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Liquid Crystals

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From Nanostructured Liquid Crystals to Polymer-Based Electrolytes**

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The importance of lithium-ion batteries has increased in recent years because of rising global energy demand.[1,2] Rechargeable lithium-ion batteries are expected to be used more widely for hybrid and completely electric vehicles as well as for portable electronics. For the construction of these batteries, the development of electrolytes, which ionically connect electrodes (cathode and anode), is essential.[1,2] A variety of electrolytes consisting of liquids, gels, and polymers have been developed.[2] The technological requirements for new electrolytes are: 1) high lithium-ion conductivity above $10^{-3}\,\mathrm{S\,cm^{-1}}$ at ambient temperature and a high lithium-ion transference number, 2) chemical, electrochemical, and thermal stability, 3) mechanical stability suitable for fabrication, 4) no electrolyte leakage for durability and safety. It is not easy to satisfy all of these demands, but use of nanomaterials may be one of promising approaches to the development of future electrolytes.

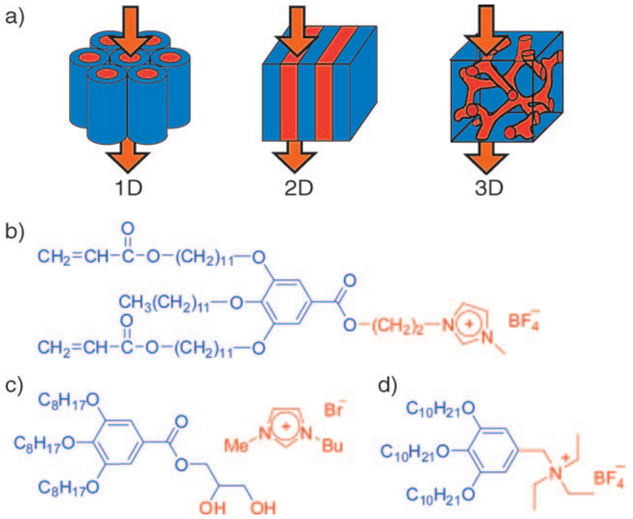

Figure 1. a) Nanostructures of liquid crystals: columnar (1D), smectic (2D), and bicontinuous cubic (3D) phases; b) polymerizable columnar ionic liquid crystal for 1D ion-conductive films;[6] c) two components for 1D ion-conductive columnar assembly;[7a] d) ionic bicontinuous cubic liquid crystal forming 3D ion channels.[8]

Liquid-crystalline nanostructures can be used to develop new electrolytes. Nanosegregated liquid crystals such as smectic, columnar, and bicontinuous cubic phases lead to the formation of nanoscale ion-pathways capable of transporting ionic species efficiently (Figure 1).[3–10] The approaches to the development of low-dimensional ion conductors by using liquid-crystalline self-organized nanostructures have been described.[3–8] Organic ionic species such as imidazolium and ammonium salts (Figure 1 b–d) have been used to design ion conductors.[5–8] For example, uniaxially aligned columnar liquid crystals of imidazolium salt derivatives exhibit anisotropic ion conduction.[6] The design and processing of suitable materials needed to obtain these efficient ion conductors include: 1) the preparation of nanostructured solid films having aligned ion channels obtained by in situ polymerization of the liquid crystals[6] (Figure 1 b), 2) the introduction of mobile ionic species into liquid-crystalline nanostructures to improve conductivity[7] (Figure 1 c), 3) the use of 3D interconnected ion channels based on bicontinuous cubic phases for the formation of continuous ion pathways (Figure 1 d).[8]

Recently, Gin and co-workers have described[9] a new elegant design approach to lithium-ion conductive materials prepared by combining the prior approaches outlined above (Figure 2). They prepared nanostructured polymeric ion conductors having 3D interconnected pathways filled with liquid electrolytes. This polymer electrolyte film shows high ion conductivities of about $10^{-3}\,\mathrm{S\,cm^{-1}}$ over a wide temperature range from ambient temperatures to −50 °C. This ion-conductive polymer material was obtained by polymerization of a lyotropic (i.e. containing liquid solvent) liquid-crystalline molecular assembly exhibiting a bicontinuous cubic phase. The liquid-crystalline materials were prepared by mixing polymerizable benzoic acid–based lithium sulfonate salt **1** with 15 wt % of conventional lithium battery electrolyte solution consisting of propylene carbonate (PC) and $LiClO_4$ (0.245 M). Compound **1** has three alkyl chains with the acryloyl groups at the periphery. These liquid-crystalline mixtures that form bicontinuous cubic structures gave 3D

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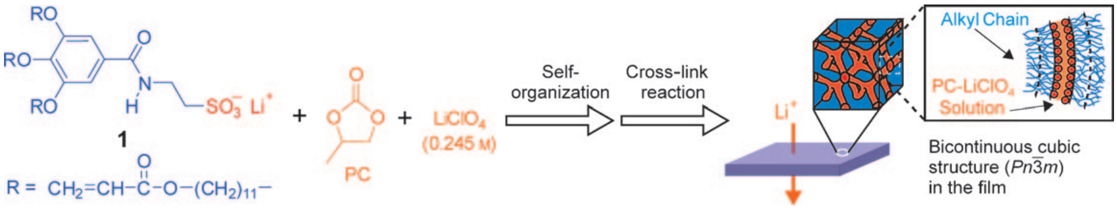

Figure 2. Preparation of nanostructured films having 3D interconnected ion-conductive pathways.[9]

ionic pathways as a consequence of the nanosegregation of ionic and nonionic moieties. After this self-organization, the nanosegregated 3D structures were preserved by in situ cross-linking polymerization.

The electrolyte films prepared by Gin and co-workers have achieved high conductivities comparable to the values of conventional gelled polymer electrolytes currently used in lithium-ion batteries that contain much larger amounts (60–80 wt %) of liquid electrolytes. These latter gelled polymer electrolytes consist of electrolyte solutions such as PC and ethylene carbonate with lithium salts and vinyl polymers such as poly(acrylonitrile) and poly(vinylidene fluoride).[2] For these materials, larger amounts of the mobile electrolyte solutions contribute to the higher ionic conductivities. For Gin's material, however, only 15 wt % ionic solution present in the confined 3D nanopores affords high conductivities in the range of $10^{-3}\,S\,cm^{-1}$ at ambient temperature. This observation suggests that self-organized nanostructures are useful for the construction of functional materials for ion transportation. For further development of the materials, the compatibility of the electrolytes and electrodes should be studied. The quality of the interface between the electrolyte material and the battery electrodes is an important issue for obtaining highly efficient nanostructured electrolytes.

Solid polymer electrolytes, poly(ethylene oxide)s have been one of most studied materials for lithium batteries because they are chemically and structurally stable, easily processable, and low cost.[2] But, as the ions are transported by segmental motion of the backbone of the polymer, the ion conductivities are in the range of 10^{-6}–$10^{-7}\,S\,cm^{-1}$ at ambient temperature below 60 °C. The approaches to the design of new efficient electrolytes have been reported. Liquid-crystalline polymers having mesogenic groups with oxyethylene chains have been prepared.[10] They form nanosegregated structures consisting of ionic and nonionic layers, thus leading to the formation of nanoscale ion channels. Gin's polymers may offer higher conductivities at lower temperatures as a result of the introduction of liquid electrolytes into the nanoionic channels.[9] Moreover, their liquid-crystal-based materials have a stable covalent-bond network, which results in the formation of mechanically robust films.[9] For traditional gelled polymer electrolytes, the materials are prepared by mixing linear polymers and electrolyte solution, and the polymers are simply swollen in the electrolytes.[2a] Owing to the higher amount of the liquid electrolytes and weaker interactions between polymers and the electrolyte solutions, leakage of the electrolyte solution may more easily occur.

In view of materials design for liquid crystals, lyotropic liquid crystals with functional solvents such as liquid electrolytes can be new functional liquid crystals.[7,9] It is also possible to classify these non-aqueous lyotropic liquid crystals as thermotropic liquid crystals consisting of two molecular components.[7,9] This classification means that non-aqueous lyotropic liquid crystals are between thermotropic and lyotropic liquid crystals.[7,9,11] These materials are designed on the same concept of micro(nano)segregation.[12]

Although further development and improvement are required for these materials to be used for battery systems, use of nanostructured materials promises to allow a versatile approach to the development of new transport materials.

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