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New Type of Li Ion Conductor with 3D Interconnected Nanopores via Polymerization of a Liquid Organic Electrolyte-Filled Lyotropic Liquid-Crystal Assembly

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Polymer electrolytes with high ion conductivity are critical for Li ion battery performance.[1] They are typically based on amorphous poly(ethylene oxide) (PEO) and related polymers doped with Li salts[1] and can be solvent-free Li salt−polymer blends with ion conductivities of $\leq 10^{-4}$ S cm^{-1} or gelled systems containing Li salt−liquid electrolyte solutions with conductivities of $\geq 10^{-3}$ S cm^{-1}.[1a] Liquid electrolytes have higher conductivity, but solid polymers are preferred because liquid electrolytes can leak and have poorer fabrication properties.[1] Unfortunately, PEO-based electrolytes have poor low-temperature conductivity. The segmental chain motion needed for ion transport is quickly lost upon cooling below the glass transition temperature.[1] Aside from the addition of liquid electrolytes, other methods for improving polymer electrolyte ion conductivity include adding plasticizers to maintain chain motion or fillers to increase void volume.[1a] Polymer electrolytes with order and permanent ion transport pathways are expected to have enhanced conductivity.[1d,2]

A new approach for making solid electrolytes involves the use of liquid crystals (LCs),[3] which have properties intermediate between crystalline solids and isotropic liquids.[4] LC-based electrolytes offer many of the advantages of polymers plus some fluidity for better ion mobility. *Solvent-free* LC electrolytes have included oligo(EO)-LCs blended with Li salts;[5,6] Li-salt-doped PEO-,[7] crown ether-,[8] and carbonate-functionalized[9] LCs and block copolymers;[10] and LCs and LC polymers with an attached ionophore as the charge carrier.[11] These systems typically have conductivities of 10^{-6} S cm^{-1} below 40 °C,[5−11] although one oligo(EO)-LC system showed a conductivity of 10^{-3} S cm^{-1} at room temperature (RT).[5d] *Solvent-containing* (i.e., lyotropic) LC (LLC) systems formed around ionic liquids (conductivity = 10^{-4} to 10^{-3} S cm^{-1}) have also been reported, but their structures are not temperature-stable.[12] Recently, polymerization of LC electrolytes has been found to afford more stable materials and conductivity behavior.[11c] Also, bicontinuous cubic (Q) phases with three-dimensional (3D) interconnected nanochannels have been found to afford better conductivity than other LC phases.[11d] Ideally, what is desired is a liquid-electrolyte-containing, ordered polymer composite with all of these features in a single system. Herein, we describe a new type of polymer electrolyte with ordered, 3D interconnected liquid nanopores based on the LLC assembly of **1** around a Li salt solution of the liquid electrolyte, propylene carbonate (PC). The resulting cross-linked Q_{II}-phase solid−liquid nanocomposite (Figure 1) exhibits an ion conductivity of 10^{-4} to 10^{-3} S cm^{-1} at RT (21 ± 2 °C) when formed with 15 wt % 0.245 M $LiClO_4$−PC solution. This material exhibits liquidlike diffusion in the nanopores and retains good ion conductivity (∼10^{-4} S cm^{-1}) down to −35 °C and lower.

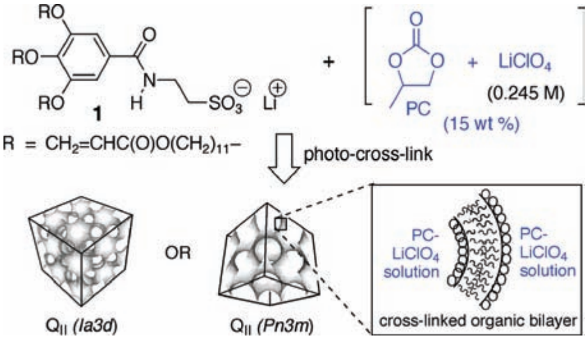

Figure 1. Li ion-conducting solid−liquid nanocomposite based on cross-linking of a Q_{II} phase formed by **1** with a PC−$LiClO_4$ solution.

Monomer **1** was synthesized by first reacting 3,4,5-tris(11′-acryloyloxyundecyloxy)benzoyl chloride with lithium 2-aminoethanesulfonate. The crude amide product was then washed with ultrapure water to remove salt impurities, which exaggerate the ion conductivity. After elemental analysis to determine the purity and the exact amount of Li^+ lost during the water wash, the monomer was then titrated with LiOH to afford pure **1** (see the Supporting Information). Since PC and related carbonates are the liquid electrolytes of choice in Li ion batteries,[1] the LLC behavior of **1** with PC solutions was explored. Pure **1** forms LLC phases with pure PC and a PC solution containing 0.245 M $LiClO_4$. Only a small number of nonaqueous LLC systems are known,[12,13] and a PC-based LLC system is unprecedented. Characterization of the **1**−PC and **1**−(0.245 M $LiClO_4$−PC) systems via polarized light microscopy (PLM) and powder X-ray diffraction (XRD) revealed in each case a Q phase containing 5−20 wt % PC at RT. The Q phases were identified by XRD *d* spacings in the ratio $1/\sqrt{6}:1/\sqrt{8}:1/\sqrt{11}\cdots$ and a black PLM optical texture.[14] The Q phases are tentatively assigned as type II because they form at low solvent content, and crude **1** forms a lamellar LLC phase at higher PC levels (see the Supporting Information).[14]

Free-standing polymerized films of the Q_{II} phases were prepared for ion conductivity studies by placing monomer mixtures [84.0/15.0/1.0 (w/w/w) **1**/PC or PC−$LiClO_4$ solution/radical photoinitiator] between heated (55 °C) quartz disks and pressing them together using manual hand pressure. The sandwiched films were cooled to RT and then radically photo-cross-linked with UV light under Ar; *d* spacings with a ratio of $1/\sqrt{6}:1/\sqrt{8}\cdots$ in the XRD profiles of the films (Figure 2) confirmed that the Q_{II} phase was retained after polymerization. The degree of acrylate polymerization was typically 85−95% according to FT-IR analysis (see the

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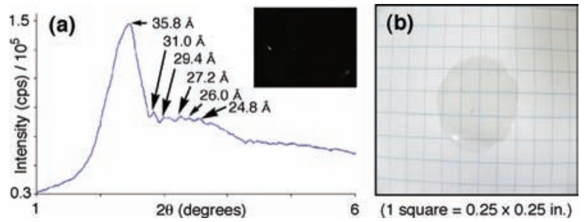

Figure 2. (a) XRD profile (inset: PLM image) and (b) photo of a cross-linked Q_{II}-phase film of **1** with 15 wt % 0.245 M $LiClO_4$−PC.

Supporting Information). The resulting colorless, transparent films were flexible and mechanically robust, and showed no sign of PC solution leaching even upon contact or blotting.

Table 1 shows RT ion conductivity values for the cross-linked Q_{II} films and several comparison materials obtained using conventional AC impedance analysis methods (Nyquist plots) (see the Supporting Information).[15] The RT conductivity of the Q_{II} network of **1** with 15 wt % pure PC was only $(6 \pm 2) \times 10^{-7}$ S cm^{-1}. This value is consistent with that reported for Li salts of ionic polymers (i.e., polyelectrolytes) containing no added free salt ($\leq 10^{-6}$ S cm^{-1}), where polymer-bound anions afford limited Li^+ mobility.[1c] In contrast, the RT conductivity of the Q_{II} network of **1** with 15 wt % 0.245 M $LiClO_4$−PC was found to be $(9 \pm 4) \times 10^{-4}$ S cm^{-1}, which is similar to that of gelled PEO systems containing substantially more (40−60 wt %) liquid electrolyte with a higher Li salt concentration (1 M).[1c] This value is also similar to that of a film of 0.245 M $LiClO_4$−PC solution measured by the same method, suggesting liquidlike mobility in the Q_{II} channels. Nafion-1135 was used as a calibration standard, and its observed conductivity matched reported values.[16] It was not possible to directly confirm the importance of the Q_{II} phase with respect to ion transport. Attempts to prepare **1**/$LiClO_4$−PC films with the same composition as the Q_{II} films but in a different phase were unsuccessful (because **1** has such a strong tendency to form the Q_{II} phase; see the Supporting Information).

Table 1. Observed RT Ion Conductivity Values (Values Listed Are Averages of ≥3 Independent Sample Runs with Standard Deviation Error Bars)

film sample	conductivity (S cm^{-1})
1 + 15% pure PC (Q_{II} network)	$(6 \pm 2) \times 10^{-7}$
1 +15% 0.245 M $LiClO_4$−PC (Q_{II} network)	$(9 \pm 4) \times 10^{-4}$
Nafion-1135	$(7.0 \pm 0.3) \times 10^{-3}$
0.245 M $LiClO_4$−PC solution	$(1.79 \pm 0.01) \times 10^{-3}$

Preliminary variable-temperature (VT) conductivity studies revealed that the conductivity of the Q_{II}-phase **1**−(0.245 M $LiClO_4$−PC) films drops less than 1 order of magnitude as the temperature goes from RT to −35 °C (and even down to −65 °C). It also remains within the same order of magnitude upon heating to 55 °C (see the Supporting Information). This behavior is not observed in gelled PEO−Li salt or LC-based materials but is important for good battery performance over a wide temperature range. Retention of liquidlike behavior at low temperatures was corroborated by VT-NMR DOSY measurements. The diffusion constant (D) of the PC in a Q_{II} composite containing 15 wt % 0.245 Li salt−PC was found to be very similar to that of pure PC and 0.245 M $LiClO_4$−PC at RT. At −35 °C, D for the PC in the Q_{II} composite was 58% of that for pure liquid PC and 66% of that for 0.245 M $LiClO_4$−PC at −35 °C (see the Supporting Information). This implies that significant liquidlike character still exists at −35 °C. Studies down to −65 °C are in progress.

In summary, a nanostructured, liquid-electrolyte-filled polymer material has been developed that has many of the best features of gelled polymers and LC-based electrolytes plus very stable, liquidlike ion conductivity over a wide temperature range that has not been observed in either of those other types of materials. Conductivity and NMR DOSY studies on this material over a wider temperature range are underway. We are also exploring ways to improve the conductivity of this material by removing the film surface layer/crust, increasing the amount of PC solution and its Li salt concentration in the films, and varying the type of liquid electrolyte used. New Q-phase LLC monomer designs are also being explored.

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Supporting Information Available: Preparation and polymerization of **1** and its LLC phases, phase diagrams, ion conductivity measurement methods, VT conductivity and NMR DOSY data, and initial thermal analysis data. This material is available free of charge via the Internet at http://pubs.acs.org.

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