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Novel Li_3ClO based glasses with superionic properties for lithium batteries

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Three types of next generation batteries are currently being envisaged among the international community: metal-air batteries, multivalent cation batteries and all-solid-state batteries. These battery designs require high-performance, safe and cost effective electrolytes that are compatible with optimized electrode materials. Solid electrolytes have not yet been extensively employed in commercial batteries as they suffer from poor ionic conduction at acceptable temperatures and insufficient stability with respect to lithium-metal. Here we show a novel type of glasses, which evolve from an antiperovskite structure and that show the highest ionic conductivity ever reported for the Li-ion (25 mS cm^{-1} at 25 °C). These glassy electrolytes for lithium batteries are inexpensive, light, recyclable, non-flammable and non-toxic. Moreover, they present a wide electrochemical window (higher than 8 V) and thermal stability within the application range of temperatures.

Introduction

In lithium-ion batteries the safety issue remains a major barrier.[1] Battery manufacturers are now able to produce high-quality lithium-ion cells for consumer electronics, with less than one reported safety incident for every one million cells produced.[2] However, this failure rate is still too high for applications in plug-in hybrid electric vehicles and pure electric vehicles, since several hundreds of lithium-ion cells will be needed to power a vehicle. The failure of a single cell can generate a large amount of heat and flame, both of which can then trigger thermal runaway of neighbouring cells, leading to failure throughout the battery pack. Consequently, there is a wide effort to tackle the safety issue of lithium batteries.[2] Chen and co-workers[3] showed that a higher graphite negative electrode surface area in a lithium-ion cell can result in a more solid electrolyte interphase (SEI) and therefore more heat generation during thermal decomposition. This initial reaction, which occurs at ~110 °C, can further trigger other exothermal reactions in the cell. Therefore, the latest work on graphitic anodes mainly focuses on the development of a stable artificial solid electrolyte interphase to stabilize the lithiated graphite and improve both safety and cycling performance.

Recently, lithium batteries using oxygen from air at the positive electrode (lithium-air batteries) have attracted worldwide attention. In this open system, the use of electrolytes with low volatility is strictly required. For lithium-air batteries a major focus of attention has been the lithium-metal anode protected by a lithium-ion conducting ceramic electrolyte.[2] The LISICON ($Li_{(1+x+y)}Al_xTi_{2-x}Si_yP_{(3-y)}O_{12}$)[4] electrolyte has been used for the previous purpose with a major inconvenient which is related to being reduced in contact with Li-metal following-on a Li-metal/ceramic interface difficult to cycle.[2]

Promising results were recently obtained with a $Li_{10}GeP_2S_{12}$ solid electrolyte.[5] In this solid electrolyte medium, Li^+ ions are conducted at 0.012 mS cm^{-1} and 12 mS cm^{-1} at −100 °C and 25 °C, respectively, which is considered to be a high conductivity. Mo *et al.*[6] found that $Li_{10}GeP_2S_{12}$ is not stable against reduction by lithium at low voltage or extraction of Li with decomposition at high voltage.

On a different front, sulfide glasses have been studied due to their high ionic conductivity. A glass of the Li_3PO_4–Li_2S–SiS_2 system is formed at ambient pressure by quenching $0.03Li_3PO_4$–$0.59Li_2S$–$0.38SiS_2$ in liquid nitrogen. Its conductivity at room temperature is 0.69 mS cm^{-1} (ref. 7) and its stability against electrochemical reduction is as wide as 10 V.[8]

We have developed and optimized a glassy electrolyte with ultra-fast ionic conduction based on an antiperovskite $Li_{3-2x}M_xHalO$ structure, in which M is a higher valent cation such as Mg^{2+}, Ca^{2+} or Ba^{2+} and Hal is a halide like Cl^- or I^- or a mixture of halides.

The glass–liquid transition is the reversible transition in amorphous materials from a hard and relatively brittle state into a molten or rubber-like state.[9] The glass transition of a liquid to a solid-like state may occur with either cooling or

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