水安定で水透れ防止するリチウムイオン伝導性固体電解質をNASICON-型構造を有するカソード保護フィルムとしての水素燃料電池用の電解質の開発

学位論文の要旨

専攻名 材料科学 専攻 氏名 ZHANG PENG

学位論文題目 Water-stable and water penetration-free lithium ion conducting solid electrolyte with NASICON-type structure as anode protection film for aqueous lithium-air batteries

The lithium-air battery is a promising power source for electric vehicles because of its high theoretical specific energy density. To date, two types of lithium air batteries, non-aqueous and aqueous, have been investigated. The non-aqueous system is relatively simple which consists of a lithium metal electrode, a non-aqueous electrolyte, and an air electrode. Corresponding to the non-aqueous system, The aqueous system consists of a lithium metal protected by a water-stable lithium conducting solid electrolyte, an aqueous electrolyte, and an air electrode. The non-aqueous system has higher energy density (3460 Wh kg⁻¹) than that of the aqueous system (1910 Wh kg⁻¹); However, it has some severe problems that must be addressed, such as lithium corrosion by water and CO₂ from the air, electrolyte decomposition, and high polarization for the reduction of Li₂O₂. Fortunately, the aqueous system lithium air battery can avoid these problems effectively.

It is well known that lithium metal has a fierce oxidation-reduction reaction with water if they contact each other directly. So one of key parts of the aqueous lithium-air battery is the lithium conducting water-stable solid electrolyte for protecting lithium anode from water. The water-impermeability and conductivity –stability for solid electrolyte in aqueous LiCl and LiOH solution are very concerned. At present, we usually use the NASICON-type lithium conducting oxides of Li₁⁺ₓAl₉(Ti, Ge)₂₋ₓP₃₋ₓSiₓO₁₂ (LATP) glass ceramic supplied by Ohara Co., Japan, which is prepared by quenching from the melt and crystallization at high temperature, and its long-term stability immersed in saturated LiCl and LiOH solution has been proved. Unfortunately, the LATP glass ceramics sheet is very expensive due to its complex manufacturing process. Moreover, the lithium ion conductivity is still not so high (~10⁻⁴ S cm⁻¹) which contributes to high polarization of lithium air battery in both of charge and discharge processes. In this thesis, it was focused on the investigation of new and cheap NASICON-type water-impermeable film with high lithium ion conductivity.

The NASICON-type lithium ion electrolytes were synthesized by sol-gel method, and the high conductivity was obtained by element doping and replacement, rational sintering process. The electrical conductivity was examined as a function of x in Li₁⁺₄Al₀.₄⁻ₓTi₁₋₁₋ₓGeₓ(PO₄)₃ (x=0-1.6), Li₁⁺₄FeₓAl₀.₄₋ₓTi₁₋₁₋ₓ(PO₄)₃ (x=0-0.4) , Li₁⁺₄CrₓAl₀.₄₋ₓTi₁₋₁₋ₓ(PO₄)₃ (x=0-0.4) at various sintering temperatures and for various sintering periods in Chapter 1, chapter 2, and chapter 3 respectively. The highest total electrical conductivity was obtained for Li₁⁺₄Al₀.₄Ti₁₋₁₋ₓGe(PO₄)₃
(x=0-0.4) sintered at 900 °C for 11 h in air. The total and bulk conductivities of the sintered pellet observed for Li1.4Al0.4Ti1.4Ge0.2(PO4)3 were 1.29 × 10⁻³ and 2.35 × 10⁻³ S cm⁻¹ at 25 °C, respectively. It was found that no significant increase of the bulk and grain boundary resistance for all of Li1.4Al0.4Ti1.6-xGex(PO4)3 (x=0-1.6), Li1.4FexAl0.4-xTi1.6(PO4)3 (x=0-0.4), Li1.4CrxAl0.4-xTi1.6(PO4)3 (x=0-0.4) was observed after immersion in a saturated aqueous solution of LiOH and LiCl. The high lithium ion conductivity and stability in LiOH and LiCl aqueous solution of Li1.4Al0.4Ti1.4Ge0.2(PO4)3 suggests that this compound is an attractive candidate as the protective layer for the lithium metal electrode in aqueous lithium-air batteries.

A super thin sheet with high lithium ion conductivity and water-penetration free is eager for high-efficiency aqueous-system lithium air batteries with long-period stability. The chief advantage of tape-casting process is that it is the best way to form large-area, thin, flat ceramic or metallic parts, and it is very impossible to prepare thin high lithium ion solid electrolyte film by other methods presently. In chapter 4, a Li1.4Al0.4Ti1.4Ge0.2(PO4)3 (LAGTP) film was prepared by tape-casting using fine LAGTP powder prepared by sol-gel method. In order to prohibit water penetration through LAGTP film, a epoxy film was formed on the surface of film to fill its pores. Then the LAGTP composite film formed with epoxy resin was water impermeable and high mechanical strength. The highest electrical conductivity of 5.26×10⁻⁴ S cm⁻¹ at 25 °C was obtained for the composite film with approximately 2 wt% epoxy resin. The composite film was stable in an aqueous solution with a high content of lithium ions.

The three-point bending strength of the 75 µm thick LAGTP-epoxy composite film was 125 N mm⁻². However, the total electrical conductivity of the composite film was decreased to 3.3×10⁻⁴ S cm⁻¹ after storage for 20 days in an air atmosphere. The degradation of conductivity in the air atmosphere may be due to an exchange reaction of Li⁺ in LAGTP and H⁺ in water. The tape-casting LAGTP-epoxy resin composite film is stable in an aqueous solution with saturated LiOH and saturated LiCl. The water-impermeable composite film with excellent mechanical properties is an attractive candidate for the water-stability lithium electrode in rechargeable aqueous lithium-air batteries.