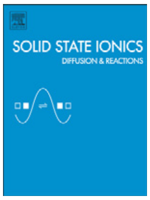
Solid State Ionics 180 (2009) 392–397

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi



New nanocomposite polymer electrolyte comprising nanosized $ZnAl_2O_4$ with a mesopore network and PEO-$LiClO_4$

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A R T I C L E I N F O

Article history:
Received 11 September 2008
Received in revised form 24 December 2008
Accepted 11 February 2009

Keywords:
Lithium polymer battery
Nanocomposite polymer electrolyte
Poly(ethylene oxide)
$ZnAl_2O_4$
Nanosized
Mesopore

A B S T R A C T

A novel poly(ethylene oxide) (PEO)-based nanocomposite polymer electrolyte (NCPE) has been developed by using nanosized, high surface area $ZnAl_2O_4$ with a mesopore network as the filler. X-ray diffraction (XRD), differential scanning calorimetry (DSC), and field emission scanning electron microscopy (FESEM) were used to characterize the NCPE. The results showed that the presence of the nanosized $ZnAl_2O_4$ powder leads to a reduction in the crystallinity of the PEO phase. The ionic conductivity and lithium ion transference number of the PEO-based polymer electrolyte were enhanced by the addition of the nanosized $ZnAl_2O_4$ powder. A broad electrochemical stability window suggests that the PEO-$LiClO_4$-$ZnAl_2O_4$ NCPE is a viable candidate for the electrolyte material in lithium polymer batteries.

1. Introduction

Advantages such as non-leakage of electrolyte, high energy density, good cyclability, flexible geometry, mechanical strength and safety have drawn the attention of many researchers to the development of all-solid-state lithium polymer batteries. Poly(ethylene oxide)(PEO)-based polymer electrolytes have gained an unprecedented significance in the past three decades since the discovery of ionic conductivity in complexes of PEO and alkaline salts in 1973 [1]. The transport of Li^+ cations in the PEO-based polymer electrolyte is coupled with the local relaxation and segmental motion of the PEO chains [2], which can only occur when PEO is in its amorphous state. However, due to its particular structure, PEO often shows relatively high crystallinity in sub-ambient temperature regions, and in such cases its ionic conductivity is lower than 10^{-7} S cm^{-1} at room temperature [3,4]. This is a serious limitation as far as its applications in home electronic appliances are concerned.

Many efforts have been devoted to improving the low temperature ionic conductivity of PEO-based polymer electrolytes. To date, most of the effective work has involved adding nanosized or mesoporous materials as fillers in order to enhance the conductivity of the polymer electrolyte. Nanosized materials such as SiO_2 [5–7], Al_2O_3 [8–10], TiO_2 [11], ZnO [12,13], ZrO_2 [14,15], and lithium aluminate nanosheets [16], have been used as the fillers in composite polymer electrolytes (CPEs) in previous work. Electrochemical investigations have consistently demonstrated that the presence of nanosized fillers leads to an enhancement of the ionic conductivity, both below and above the PEO crystallization temperature. These effects have been interpreted by assuming that the nanosized fillers play a role in inhibiting the PEO chain crystallization kinetics, as well as providing specific surface interactions with the electrolyte components. Mesoporous materials such as MCM-41 [17,18], ZSM-5 [19,20], SBA-15 [21,22], and P123@SBA-15 [23] have attracted much attention as fillers in CPEs due to their well ordered microstructures and large pore sizes. Porous materials have obvious advantages compared with traditional ceramic fillers because of their tunable pore/cage sizes and base/acid sites. Many workers have proposed that two major types of conduction mechanisms for porous fillers can be identified: one involving conventional amorphous PEO and a second involving hopping in a sequential manner by replacing the nearby vacancies (‘holes’) on the surface (both interior and exterior) of the porous materials [17,18,21,22]. Although synergistic effects can be expected to lead to an improved performance if a material with both nanosized domains and a mesopore network is used as the filler in a nanocomposite polymer electrolyte (NCPE), to the best of our knowledge no such study has been reported.

In this work, a novel PEO-$LiClO_4$-$ZnAl_2O_4$ NCPE has been developed, in which nanosized $ZnAl_2O_4$ with a mesopore network is used as the filler. The effects of adding such a filler on the ionic conductivity, lithium ion transference number and electrochemical stability of the PEO-based polymer electrolyte are investigated.

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doi:10.1016/j.ssi.2009.02.015

2. Experimental

2.1. Synthesis of nanosized $ZnAl_2O_4$ with a mesopore network

The synthesis of $ZnAl_2O_4$ powder was conducted as described in reference [24], and included three main parts as follows:

(1) A method developed in our laboratory involving separate nucleation and aging steps, which facilitates the synthesis of layered double hydroxides (LDH) with smaller and more uniform crystallite size than conventional coprecipitation techniques, was employed to synthesize ZnAl-LDH [25]. Solution A: $Zn(NO_3)_2.6H_2O$ and $Al(NO_3)_3.9H_2O$ with a Zn^{2+}/Al^{3+} molar ratio of 3.0 were dissolved in 100 mL of deionized water to give a solution with a total cation concentration of 1.2 M. Solution B: NaOH and Na_2CO_3 were dissolved in 100 mL of deionized water to form a mixed base solution. The concentrations of the base were related to those of the metal ions in solution A as follows: $[CO_3^{2-}] = 2.0\ [Al^{3+}]$, $[OH^-] = 1.6\ ([Zn^{2+}] + [Al^{3+}])$. Solutions A and B were simultaneously added rapidly to a colloid mill with the rotor speed set at 3000 rpm and mixed for 2 min. The resulting suspension was aged at 90 °C for 4 h, centrifuged, washed thoroughly with distilled water, and finally dried at 60 °C overnight.

(2) Samples of the above-synthesized ZnAl-LDH (Zn/Al = 3.0) precursor were calcined in air at 700 °C for 2 h with a heating rate of 10 °C min^{-1}. The resulting products were slowly cooled to room temperature.

(3) 1.0 g of the calcined material was subsequently treated with 25 mL of aqueous sodium hydroxide solution (10 M) at 60 °C for 2 days under moderate stirring. The final products were separated by centrifugation several times and dried at 80 °C overnight.

2.2. Preparation of the PEO_{16}-$LiClO_4$-$ZnAl_2O_4$ NCPE films

PEO with molecular weight 100,000 and $LiClO_4$ supplied by Alfa Aesar were dried under vacuum at 50 °C and 100 °C, respectively, for at least 48 h before use. $ZnAl_2O_4$ powder prepared as above was heated under vacuum at 150 °C for 48 h to remove water before use. Films were prepared by the conventional solution cast technique as follows: Various amounts of $ZnAl_2O_4$ powder of PEO were dispersed in acetonitrile with the aid of ultrasonic dispersion, followed by the addition of PEO and $LiClO_4$ with fixed [EO]/[Li] molar ratio of 16. The solution was stirred at room temperature for 24 h until complete homogenization of the mixture had occurred. The slurry was then cast onto a self-designed Teflon plate and solvent allowed to evaporate slowly at room temperature for 24 h. Finally, the samples were dried under vacuum at 50 °C for 48 h. The films obtained were 150–200 µm in thickness. The NCPEs containing $ZnAl_2O_4$ are designated PEO_{16}-$LiClO_4$-x wt.% $ZnAl_2O_4$, where x denotes 0, 3, 5, 8, 10 or 15.

2.3. Characterization of samples

X-ray diffraction (XRD) patterns of the samples were obtained by using a Shimadzu XRD-6000 diffractometer with Cu-K_α radiation (40 kV and 30 mA) at a scanning rate of 5°min^{-1}.

The specific surface area determination and pore volume and size analysis were performed by BET and BJH methods using a Quantachrome Autosorb-1C-VP Analyzer. Prior to the measurements, samples were outgassed at 200 °C for 2 h.

Differential scanning calorimetry (DSC) was used to determine the melting point (T_m) and the glass transition temperature (T_g) of the polymer electrolyte by using a NETZSCH-DSC-204-F1 instrument. The measurements were carried out at a heating rate of 10 °C min^{-1} from −60 °C to 100 °C. A flow of dry nitrogen gas was maintained over the perforated pan to avoid any contact with atmospheric moisture. Sample weights were in the range 3–5 mg and an empty aluminum pan was used as a reference.

Sample morphologies were investigated using a Hitachi S4700 field emission scanning electron microscope (FESEM).

Transmission electron microscopy (TEM) images were recorded with Hitachi H-800 instrument.

The ionic conductivity of the samples was measured by sandwiching the samples between two stainless steel blocking electrodes using AC impedance techniques. The measurements were performed using an electrochemical workstation (IM6e, Germany) between 100 kHz and 10 Hz at various temperatures ranging from 25 °C to 80 °C. A thermostatic bath (Julabo Labortechnik GmbH, Germany) was utilized to control the temperature to within ±0.1 °C of the target value. The samples were thermally equilibrated at each temperature for at least 2 h prior to the measurements. The bulk resistance (R_b) was obtained by reading the intercept of the impedance spectrum, and the ion conductivity was calculated from the expression

$$\sigma = L / (R_b A) \tag{1}$$

where L is the thickness of the electrolyte film and A represents the electrode area.

The lithium ion transference number, t_+ of the samples was measured by utilizing the method reported previously [26,27]. The NCPE film was sandwiched between two lithium-unblocking electrodes to form a symmetrical Li/electrolyte/Li cell. After the initial lithium interfacial resistance (R_o) of the cell was measured, a DC voltage pulse (ΔV) was applied to the cell for the chronoamperometric analysis until a steady condition was obtained, recording the steady current (I_s), and the final interfacial resistance (R_s) was then measured. By using the above values, the value of t_+ can be calculated using the equation:

$$t_+ = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)} \tag{2}$$

The initial current (I_o) is calculated from the voltage and the overall cell resistance by

$$I_o = \Delta V / (R_e + R_o) \tag{3}$$

where R_e is the electrolyte resistance.

The electrochemical stability window of the NCPE was determined by running a linear sweep voltammogram in three-electrode cells using stainless steel as the blocking working electrode and lithium as both the counter and the reference electrode. An IM6e electrochemical workstation was used with a scanning rate of 1 mV s^{-1}.

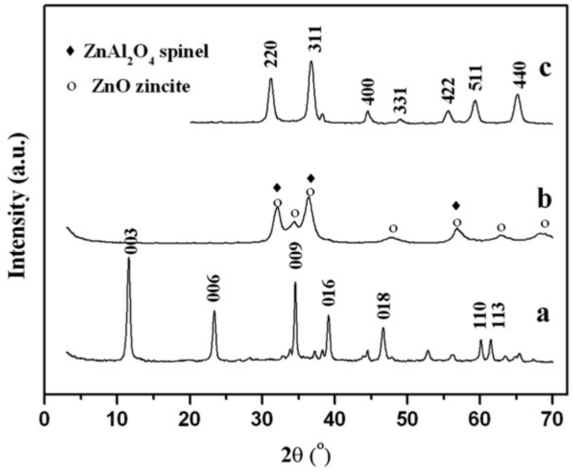

Fig. 1. Powder XRD patterns of (a) the ZnAl-LDH precursor, (b) ZnAl-LDH calcined at 700 °C for 2 h, and (c) $ZnAl_2O_4$.