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NEW POLYMER AND LIQUID ELECTROLYTES FOR LITHIUM BATTERIES

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Abstract

All non-aqueous lithium battery electrolytes are Lewis bases that interact with cations. Unlike water, they don't interact with anions. The result is a high degree of ion pairing and the formation of triplets and higher aggregates. This decreases the conductivity and the lithium ion transference and results in polarization losses in batteries. Approaches that have been used to increase ion dissociation in PEO based electrolytes are the use of salts with low lattice energy, the addition of polar plasticizers to the polymer, and the addition of cation complexing agents such as crown ethers or cryptands. Complexing of the anions is a more promising approach since it should increase both ion dissociation and the lithium transference. At Brookhaven National Laboratory (BNL) we have synthesized two new families of neutral anion complexing agents, each based on Lewis acid centers. One is based on electron deficient nitrogen sites on substituted aza-ethers, wherein the hydrogen on the nitrogen is replaced by electron withdrawing groups such as CF_3SO_3^- . The other is based on electron deficient boron sites on borane or borate compounds with various fluorinated aryl or alkyl groups. Some of the borane based anion receptors can promote the dissolution of LiF in several solvents. Several of these compounds, when added in equivalent amounts, produce 1.2 M LiF solutions in DME, an increase in solubility of LiF by six orders of magnitude. Some of these LiF electrolytes have conductivities as high as $6 \times 10^{-3} \text{ Scm}^{-1}$. The LiF electrolytes with borane anion acceptors in PC:EC:DEC solvents have excellent electrochemical stability. This has been demonstrated in small Li/LiMn₂O₄ cells.

Introduction

The key problems with polymer electrolytes are low conductivity at ambient temperature and low lithium ion transference. Together these features lead to poor material utilization, particularly at high discharge rates, resulting in low energy density and low cycling efficiency (1). Since Armand proposed the application of poly(ethylene oxide) (PEO) based polymer electrolytes for lithium batteries, in 1978 (2), there has been extensive research in the field. Early on it was established that ion mobility was related to the segmental motion of the polymer chains, and significant conductivity only occurred in the amorphous part of the polymer (3). Electrochemical and Raman spectroscopy studies in liquid polymer solvents such as poly(propylene glycol) indicated that ion-ion and ion-solvent interactions were very different from those found in aqueous solvents (4-7). In all cases there is a high degree of ion pairing and the formation of triplets and higher aggregates. Raman studies also showed an increase in ion pairing with increasing temperature for several salts in low molecular weight polymer solvents (5, 6,

8). Yang *et al.* used x-ray absorption spectroscopy (XAS) at the potassium K. edge to study ion pairing of potassium salts in liquid polar carbonate solvents and in high molecular weight PEO (9, 10). The results confirmed a high degree of ion pairing in PEO based electrolytes and an increase in ion pairing with increasing temperature. EXAFS studies of $\text{RbBr}(\text{PEO})_8$ confirmed the formation of cluster species with the composition of approximately $\text{Rb}_{12}\text{Br}_{12}$ (11). Ion pairing and aggregate formation decrease the number of charge carriers, the ionic conductivity and the cation transport number. Depending on the measurement method and the salt concentration, lithium ion transference numbers in PEO based electrolytes vary between 0 to 0.5 (12). Measurements by the Hittorf method give a lithium ion transference number of 0.06 for $\text{LiClO}_4(\text{PEO})_8$ at 120°C (13). Ion pairing and aggregate formation are the cause of both the low conductivity and the low lithium ion transference. There is ample evidence that in many cases ion pairing increases with increasing temperature (13). This has been ascribed to a negative entropy of solvation (14).

Approaches that have been used to increase ion dissociation in PEO based electrolytes are the use of salts with low lattice energy (15), the addition of polar plasticizers to the polymer (16), and the addition of cation complexing agents such as crown ethers or cryptands (17). Complexing of the anions is a more promising approach since it should increase both ion dissociation and the lithium transference.

Water is an excellent solvent because it can accommodate both cations and anions. The lone electron pair on the oxygen is a hard Lewis base that can accommodate cations. The hydrogen can hydrogen bond to anions and function as a hard Lewis acid. All of the organic solvents for lithium batteries, including PEO, are Lewis bases. As a result they only accommodate cations. This is a large contributor to ion pairing in these solvents. Our approach to the design of new electrolytes is to incorporate anion binding Lewis acid agents in the electrolyte.

The design and synthesis of receptor molecules for the selective complexation of anions has been an active area of research for the past two decades (18, 19). Most of the work is in the biological area with emphasis on molecular recognition and mimicking of processes in biological membranes. To accomplish anion binding, most of the host molecules contain either positively charged sites or are electroneutral hosts based on Lewis acid metal centers or on hydrogen bonding (19). A survey of the literature indicated that none of these were suitable anion receptors for use in a lithium battery environment. At Brookhaven National Laboratory (BNL) we have synthesized two new families of neutral anion complexing agents, each based on Lewis acid centers. One is based on electron deficient nitrogen sites on substituted aza-ethers, wherein the hydrogen on the nitrogen is replaced by electron withdrawing groups such as CF_3SO_3^- (20). The other is based on electron deficient boron sites on borane or borate compounds with various fluorinated aryl or alkyl groups (21). Zhang and Angell have reported on the use of the Borate Ester of Glycol (BEG) as a co-solvent with alkene carbonates for lithium battery electrolytes (22). Later Metha and Fujinami prepared and tested polymer electrolytes incorporating boroxine rings with pendant oligoether side chains and a variety of dissolved lithium salts (23). The present work introduces hard Lewis acid centers in the electrolyte that complex anions and greatly enhance the degree of ion dissociation and the conductivity of the electrolyte.

In designing new electrolytes with Lewis acid anion hosts it is necessary to consider the problem of competition between the anion and the solvent for the host. Also interactions of the host with the solvent could increase the viscosity of the electrolyte (22). Important parameters are the relative size of the solvent molecules and the anions, steric effects, the Lewis acidity of the binding agent, and the Lewis basicity of the anions and the solvent. Fortunately there are many anions and solvents to choose from, and the properties of the binding hosts can be manipulated by molecular design.

Experimental

Synthesis of aza-ether anion receptors: Figure 1 shows examples of aza-ether receptors that we have synthesized. Details of the synthetic methods have been published (20). An electron withdrawing group (R), $R = CF_3SO_2$, was used to substitute the amine hydrogen atoms in linear, branched or cyclic aza-ethers. The varied geometry permits the design of complexing agents for various polyatomic anions. Figure 1 includes abbreviated codes for each of the compounds. These codes are used in the discussion, Table 1 and the caption for Fig. 3.

Synthesis of aza-ether based polymer electrolytes: Several new polymer electrolytes, based on the complexing of anions, were synthesized by grafting the aza anion receptors onto a siloxane polymer backbone. Details of the synthesis are given elsewhere (24).

Synthesis of boron-based anion receptors: Figure 2 shows examples of the boron-based anion receptors. Several borane, borate and boronate compounds have been synthesized. Details of the synthesis are given elsewhere (21).

Electrolyte stability studies: Electrolyte stability studies were done in a three-electrode cell with a glassy carbon working electrode (7.0 mm^2), a platinum wire counter electrode, and a lithium metal foil reference electrode. The measurement consisted of anodic sweep cyclic voltammetry at 20 mV/s .

Cell testing: electrolytes containing the anion receptors were evaluated in small Li/LiMn₂O₄ cells. The cell consisted of a LiMn₂O₄ disc cathode, a lithium foil disc anode and a Celgard separator. Both electrodes had an area of 2.82 cm^2 . The LiMn₂O₄ cathode was made coating a slurry of LiMn₂O₄ powder with 10% acetylene black and 10% poly(vinylidene fluoride) binder in a 1-methyl-2-pyrrolidone solvent on aluminum foil. The electrode was dried in vacuum at 100°C . Two types of electrolytes were evaluated. One was 1 M LiF + 1 M tris(pentafluorophenyl) borane (TPFPB) in a dimethoxyethane (DME) solvent. The other electrolyte was identical except that the solvent was a 1:1:3 mixture of propylene carbonate (PC):ethylene carbonate (EC):dimethyl carbonate (DMC). Cycling was carried out on an Arbin battery test system and the cells were cycled at the C/3 rate between 3.5 and 4.3 V.

Results and Discussion

Aza-ether anion receptors in liquid electrolytes: The effect of the aza ether anion receptors was investigated in several electrolytes with a tetrahydrofuran (THF) solvent. The addition of the aza compounds greatly increased the solubility of LiCl in THF. In electrolytes with 0.2 M LiCl + 0.2 M of the linear aza compound, the conductivity

increased with increasing chain length (20). With L4R as an additive the conductivity was $8.4 \times 10^{-5} \text{ Scm}^{-1}$. As the number of R groups increased to 5, 6, and 8, the corresponding conductivity increased to 1.4×10^{-4} , 7.2×10^{-4} , and $1.4 \times 10^{-3} \text{ Scm}^{-1}$. The increase in conductivity also depended on the salt. Table 1 shows conductivity data for electrolytes of various salts in THF with equivalent additions of the C4R aza-crown ether. The addition of the anion acceptor increases the conductivity in all cases. There is a large increase in conductivity for salts with anions that are hard Lewis bases, such as chloride. The increase in conductivity is less for the triflate salt, whose anion is a soft Lewis base.

The formation of anion complexes was confirmed by x-ray absorption studies. Figure 3 shows x-ray absorption spectra at the Br K edge for 0.2 M LiBr in tetrahydrofuran (THF) with equivalent additions of various aza anion acceptors. The features at the Br K edge are due to bound state transitions from $1s$ to $4p$ states. In pure THF the Br^- is symmetrically coordinated with solvent molecules and the $4p$ states are degenerate. The result is a single broad peak (white line) at 13476 eV. L2R shows almost no effect because it does not bind with Br^- . Beginning with L4R the white line is split and the effect becomes more pronounced as the chain length of the aza compound increases. The splitting of the white line is due to coordination of the acceptor with the anion and the lifting of the degeneracy of the $4p$ states.

Recently D'Aprano and co-workers have done conductance measurements for LiClO_4 and the anion receptor C4 in different aprotic solvents (24). Their results show that the anion-ligand formation constants increase with decrease of the dielectric constants of the solvents and that the presence of the ligand increases the ionization of LiClO_4 and enhances transference number of the Li^+ ion. In propylene carbonate the Li^+ ion transference number was increased by 30%.

Aza-ether based polymer electrolytes: The siloxane polymer with the grafted aza-ether anion acceptor groups dissolved lithium salts such as LiCl to yield a new type of polymer electrolyte that contains no ethylene oxide groups (25). The lone pair electrons on the O atoms in poly(ethylene oxide) form an array of hard Lewis bases that complex hard Lewis acids such as Li^+ . The N atoms in the new polymers act as an array of Lewis acids that complex hard Lewis bases such as Cl^- . Some of these polymers have conductivities of 10^{-5} Scm^{-1} at 25°C .

Even though the substituted aza-ethers are excellent anion acceptors, the di-substituted terminal NR_2 groups in the linear and branched compounds are inherently unstable. Also the molecular weight of many of these compounds is large and some of them have low solubilities in non-aqueous solvents. These factors and the prospect of making stronger Lewis acids were the motivation for the development of the boron-based anion receptors.

Boron-based anion receptors: Some of the boron based anion acceptors can promote the dissolution of normally insoluble salts, such as LiF, in several non-aqueous solvents (26). Amongst the compounds in Fig. 2, compounds 3, 4, 5, 8, 9, 10, 11 and 14 promote the dissolution of LiF in several solvents, including dimethoxyethane (DME) and mixtures of PC:EC:DMC. The normal solubility of LiF in non-aqueous solvents is about 10^{-5} M . This was a factor that prevented the development of rechargeable batteries based on metal fluoride cathodes (27, 28) Several of these receptor compounds, when added in

equivalent amounts, produce 1.2 M LiF solutions in DME, an increase in solubility of LiF by six orders of magnitude.

The boron-based anion receptors, in particular the borane compounds, have remarkable electrochemical stability (29). Figure 4 shows anodic voltammograms on glassy carbon for electrolytes with 1 M salt + 1 M TFPFB in DME and PC:EC:DMC solvents. Stability windows in excess of 5.1 V are observed, with the stability limited by the PC:EC:DMC solvent. LiF itself has a thermodynamic stability window of 5.92 V.

Some of these LiF based electrolytes have very good conductivity. The respective conductivity of 0.8 M solutions of LiF in DME with equivalent amounts of compounds 7 and 14 are 6.4×10^{-3} and $6.6 \times 10^{-3} \text{ Scm}^{-1}$ at 25°C. This compares with a conductivity of $\sim 8 \times 10^{-3} \text{ Scm}^{-1}$ for 0.8 M LiPF₆ in DME. Highly conductive electrolytes can also be made with LiF and these anion receptors in conventional solvent mixtures such as 1:1:3 PC:EC:DMC. Several LiF based electrolytes of this type have been successfully evaluated in rechargeable Li/LiMn₂O₄ cells (25). Figure 5 shows capacity versus cycle life for such a cell when cycled at the C/3 rate. The capacity maintenance is remarkably good.

We plan to incorporate some of these boron anion receptor structures into polymer electrolytes.

Acknowledgement

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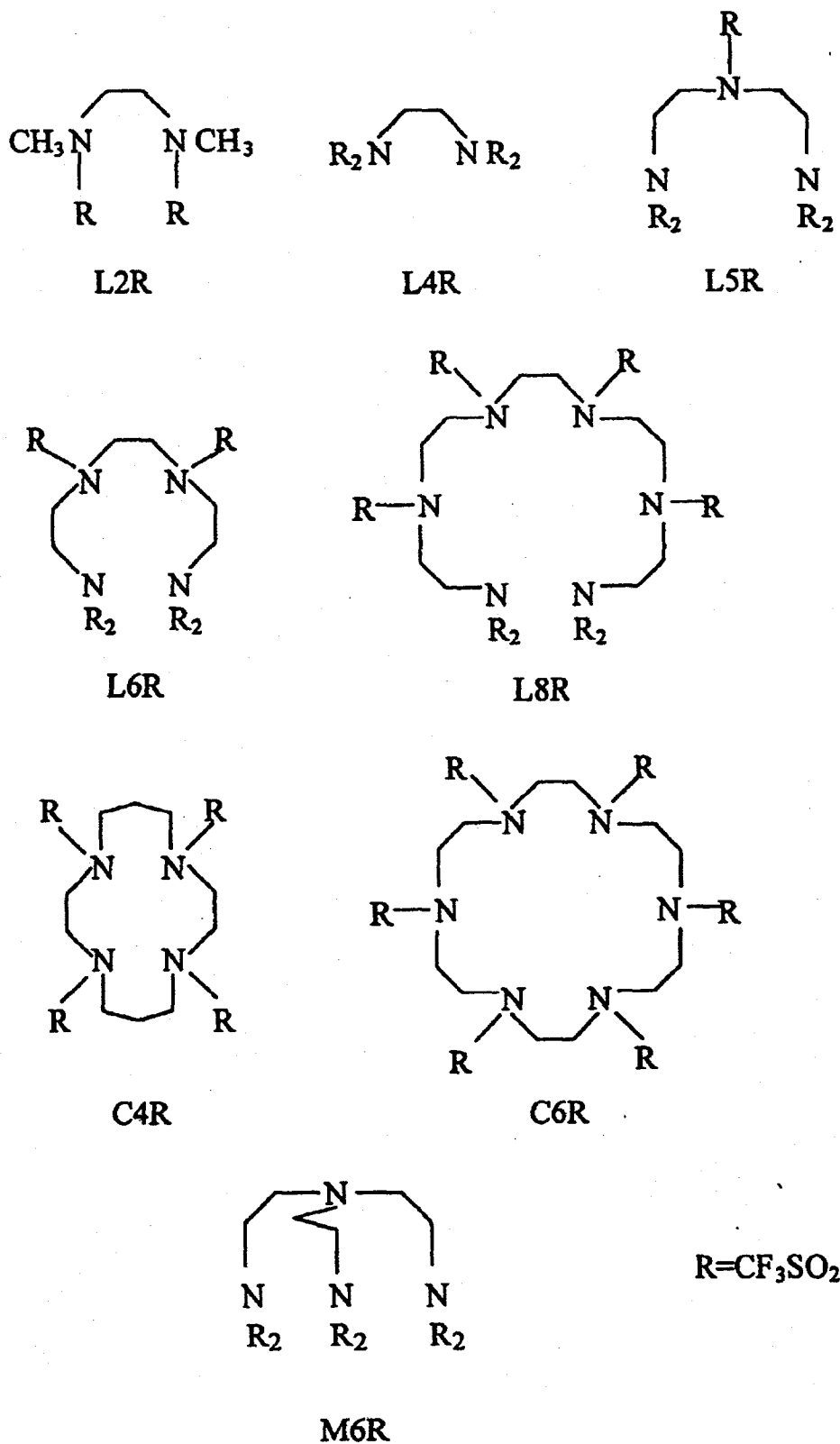
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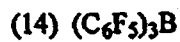
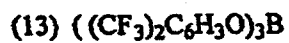
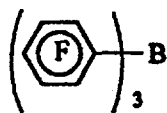
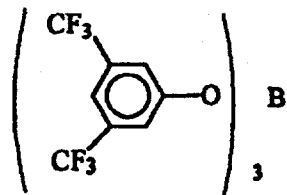
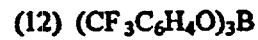
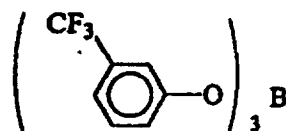
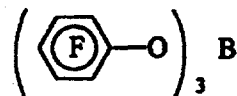
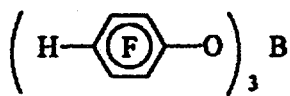
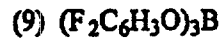
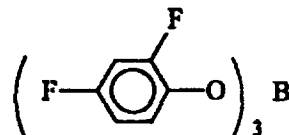
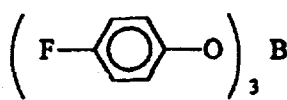
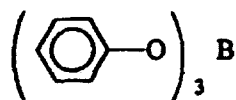
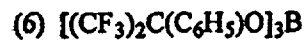
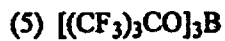
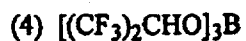
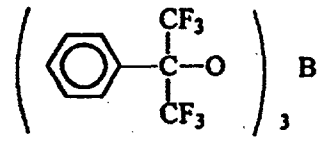
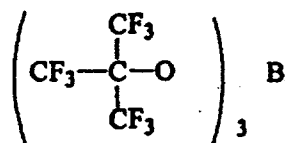
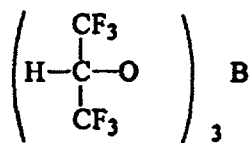
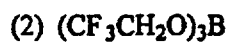
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Table 1 The effect of the addition of equivalent amounts of the aza-crown ether C4R on the conductivity of lithium salt electrolytes in THF

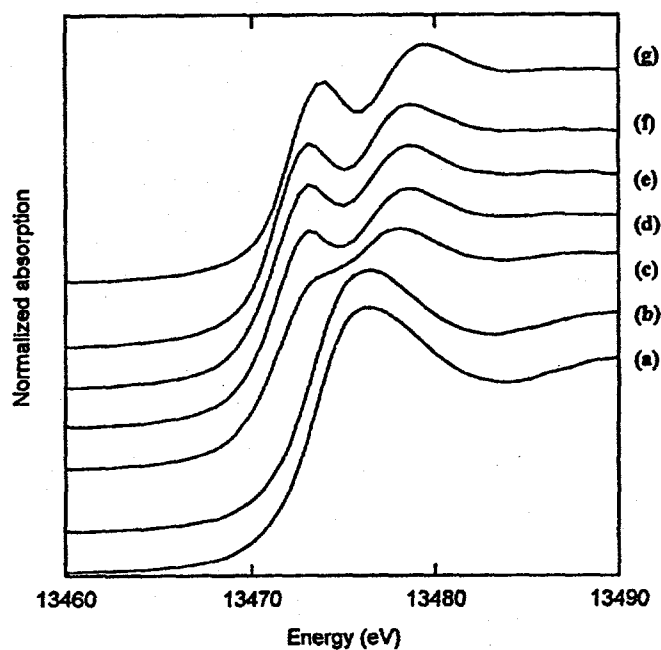
Salt	Conductivity (S/cm)	
	Pure salt	Salt + C4R
0.1 M LiCl	1.6×10^{-6}	3.4×10^{-4}
0.1 M LiBr	7.3×10^{-6}	7.3×10^{-4}
0.1 M LiI	6.7×10^{-5}	1.6×10^{-3}
0.1 M LiCF ₃ SO ₃	1.7×10^{-4}	9.6×10^{-4}
1.0 M LiCF ₃ SO ₃	9.1×10^{-4}	1.4×10^{-3}
0.1 M LiClO ₄	3.4×10^{-4}	1.3×10^{-3}



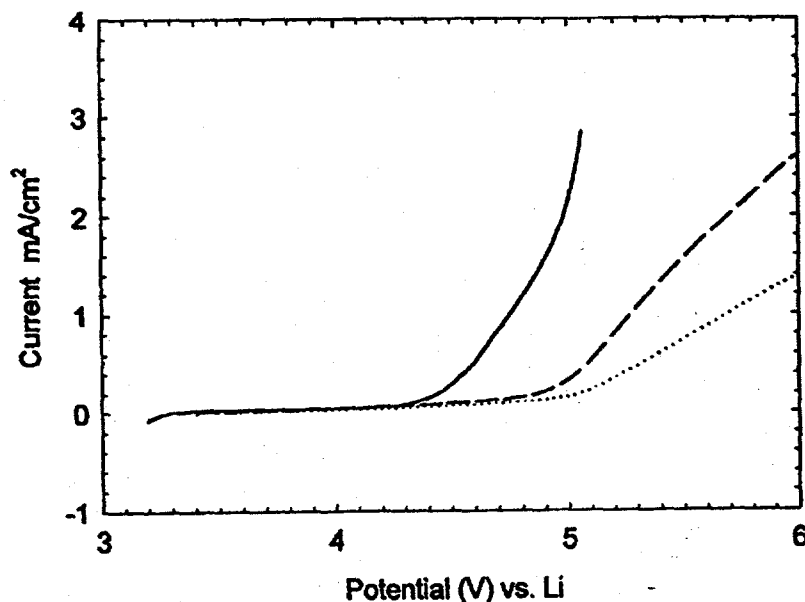
1. Structures of linear, cyclic and branched aza-ether based anion receptors.



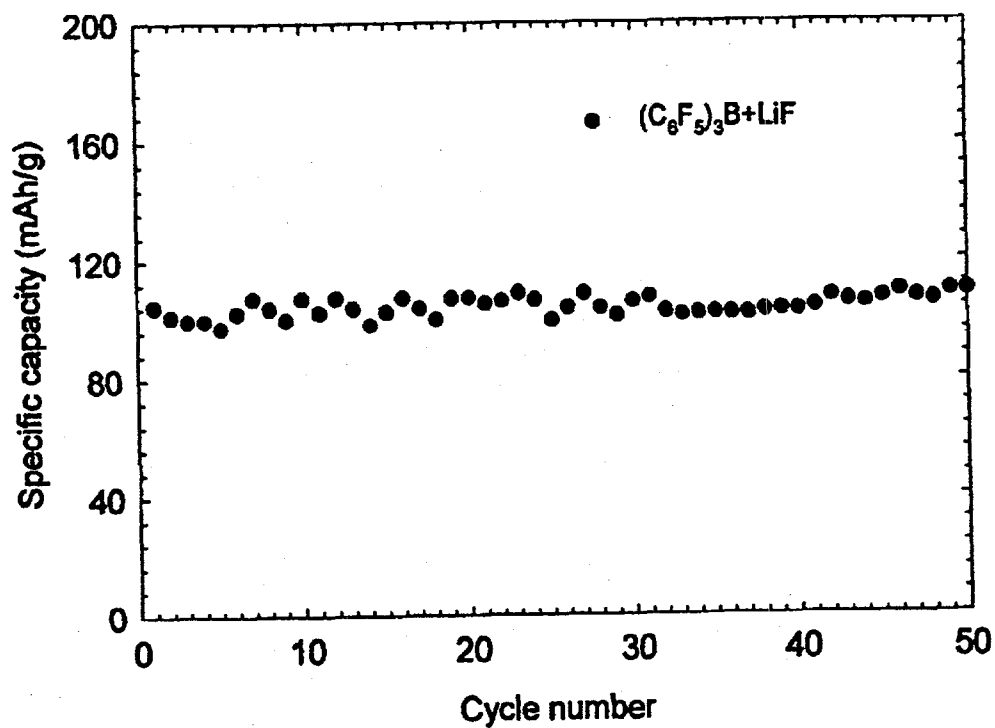
2. Structures of borate and borane anion receptors.



3. X-ray near edge absorption spectra at the Br K edge for 0.2 M LiBr in tetrahydrofuran (THF) with equivalent additions of various anion receptors, (a) LiBr in pure THF and in electrolytes with 0.2 M additions of (b) L2R, (c) L4R, (d) L5R, (e) L6R, (f) L8R and (g) M6R. The spectra are offset along the Y-axis for clarity.



Anodic cyclic voltammograms on glassy carbon (20 mV/s) in (a) 1 M LiF + 1M TPFPB in DME (—), (b) 1 M $\text{CF}_3\text{CO}_2\text{Li}$ + 1M TPFPB in 1:1:3 PC:EC:DMC (---), (c) 1 M LiF + 1M TPFPB in 1:1:3 PC:EC:DMC (.....).



4. Capacity cycle life behavior for a $Li/LiMn_2O_4$ cell with a 1 M $LiF + TPF PB$ in 1:1:3 PC:EC:DMC electrolyte. Cell was cycled at the C/3 rate between 3.5 and 4.3 V.