Title	ケイホウ酸ガラス型有機・無機ハイブリッドの設計とその二次電池デバイスへの電気化学的応用
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Borosilicate Type Organic-inorganic Hybrid Ion-gels and their Electrochemical Applications in Secondary Battery Devices

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ABSTRACT

Nowadays, lithium ion batteries are widely employed as energy storage media in numerous electrical appliances. Although these batteries have higher energy density, flammability of electrolyte and lower transference number endanger their reliability for persistent usage in daily life. With the Boeing Dreamliner mishap due to faulty lithium-ion batteries, a deliberate and conscientious effort towards improvement safety parameters of the batteries apart from production efficiency in terms of cost, conductivity and other mechanical and thermal factors.

The present doctoral work mainly concerns with the design of novel ionic liquid based lithium ion conducting electrolytes for LiBs aiming at the improvement of the abovementioned issues, divided n the chapters 2,3 and 4 in the doctoral thesis. Hybrid ion-gel electrolytes via borosilicate glass formation is one of approach for such novel electrolytes. In-situ sol-gel condensation reactions of alkoxysilane/alkoxyborane in ionic liquid media resulted in the formation of organic-inorganic hybrids, which constitutes the principle subject of Chapter-2. Such, organic-inorganic hybrids have the dual advantages of high ionic conductivity due to the organic component and high thermal stability due to the inorganic component. Incorporation of boron improves ionic conductance by facilitated salt dissociation. Enhanced salt dissociation may be due to the possible interactions between the empty p-orbital of boron atom and the anion moiety. The main aspects of this chapter are highlighted in Fig. 1.

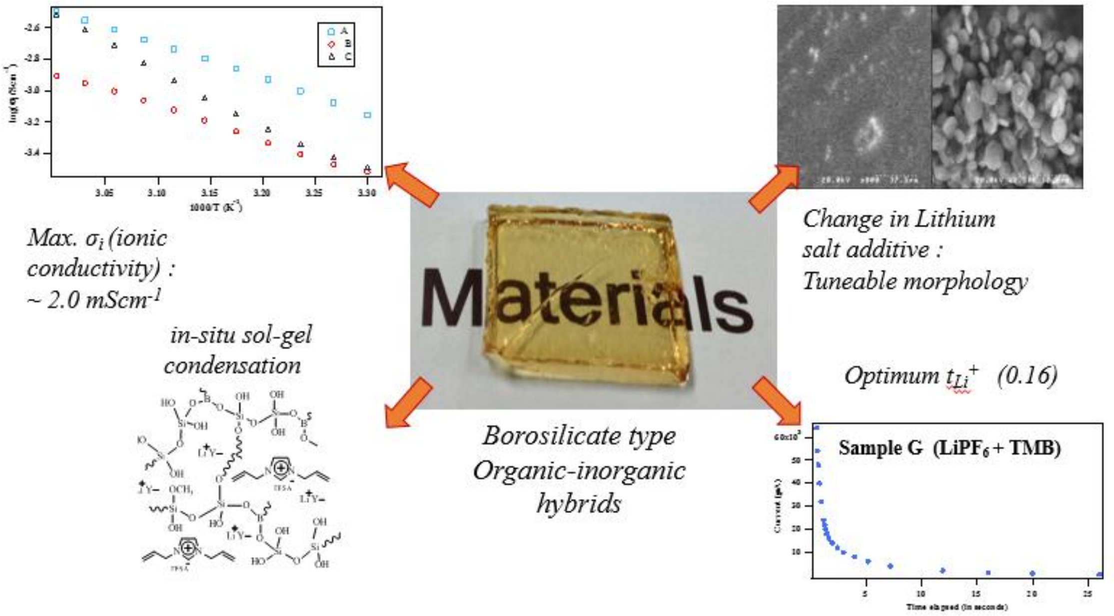

Figure 1. Highlights of Chapter 2

In the subsequent chapter, i.e. Chapter-3, the viability of the organic-inorganic hybrids as electrolytes for lithium batteries was studied by the fabrication of anodic half-cells, and their subsequent cycling at various charging current rates. The conventional protocol was employed for charge-discharge studies. Having obtained results not in terms with the typical patterns of batteries, a variant of the

Electrochemical Impedance spectroscopic technique was further employed to determine the causes of such anomalous behaviour. Given the novelty of the material, to get a clear view of the internal kinetics of cells, the impedance profiles of the anodic half-cells were studied over a range of potential utilising Dynamic Electrochemical Impedance Spectroscopy. It was observed that high capacitive tail-ends were observed at higher potentials in these anodic-half cells, with anomalous charge-discharge profiles at such potentials. Hence, utilising such non-destructive DEIS technique, and interpreting the results in terms effect of potential on the passivation of the electrolyte, the voltage cut-offs were revised. The revised protocol, which comprised of DEIS experiments followed by charge-discharge studies, provided notable results. The gist of this chapter is shown in Figure 2. The $LiPF_6$ based hybrids with various alkoxyboranes were considered for the studies in this chapter on account of their high ionic conductivities.

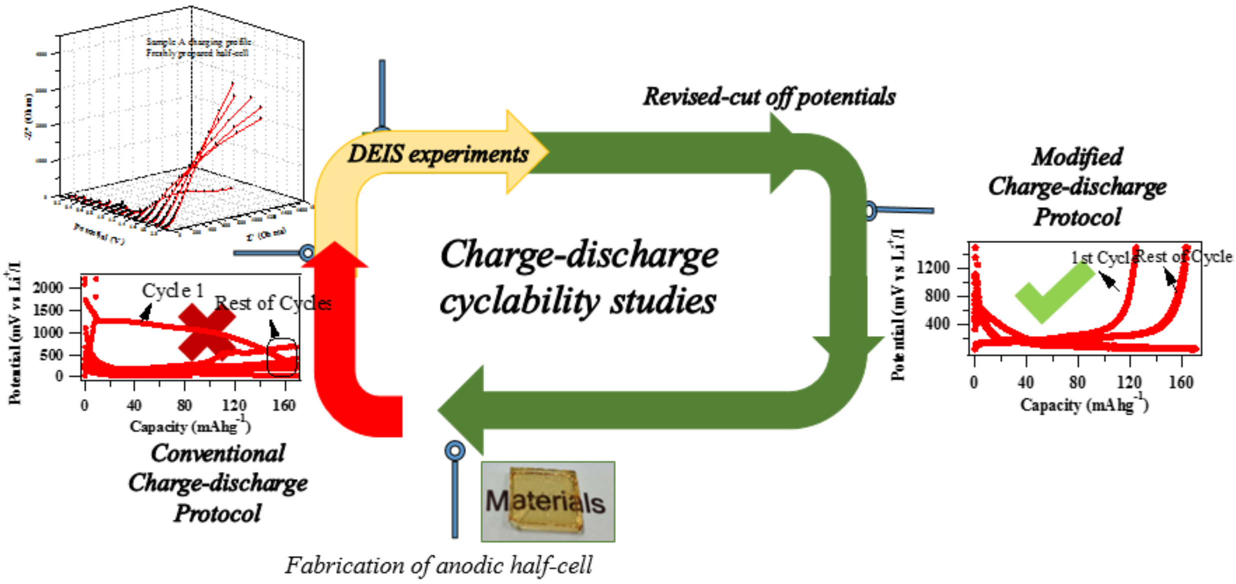

Figure 2. Highlights of Chapter 3

The major focus of the final chapter (Chapter-4) was on the flammability studies and thermogravimetric studies of the organic-inorganic hybrids to evaluate their thermal stability in a comparative manner with that of the commercially available electrolytes for lithium-ion batteries. Thermogravimetric analysis (TGA) showed morphologically uniform hybrids were stable up to 350°C. The highly homogenous hybrids with LiTFSA salt additive showed greater thermal stability in naked flame studies as well. While $LiPF_6$ based hybrids which characteristically showed heterogeneous behaviour showed higher susceptibility to flame tests, and showed lower range of thermal stability in thermogravimetric experiments. However, the hybrid electrolytes showed self-extinguishing features, which is absent in case of commercially used electrolytes in lithium ion batteries.

Thus, the doctoral work encompasses an overall study comprising of three steps. The first step being the design and synthesis of novel borosilicate type organic-inorganic hybrids along with the study of its conductivity and lithium-ion diffusivity aspects. The second phase includes the study of fabricated anodic half-cells using organic-inorganic hybrids for a practical demonstration of these hybrids in lithium batteries. In addition, Dynamic electrochemical impedance spectroscopy was used as a diagnostic tool to evaluate an optimum working rage for these cells. In the third and final step, the thermal stability of these hybrids was verified through thermogravimetric and naked flame studies.

Keywords: Organic-inorganic hybrids, ion-gels, in-situ sol-gel condensation, lithium-ion borosilicate, charge-discharge