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論文の内容の要旨

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.

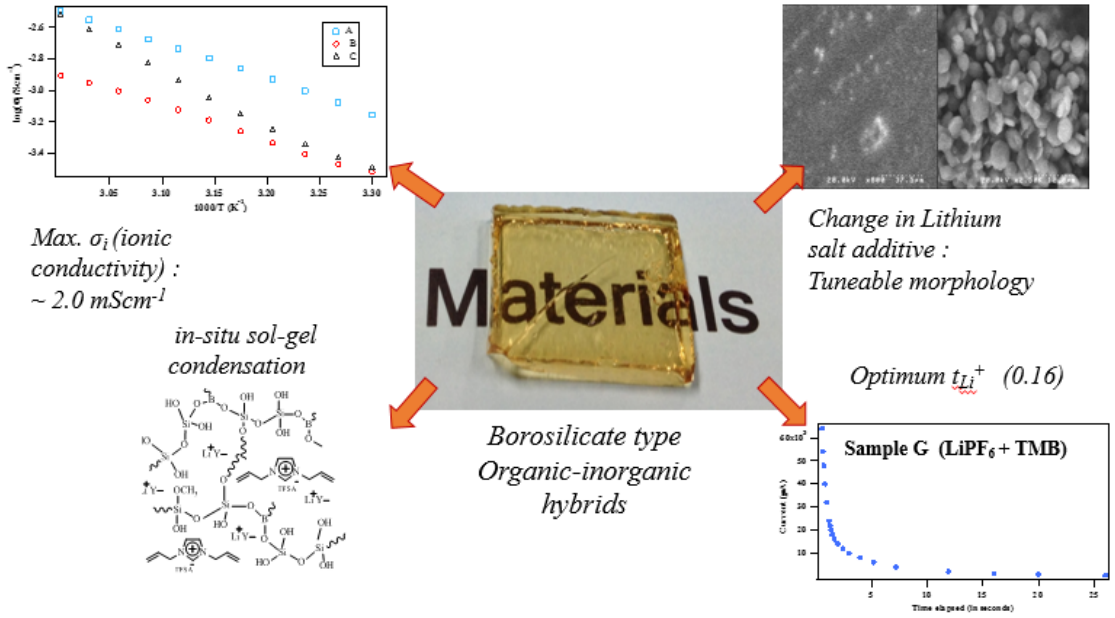

Figure 1. Highlights of Chapter 2

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.

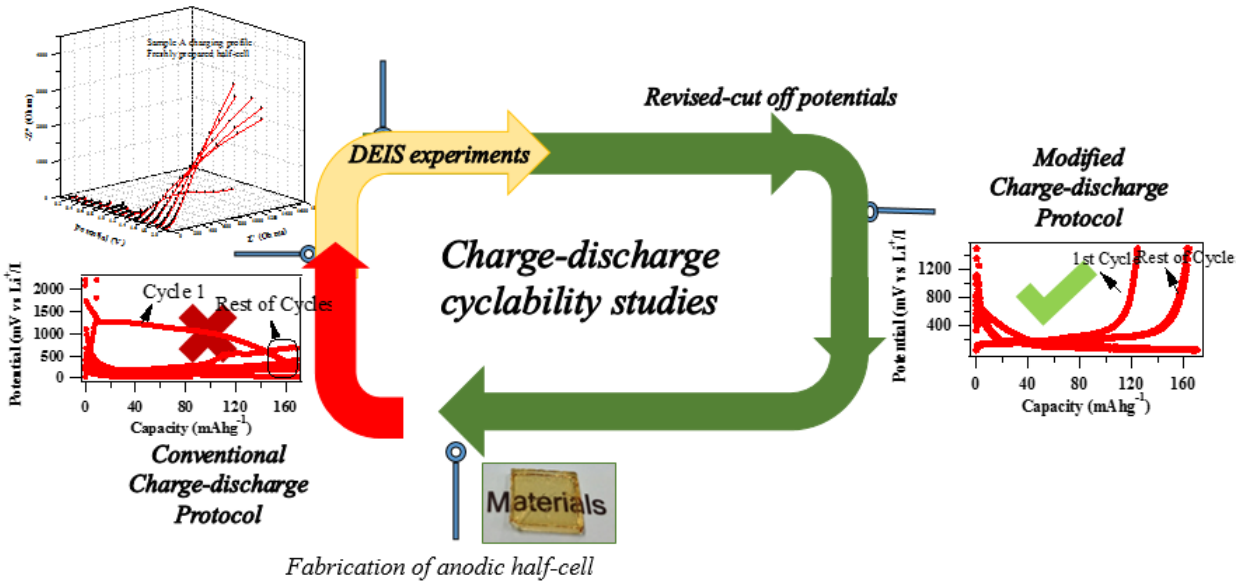

Figure 2. Highlights of Chapter 3

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

論文審査の結果の要旨

本論文では、ケイホウ酸ガラスと低粘度イオン液体から成る有機・無機ハイブリッド型イオンゲル電解質を in-situ ゾル―ゲル法により合成し、それらのイオン伝導性、モルフォロジー特性を検討した。得られた電解質材料を用いてリチウム箔を陽極、グラファイトを負極としたハーフセルを構築し、充放電特性評価を行った。また、電解質材料の耐熱性及び難燃性に関しても併せて評価した。

得られた電解質のイオン伝導特性は、優れた系では 10^{-3} Scm^{-1}を上回り、実用レベルに達した。また、SEM 観察によりモルフォロジーを検討したところ、LiTFSA 添加系では均一なモルフォロジーを示すのに対し、$LiPF_6$添加系では相分離オーダーが大きくなることが分かった。また、観測されたモルフォロジーの相違はイオン伝導特性と耐熱性の両面に影響を与えることが分かった。$LiPF_6$添加系では大きな相分離オーダーによりイオン伝導パスの接続が容易になり、結果として高いイオン伝導度を示した。一方、耐熱性においては有機成分と無機成分が均一に混和した LiTFSA 添加系が優れた特性を示した。

また、作製した電解質を用いて構築したハーフセルは可逆的な充放電特性を示した。同時に、良好な放電容量とサイクル特性を示し、固体電解質を用いた系としては非常に優れた特性を示した。更に本研究においては、構築した電池セルの終止電圧を非破壊的に簡易に決定する新たな手法を提案した。充放電曲線上と同様の条件において in-situ での DEIS（Dynamic Electric Impedance Spectroscopy）測定を連続的に行うことによって電解質―電極界面の界面電荷移動抵抗をモニタリングしつつ終止電圧を決定することにより、多くの電池セルに異なる条件で試行錯誤的に充放電試験を重ねる必要なく最適な充放電条件を見出すことに成功した。

電解質の安全性を調べるため、熱重量分析と燃焼試験を行った。汎用の電解質であるエチレンカーボネートとジエチレンカーボネートの混合系は炎を作用させることで容易に着火、燃焼したが、本研究で作製した各電解質に炎を作用させても着火することはなく、自己消炎性を有していることが分かった。

以上のように本研究で見出された電解質材料及び電気化学的分析手法は実学的及び学術的に多くの有益な知見を含んでおり、博士学位論文として相応しいものと認められる。