

# 博士論文

## **Development of Liquid-Crystalline Self-Organized Electrolytes for Energy Devices**

(エネルギーデバイスのための  
液晶性自己組織化電解質の開発)

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## Chapter 1. Introduction

Self-assembly is a process in which certain components spontaneously form organized structures or patterns as a consequence of specific, local interactions among the components themselves. For molecular systems, by considering intermolecular interaction, nanosegregation and molecular shapes, appropriately designed molecules form various nanostructures. If we introduce functional moieties, such as electrical and optical properties into these systems, we can control the function of materials as well as their nanostructures.

Liquid crystals are representative self-assembling materials. They have characteristics of both crystal and liquid such as anisotropic and dynamic properties. Some amphiphilic molecules consisted of immiscible parts exhibit various liquid-crystalline (LC) nanosegregated structures. Use of dynamic properties and nanostructures of liquid crystals are promising approach for development of ion-conductive materials. Ion-conductive liquid crystals have ion-conductive moieties such as carbonate, oligoethylene oxide and ionic moieties, combined with certain mesogenic moieties. They form self-assembled nanostructures depending on their molecular structures and exhibit different ion-conducting behavior. Efficient ionic conductivities of 1D, 2D and 3D in their columnar, smectic, and bicontinuous cubic LC assemblies can be achieved. Ion-conductive liquid crystals can be applied to electrolytes of energy devices. For examples, Li-ion conductors and iodides-ion conductors are applied to lithium-ion batteries (LIBs) and dye-sensitized solar cells, respectively. Proton conductors have potential application for fuel cells (FCs). Among these devices, the author focuses on the development of LC Li-ion conductors and proton conductors. Both LIBs and FCs play central rolls in energy storage and conversion systems for sustainable society. Commercial use of these devices has been wide-spreading and demands for these devices have been growing rapidly. For both LIBs and FCs, the three main components are anodes, cathodes and electrolytes. Electrolytes are electrically insulating but ionically conducting materials and important factor affecting the power performances and reliability of these devices.

In these backgrounds, the objective of this thesis is development of LC ion-conductors for Li-ion and proton. For development of Li-ion conductors, enhanced performances of LC electrolytes for LIBs by noncovalent approach, and development of novel LC Li-ion conductors having a fluorinated oligoethylene oxide moiety are described in chapter 2 and chapter 3, respectively. For development of proton conductors, proton conductive hybrid materials consisted of organic molecules having an imidazole moiety and polyoxometalates as proton source are described in chapter 4.

## **Chapter 2. Improvement of Performances of Liquid-Crystalline Electrolytes for Li-Ion Batteries by Noncovalent Approach**

In this chapter, achievement of high performance LIBs with LC electrolytes is described. LIBs are high-performance secondary batteries with high voltage, high energy density, and excellent cyclability. For commercial LIBs, carbonate-based organic solutions of lithium salts are used because of their electrochemical stability and high ionic conductivity. However, intrinsic safety concerns such as leakage, evaporation and flammability sometimes cause serious troubles. As one of the approaches to tackle this problem, LC states as quasi-solid electrolytes can be beneficial. Previously, columnar liquid crystals having a cyclic carbonate group was developed, and the mixtures with a lithium salt showed 1D ionic conductivities. To improve ionic conductivity and electrochemical stability, a calamitic molecule forming smectic LC assemblies was developed and applied to electrolytes of LIBs for the first time. However, high rate charge-discharge operation based on LC electrolytes have not yet been achieved owing to the still low ionic conductivities. Higher ionic conductivities of LC electrolytes are required for improvement of power performances including room-temperature operation. The author employed a noncovalent approach for enhancement of ionic conductivity. Organization of mobile small electrolyte molecules into the LC ion-transporting nanostructures can be an effective strategy to achieve highly conductive materials for LIBs.

In the present study, the author has applied ternary mixtures of a calamitic molecule having a cyclic carbonate moiety, a lithium salt, and ethylene carbonate (EC) or propylene carbonate (PC). The author expected that small carbonate molecules would be organized into the self-assembled structure with structure-directing calamitic molecules through noncovalent interactions. The ternary mixtures are expected to provide highly Li-ion conducting 2D channels, leading to the construction of high-performance LIBs. The LC properties of ternary mixtures with different weight ratio of EC are investigated. The mixtures showed stable smectic A (SmA) phases in a wide temperature range. The mixtures showed the lower isotropization temperatures as the EC content in the mixtures increased. However, the thermal stability of LC phase is sufficient even for the mixture containing 29 wt% of EC whose isotropization temperature is 80 °C. To investigate the nanostructures of the LC mixtures, X-ray diffraction were measured. The pattern for the mixture containing 29 wt% of EC showed three reflection peaks corresponding to the reflections of a layered structure with a spacing of nearly twice the molecular length which was estimated by molecular mechanics calculations. These results indicate the formation of a bilayered structure of the SmA phase. Ionic conductivities of the mixtures were examined by the alternating current impedance method. The results reveal that

the higher EC content resulted in the higher ionic conductivities. The conductivities of the mixture containing 29 wt% of EC at 60 and 25 °C were approximately 20 and 60 times higher, respectively, than those of the binary mixture of the calamitic molecule and a lithium salt. For the ternary mixture, Li-ions were transported efficiently with highly mobile EC molecules within the conductive layers of the smectic structures. These LC electrolytes were evaluated on the basis of electrochemical performance of half cells composed of Li metal and LiFePO<sub>4</sub>, which is one conventional positive electrode material for LIBs. The rate performances were evaluated by charging/discharging at different current rates at 60 °C. It is noteworthy that the initial and final capacities of approximately 150 mAh g<sup>-1</sup> at a low current density of 5 and 25 mA g<sup>-1</sup> were close to the theoretical capacity of LiFePO<sub>4</sub> (172 mAh g<sup>-1</sup>). Remarkably, in the case of the mixture containing 29 wt% of EC, the capacity was retained at high values (more than 100 mAh g<sup>-1</sup>) even at relatively high current densities of 500 mA g<sup>-1</sup>. These rate performances for the LC electrolytes came from the highly ion-conductive properties. In the charge/discharge profiles at different current densities, the potential plateaus for the mixture containing 29 wt% of EC show a small polarization even at a high current density, indicating the low resistance of the LC electrolyte. From these results, the rate performances and polarization of potential plateaus were strongly related to the ionic conductivities of the electrolyte. For LC electrolyte of this composition, operation at room temperature were also examined. This LC electrolyte retained high values of 100 mAh g<sup>-1</sup> even at relatively high current density of 100 mA g<sup>-1</sup>. It is concluded that the use of noncovalent approach for the enhancement of the performance in the LC electrolytes is effective, achieving the room-temperature operation. The detailed discussion of this study is presented in paper [1].

### **Chapter 3. Block-Structured Molecules Having a Perfluorinated Oligoethylene Oxide Moiety for Lithium-Ion Conduction**

In this chapter, the LC properties of block-structured molecules having a perfluorinated oligoethylene oxide moiety and ion-transporting properties of their complexes with lithium salts are described. Perfluoropolyether-based electrolytes have great potential for electrolytes of LIBs with enhanced safety and durability because of their nonflammability, thermal stability and electrochemical stability. For exploration of novel LC Li-ion conductors, block-structured molecules comprising a perfluorinated oligoethylene oxide monoalkyl ether and a terminal methyl carbonate moiety have been developed. The fluorinated molecules showed highly ordered smectic phases around room temperature. The fluorinated molecule exhibited lower isotropization temperature than

the non-fluorinated analog. As for ionic conductivity, the complex of the fluorinated molecule with a lithium salt showed lower conductivities compared to that of the non-fluorinated molecule. It can be explained that dissociation and transport of Li-ions are caused solely by carbonate moieties in the case of the fluorinated molecule. The detailed discussion of this study is presented in paper [2].

## **Chapter 4. Structural Control and Proton Conductivities of Polyoxometalate-Organic Liquid-Crystalline Hybrids**

In this chapter, development of LC proton conductors consisted of organic proton accepting molecules and polyoxometalates is described. Conventional proton conductors for proton exchange membrane for FCs are perfluorinated polymers with sulfonic groups. They have concerns of high cost and environmental burden. Non-fluorinated polymers such as sulfonated aromatic polymers and acid-base polymer complexes have been developed to replace perfluorinated ones. However, there are still needs for efficient anhydrous proton conductors which can be used over 100 °C. Several LC anhydrous proton conductors were reported. For examples, 2-alkylated imidazole or wedge-shaped sulfobetaine are complexed with Brønsted acids to form 2D or 1D and 3D proton-transporting nanochannels. By the addition of Brønsted acids, the mesogenic proton accepting molecules work as the efficient proton-transporting medium. For exploration of novel LC anhydrous proton conductors, polyoxometalates as Brønsted acids have attracted the author's attention. Polyoxometalates, especially for Keggin-type heteropoly acids, have strong acidity and redox activity, thus are promising materials for FCs because of their high proton conductivities in solid hydrate state and catalytic activities for both reduction of oxygen and oxidation of carbon monoxide. To fully exploit these properties and achieve desired functions, control of their aggregated structures from molecular-level to macroscopic scale is essential. Our strategy here is use of thermotropic LC nanostructures for structural control of polyoxometalates from nano- to macro-scopic scale.

In the present study, proton conductive hybrid materials have been developed by complexation of wedge-shaped molecule having an imidazole moiety with phosphotungstic acid. Imidazole is promising for anhydrous proton-transporting material which can be used in the temperature region over 80 °C. Solid materials incorporating imidazole molecules in regular nanostructures can be used for proton-exchange membrane materials for FCs. In the present system, regular nanochannel formed by imidazole moieties and phosphotungstic acids can be advantageous for proton-transport. The LC behaviors of mixtures of imidazole derivatives with phosphotungstic

acid were examined. While the derivatives themselves did not show any LC phases, the mixtures showed LC phases including hexagonal columnar ( $\text{Col}_h$ ) phases, bicontinuous cubic ( $\text{Cub}_{bi}$ ) phases and smectic A ( $\text{SmA}$ ) phases depending on mol% of the acid and temperature. The imidazole derivatives with different number (two or three) of dodecyl chains at the periphery showed different LC properties. The mixtures of that of three dodecyl chains exhibited only  $\text{Col}_h$  phases. This can be explained that the volume ratio of ionophobic domain of dodecyl chains is larger, resulting in favored formation of  $\text{Col}_h$  structures rather than  $\text{Cub}_{bi}$  or  $\text{SmA}$  structures. As for the stability of LC phases, increase of the acid resulted in higher isotropization temperatures. This is ascribed to the formation of acid-base ion-pairs between imidazole derivatives and the acid. Increase of the ion pairs lead to stronger intermolecular interactions, which stabilize the molecular arrangement. For further analysis on the LC structures, the mixtures containing 10 mol% of the acid were investigated. The mixture of the derivative with two dodecyl chains showed  $\text{Cub}_{bi}$  phases at room temperature. X-ray diffraction measurement of this mixture in the  $\text{Cub}_{bi}$  phase revealed that the lattice constant is estimated to be 105 Å. Direct observation by transmission electron microscopy (TEM) was conducted. The result of TEM observation also indicated the nanosegregated structure of the  $\text{Cub}_{bi}$  phase. In contrast, the mixture of the derivative with three dodecyl chains showed a  $\text{Col}_h$  phase at room temperature. In the TEM image for this mixture, striped patterns were observed, resulting from the  $\text{Col}_h$  structure oriented parallel to the surface of substrate. The interval of the stripe, which may correspond to the projected intercolumnar distance, is approximately 35 Å, which is related to 41 Å for the reflection of  $d_{100}$  in the X-ray diffraction measurement. For columnar assemblies of these mixtures, uniaxial orientation of column axis was achieved by applying shear force owing to dynamic properties of these LC mixtures. Control of 1D arrangement of polyoxometalate in macroscopic scale was achieved. This was confirmed by polarizing optical microscopic observation under crossed Nicols condition. The anisotropic ionic conductivities were measured for the mixtures on heating process. For the mixture of the derivative with two dodecyl chains, no anisotropic behavior was observed in the  $\text{Cub}_{bi}$  phase. As the  $\text{Cub}_{bi}$ – $\text{Col}_h$  phase transition occurred around 100 °C, the anisotropy in conductivities appeared. In the case of the derivative with three dodecyl chains, ionic conductivities were one-order lower than that with three dodecyl chains. This is because the proton conducting moieties of that with two dodecyl chains are more closely packed and protons can be efficiently transported. The detailed discussion of this study is presented in paper [3].

## Chapter 5. Conclusion and Perspective

The present thesis describes the development of LC electrolytes for Li-ion and proton. By designing molecular structures and intermolecular interaction, the LC ion-conductors with various well-defined nanostructures have been obtained and their LC properties and ion-transporting properties are elucidated.

Chapter 1 describes general introduction on LC electrolytes and objective of this thesis.

In chapter 2 and chapter 3, the development of LC Li-ion conductors is mentioned. Chapter 2 describes enhanced performances of LIBs using LC electrolytes through organization of small carbonate molecules into nanosegregated layered structures. These results would expand the possibility of LC electrolytes for the application of LIBs. In chapter 3, the effects of a fluorinated oligoethylene oxide moiety on LC properties and ionic conductivities are presented. It is reported that the lower isotropization temperatures were observed for block-structured fluorinated molecules having a fluorinated oligoethylene oxide moiety compared to their non-fluorinated analogs.

In chapter 4, the development of LC Li-ion conductors is mentioned. Chapter 4 reports the controlled structures of polyoxometalate-organic LC hybrids for proton conductors. The approach in the study for structural control of polyoxometalates in nano- to macro-scopic scale can be a powerful method not only for development of electrolytes but also for exploration of other functional materials.

In conclusion, this thesis demonstrates the potential of liquid crystals as effective platform for development of electrolytes for energy devices such as LIBs and FCs. The results in this thesis would open up a new avenue for the development of self-organized electrolytes.

## List of Publications

### Original Papers

- [1] “Noncovalent Approach to Liquid-Crystalline Ion Conductors: High-Rate Performances and Room Temperature Operation for Li-Ion Batteries”  
Taira Onuma, Eiji Hosono, Motokuni Takenouchi, Junji Sakuda, Satoshi Kajiyama, Masafumi Yoshio, Takashi Kato, *ACS Omega* **3**, 159–166 (2018).
- [2] “Liquid-crystalline behavior and ion-transport properties of block-structured molecules containing a perfluorinated ethylene oxide moiety complexed with a lithium salt”  
Taira Onuma, Masafumi Yoshio, Masaki Obi, Kimiaki Kashiwagi, Shinya Tahara, Takashi Kato, submitted.
- [3] “Self-Assembly and Proton Conductivities of Polyoxometalate-Surfactant Complexes: 1D, 2D and 3D Structural Control Achieved by One Surfactant”  
Taira Onuma, Masafumi Yoshio, Takashi Kato, in preparation.