SYNTHESIS AND STUDIES OF BORON BASED ANION RECEPTORS AND THEIR USE IN NON-AQUOUES ELECTROLYTES FOR LITHIUM BATTERIES

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ABSTRACT

A new family of anion receptors based on boron compounds has been synthesized. These compounds can be used as anion receptors in lithium battery electrolytes and can greatly increase solubility and ionic conductivities of various lithium salts, such as LiF, LiCl, CF_3COOLi and C_2F_5COOLi, in DME solutions. Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy studies show that Cl^- anions of LiCl are complexed with these compounds in DME solutions. The electrochemical stability of lithium salts and one of the boron compounds in deferent solvents was studied. For the first time, LiF has been successfully used as conducting salt in a novel electrolyte with this boron compound as an additive in DME. A rechargeable $Li/LiMn_2O_4$ cell using this electrolyte was successfully cycled 51 times. However, the capacity fades with cycling due to decomposition of the solvent. The cycling performance of the battery was greatly improved by replacing DME with PC-EC-DMC as the solvent.

INTRODUCTION

MASTER

The development of new electrolyte systems for lithium batteries is an active area of research. The goal is to reduce the cost and toxicity and to enhance the safety and performance of lithium batteries. Reduction of ion pairing in non-aqueous electrolytes for lithium batteries is an important way to improve the properties of these electrolytes. Currently, ion pair reduction is achieved by using solvents that have high dielectric constant, salts that are easily dissociated and additives that dissociate the ion pairs (1-3). There have been reports on the use of cation complexing agents such as crown ethers and cryptands as additives to increase the conductivity of non-aqueous electrolytes (4-5). However, the use of anion receptors is a more attractive approach for a lithium battery electrolyte, because anion receptors enhance the dissociation of ion pairs and increase population of free cations in electrolyte which result in an increase of both conductivity and cation transference number.

Previously, we have reported on the synthesis of a series of aza-based anion receptors with electron withdrawing groups (CF_3SO_2) on the nitrogen atoms (6). Recently, we have synthesized a new family of boron based anion receptors. The details about synthesis of

these compounds were reported elsewhere (7). The effect of these boron compounds on the conductivity of simple lithium salts, LiCl, LiF, CF_3COOLi, and C_2F_5COOLi in non-aqueous solvents was studied. Compared to lithium salts used for commercial lithium battery electrolytes, such as $LiPF_6$ and $LiAsF_6$, these salts are low cost and less toxic. The increase of ionic conductivity of these salts in electrolytes with boron based anion receptors as additives will offer the possibility of replacing $LiPF_6$ or $LiAsF_6$ by these salts. The relationship between the conductivity enhancement and the structure of the anion receptors will be discussed. Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy at the Cl K edge was used to study the complexation between these anion receptors and Cl⁻ anion.

In order to further study the possibility of using these boron compounds in electrolyte for lithium batteries, the electrochemical stability of new composite electrolytes were examined. The feasibility of new electrolytes was also tested in rechargeable $Li/LiMn_2O_4$ cell. This paper is a report on these preliminary studies.

EXPERIMENTAL

Materials
The structures of the synthesized compounds and the reference compounds are given in figure 1. Compounds **1** and **7** are commercially available and were used as reference compounds in this study. The other 12 compounds in Fig. 1 were synthesized as described in our previous paper (7). 1 M LiPF6 in PC-EC-DMC (1:1:3) used as the electrolyte in the reference cell was obtained from EM Industries Inc. The $LiMn_2O_4$ cathode material in the test cells was also purchased from EM Industry Inc.

Conductivity Measurements
Conductivity measurements were made at 25 °C using a Hewlett-Packard 4129A Impedance Analyzer in the frequency range from 5Hz to 10 MHz. Cells with Pt electrodes were used for the measurements.

NEXAFS Measurements
NEXAFS measurements were made at the Cl K edge. The measurements were done at Beam Line X19A of the National Synchrotron Light Source. The data were collected as fluorescence excitation spectra using a large solid angle ionization chamber as the fluorescence detector. The solutions after being used in conductivity measurements were poured into cells with thin Mylar windows for NEXAFS studies.

Electrochemical Stability
A Solatron SI 1287 Electrochemical Interface System was used to perform anodic sweep cyclic voltammetry experiments under software control. The scan rate is 20 mV/s. The cell comprised three electrodes, a glassy carbon working electrode (7.0 mm^2), a platinum wire counter electrode and a lithium metal foil reference electrode.

Cell Construction
The composite $LiMn_2O_4$ electrode was made by mixing $LiMn_2O_4$ powder with 10%

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acetylene black and 10% poly(vinylidene fluoride) (PVDF) (KynarFlex 2801, Atochem) in 1-methyl-2-pyrrolidinone, coating this slurry onto a aluminum foil and then drying the electrode in vacuum at 100 °C. The test battery was a two-electrode hermetically sealed prototype cell, consisting of a $LiMn_2O_4$ (EM Industries, Inc) cathode, a lithium foil anode and a Celgard separator. Cell assembly was carried out under an Ar atmosphere. The lithium foil served as both the counter and reference electrodes.

Cycling Performance

Cycling of test batteries was carried out on an Arbin battery test system and the cells were cycled at the C/3 rate between 3.5 and 4.3V.

RESULTS AND DISCUSSION

Table I lists the ionic conductivities of 0.2M lithium salts in DME solutions, as well as the data for solutions with 0.2M various boron based compounds as additives. The ionic conductivities of all the lithium salts in DME solutions are very low. The LiF is insoluble in DME. Addition of compound 1, the unfluorinated alkyl borate, $(CH_3O)_3B$, had a minimal effect on conductivity. However, upon addition of compound 2-6 which have fluorinated electron withdrawing groups attached to the alkyl chain, the solubility of the salts and the conductivies of the solutions were both increased significantly. The conductivities increased with increase of fluorination of these compounds. The most significant increase of conductivity of the lithium salt solutions was obtained by using compound 4 $[(CF_3)_2CHO]_3B$. This is due to the two branched CF_3 groups which have much stronger electron withdrawing effect than a linear structure. The ionic conductivity reached as high as 3.9×10^{-3} S/cm for CF_3COOLi, 4.6×10^{-3} S/cm for C_2F_5COOLi, and 3.8×10^{-3} S/cm for LiCl. However, the solubility of LiF in DME was not significantly improved by using compound 4 as an additive and the conductivity was only 1.3×10^{-5} S/cm. The conductivities of solutions containing compounds 5 and 6 were lower than those containing compound 4 although extra CF_3 in compound 5 and a phenyl group in compound 6 were added. This indicates that steric hindrance effect may impair the ability of boron compounds to complex with anions.

Compounds 7-11 are triaryl borate compounds with a different number of H atoms substituted by fluorine. The unfluorinated compound 7 has very weak effect on conductivities of solutions of lithium salts as was found with compound 3. The ionic conductivities also increased with increasing number of fluorine atom substitutions for compounds 8-11. When these compounds were added to a LiF/DME solution, the conductivities increased from 1.7×10^{-5} S/cm to 2.9×10^{-3} S/cm in going from compound 8 to 11. The conductivities of solutions of all the other salts followed a similar trend. The fully fluorinated triaryl borane, compound 14, also had a large effect on conductivity enhancement.

The effects of the concentration of additives and salts on conductivity were also studied. The three additives, compounds 4, 11 and 14, showing the best conductivity enhancement at 0.2 M concentration, were further studied at higher concentrations and the results are listed in Table II. Because the solubility of these salts is related to the

concentration of the additives, the concentrations of salts are same as those of additives in each solution. A maximum conductivity was reached around 0.8 M. For all of the salt/additive combinations studied, at least one concentration reached conductivity of 6 x 10^{-3} S/cm.

Since both the anion and cation participate in ionic conduction, conductivity studies alone are insufficient evidence for anion complexation by these boron based compounds. Near Edge X-ray Absorption Fine Structure (NEXAFS) technique was used to study the coordination symmetry of anions in solution. The fine structure of the absorption spectrum near the edge provides the information about coordination symmetry of Cl^- anion. Figure 2 shows how the boron based additives with different electron withdrawing groups have a dramatic effect on fine structure of the absorption spectra. The white line in curve (a) for LiCl in DME is a broad peak, with a small shoulder on the low energy side. This is similar to the structure found for Cl^- in the free-ion state. In a symmetric environment, the transition feature for Cl^- is a broad peak. White line peak splitting can occur if there is an asymmetric distribution of atoms (or molecules) surrounding the Cl^- with strong bonding. The more asymmetric the distribution is, the stronger the splitting effect will be. The broad peak of white line for LiCl in DME is due to a spherical symmetry distribution of the solvent molecules around Cl^- ions and the weak interaction between solvent and Cl^-. In curve (b) and (c), the white line was split into two peaks. This gives strong evidence that Cl^- is indeed complexed with the boron atom of these compounds.

Conductivity data for salt solutions with compounds **8-11** indicates that the anion complexation effect increases as the number of fluorine atoms is increased in these compounds. The NEXAFS spectra at the Cl K edge for DME solutions of LiCl and compounds **8-11** are plotted in Figure 3. From curve (a) to (c) for compounds **8-10**, the white line splitting become more and more intense with increase of F substitution. This trend is in good agreement with the conductivity data in Table I. However, with the fully fluorinated compound **11**, the degree of white line splitting in curve (d) was less than curve (c). The conductivity data show a stronger anion complexation effect of compound **11** than compound **10**. The weaker white line splitting of curve (d) in Figure 3 may be due to a more symmetrical coordination by compound **11**.

To further explore the possibility of using these boron compounds in electrolytes for lithium batteries, the electrochemical stability was measured by anodic sweep cyclic voltammetry. Figure 4 shows the anodic stability limit of the electrolytes containing lithium salts and compound 14 in DME on inert glassy carbon electrode. Except for LiCl, which decomposed at 3.9V, the electrochemical stability of the electrolytes containing the other salts is acceptable for rechargeable lithium batteries. The initial decomposition of LiF and compound 14 in DME occurs at 4.46V. This decomposition voltage is very similar to previously reported results for $LiClO_4$ in DME (8). This implies that the decomposition is related to the solvent. The solubility of compound 14 and LiF in DME can reach as high as 1M. Due to the superior conductivity of this DME based electrolyte, it was chosen for testing in a $Li/LiMn_2O_4$ cells. This is the first time LiF has been used in an electrolyte for a lithium battery.

Figure 5 shows a discharge curve for the test cell, at the C/3 rate at room temperature,

with 1 M LiF and 1 M compound **14** in DME as the electrolyte. The discharge curve of the test cell exhibits the two typical plateaus at 4.1 and 3.9 V. The initial specific cathode capacity for the test cell is 100 mAh g^{-1}.

With continued cycling between 3.5-4.3 V at the C/3 rate, the capacity of the cell with the LiF and compound **14** as electrolyte decreased to 59 % of the initial capacity after 51 cycles. The voltages of two discharge plateaus also decreased during cycling. This voltage drop indicated an increase of internal resistance of the cell. This is most likely due to solvent decomposition. So a more stable solvent to improve the performance of this electrolyte system is needed.

Figure 6 shows that the electrochemical stability for solutions of LiF and compound **14** in DMC is higher than in DME. The initial decomposition begins at 4.91V in DMC while occurs at 4.46 V in DME on a glassy carbon electrode. However, the solubility of compound **14** in DMC is rather low, the highest concentration is about 0.3 M at room temperature. When solvents with high polarity, PC and EC, were added to DMC, the solubility of compound **14** was significantly increased. The onset decomposition voltages of compound **14** and three lithium salts in PC-EC-DMC (1:1:3) are listed in Table 3. It is clear that the electrochemical stabilities of all combinations in PC-EC-DMC were much higher than those in DME. The composite electrolyte with LiF is stable up to 5.0 V on a glassy carbon electrode. The ionic conductivities of these electrolytes in PC-EC-DMC (1:1:3) in Table III are lower than those electrolytes in DME due to the high viscosity of the PC-EC-DMC solvent. However, the optimization of this system may still improved the conductivity. Another Li/LiMn$_2$O$_4$ battery cell with LiF and compound **14** in PC-EC-DMC (1:1:3) was built and the cell was cycled under same condition as the DME electrolyte. The first and 50th discharge curves are shown in Figure 7. The discharge capacity for the first discharge was 109 mAh g^{-1} for the cathode and the 50th discharge ie was 104 mAh g^{-1}. The plateaus of discharge curve also decrease with the cycling but the voltage decrease is much less than that found in DME. Therefore, the cycling performance of Li/LiMn$_2$O$_4$ battery with composite electrolyte containing LiF and boron compound **14** in PC-EC-DMC is much better than that in DME due to the excellent electrochemical stability.

CONCLUSIONS

Ionic conductivity and NEXAFS studies show that a family of newly developed fluorinated alkyl and aryl borate and borane compounds form complexes with Cl$^-$ and increase the ionic conductivity by increasing the concentration of free Li$^+$ cations, when used as additives in lithium salts electrolytes. The degree of complexation and conductivity enhancement also depends on the structure of the boron compounds. The complexing agents have the ability to promote the dissolution of LiF, which is normally insoluble in organic solvents. For the first time, the potential of using an electrolyte based on a combination of LiF and a boron based anion receptor in a non-aqueous solvent (DME) has been demonstrated in a rechargeable Li/LiMn$_2$O$_4$ cell. The cycle life of the cell is further improved by replacement of DME by PC-EC-DMC as solvent.

ACKNOWLEDGEMENT

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Table I Ionic conductivity of 0.2 M boron compound + 0.2 M lithium salt in DME

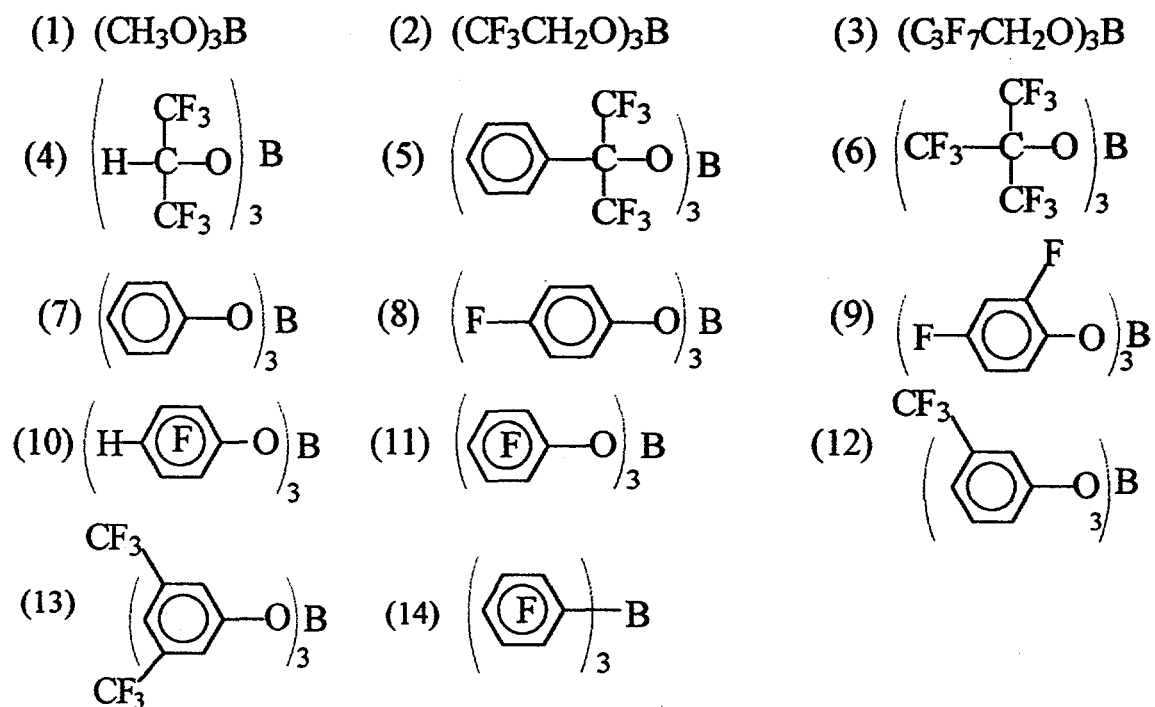| Boron Compounds (0.2 M)	Lithium Salts Conductivity (S/cm)			
	CF_3CO_2Li	$C_2F_5CO_2Li$	LiF	LiCl
Salt only	3.3×10^{-5}	2.1×10^{-5}		5.0×10^{-6}
(1) $(CH_3O)_3B$	2.3×10^{-5}	1.7×10^{-5}		5.0×10^{-6}
(2) $(CF_3CH_2O)_3B$	1.9×10^{-4}	7.0×10^{-5}		5.4×10^{-5}
(3) $(C_3F_7CH_2O)_3B$	2.6×10^{-4}	1.1×10^{-4}	1.6×10^{-5}	8.4×10^{-5}
(4) $[(CF_3)_2CHO]_3B$	3.9×10^{-3}	4.6×10^{-3}	1.5×10^{-5}	3.8×10^{-3}
(5) $[(CF_3)_3CO]_3B$	3.8×10^{-3}	3.8×10^{-3}	1.3×10^{-5}	3.0×10^{-3}
(6) $[(CF_3)_2C(C_6H_5)O]_3B$	3.8×10^{-5}	2.0×10^{-5}		4.6×10^{-6}
(7) $(C_6H_5O)_3B$	1.3×10^{-4}	6.3×10^{-5}		1.2×10^{-5}
(8) $(FC_6H_4O)_3B$	6.2×10^{-4}	4.0×10^{-4}	1.7×10^{-5}	6.2×10^{-5}
(9) $(F_2C_6H_3O)_3B$	1.5×10^{-3}	1.4×10^{-3}	1.7×10^{-4}	2.7×10^{-4}
(10) $(F_4C_6HO)_3B$	2.3×10^{-3}	2.0×10^{-3}	8.8×10^{-4}	1.7×10^{-3}
(11) $(C_6F_5O)_3B$	3.3×10^{-3}	3.7×10^{-3}	2.9×10^{-3}	3.0×10^{-3}
(12) $(CF_3C_6H_4O)_3B$	2.2×10^{-3}	2.3×10^{-3}		1.1×10^{-3}
(13) $((CF_3)_2C_6H_3O)_3B$	2.8×10^{-3}	3.4×10^{-3}		3.0×10^{-3}
(14) $(C_6F_5)_3B$	3.2×10^{-3}	3.8×10^{-3}	1.7×10^{-3}	2.6×10^{-3}

Table II Ionic Conductivity of Lithium Salts and Boron Additives with Various Concentrations in DME

(4) $[(CF_3)_2CHO]_3B$

Concentration of Salts and Additives	Conductivity (S/cm)		
	Lithium Salts		
	CF_3CO_2Li	$C_2F_5CO_2Li$	LiF
0.2M	3.9×10^{-3}	4.6×10^{-3}	
0.3M	5.5×10^{-3}	6.3×10^{-3}	
0.4M	6.6×10^{-3}	7.7×10^{-3}	
0.5M	7.9×10^{-3}	8.5×10^{-3}	
0.8M	8.9×10^{-3}	9.5×10^{-3}	
1.0M	8.9×10^{-3}	9.2×10^{-3}	
1.2M	8.2×10^{-3}	8.6×10^{-3}	

(11) $(C_6F_5O)_3B$

	CF_3CO_2Li	$C_2F_5CO_2Li$	LiF
0.2M	3.3×10^{-3}	3.2×10^{-3}	4.1×10^{-3}
0.3M	3.7×10^{-3}	4.4×10^{-3}	4.1×10^{-3}
0.4M	4.5×10^{-3}	5.5×10^{-3}	5.6×10^{-3}
0.5M	5.9×10^{-3}	6.1×10^{-3}	6.0×10^{-3}
0.8M	5.6×10^{-3}	6.4×10^{-3}	
1.0M	5.2×10^{-3}	5.8×10^{-3}	6.8×10^{-3}
1.2M	4.4×10^{-3}	5.4×10^{-3}	

(14) $(C_6F_5)_3B$

	CF_3CO_2Li	$C_2F_5CO_2Li$	LiF
0.2M	3.2×10^{-3}	3.0×10^{-3}	1.7×10^{-3}
0.3M	5.1×10^{-3}	4.2×10^{-3}	3.5×10^{-3}
0.4M	6.3×10^{-3}	4.9×10^{-3}	4.7×10^{-3}
0.5M	6.8×10^{-3}	5.4×10^{-3}	6.4×10^{-3}
0.8M	6.7×10^{-3}	5.9×10^{-3}	6.6×10^{-3}
1.0M	6.0×10^{-3}	5.4×10^{-3}	6.2×10^{-3}
1.2M	5.4×10^{-3}	4.4×10^{-3}	

Concentrations of salts and additives are the same in all solutions.

Table III Comparison of Initial decomposition on glassy carbon electrode and ionic conductivity of 1 M lithium salts and 1 M boron compound 14 in DME and PC-EC-DMC (1:1:3).

Lithium Salt	$(C_6F_5)_3B$			
	Decomposition voltage (V)		Ionic Conductivity (S/cm)	
	DME	PC-EC-DMC	DME	PC-EC-DMC
LiF	4.46	5.00	5.52×10^{-3}	1.20×10^{-3}
CF_3CO_2Li	4.20	4.96	7.43×10^{-3}	3.67×10^{-3}
$C_2F_5CO_2Li$	4.34	4.76	5.52×10^{-3}	3.51×10^{-3}

(1) $(CH_3O)_3B$ (2) $(CF_3CH_2O)_3B$ (3) $(C_3F_7CH_2O)_3B$

(4) $\left(H-\underset{CF_3}{\overset{CF_3}{C}}-O \right)_3 B$ (5) $\left(C_6H_5-\underset{CF_3}{\overset{CF_3}{C}}-O \right)_3 B$ (6) $\left(CF_3-\underset{CF_3}{\overset{CF_3}{C}}-O \right)_3 B$

(7) $\left(C_6H_5-O \right)_3 B$ (8) $\left(F-C_6H_4-O \right)_3 B$ (9) $\left(F_2C_6H_3-O \right)_3 B$

(10) $\left(H-C_6H_3F-O \right)_3 B$ (11) $\left(C_6H_4F-O \right)_3 B$ (12) $\left(CF_3C_6H_4-O \right)_3 B$

(13) $\left((CF_3)_2C_6H_3-O \right)_3 B$ (14) $\left(C_6H_4F \right)_3 B$

Figure 1. Chemical structure of boron based anion receptors and related reference compounds. The numbers in brackets correspond to the compound number in the text.
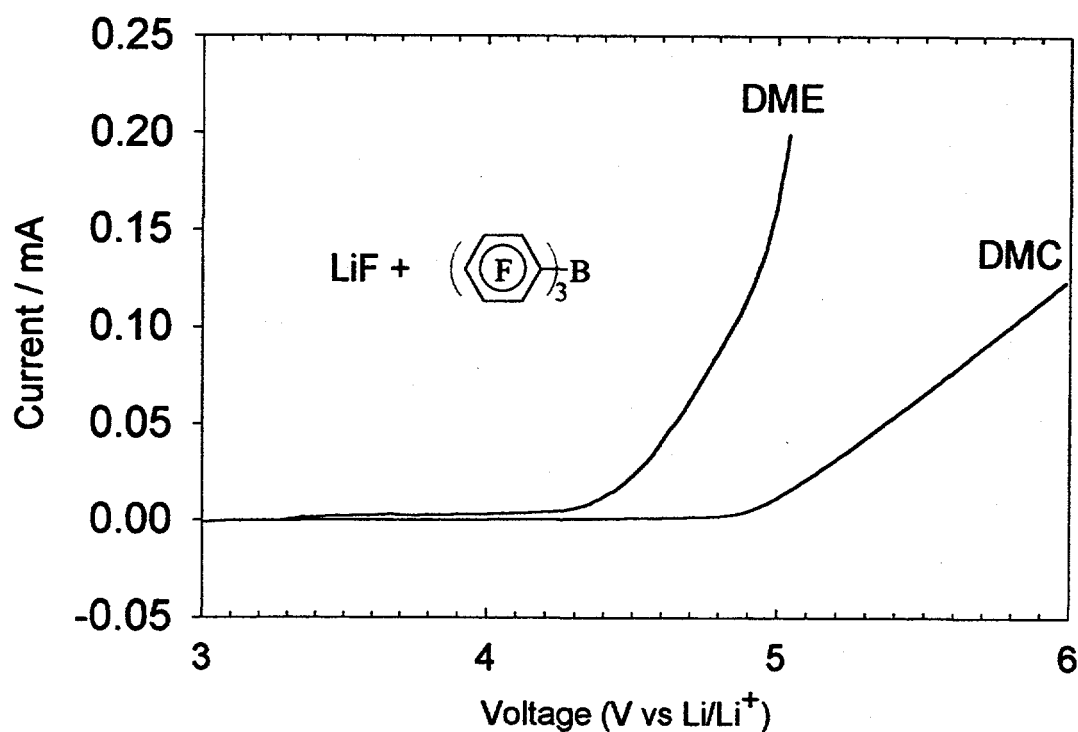
Figure 6. Comparison of cyclic voltagramms for 1M LiF and compound 14 in DME, 0.2 M LiF and compound 14 in DMC at a glassy carbon electrode.
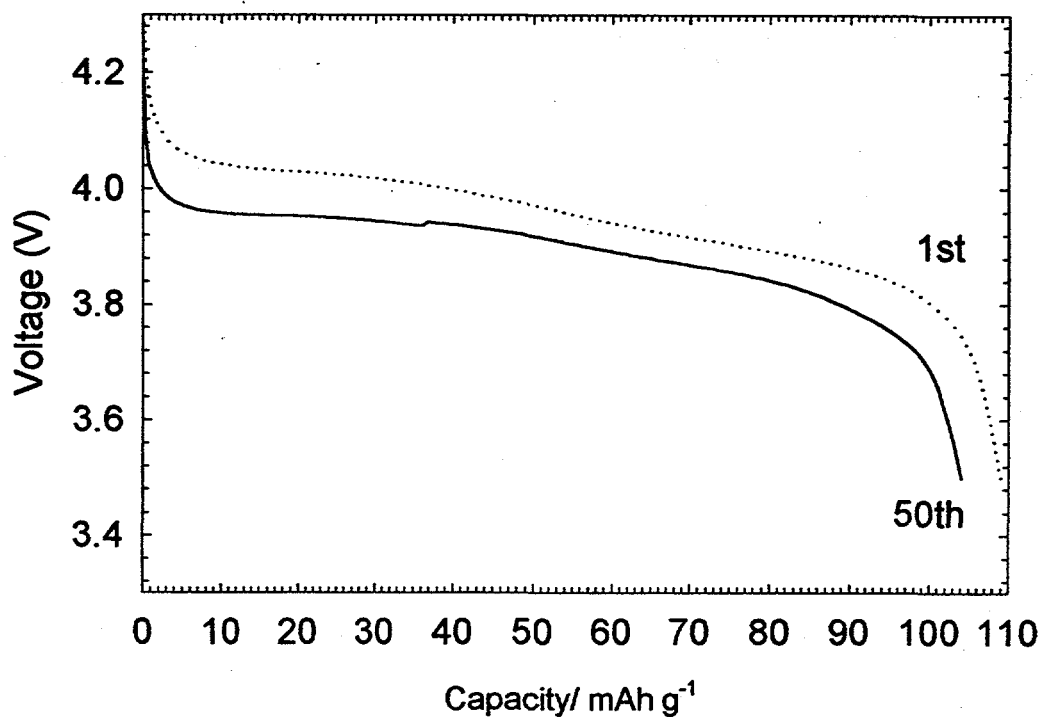

Figure 7. 1st and 50th discharge curves of Li/ LiMn$_2$O$_4$ battery with LiF and boron compound 14 in PC-EC-DMC (1:1:3) as electrolyte.