A lithium superionic conductor as a new solid-state battery electrolyte

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The sustainable production of renewable energy such as solar and wind energy depends on a number of natural conditions such as duration of the day or night, and velocity and direction of the wind. However, supply of such renewable energies is non-continous. Therefore, high performance energy storage devices are essential to store the generated energy and to stabilize the connected electricity grid. Current research and development on electrochemical power sources are mainly focused on fuel cells, batteries and electrochemical capacitors and are directed towards obtaining high specific energy, high specific power, long cycle life, etc. at relatively low cost. Batteries have great importance in modern society. They are used to power electric and hybrid electric vehicles and to store wind and solar energy in smart grids. Electrochemical devices with high energy and power densities can currently be powered only by batteries with organic liquid electrolytes. However, such batteries require relatively rigorous safety measures, making large-scale systems complex and expensive. The increasing requirement of energy storage systems has brought great interest in academic research activities as well as huge investments of money in the field of rechargeable batteries. The introduction of lithium-ion battery by Sony corporation in 1991 (ref. 1) has brought a new dimension in the research of battery and it is now being used in the everyday life of a consumer. Lithium-ion battery followed the reversible insertion and extraction of lithium ion from $LiCoO_2$ and graphite electrodes respectively. Therefore, the performance of the lithium-ion battery not only depends on the electrode properties, but also on the movement of ions through the electrolyte during the charge and discharge cycles. Figure 1 is a schematic diagram of graphite intercalated with lithium. The high operating voltage of a lithium ion electrochemical cell inhibits the use of aqueous electrolyte and most commercial cells use solutions of dissociated salts. However, these electrolytes can still undergo unwanted reactions with the electrodes made from structurally unstable layered transition metal oxides at high operating voltage, which are unfavourable for the long-term cyclability and stability of lithium-ion battery-based electrochemical cells. Many alternative materials such as solid polymers, ionic liquids and inorganic (ceramic) electrolytes have been implemented in real batteries[2]. However, most of them suffer from slow ionic transport at room temperature and high cost.

Fast ion conductors, which are also known as solid-state electrolytes and superionic conductors, are materials that act as solid-state ion conductors and are used primarily in solid oxide fuel cells. As solid electrolytes, they conduct due to the movement of ions through voids or empty crystallographic positions in their crystal lattice structure. The most commonly used solid electrolyte is yttria-stabilized zirconia (YSZ). One component of the structure, the cation or anion, is essentially free to move throughout the structure, acting as a charge carrier. Solid-state electrolytes find use in all solid-state supercapacitors, batteries, fuel cells and also in various kinds of chemical sensors. However, the application of solid electrolytes is limited at present due to the low conductivities in comparison to organic liquid electrolytes. They attain moderate conductivities (10^{-2} S cm^{-1}) only at a temperature between 50°C and 80°C, which is still one order magnitude lower than the conductivities of organic liquid electrolytes.

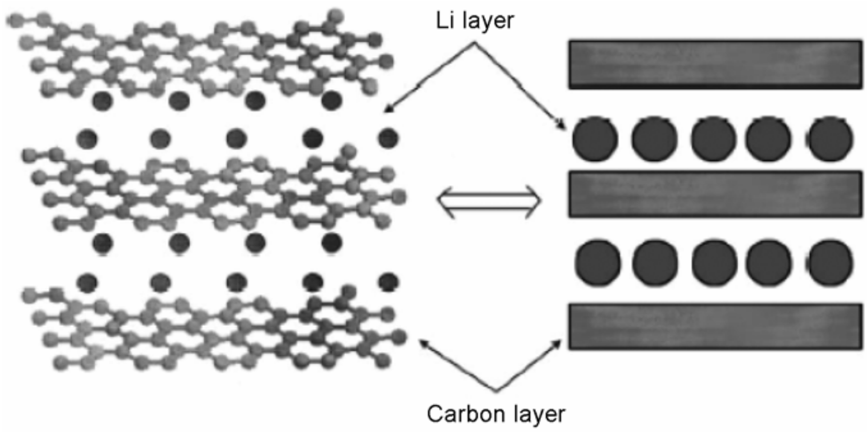

Figure 1. Schematic diagram showing the intercalation of graphite with lithium.

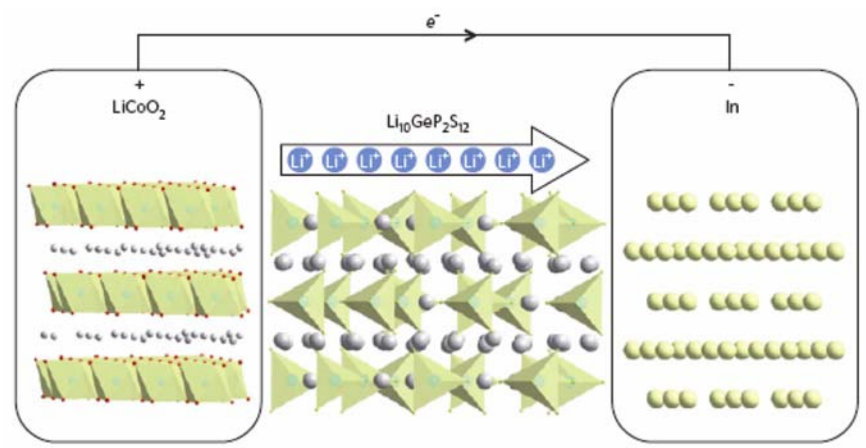

Figure 2. Schematic diagram of the all-solid-state lithium-ion battery reported by Kamaya *et al.*[4]. An all-solid-state battery with the structure $LiCoO_2/Li_{10}GeP_2S_{12}/In$ (from Masquelier[3], reprinted with permission from Nature Publishing Group).

Recently, researchers at the Tokyo Institute of Technology and Toyota Motor Corporation, Japan, introduced a novel crystalline solid inorganic electrolyte, whose lithium ion conductivity exceeds that of organic liquid electrolyte-based systems and can be used in energy storage systems[3,4]. They reported a new lithium ion superionic conductor, $Li_{10}GeP_2S_{12}$, which exhibits the highest lithium ion conductivity ever measured for a solid electrolyte (~ 12 mS cm^{-1} at 300 K) at room temperature. The material possesses a three-dimensional structure, which consists of $(Ge_{0.5}P_{0.5})S_4$ tetrahedra, PS_4 tetrahedra, LiS_4 tetrahedra and LiS_6 octahedra. The composition and structure of this material were elucidated by synchrotron X-ray diffraction and neutron diffraction measurement. The new material exhibits an extremely high bulk conductivity of over 10^{-2} S cm^{-1} at room temperature.

Lithium superionic conductors, which can be used as solid electrolytes, exhibit high ionic diffusion in the mobile ion sublattice at temperatures well below their melting point. Therefore, it is important to understand the mechanism of fast ionic transport in solids. Figure 2 is a schematic diagram of the all-solid-state lithium-ion battery reported by Kamaya *et al*.[4]. They used $LiCoO_2$ as the positive electrode and indium (In) as the negative electrode, with an operating voltage of 3.3 V. An all-solid-state battery with the structure $LiCoO_2/Li_{10}GeP_2S_{12}/In$ exhibits an excellent battery performance with excellent reversibility. During charging, lithium ions travel with high mobility from the positive $LiCoO_2$ electrode to the negative In electrode via partially occupied LiS_4 tetrahedra and interstitial positions in the new superionic conductor $Li_{10}GeP_2S_{12}$. Moreover, this new solid-state battery electrolyte exhibits wide electrochemical stability, which is important for cycling stability and safety issues. Other superionic conductors such as Li_3N, $Li_{1/3-x}Li_{3x}NbO_3$ and $LiBH_4$–LiI suffer from major drawbacks in terms of cycling stability and safety issues. This is the major advantage of $Li_{10}GeP_2S_{12}$ over other superionic conductors. Therefore, this new lithium ion superionic conductors has many advantages in terms of device fabrication (efficient shaping, patterning and integration), stability, safety (non-explosive) and electrochemical properties (high conductivity and wide electrochemical potential window).

The new electrolyte ($Li_{10}GeP_2S_{12}$) was examined as a solid electrolyte for practical lithium-ion battery. The battery exhibits a discharge capacity of over 120 mA h g^{-1} and excellent discharge efficiency of about 100%, demonstrating that it is applicable as a practical electrolyte for all-solid-state batteries.

It is expected that discovery of this new solid electrolyte will result in a wide range of fundamental studies on ionic mobility in bulk materials and this will lead to the development of the next generation of batteries. The discovery will probably renew interest in ceramic solid electrolytes. Finally, it will make a breakthrough in terms of application of batteries for further development of pure electrical and hybrid vehicles.

1. Armand, M. and Tarascon, J. M., *Nature*, 2008, **451**, 652–657.
2. Knauth, P., *Solid State Ionics*, 2009, **180**, 911–916.
3. Masquelier, C., *Nature Mater*., 2011, **10**, 649–650.
4. Kamaya *et al*., *Nature Mater*., 2011, **10**, 682–686.

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