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Solid lithium electrolytes based on an organic molecular porous solid†

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A new type of solid lithium-ion conducting electrolytes prepared by incorporation of Li+ ions into a cucurbit[6]uril (CB[6])-based organic molecular porous solid shows high Li+ ion conductivity ($\sim 10^{-4}$ S cm^{-1}) and mobility (transference numbers, t_{Li}^+ = 0.7–0.8). In addition, the solid electrolytes show excellent, thermally stable performance even after several temperature cycles.

Lithium-ion batteries (LIB) hold great potential for application in powering electric vehicles and portable electric devices because of their high energy density, high (operating) voltage, and long duration compared to other rechargeable batteries.[1,2] Over the last decade, significant progress has been made in the development of high energy density electrode materials. By contrast, no remarkable advancement was made in electrolyte materials, which play an important role in preventing direct contact between two electrodes and reversibly transporting ions to compensate for the system charge. Although widely-used liquid electrolytes have high ionic conductivity, their short-comings such as restriction of battery shape, usage of flammable/ volatile electrolyte solvents and risk of their leakage limit their applications.[3,4] Furthermore, a low Li+ ion transference number (typically in the range of 0.2–0.5), which results in a short cell lifetime, slow charging rate, and low energy density, has been another serious drawback of liquid electrolytes.[5,6] To overcome the limitations, solid-type electrolyte materials such as ceramic and polymer type electrolytes have been studied extensively.[7–10] Very recently, crystalline porous materials with well-defined pores

including metal–organic frameworks (MOFs) have been explored as Li+ ion conducting materials,[11–15] some of which showed good Li+ ionic conductivity by grafting lithium precursors into open metal sites. However, low ionic conductivity, low cationic mobility, high interfacial resistance, and poor lithium compatibility of these solid-type electrolytes still hinder their practical applications.[3,4,16] Thus, the design and fabrication of a safe, high-performing solid electrolyte material still remains a challenge.

Recently, we reported an organic molecular porous material (porous CB[6]) made of cucurbit[6]uril, a pumpkin-shaped host molecule, which has a honeycomb-like structure with one-dimensional (1D) channels along the c-axis (average pore diameter 7.5 Å; pore aperture 6 Å). The porous CB[6] with permanent porosity and high thermal stability has been proved to be useful for a variety of applications including selective gas sorption and proton conduction.[17–19] Especially, the porous CB[6] with 1D channels filled with water and acids showed both high and highly anisotropic proton conductivity,[20] demonstrating that the 1D channels provide an excellent ion transport pathway. These previous findings and versatile properties of the porous CB[6] prompted us to investigate the Li+ ion conduction in the 1D channels of the porous CB[6] matrix. Considering the confinement effect in the pores of a solid matrix, we thought that the intrinsic thermal runaway problem of liquid and the sudden decrease in conductivity at low temperature by crystallization, which is commonly observed in polymer matrices,[21–23] can be avoided by using the porous CB[6] solid matrix. In addition, the crystalline porous CB[6] can be synthesized easily using common shelf reagents, and used without any tedious post-synthetic modification. We thus decided to incorporate the Li+ electrolyte inside the channels to produce a safe and stable Li+ ion conducting solid electrolyte.

Herein, we report a new type of solid lithium-ion conducting materials synthesized by incorporation of Li+ ions into a cucurbit[6]uril (CB[6])-based organic molecular porous material (Scheme 1), which exhibits high Li+ ion conductivity ($\sim 10^{-4}$ S cm^{-1}) and high cationic transference number (t_{Li}^+ = 0.7–0.8). In addition, the solid electrolyte shows excellent, thermally stable performance

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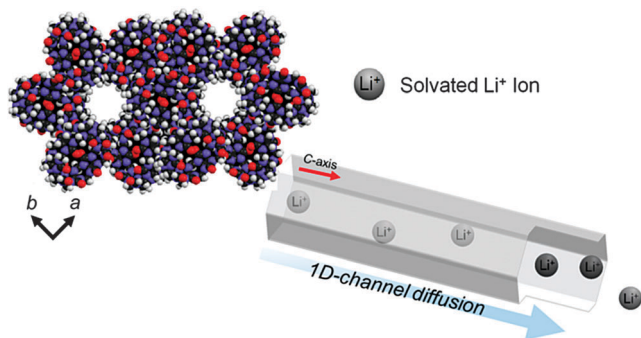
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Scheme 1 Porous CB[6]-based solid lithium electrolyte showing a Li$^+$ ion transport pathway in the 1-D channels.

Fig. 1 Nyquist plots of the ac impedance data obtained for pellets of **3a**, **3b**, and **3c**.[48]

even after several temperature cycles. To the best of our knowledge, this is the first example of highly thermally stable, organic molecular porous material-based Li$^+$ ion conducting solid materials that simultaneously exhibit both high ionic conductivity and high cationic transference number.

Porous CB[6] (**1**) was prepared by recrystallization from aqueous HCl solution, following the previously reported procedure[20] with some modifications. Solvent molecules filling the channels were removed by heating under a dynamic vacuum for the formation of guest free porous CB[6] (**2**), which was characterized using powder X-ray diffraction (PXRD), thermo-gravimetric analysis (TGA) and elemental analysis (EA) (see ESI†).

To introduce Li$^+$ ions into the channels of **2**, we chose propylene carbonate (PC) or dimethylcarbonate (DMC) as a solvent to dissolve lithium salts since they are widely used as solvents for Li$^+$ ion electrolytes due to high dielectric constant and solvating power (PC) or low viscosity and high lithium ion conductivity (DMC). We first tested and confirmed the excellent stability of **2** in the organic solvents using PXRD (Fig. S3, ESI†). Soaking **2** in 1 M solution of LiPF$_6$ or LiClO$_4$ in PC, or 1 M solution of LiPF$_6$ in DMC, for 12 h followed by rapidly washing with THF to remove residual Li salts on the surface and drying under reduced pressure furnished Li$^+$ ion incorporated porous CB[6], **3a**, **3b**, or **3c**, respectively, as a free-flowing, dry powder, which could be easily pressed into pellets without a binder (Fig. S5, ESI†). The amount of Li$^+$ ions incorporated into the organic molecular porous solid was established by elemental analysis and inductively coupled plasma (ICP) analysis; **3a**, **3b**, and **3c** have a molecular formula of CB[6]·0.8LiPF$_6$·3PC, CB[6]·0.4LiClO$_4$·3.4PC, and CB[6]·1.1LiPF$_6$·2.2DMC, respectively. PXRD analysis indicated that the crystal structure of the framework was maintained after the impregnation process (Fig. S6, ESI†). The presence of solvated Li$^+$ ions inside the channels of porous CB[6] crystals was further corroborated using FT-IR spectroscopy. In the FT-IR spectra of **3a** and **3b**, a band associated with the C=O stretching modes of coordinated PC appears at 1785 cm^{-1}. The emergence of two new broad peaks at 843 cm^{-1} and 1088 cm^{-1} are attributed to the symmetric P–F stretching modes of free PF$_6^-$ and the asymmetric stretching vibration modes of free ClO$_4^-$, respectively (Fig. S11, ESI†).[24–27]

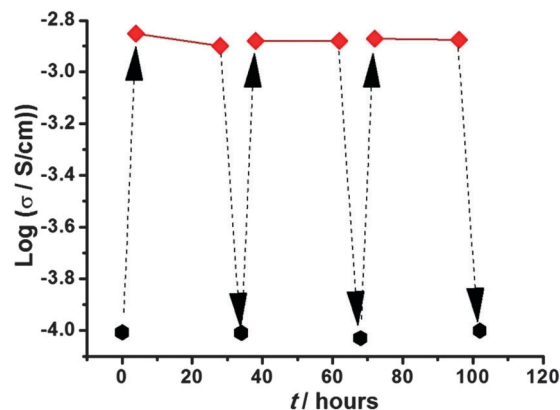The Li$^+$ ion conductivity of **3a**, **3b** and **3c** was measured on pellets by ac impedance spectroscopy (Fig. 1). Regardless of the
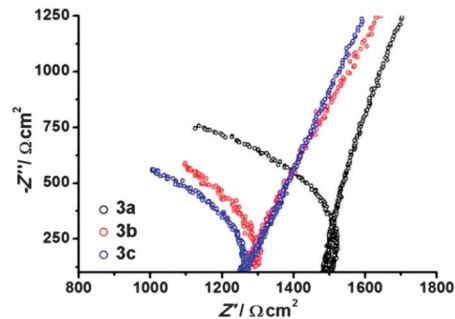
counter ions and solvents, they all exhibited similar conductivity values (0.8–1.0 × 10^{-4} S cm^{-1}) at room temperature (Table 1), which is almost four orders of magnitude higher than that of **2** (<1.5 × 10^{-8} S cm^{-1}) (Fig. S7, ESI†), suggesting that facile migration of solvated Li$^+$ ions along the 1D channel of **2** is responsible for the high ionic conductivity values.[14] These values are much higher than those of typical polyether-based polymer electrolytes ($\sim$10^{-8}–10^{-5} S cm^{-1})[28,29,32] and are comparable to the best values for MOF-based lithium solid electrolytes ($\sim$10^{-6}–10^{-4} S cm^{-1}).[14,15] Most importantly, the Li$^+$ ion conductivity of **3a**, **3b** and **3c** is just one order of magnitude lower than that of the desired battery electrolytes (10^{-3} S cm^{-1}).

Temperature-dependent conductivity measurements of **3a**, **3b**, and **3c** revealed a typical Arrhenius-type activated behavior with activation energies in the range of 0.32–0.38 eV (31–37 kJ mol^{-1}) (Fig. 2 and Table 1). These activation energy values are much lower than that of the well-established ceramic electrolyte LIPON–Li$_3$PO$_4$ (0.55 eV, 53.0 kJ mol^{-1})[30] and comparable to that observed in LISICON–Li$_{14}$ZnGe$_4$O$_{16}$ (0.40 eV, 38.5 kJ mol^{-1}).[31] Furthermore, our materials showed 5 times lower activation energy compared to the PEO/Li$^+$ polymer electrolyte (1.66 eV, 160.4 kJ mol^{-1}) and 2 times lower than that of the solid polymer electrolyte α-CD (α-cyclodextrin)-PEO/Li$^+$ (0.78 eV, 75.1 kJ mol^{-1}) made of PEO and the macrocyclic compound α-CD.[32] With a high conductivity in the order of 10^{-4} S cm^{-1} and activation energy less than 0.4 eV, these Li$^+$ ions incorporated into organic molecular porous solids can be classified as a superionic conductor.[14] It is worth noting that the portals of each CB[6] are blocked by two neighboring CB[6] molecules in **2**[18] (and presumably in **3** as well), thereby preventing the direct interaction of Li$^+$ ions with the carbonyl oxygen atoms of CB[6]. While a large shift ($\sim$15 cm^{-1}) in the C=O stretching frequency was observed upon metal coordination to the carbonyl portals of CB[6],[32] almost no shift in the C=O stretching frequency in **3a**, **3b**, and **3c** compared to that in **2** (Fig. S11, ESI†) is consistent with the lack of direct interactions between Li$^+$ ions and the carbonyl oxygen atoms of CB[6]. Such an arrangement of CB[6] molecules in **3** may allow a relatively free movement of Li$^+$ ions in the 1D channels whereas in the case of polyether-based polymer electrolytes, the movement of the ions may be hindered by favorable charge–dipole interactions with the oxygen atoms of the polymer chains.[33,34]

Table 1 Lithium ion conductivity at RT, molar Li$^+$ concentration, molar conductivities, and activation energies of **3a**, **3b**, and **3c**

Compounds	Electrolyte (per one CB[6])	σ ($\times 10^{-4}$)/S cm^{-1}	C_{Li}^+/M	Λ_M ($\times 10^{-5}$)/S cm^{-1} M^{-1}	E_a/eV
3a	0.8LiPF$_6$·3PC	0.9 ± 0.4	1.7	5 ± 2	0.38
3b	0.4LiClO$_4$·3.4PC	0.8 ± 0.4	0.99	8 ± 4	0.32
3c	1.1LiPF$_6$·2.2DMC	1.0 ± 0.2	1.2	8 ± 2	0.34
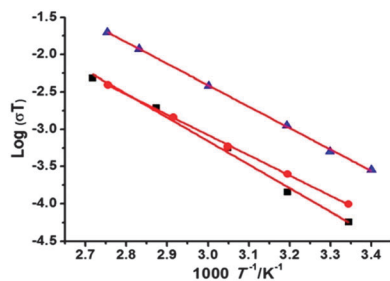
Fig. 2 Arrhenius plots of ionic conductivity data obtained from **3a** (■), **3b** (●), and **3c** (▲).

Fig. 3 Temperature cycling of **3c** at elevated temperatures of up to 373 K.

Table 2 Measured parameters for calculating transference number^a

Compounds	R_{ss}/Ω	R_0/Ω	I_0/μA	I_{ss}/μA	t_{Li}^+
3a	538	437	1.15	0.92	0.8
3b	569	433	127	91	0.7

^{a} Voltage bias = 0.5 V.

One of the serious limitations of Li$^+$ electrolytes is the narrow operational temperature and limited electrochemical window.[35] Although LiPF$_6$ and LiClO$_4$ show a good performance at low temperature and good compatibility using electrode current collectors (Cu and Al), they are easily decomposed or deteriorated at 60–80 °C.[36] Thus, prevention of electrolyte deterioration and side reaction at high temperatures can increase the battery life. We thus decided to investigate the thermal stability and electrochemical stability of our materials. First of all, the crystal structures of **3a**, **3b**, and **3c** were maintained at high temperatures up to 373 K, as confirmed by PXRD (Fig. S10, ESI†) and IR spectroscopy (Fig. S11, ESI†), which suggests that they have a good thermal stability even above 80 °C, a typical upper temperature window in liquid Li electrolytes and polymer electrolytes.[37] We have also tested electrochemical stability of **3a**, **3b**, and **3c** via cyclic voltammetry. Cyclic voltammograms were obtained between +3 V and +6 V for **3a** and between +2 V and +5 V for **3b** and **3c** at room temperature and 373 K (Fig. S12, ESI†). No electrolyte decomposition or electrochemical parasitic reaction in the operating voltage range was apparent as judged by a small current level across the sweeping voltages and no abrupt current increase was observed between 4 and 4.5 V, which is known to be associated with electrolyte decomposition.[1,38]

Although DMC is widely used as a co-solvent in commercial Li electrolytes due to its low viscosity and high ionic conductivity, one of the shortcomings of the solvent is its high flammability and volatility.[35] It thus prompted us to test the stability of **3c** having a molecular formula of CB[6]·1.1LiPF$_6$·2.2DMC by measuring its ionic conductivity, while cycling the temperature between 298 K and 373 K (Fig. 3, and Fig. S9, ESI†). Almost no change in conductivity was observed after each cycle for 4 days as shown in Fig. 3, which demonstrates a safe and high conducting behavior of **3c** even at elevated temperatures.[39,40]

Having established that these Li$^+$ ion incorporated-organic molecular porous solids have excellent Li$^+$ ion conductivities, we measured the lithium transference number (t_{Li}^+) of the solid

electrolytes, another important parameter for battery applications, using the ac impedance method combined with the steady-state current technique.[40,41] The measured t_{Li}^+ values are 0.8 and 0.7 for **3a** and **3b**, respectively, at room temperature (Fig. S13, ESI†), which is in sharp contrast to the fact that those for conventional liquid electrolytes and PEO/Li$^+$ polymer electrolyte are in the range of 0.2–0.5.[42–44] The high t_{Li}^+ values observed for **3a** and **3b** (Table 2) suggest that the narrow 1D channels (pore diameter 7.5 Å; aperture 6 Å) in the molecular porous materials may hinder the movement of the bulky anions (2.4–2.6 Å) while allowing a relatively fast movement of the small Li$^+$ ion (0.76 Å).[45–47]

In summary, we have developed a new type of solid lithium-ion conducting materials prepared from an organic molecular porous solid made of cucurbit[6]uril. Most significantly, the incorporation of Li$^+$ ion into the 1D channels of guest-free porous CB[6] can lead to high Li$^+$ ion conductivity (10^{-4} S cm^{-1}) and transference numbers (t_{Li}^+ = 0.7–0.8). In addition, they showed an excellent performance in the temperature cycling test, confirming a stable ion conducting behavior even at elevated temperatures. To the best of our knowledge, this is the first example of highly thermally stable organic molecular porous material-based Li$^+$ ion conducting materials. The results described here represent significant progress in the designing and tailoring of a safe and high-performing solid electrolyte, which can address the existing challenges in

lithium ion battery technologies and may provide new insight into the development of advanced lithium ion batteries.

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