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Development of Ion-Conductive Liquid Crystals Having Fluorinated Mesogens towards Electrolytes for Lithium-Ion Batteries

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Abstract

Ion-conductive nanostructured liquid crystals having fluorinated mesogens have been developed for improvement of the oxidation resistance towards electrolytes for lithium-ion batteries. These liquid-crystalline (LC) electrolytes form 2D ion-conductive pathways by self-assembly. The LC electrolytes show oxidation resistance up to 4 V versus Li/Li$^+$. Lithium half-cells composed of LiFePO$_4$ and the LC electrolytes exhibit high coulombic efficiency and no obvious decrease of the capacity within 30 cycles.

1. Introduction

Ion-conductive nanostructured liquid crystals have attracted attention as quasi-solid electrolytes for energy devices because they provide efficient ion-conductive pathways by self-assembly[1)]. We have developed carbonate-based smectic liquid crystals forming 2D ion-conductive pathways and successfully operated lithium-ion batteries with these LC electrolytes[2)-4)]. Here we report design and synthesis of compound **1** as a new LC electrolyte molecule having a fluorinated mesogen for improvement of the oxidation resistance (Fig. 1a). We expected that introduction of fluorine atoms to the mesogen would lower the highest occupied molecular orbital (HOMO) level of the LC molecule and enhance the oxidation resistance compared to non-fluorinated LC compound **2** (Fig. 1b).

2. Experiment

Compound **1** was designed and synthesized for improvement of the oxidation resistance (Fig. 1a). The LC properties of compound **1** and its mixtures with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in molar ratios of 9:1 to 5:5 were characterized. The ionic conductivities of the mixtures were measured by alternating current impedance method. The electrochemical stability of the mixture of **1**/LiTFSI in the molar ratio of 8:2 was studied with cyclic-voltammetry (CV) measurements. The performance of lithium-ion batteries using the mixture of **1**/LiTFSI was examined with a half-cell composed of LiFePO$_4$ and lithium metal at 60 °C.

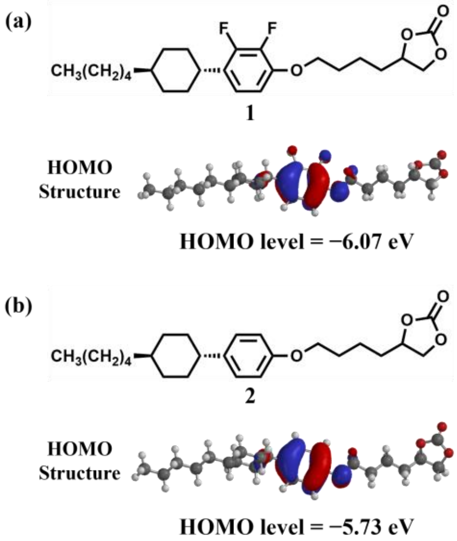

Fig. 1 Molecular structures, HOMO structures and HOMO levels of **1** and **2**.

3. Results and discussion

Compound **1** and the mixtures of **1**/LiTFSI exhibited smectic A phases over wide temperature range. The isotropization temperatures of the mixtures were higher than that of **1** alone due to the ion-dipole interactions between lithium ions and carbonate groups. The mixture of **1**/LiTFSI in the 8:2 molar ratio showed the highest ionic conductivity among the mixtures, which was comparable to that of the mixture of **2**/LiTFSI[2)].

Fig. 2 shows the CV curves of **1**/LiTFSI and **2**/LiTFSI[2),4)]. The peaks corresponding to the lithium deposition and dissolution were observed around 0 V versus Li/Li$^+$. In the high potential region, the mixture of **1**/LiTFSI was stable up to 4 V, while the decomposition peak was observed for the mixture of **2**/LiTFSI before reaching to 4 V. These results suggest that the fluorination of the mesogen improved the oxidation resistance.

The charge-discharge curves were obtained for a lithium half-cell composed of $LiFePO_4$ and the LC electrolyte of **1**/LiTFSI (Fig. 3). No obvious decrease of the capacity was observed within 30 cycles. The cyclability and coulombic efficiencies were higher than those of the cell using **2**/LiTFSI. These results suggest that the improvement of the oxidation resistance suppressed undesired side reactions to provide enhanced battery performance.

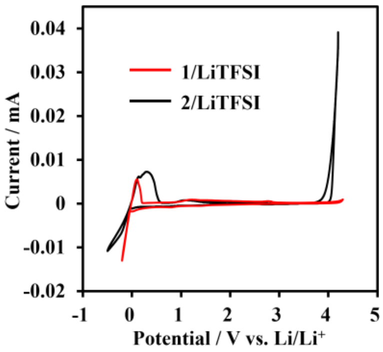

Fig. 2 Cyclic voltammograms of **1**/LiTFSI and **2**/LiTFSI.

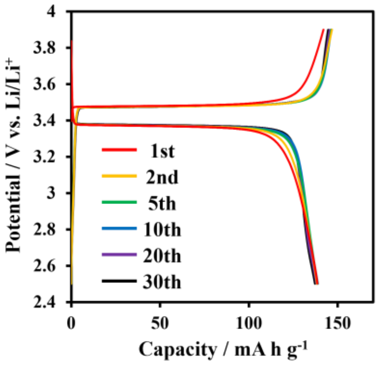

Fig. 3 Charge–discharge curves of the lithium half-cell composed of $LiFePO_4$ and the LC electrolyte of **1**/LiTFSI.

4. Conclusions

We have developed new LC electrolytes having fluorinated mesogens for improvement of the oxidation resistance. These LC electrolytes formed 2D ion-conductive pathways in the smectic A phases. The fluorination of the mesogen provides improved electrochemical stability for the LC electrolytes, leading to the enhancement of the battery performance of lithium half-cells composed of $LiFePO_4$ and the LC electrolytes.

Acknowledgments

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