Lithium-ion batteries are currently produced on a large scale mainly as equipment for powering portable electronic devices, but simultaneously intensive research is carried out on the development of large and high power batteries for powering hybrid electric vehicles (HEVs) and plug-in HEVs.

We have reported that boric ester electrolytes showed the high oxidation potential. Boric esters exhibit preferable physical and electrochemical properties that are tunable due to substituents R (Fig. 1). The boron atom possesses a vacant *p*-orbital and thus Lewis acid. They are able to bind the counter anions of lithium salts and solvent molecules. Boric esters could be synthesized from inexpensive starting materials such as boric acid (B(OH)₃) and alcohols. A boric ester is found to have a high oxidative stability, therefore the use of LiNi_{0.5}Mn_{1.5}O₄ (LNM) can be expected. In this study, we measured charge-discharge of Li/LNM cell in boric ester electrolyte.

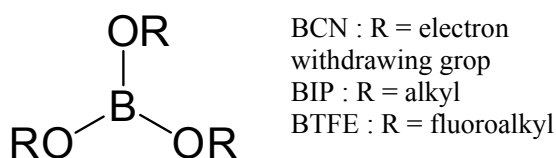


Fig. 1 Chemical structures of boric esters.

Table 1 Compositions of electrolytes.

| Electrolyte | Salts [mol kg ⁻¹] | Solvents |
|-------------|-------------------------------|--|
| A | LiBF ₄ = 1.0 | EC/EMC = 1/1 (vol) |
| B | LiBF ₄ = 0.7 | BIP/BCN = 1/2 (mol) |
| C | LiBF ₄ = 1.0 | BTFE/BCN = 1/2 (mol) + EC/EMC = 1/1 (vol) = 1/1 (vol) |

Experimental

Boric ester synthesized boric acid (B(OH)₃) and alcohols. Composition of liquid electrolytes were shown in Table 1. Li/LNM cell was prepared, then the cell charge-discharge measurement was performed.

Result and discussion

Charge-discharge behaviors of Li/LNM cell in electrolyte A indicate the large irreversible current probably resulting from oxidative decompose of EC/EMC. However, the cell was operated in electrolyte B and C up to 20 cycles. This is considered to be for high anodic stability of boric ester electrolyte.

Conclusion

The Li/LNM cell with high potential cathode was operated in boric ester electrolyte.

Reference

- 1) Y. Yalyosef, et al, *J. Power Sources*. 106 (2005)

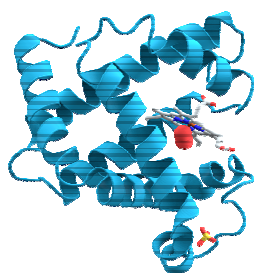
Synthesis and evaluation of a molecule which has the molecule oxygen capture ability

Shota TEZUKA

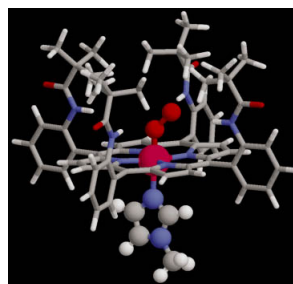
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Blood is an electrolyte in which salts and proteins are dissolved. One of the functions of blood is to bind the molecular oxygen at the lung and to bring them to distal cells to maintain an animal life. Heme proteins such as myoglobin (1) play a central role for absorption and desorption of the molecular oxygen. Eventually the molecular oxygen immediately dissolves in blood than in normal saline. Attention has been long paid to pioneer the artificial blood system so as to create a blood substitute for instance.

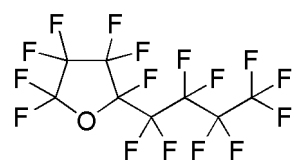
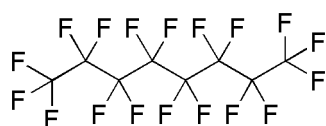
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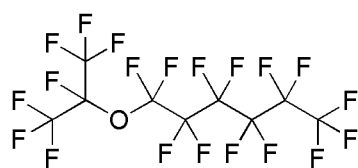
Myoglobin (1)



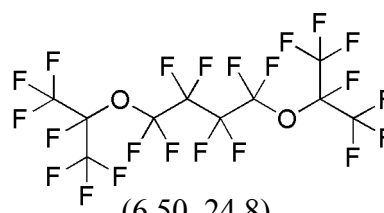
Picket fence porphyrin (2)



(5.60, 22.3)



(6.60, 25.0)

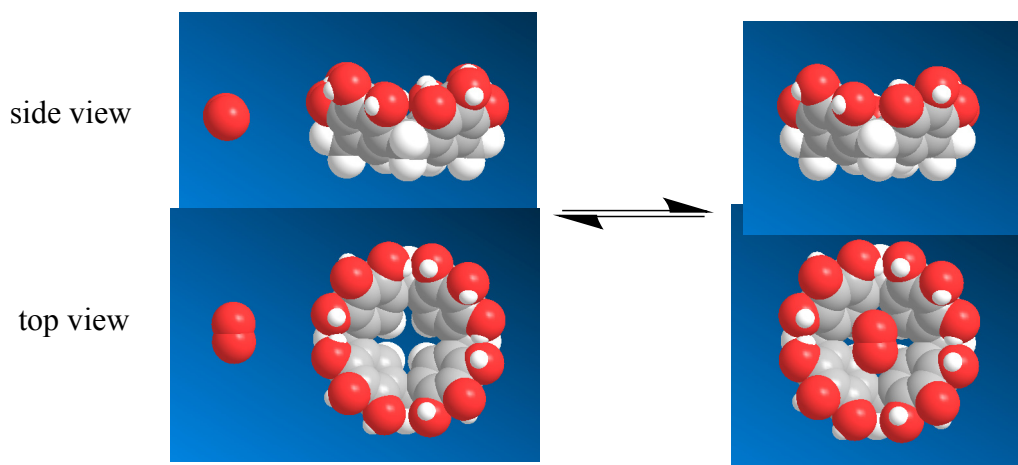


(6.50, 24.8)

Perfluorocarbons (3): the numbers in parentheses denote the solubility of molecular oxygen and carbon dioxide as molar ratio (solute mol $\times 10^3$ /solvent mol).

Synthetic hemes, such as iron (II) picket fence porphyrin (2),¹ took part in this exploration giving rise to a clue to the rudimentary knowledge of the blood function, but these synthetic molecules were unsuitable for quantity production. Perfluorocarbons (3) also absorb the molecular oxygen but the practical application of these remains mostly

unexploited.^{2,3,4}



Scheme 1 Schematic representation of reversible molecular oxygen absorption-desorption with a synthetic aromatic

Recently we have found that a newly designed electron-sufficient aromatic is capable of interacting with the molecular oxygen in solution. The fluorescence from the aromatic decreases as the oxygen gas was introduced into the solution probably because of the resulting proximity of the oxygen to the aromatic: the photo-excited energy at the aromatic seems to be inactivated by the O-O vibration in the molecular oxygen bound. The fluorescence intensity partially recovers upon introducing an inert gas (N_2 , Ar) into the solution indicating that the interaction observed is reversible (Scheme 1). A simple phenol derivative also decrements its fluorescence when the oxygen gas was introduced but the bathochromic shift occurs simultaneously. Furthermore the decrescence and shift are irreversible. These exhibit that the aromatic enables the reversible oxygen absorption while a simple phenol derivative merely undergoes irreversible oxidation.

1. "Picket fence porphyrins. Synthetic models for oxygen binding hemoproteins," Collman, J. P.; Gagne, R. R.; Reed, C.; Halbert, T. R.; Lang, G.; Robinson, W. T. *J. Am. Chem. Soc.*, **1975**, *97* (6), 1427–1439.
2. "Survival of Mammals Breathing Organic Liquids Equilibrated with Oxygen at Atmospheric Pressure," Clark, L. C., Jr.; Gollan, F. *Science* **1975**, *152*, 1755–1756.
3. "The Effects of Structure on the Viscosities of Perfluoroalkyl Ethers and Amines," Brice, T. J.; Coon, R. I. *J. Am. Chem. Soc.* **1953**, *75*, 2921–2925.
4. "Physical Properties and Gas Solubilities in Selected Fluorinated Ethers," Tham, M. K. et al. *J. Chem. Eng. Data* **1973**, *18*, 385–386.

Charge-discharge behaviors of carbonate ester electrolytes containing alkoxyboroxine

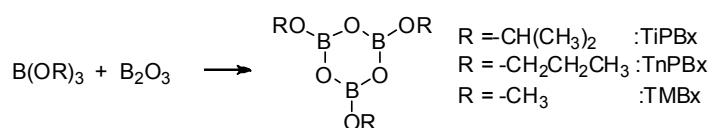
50912098 Naoki Numada

Introduction

We have recently shown that a specific alkoxyboroxine of tri-isopropoxy boroxine (TiPBx) highly stabilized interfacial reactions between both the cathode/anode and carbonate ester electrolyte probably resulting from formation of a stable solid state electrolyte interface (SEI).¹⁾ Here we report on the further efficiency of alkoxyboroxines at low concentration (ca. 0.01 mol kg⁻¹) and on charge-discharge behaviors of the lithium ion battery with the electrolyte containing alkoxyboroxines.

Experimental

Alkoxyboroxines were synthesized from boric acid anhydride (B₂O₃) and corresponding boric esters (B(OR)₃). The electrolytes were prepared from alkoxyboroxines dissolving into 1.0 mol kg⁻¹ LiBF₄ in EC (ethylene carbonate)/EMC (ethyl methyl carbonate) (1/1 vol). The charge-discharge behaviors were conducted with the LiMn₂O₄ cathode and Li metal anode. The anodic stability of electrolytes was evaluated by Cyclic voltammetry (CV) with LiMn₂O₄ thin film cathode.



Scheme.1 synthesis of Alkoxyboroxines

Result and discussion

Chemical structures of alkoxyboroxines were drawn in the inset of Fig.1 and the discharge capacity as the index of charge-discharge behavior was shown in Fig.1. The capacity decreased for the electrolyte without TiPBx while it was improved on addition of a small amount of TiPBx (0.01 mol kg⁻¹). In contrast to TiPBx, TnPBx showed low effect. TMBx indicated rather negative effect as compared with additive free. CV measurements exhibited that the interface of electrolytes/LiMn₂O₄ thin film was highly stabilized at the high voltage even at the low TiPBx concentration presumably because of formation of stable SEI. In fact the secondary ion-microprobe mass spectrometry indicated existence of B atom at the LiMn₂O₄ thin film surface.

Acknowledgement

We acknowledge NEDO of Japan for finance support.

References

1) T. Horino et al., *J.Electrochem.Soc.*, 157 (2010) 677.

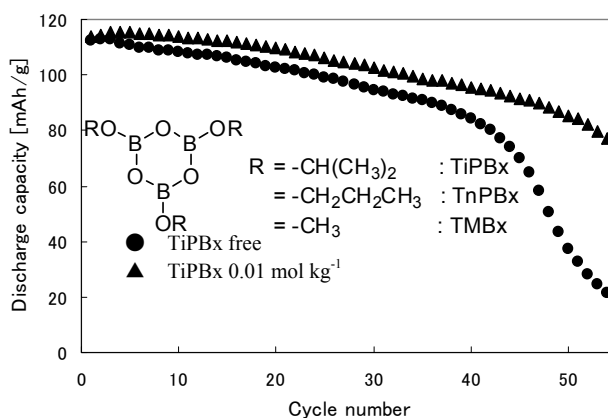


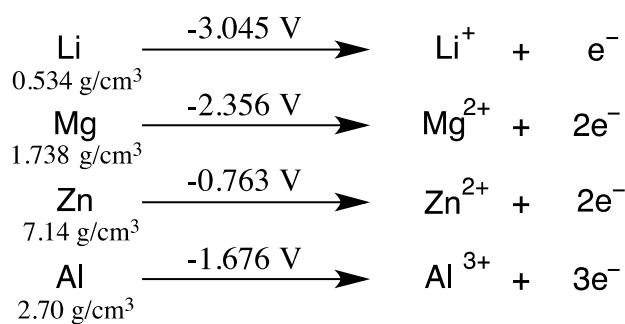
Fig.1 Discharge capacity vs cycle number. electrolyte: 1.0 mol kg⁻¹ LiBF₄ in EC/EMC (1/1 vol) with/without TiPBx, cathode: LiMn₂O₄, anode: Li, cut-off voltage: 3.5-4.7 V, rate: 0.5 C, temperature: 30⁰C.

Synthesis of magnesium salt for multivalent ion secondary battery

Kosuke MIZUNO

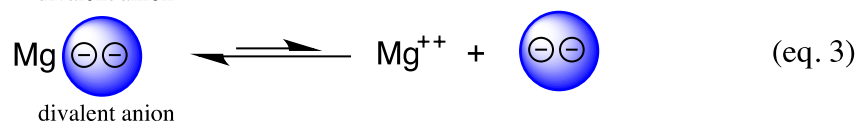
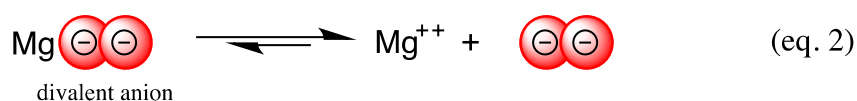
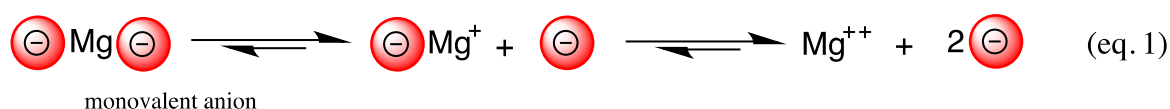
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The urgent and general requirements for secondary batteries are to be small and light: thus a battery possessing high energy density per unit volume ($V \cdot A \cdot \text{hour}/\text{dcm}^3$) and mass ($V \cdot A \cdot \text{hour}/\text{kg}$) is highly demanded. Alkali metals such as lithium and sodium lose one electron upon oxidation while multivalent metals such as magnesium, zinc, or aluminum give multi electrons. Therefore a multivalent ion battery may increase its energy density. The oxidation reactions, redox potentials, and densities of the metals are summarized in Scheme 1.



Scheme 1 Oxidation reactions, redox potentials, and densities of lithium, magnesium, zinc, and aluminum.

The magnesium recently attracts attentions among the multivalent metals due to low reactivity and abundance. Thus magnesium metal could be adopted as the anode material bringing about the extremely high capacity battery. However battery materials especially for the cathode and electrolyte are still underdeveloped and bound candidates are not yet brought forward so far. A magnesium supporting salt as an electrolyte component is also well unexplored yet. A salt pairing with two monovalent anion such as chloride (Cl^-) involves the two-step dissociation which always indicates low dissociation constant in total (equation 1). A salt pairing with one divalent anion such as sulfonate (SO_4^{2-}) also shows low dissociation constant because of the localized two negative charges (equation 2). A divalent anion in which the charges are delocalized is required (equation 3).



Recently we have found that a divalent anion possessing cluster structure exhibits the two negative charges are delocalized on all over anion surface promising high dissociation degree (**Figure 1**). Then we have synthesized the magnesium salt with the dianion by means of the cation exchange procedure.

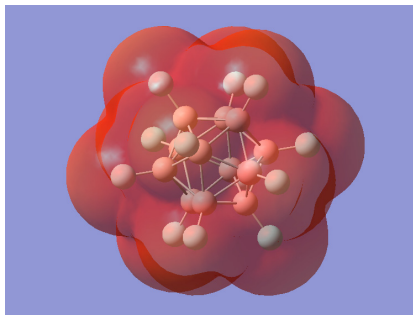


Figure 1 The most stable structure and electron distribution (red) of the cluster dianion by theoretical calculation (B3LYP/6-311+G(d,p))

1. "Picket fence porphyrins. Synthetic models for oxygen binding hemoproteins," Collman, J. P.; Gagne, R. R.; Reed, C.; Halbert, T. R.; Lang, G.; Robinson, W. T. *J. Am. Chem. Soc.*, **1975**, 97 (6), 1427–1439.
2. "Survival of Mammals Breathing Organic Liquids Equilibrated with Oxygen at Atmospheric Pressure," Clark, L. C., Jr.; Gollan, F. *Science* **1975**, 152, 1755–1756.
3. "The Effects of Structure on the Viscosities of Perfluoroalkyl Ethers and Amines," Brice, T. J.; Coon, R. I. *J. Am. Chem. Soc.* **1953**, 75, 2921–2925.
4. "Physical Properties and Gas Solubilities in Selected Fluorinated Ethers," Tham, M. K. et al. *J. Chem. Eng. Data* **1973**, 18, 385–386.

Novel liquid electrolyte with nitrile compound possessing high oxidation potential

50912100 Miho Hatazaki

Introduction

The urgent and general requirement for lithium ion batteries installed in vehicles is to be small and light: thus a battery exhibiting high energy density per unit volume ($V \cdot A \cdot \text{hour}/\text{cm}^3$) and mass ($V \cdot A \cdot \text{hour}/\text{kg}$) is highly demanded. Attention has been therefore paid to development of a novel liquid electrolyte possessing high oxidation potential. Nitrile compounds such as adiponitrile generally have high oxidation potential but lack the high dipole moment resulting in low dielectric constant. Here we synthesize a nitrile compound with high oxidation potential as well as high dipole moment.

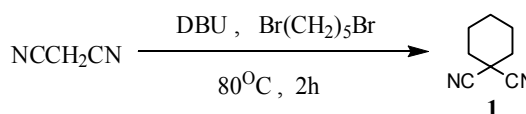
Experimental

1 was synthesized from malononitrile and 1,5-dibromopentane according to Scheme 1. Liquid electrolytes were prepared by dissolving of LiPF_6 in a mixed solvent of ethylene carbonate/ethyl methyl carbonate /**1** (1/1/1 weight, 1.0 mol/kg). I measured ionic conductivity of this electrolyte. Oxidation potential of the electrolytes was evaluated by linear sweep voltammetry (LSV). Intermolecular interaction of carbonate and **1** molecules was estimated by ^1H - and ^{13}C -NMR spectroscopy.

Results and discussions

Ab initio calculation with B3LYP/6-311+G** indicates that **1** has the high dipole moment of 5.246 debye while adiponitrile has 0.0 debye. The ionic conductivity has improved when **1** was added into EC/EMC (**Fig. 1**). This was derived from the valid dielectric constant of the electrolyte

resulting from high dipole moment in **1**. LSV indicated that the carbonate ester electrolyte showed the oxidation potential at 4.5 V while the electrolyte with **1** showed at 5.3 V (**Fig. 2**). NMR spectroscopy suggested the intermolecular interaction between carbonate and **1** molecules. The electron deficient molecule of **1** carrying electron withdrawing nitriles reduced the electron density on the carbonate molecules through the interaction eventually giving high oxidation potential.



Scheme 1 Synthesis of **1**

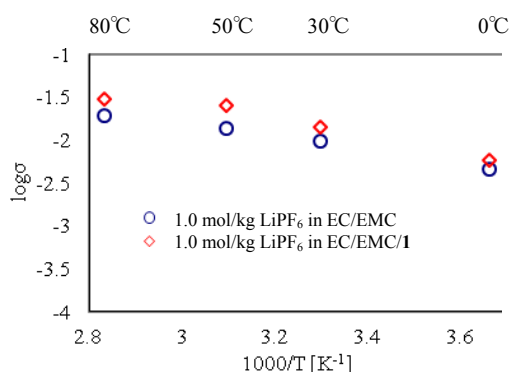


Fig.1 Ionic conductivity for electrolytes. applied voltage: 10 mV, range of frequency: $10^6 \sim 0.1$ Hz

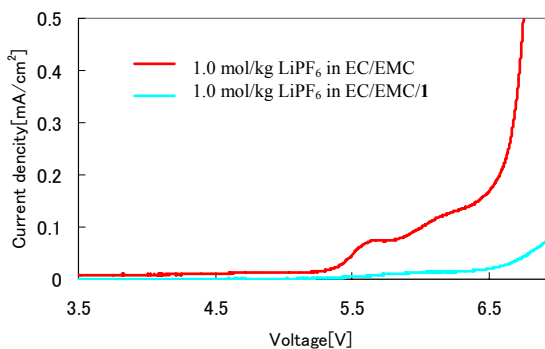


Fig.2 LSV (V vs Li/Li^+) for electrolytes. scan rate: 0.1 mV/sec, working electrode: C, reference electrode: Li.