Novel Electrolytes for Lithium-Ion Batteries

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ABSTRACT

For many applications in consumer electronics lithium ion batteries (LIBs) are the energy source of choice because of their high energy-to-weight-ratio, lack of memory effect and low discharge when not in use. However, over the past years serious problems occurred as a consequence of short-circuit currents which led to overheating and ignition of the organic solvents used in the formulation of the electrolytes.

Ionic liquids (ILs) show interesting profiles of physical and chemical properties which allow their use as safe electrolytes in batteries. These properties include tunable viscosities and conductivities, chemical and thermal stability as well as large electrochemical windows, incombustibility and a low vapor pressure.

In this presentation we will report on our recent developments in the field electrolytes for LIBs based on ionic liquids. The focus of this talk will be the use of mixtures of ionic liquids and additives in order to increase the performance and the safety of such electronic devices.

Keywords: lithium ion battery, ionic liquid, electrolyte, mixture, additive

1 INTRODUCTION

Lithium ion batteries are today not only used as power sources for mobile electronic devices but also for a growing amount of electronic means of transportations.[1] The electrolyte of a lithium ion battery has a great influence on the performance of lithium ion batteries. Important requirements for the electrolyte of lithium ion batteries are a large electrochemical stability, a wide liquid range, a high thermal stability, a low vapor pressure, incombustibility, a low viscosity, a high lithium ion conductivity, a high capacity and high cycling rates.[2] The major problems of lithium ion batteries with conventional electrolytes are that short circuits often lead to overheating and ignition of the organic solvents, which are part of conventional electrolytes.[3]

Ionic Liquids (ILs) are a new class of materials, consisting entirely of ions, which are liquid at unusual low temperatures.[4] Typical structural motifs combine organic cations with inorganic, or, more rarely, organic anions (Figure 1). Ionic liquids possess a unique combination of properties, like a wide liquid range and a high thermal stability. In particular their low vapor pressure and their incombustibility is making them safer alternatives for low volatile organic solvents, which are an important components of conventional electrolytes for lithium ion batteries.[5] Therefore, ionic liquids based electrolytes became more and more important and thus part of many investigations during the last years.[6-14]

Figure 1: Examples of typical cations and anions.

Ionic liquids can also be used as additives for increasing the conductivity of conventional electrolytes.[15] In order to obtain insight in the nature of the solid electrolyte interface (SEI) layer between the electrolyte and the electrode in situ transmission electron spectroscopy[18] and impedance spectroscopy[19] of lithium ion batteries with ionic liquids based electrolytes were performed. Investigations of interfacial layers between ionic liquids and Au(111) surfaces were performed by Endres et al.[20]

Despite their advantages, most ionic liquids-based electrolytes show lower conductivities than conventional electrolytes. This is mostly due to the higher viscosity of ionic liquids in comparison to conventional organic solvents. In order to decrease the viscosity and to increase the conductivity of ionic-liquid based electrolytes, we investigated mixtures of different ionic liquids and ionic liquids with additives.

2 MIXTURES OF IONIC LIQUIDS

For the use as components in electrolytes of lithium ion batteries the optimal ionic liquids should possess a low viscosity and a high conductivity to overcome transport limitations. In particular ionic liquids based on bis(trifluoromethylsulfonyl)imide, bis(fluorosulfonyl)imide or trifluoromethylsulfonate anions are interesting candidates for battery applications due to their high electrochemical stability (Figure 2-5).
As Figure 2 and 3 demonstrates, ionic liquids with bis(trifluoromethylsulfonyl)imide anions are electrochemically a little bit more stable than those with trifluoromethanesulfonate anions.

The absence of an extremely protic C-H bond like the C2-H bond between the two nitrogen atoms of the imidazolium cation leads to a higher electrochemical stability of ionic liquids with pyrrolidinium cations in comparison to those with imidazolium cations (Figure 2 and 3).

The electrochemical stability of ionic liquids with bis(fluorosulfonyl)imide anions is only slightly lower than those of ionic liquids with bis(trifluoromethylsulfonyl)imide anions (Figure 4 and 5).

Due to their lower viscosity and higher conductivity ionic liquids with bis(fluorosulfonyl)imide anions might be good electrolyte components, according to the application area of the batteries.

We were interested in the viscosity and the conductivity of binary mixtures of ionic liquids, because the increased entropy of the components of an eutectic mixture usually leads to a decrease of the melting temperature. First of all we investigated binary mixtures of ionic liquids like mixtures of 1,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide (DiMIM BTA) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM BTA).

The viscosity of different mixtures of these ionic liquids in comparison to the viscosity of the pure substances is shown in Figure 7. The mixture of 10 mol% DiMIM BTA and 90 mol% EMIM BTA shows a lower viscosity than the pure EMIM BTA and the pure DiMIM BTA. It is also significantly lower than the viscosities of the other mixtures of EMIM BTA and DiMIM BTA.

The conductivity of these mixtures is shown in Figure 8. As expected, the conductivity of the mixture of 10 mol% DiMIM BTA and 90 mol% EMIM BTA is at 30 °C with 8.828 mS/cm significantly higher than the conductivity of the pure ionic liquids EMIM BTA or DiMIM BTA.
Figure 8: Temperature-dependent viscosity of EMIM BTA, DiMIM BTA and selected mixtures.

Promising results were also obtained for mixtures of 1-allyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (AllylMIM BTA) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM BTA). While the viscosity of the mixtures is not lower than the viscosity of the pure ionic liquids (Figure 9), the mixture of 10 mol% AllylMIM BTA and 90 mol% EMIM BTA has a significantly higher conductivity than the pure ionic liquids (Figure 10).

The Arrhenius plot of the mixtures of AllylMIM BTA and EMIM BTA as well as of the pure ionic liquids (Figure 11) shows a deviation from Arrhenius-like behaviour. Instead, the selected ionic liquids and mixtures fit to a Vogel-Fulcher-Tammann behaviour, indicating that EMIM BTA, AllylMIM BTA, and the selected mixtures of these two ionic liquids are supercooled liquids.

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Figure 11: Arrhenius-Plot for the temperature dependent viscosity of AllylMIM BTA, EMIM BTA and selected mixtures.

3 INFLUENCE OF ADDITIVES

Conventional electrolytes for lithium ion batteries have a conductivity of at least 10 mS/cm.[22] The mixtures shown in this paper have after addition of Li BTA a conductivity which is significantly lower. This shows that further optimizations are necessary before using an electrolyte consisting of pure ionic liquids for commercial lithium ion batteries. Thus, we also investigated the influence of additives on the viscosity and conductivity of mixtures of ionic liquids. We therefore used additives which we assumed to have a positive influence on the lithium ion conductivity. One example for those additives is substance X.

Figure 12: Temperature-dependent viscosity of mixtures of ionic liquids with and without additive X.

As can be seen in Figure 12 the viscosity of the mixtures is slightly increased by the addition of additive X, which is due to a relatively high viscosity of additive X.
Consequently, the conductivity of the mixtures is reduced in the presence of additive X (Figure 13).

It is well known that the addition of lithium bis(trifluoromethylsulfonyl)imide leads to a decrease of the conductivity of ionic liquids. This is also observed in the presence of additive X (Figure 14). But additive X reduces the drop of the conductivity significantly.

![Figure 13: Temperature-dependent conductivity of mixtures of ionic liquids with and without additive X.](image)

![Figure 14: Temperature-dependent conductivity of mixtures of ionic liquids.](image)

4 CONCLUSION

We were able to demonstrate that the viscosity of ionic liquids can be reduced by mixing different ionic liquids. The reduction of the viscosity leads to an increase of the conductivity. We were also able to increase the conductivity in the presence of lithium bis(trifluoromethylsulfonyl)imide by addition of non-ionic additives. The use of mixtures of ionic liquids has a large potential for electrochemical applications in general and for lithium ion batteries in particular. In addition, further investigations are necessary to understand the influence of the bulk structure of the ionic liquids on the viscosity and the conductivity of the mixtures of different ionic liquids and to identify mixtures of ionic liquids which have even higher conductivities.

5 REFERENCES