

Title	リチウムイオン 2 次電池の性能向上のための有機ホウ素系固体電解質 / 固体電解質界面設計
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Design of Organoboron Solid Electrolytes/Solid Electrolyte Interface for Enhanced Performance of Lithium Ion Secondary Batteries

Background:

Lithium ion batteries (LiBs) are one of the most competitive energy storage devices amongst all conventional sources of energy storage. This is because of their high energy density and high power through put. The high research interest in this area is diverted mainly towards the improvement of capacity of these batteries, though there is a scope of improvement in increasing the energy density as well. The panacea for such problems has been identified to be the tailoring the Solid Electrolyte Interface (SEI)¹. SEI between the negative electrode and the electrolyte of a Li ion battery is considered as a factor influencing the overall battery performance. Low irreversible capacity loss, good charge transfer kinetics and good storage properties are the main characteristics of a good performing battery². This interface which allows Li⁺ ions to be

transported through the film during the subsequent intercalation and deintercalation processes³, can be achieved either by the use of *a*) low molecular weight electrolytes with highly ordered structures or *b*) by highly conducting electron rich conjugated polymers and self-polymerizing them over anode for better SEI characteristics. Hence, in this research theme (Fig. 1), we synthesized various low molecular weight solid organoboron electrolytes as highly ordered structures for interfacial studies at carbon electrode as the first part of modifying the SEI using electrolytes. In the second part of modifying the anode⁴, we utilized an organoboron monomer to reduce the interfacial resistance at SEI by using charge discharge analysis and Electrochemical Impedance

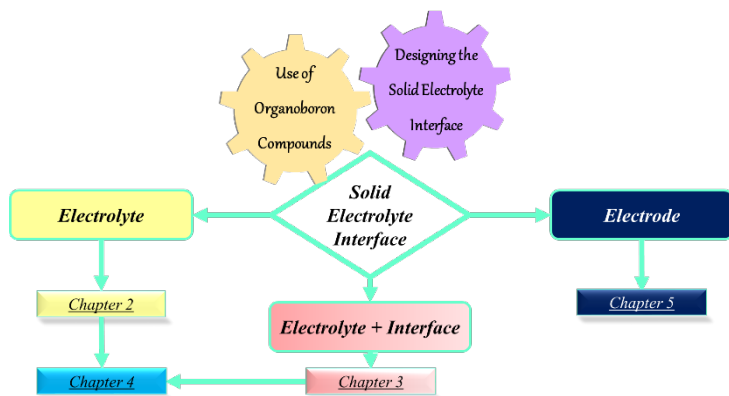


Fig. 1. Schematic of the research work

Spectroscopy (EIS). Designing a well-defined organoboron SEI can help in multifold increase in the performance of LiBs.

Aim:

- Design and synthesis of organoboron compounds (electrolytes and conducting monomer for surface coating) that will result in the tuning of the electrode-electrolyte interface, conductive and stable Solid Electrolyte Interface (SEI) layer over the anode (graphene) and
- To determine the charge-discharge characteristics of the electrode and interfacial resistance after tuning the SEI for understanding of the Li ion battery.

Experimental and Results & Discussion

- Design of a Crystalline Low Molecular Weight Electrolyte for Obtaining a Conducting Interface over Anodes (Chapter 2)**

Experimental:

Dehydrocoupling reaction between ethylene glycol and mesityl borane resulted in a novel low molecular weight cyclic organoboron crystalline compound (Scheme 1) obtained as needle shaped crystals (Fig. 2) which was characterized for its structure and other thermal properties.

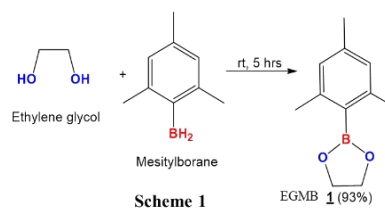


Fig. 2 Needle Crystals of 1

Results and Discussion:

The electrochemical properties of the electrolyte derived by ethylene glycol (**1**), were studied under specific composition of Li salt inserted via two external methods, viz. a) facile grinding and b) conventional method (using solvent dissolution and evaporation). The presence of crystallinity in the electrolyte can be considered as an important factor behind the high ionic conductivity and high lithium ion transference number in an all solid electrolyte of this type. The ionic conductivities for the samples prepared by grinding method were significantly higher at the optimal concentration of lithium salt which can be due to the retainment of crystallinity of a Lewis acidic ordered structure by grinding which otherwise might be lost in the case of conventional samples due to solvation (Table 1).

Table 1 Comparison of VFT parameters for the samples prepared by conventional method and grinding

Sample ($\underline{1}$:LiTFSI)	S. No.	Grinding Method				S. No.	Conventional Method			
		A ($\text{Scm}^{-1} \text{K}^{1/2}$)	B (K)	R^2	σ_i at 51°C (Scm^{-1})		A ($\text{Scm}^{-1} \text{K}^{1/2}$)	B (K)	R^2	σ_i at 51°C (Scm^{-1})
4:1	<u>1</u>	2.52	1607	0.9997	1.4×10^{-5}	<u>7</u>	4.74	1555	0.9964	6.6×10^{-5}
2:1	<u>2</u>	6.90	1209	0.9992	3.6×10^{-4}	<u>8</u>	4.81	1583	0.9992	2.7×10^{-4}
1:1	<u>3</u>	1.72	765.3	0.9995	3.9×10^{-4}	<u>9</u>	59.2	1796	0.9988	1.1×10^{-4}
1:2	<u>4</u>	15.7	1236	0.9994	7.1×10^{-4}	<u>10</u>	2.17	1350	0.9992	5.2×10^{-5}
1:3	<u>5</u>	33.7	1707	0.9998	3.9×10^{-5}	<u>11</u>	1.25	1071	0.9997	9.4×10^{-5}
1:4	<u>6</u>	0.66	1331	0.9992	3.6×10^{-5}	<u>12</u>	1.32	1232	0.9990	6.1×10^{-5}

The conduction mechanism can be associated with the formation of regulated ion conductive path (ionic channel) templated by crystalline boron compound along with the effective trapping of the TFSI⁻ anions by the vacant p-orbitals of boron.

ii) Specifically Designed Lithium Borate Type Electrolytes for a Highly Conducting Electrode-Electrolyte Interface (Chapter 3)

Experimental:

Two electrolytes were synthesized via dehydrocoupling reaction between lithium mesitylhydroborate and glycerol (Scheme 2) /oxalic acid (Scheme 3) in order to generate a single cation conducting electrolyte with controlled formation of ion conduction channels by direct incorporation of Li⁺ itself in the molecule. Both the synthesized electrolytes, 2 and 3, were studied for their conductive properties.

Results and Discussion:

The electrolytes exhibited ionic conductivities in the range of 10^{-2} to 10^{-3} Scm^{-1} when measured in presence of an ionic liquid viz., AMImTFSI. Highest transference number of 0.81 was obtained for electrolyte derived from oxalic acid in ionic liquid. The properties were compared with the commercially available Li salt, lithium bis (oxalato) borate (LiBOB) (Fig.3).

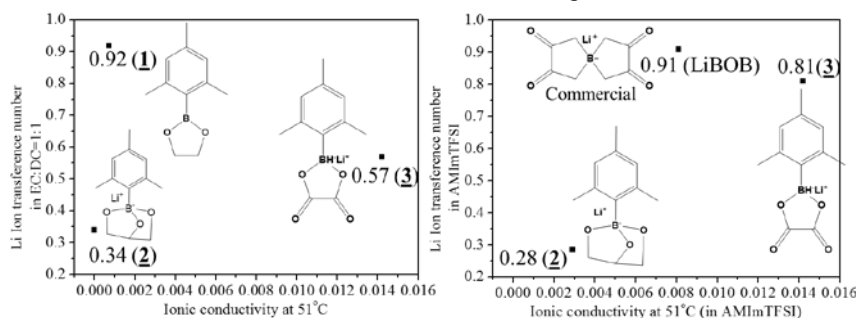
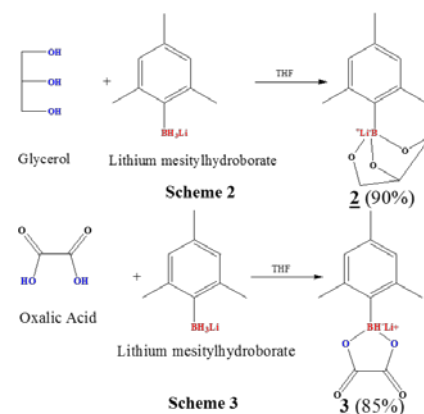


Fig. 3 Comparison of ionic conductivity and Li ion transference number of a) 1, 2 and 3 in EC: DEC=1:1 and of b) 2, 3 and LiBOB in AMImTFSI

iii) Charge-Discharge Characteristics of the Designed Low Molecular Weight Electrolytes (Chapter 4)

Experimental: For charge-discharge studies, graphite based anodic half-cells were prepared and the prepared graphite based anodic half-cells were charged and discharged in a galvanostatic mode with restriction in potential.

Results and Discussion:

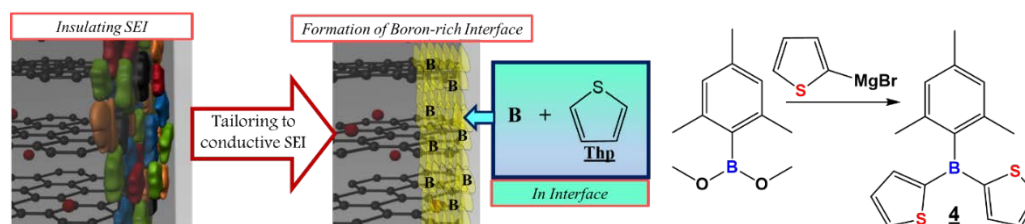
The synthesized low molecular weight electrolytes, 1, 2 and 3, were evaluated as electrolytes for lithium ion batteries through charge-discharge studies in anodic-half cell configuration using graphite anodes. All the Li ion cells showed reversible charge-discharge characteristics. All the above results confirm a real-time application of these electrolytes in lithium ion batteries (Table 2). The average capacity for alkylborane type electrolyte 1, ranged from 150-200 mAh/g. Lithium borate type electrolytes 2 and 3, exhibited charge-discharge capacity in the range of 150-200 mAh/g and 75-80 mAh/g respectively. Their interfacial characteristics were also studied via Electrochemical Impedance Spectroscopy (EIS). Electrolytes 1 and 3 showed reduced interfacial resistance indicating the formation of a stable and conductive SEI layer.

Table 2 Comparison of charge-discharge capacities and interfacial for the three samples **1**, **2** and **3**

Electrolyte	Charge-Discharge Capacity of 1 st cycle (mAh/g)	Average capacity (mAh/g)	Interfacial resistance after 10 cycles (Ω)/before 10 cycles(Ω)
1 :LiTFSI=1:2 + 30 μ L of EC:DEC=1:1	200 (Capacity of Carbon used = 220 mAh/g)	200-150	26.09/237.2
2 + 30 μ L of EC:DEC=1:1	398 (Capacity of Carbon used = 220 mAh/g)	200-100	-
3 + 30 μ L of EC:DEC=1:1	120 (Capacity of Carbon used = 160 mAh/g)	84-78	51.07/3221

iv) **Electropolymerization of an Electron Rich Conjugated Monomer over Anode to Reduce the Interfacial Resistance at Electrode-Electrolyte Interface (Chapter 5)**

Experimental: The organoboron monomer was synthesized as shown in Fig. 4 and it was electropolymerized over graphite anodes via two methods:

**Fig. 4** Schematic of the formation of the SEI and Reaction Scheme of synthesis of organoboron-thiophene monomer, **4**

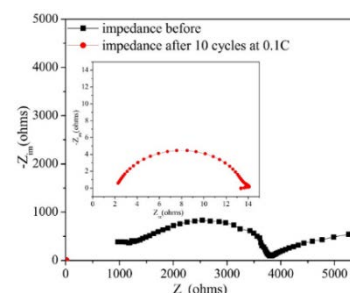
- a) *Pre-modification via cyclic voltammetry* in ionic liquid (AMImTFSI/BMImTFSI)/acetonitrile system as electrolyte
b) *In-situ modification via repeated charge-discharge cycles* in anodic half-cell configuration in 1 M LiTFSI in EC:DEC=1:1 as the electrolyte system.

Results and Discussion:

Modification of the anode surface with a boron-thiophene monomer resulted in reduction of charge-transfer resistance (Fig. 5) at the electrode-electrolyte interface and led to increased capacities. In case of *in-situ* modified anodes, the capacity obtained using boron-thiophene monomer as additive was higher as compared to thiophene. A drastic fall in charge-transfer resistance in the lithium cell containing the boron-thiophene monomer asserted the charge-discharge data without any fading and can be attributed to the formation of a highly stable and conductive interface (Table 3).

Table 3 Comparison of charge-discharge capacities and interfacial resistances of pre-modified anodes and *in-situ* modified anodes using **4**

Sample	Pre-Modification of Anode		In-situ Electropolymerization	
	Capacity: 1 st - 10 th cycle (mAh/g)	Interfacial resistance after cycling (Ω)	Capacity of 1 st cycle (mAh/g)	Interfacial resistance after cycling (Ω)
Only Graphite (No additive)	200 to 30	3500	-	-
Thiophene	-	-	20	100
4 (MBTB)	125-100	2500	60	16

**Fig. 5** Decrease in interfacial resistance after using monomer, **4**

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Keywords: Li ion battery low molecular weight electrolytes, organoboron compounds, solid electrolyte interface (SEI), lithium borates, electropolymerization, organoboron conducting polymer