博士論文

Development of Nanostructured

Liquid-Crystalline Electrolytes for

Battery Applications

（電池への応用のためのナノ構造液晶電解質

の開発）

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Self-assembly is one of promising approaches to the development of materials providing high and new functions in their condensed states. The bottom-up syntheses of materials where functional molecules spontaneously form ordered structures are expected as energy saving and environmentally friendly processes.

Liquid crystals are representative self-assembled materials. Owing to their unique properties of forming dynamic nanostructures, liquid crystals offer a variety of advantages such as organization of functional groups, anisotropic functions, and dynamic properties. The author focuses on ion-conductive liquid crystals. They form 1D, 2D, and 3D ion-conductive pathways in their columnar, smectic, and bicontinuous cubic liquid-crystalline (LC) nanostructures, respectively. Because these pathways enable the efficient and anisotropic transport of ions, ion-conductive liquid crystals have attracted attention as new electrolytes for energy devices, such as lithium-ion batteries, fuel cells, and dye-sensitized solar cells. Among these devices, the main target in this thesis is lithium-ion batteries. Lithium-ion batteries are high-performance secondary batteries with high voltage, high energy density, and excellent cyclability. Generally, electrochemical insertion and extraction of lithium ions at electrodes are the driving forces for energy storage. For electrolytes, many kinds of materials are studied. However, there is no report on LC electrolytes for the batteries because of the difficulty to satisfy the requirements for application.

In the present thesis, the development of nanostructured LC electrolytes for lithium-ion batteries is described. The author focuses on two main properties of electrochemical stability and ionic conductivity. In consideration of electrochemical stability, carbonate-based LC electrolytes have been developed in chapter 1 and chapter 2. For improvement of ionic conductivity, ionic liquid-based LC systems with highly mobile ion-conductive pathways and large conductive area have been studied in chapter 3 and chapter 4, respectively.

Chapter 1. Carbonate-Based Liquid-Crystalline Electrolytes for Lithium-Ion Batteries

This chapter describes the material design and the development of LC electrolytes with high electrochemical stability. The applicability of the electrolyte to lithium-ion batteries is demonstrated. Organic carbonates are employed as the ion-conductive moieties of LC molecules. Carbonates are practically used in lithium-ion batteries because of their high electrochemical stability and ionic conductivity. A cyclic carbonate-based rod-like molecule has been designed. LC electrolytes consisting of the molecule and a lithium salt have been developed for the formation of 2D ion-conductive pathways with high mobility and large area in their smectic LC assemblies. In this chapter, it is reported that the mixtures of the carbonate-based molecule and a lithium salt exhibit smectic LC phases in wide temperature ranges. Infrared spectroscopy shows the existence of ion-dipole interactions between carbonate groups and lithium ions in the LC mixtures. Ionic conductivity measurements by the alternating current impedance method reveal that the electrolytes exhibit higher ionic conductivities than the previously reported carbonate-based columnar liquid crystal, which is attributed to the higher ion mobility of 2D ion-conductive pathways than that of 1D ones. In addition, high electrochemical stability of the LC electrolyte for application to lithium-ion batteries is shown by cyclic voltammetry. It is concluded that the LC electrolyte can be applied to lithium-ion batteries through charge-discharge experiments for the electrochemical cells composed of the LC electrolyte and electrodes of lithium-ion batteries. This is the first demonstration of the applicability of LC electrolytes to lithium-ion batteries. The details of this study are discussed in paper [1].

Chapter 2. Liquid-Crystalline Electrolytes Based on Steroid Mesogens

This chapter describes the designs and the syntheses of ion-conductive LC molecules based on steroid mesogens in expectation of high electrochemical stability of electrolytes. In chapter 1, the gradual reduction of the LC electrolyte and the capacity fade of batteries during charge-discharge cycling have been observed. Based on this observation, carbonate-based LC molecules having a steroid mesogen have been designed. The study on frontier molecular orbitals of molecules by density functional theory calculations leads to the assumption that the employment of the mesogen without π electrons should provide LC electrolytes with high electrochemical stability. Liquid crystallinity and properties as electrolytes are reported for the ion-conductive liquid crystals consisting of the steroid-based molecules and lithium salts. The details of this study will be discussed in paper [2].

Chapter 3. Formation of Highly Mobile 2D Ion-Conductive Pathways through Self-Assembly of Ionic Liquid Crystals and Ionic Liquids

The development of highly ion-conductive LC materials is described in this chapter. Ionic liquids are selected as ion-conductive parts for LC electrolytes. Ionic liquids are organic salts showing isotropic liquid states at room temperature. They receive attention as new electrolyte materials due to their nonvolatility, nonflammability, and high ionic conductivity. The material design in this chapter is the construction of highly mobile 2D ion-conductive pathways by mixing rod-shaped ionic LC molecules and ionic liquids. This design comes from the difficulty to obtain high conductivity for one-component systems of ionic liquid crystals because of the low mobility of ions covalently bonded to the mesogens. Rod-like molecules having an imidazolium ionic moiety have been designed as the ionic LC molecules. Imidazolium salts have been employed as the ionic liquids because of their high ionic conductivity. It is reported that the ionic LC molecule and the ionic liquids are compatible over the whole range of composition and cooperatively form 2D ion-conductive pathways in the smectic LC assemblies. The isotropization temperature of mixture decreases with the increase in the mole fraction of the ionic liquid. This tendency suggests the formation of fluid LC structures by incorporation of the ionic liquid. It is demonstrated that the organization of the ionic liquid into the 2D conductive pathways leads to the enhancement of ionic conductivity of the LC electrolytes. The calculation of activation energy for ion conduction indicates the formation of pathways with higher mobility by addition of the ionic liquid. The three-component mixtures containing lithium salts have been also prepared for lithium ion-conductive electrolytes. LC and ion-conductive properties of the materials are described. The details of this study are discussed in paper [3].

Chapter 4. Ionic Liquid Crystals with Large Conductive Area

This chapter describes the design and the development of ionic liquid-based LC electrolytes with large conductive area. The intention in this chapter is that wide ion-conductive regions formed in normal-type nanosegregated LC structures lead to high ionic conductivity. Wedge-shaped molecules having imidazolium moieties on their peripheries have been designed and synthesized. It is reported that the molecules with two imidazolium moieties exhibit hexagonal columnar phases, whereas the molecule with three ionic moieties shows a micellar cubic one. By referring to the phase behavior of nanosegregated liquid crystals, it is concluded that these molecules form normal-type columnar and micellar cubic LC structures where ionic moieties are placed at the outer sides of columns and micelles. Anisotropic ionic conductivities of the columnar LC molecule have been measured by the alternating current impedance method for the oriented samples. It is revealed that ion-conductive properties are hardly affected by column orientation, which indicates the formation of 3D continuous ion-conductive matrices. The mixtures of an imidazolium ionic liquid and the columnar LC molecule have been prepared. It is demonstrated that addition of the ionic liquid induces micellar cubic LC assemblies because of the increase in volume fraction of ionic moieties in the system. Ionic conductivity measurements for the LC mixtures reveal that the conductivity increases with the increase in mole fraction of the ionic liquid. This observation leads to the conclusion that the organization of the ionic liquid into LC nanostructures results in higher mobility of ion-conductive regions. The details of this study will be discussed in paper [4].

Chapter 5. Conclusion and Perspective

The present thesis describes the design and the development of LC electrolytes aimed at the application to lithium-ion batteries. The approaches focused on two main properties of electrochemical stability and ionic conductivity are reported.

In chapter 1 and chapter 2, the development of carbonate-based LC electrolytes designed for high electrochemical stability is described. Through the material design shown in the chapters, the applicability of LC electrolytes to lithium-ion batteries is demonstrated for the first time.

Chapter 3 and chapter 4 report the development of highly ion-conductive LC electrolytes based on ionic liquids. In chapter 3, the formation of highly mobile 2D ion-conductive pathways in the LC co-assemblies of ionic liquid crystals and ionic liquids is described. The development of ionic liquid crystals with large ion-conductive area is reported in chapter 4.

In conclusion, this thesis demonstrates the potential of ion-conductive liquid crystals as electrolytes for lithium-ion batteries and gives the design strategies to develop novel high performance LC electrolytes. The results shown in this thesis may lead to the development of self-assembled electrolytes for not only lithium-ion batteries but also other types of energy devices.

List of Publications

Original Papers

[1] "Liquid-Crystalline Electrolytes for Lithium-Ion Batteries: Ordered Assemblies of a Mesogen-Containing Carbonate and a Lithium Salt"
Junji Sakuda, Eiji Hosono, Masafumi Yoshio, Takahiro Ichikawa, Takuro Matsumoto, Hiroyuki Ohno, Haoshen Zhou, Takashi Kato, *Adv. Funct. Mater.* **2015**, DOI: 10.1002/adfm.201402509.

[2] "Liquid-Crystalline Electrolytes with High Electrochemical Stability: Carbonate-Based Liquid Crystals Having a Steroid Mesogen"
Junji Sakuda, Eiji Hosono, Masafumi Yoshio, Takahiro Ichikawa, Hiroyuki Ohno, Haoshen Zhou, Takashi Kato, in preparation.

[3] "2D Assemblies of Ionic Liquid Crystals Based on Imidazolium Moieties: Formation of Ion-Conductive Layers"
Junji Sakuda, Masafumi Yoshio, Takahiro Ichikawa, Hiroyuki Ohno, Takashi Kato, submitted.

[4] "Ionic Liquid Crystals with Large Conductive Area: Wedge-Shaped Molecules Having Peripheral Imidazolium Moieties"
Junji Sakuda, Masafumi Yoshio, Takahiro Ichikawa, Hiroyuki Ohno, Takashi Kato, in preparation.

References

[1] "Hole Transport of a Liquid-crystalline Phenylterthiophene Derivative Exhibiting the Nematic Phase at Ambient Temperature"
Midori Nuita, Junji Sakuda, Yuki Hirai, Masahiro Funahashi, Takashi Kato, *Chem. Lett.* **2011**, *40*, 412–413.

[2] "Design of Amphiphilic Zwitterions Forming Liquid-Crystalline Phases and Effects of Lithium Salt Addition on Their Phase Behavior"
Takuro Matsumoto, Takahiro Ichikawa, Junji Sakuda, Takashi Kato, Hiroyuki Ohno, *Bull. Chem. Soc. Jpn.* **2014**, *87*, 792–796.

Reviews

[1] "Liquid-Crystalline Catenanes and Rotaxanes"
Junji Sakuda, Takuma Yasuda, Takashi Kato, *Isr. J. Chem.* **2012**, *52*, 854–862.

[2] "Liquid-Crystalline Catenanes and Rotaxanes"
Junji Sakuda, Takuma Yasuda, Takashi Kato, in *Handbook of Liquid Crystals, 2nd Edition*, Vol. 5 (Eds: J. W. Goodby, P. J. Collings, T. Kato, C. Tschierske, H. Gleeson, P. Raynes), Wiley-VCH, Weinheim **2014**, Ch. 11, pp. 541–555.