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Magnesium ion-conducting gel polymer electrolytes dispersed with nanosized magnesium oxide

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ABSTRACT

Experimental investigations are performed on novel magnesium ion-conducting gel polymer electrolyte nanocomposites based on poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP), dispersed with nanosized magnesium oxide (MgO) particles. The nanocomposite materials are in the form of free-standing films. Various physical and electrochemical analyses demonstrate promising characteristics of these films, suitable as electrolytes in rechargeable magnesium batteries. The optimized material with 3 wt.% MgO offers a maximum electrical conductivity of $\sim 8 \times 10^{-3}$ S cm^{-1} at room temperature ($\sim 25\,^{\circ}$C) with good thermal and electrochemical stabilities. The ion/filler–polymer interactions and possible conformational changes in host polymer PVdF-HFP due to the liquid electrolyte entrapment and dispersion of nanosized MgO are examined by Fourier transform infrared (FTIR), X-ray diffraction (XRD) and scanning electron microscopic (SEM) methods. The Mg^{2+} ion conduction in the gel film is confirmed from the cyclic voltammetry, impedance spectroscopy and transport number measurements. The Mg^{2+} ion transport number (t_+) is enhanced substantially and found to have a maximum of ~0.44 for the addition of 10 wt.% MgO nanoparticles. The enhancement in t_+ is explained on the basis of the formation of space-charge regions due to the presence of MgO:Mg^{2+}-like species, that supports Mg^{2+} ion motion.

1. Introduction

The research and development of polymer electrolyte based batteries with high specific energy, good reliability and safety has been an active area for the past three decades [1–3]. Advances in microelectronic industry, especially mobile phones and portable computers, have created a demand for new and improved power sources. Presently, world-wide efforts are directed towards the development of advanced battery technologies based on lithium negative electrodes (anode). To date, the rechargeable lithium ion battery has been one of the best choices in view of specific capacity and cyclic stability [4]. However, rechargeable lithium metal batteries with high specific power or energy are still unavailable in the market. These batteries are relatively expensive and suffer from some safety limitations. Hence, new rechargeable battery systems are required which can be made of cheap and environmental friendly materials.

Recently, the magnesium-based rechargeable battery system has attracted attention due to its performance capabilities, which are expected to be close to those of lithium-based rechargeable batteries [5–7]. Magnesium is one of the ideal materials for the negative electrode for practical batteries because it has low electrochemical equivalence (~ 12.15 g eq^{-1}), considerably negative electrode potential (−2.3 V vs. SHE), low cost due to natural abundance, and greater safer than lithium. Aurbach et al. [8] have developed a prototype high-capacity rechargeable magnesium battery using electrolyte solutions based on Mg organohaloaluminate salts. The same group reported that Chevrel phases Mo_6T_8 (T = S, Se) can insert Mg ions reversibly and can be used as practical cathode materials for rechargeable Mg-batteries [9]. Despite these studies, however, development of rechargeable Mg-batteries has not be accelerated mainly due to the lower reversibility of the Mg electrode/electrolyte charge transfer and the lack of suitable Mg^{2+} ion-conducting non-aqueous electrolytes [10,11]. Recently, the development of solid-state Mg^{2+} ion-conducting electrolytes has become one of the important issues to realize rechargeable, solid-state Mg-batteries.

Gel polymer electrolytes, an excellent substitute for liquid electrolytes, continue to attract research interest due to properties which make them suitable for application in solid-state electrochemical devices, e.g., rechargeable batteries, supercapacitors, etc. [12,13]. Such gel electrolytes are examined mostly for use in lithium systems. Mg^{2+} ion-conducting gel polymer electrolytes are not widely reported except a few systems [14–16]. Few solid-state rechargeable magnesium batteries using polymer gel electrolytes have been reported in literature [17,18]. Gel polymer electrolytes

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have some important advantages over liquid electrolytes in that the risk of leakage is reduced, and electrode interfacial contact can be maintained during volumetric changes associated with charge and discharge cycling of the battery. The ability of gel electrolytes to act as both the separator and the electrolyte leads to easy fabrication and allows the possibility of miniaturized devices. However, the main drawback associated with these materials is the tendency to flow, which is deleterious in terms of decay in conductivity and, particularly, in battery reliability and safety. This is obviously a limitation with present gel polymer electrolyte systems and various approaches are under consideration to assure membrane integrity during operation and storage.

The dispersion of nanosized ceramic filler particles, e.g., Al_2O_3, SiO_2, TiO_2, is one of the most reported approaches to improve the mechanical as well as the electrochemical and transport properties of polymer/gel electrolytes [19–21]. In general, the ceramic fillers are broadly classified into two categories, namely, active and passive fillers. The active component materials participate in the conduction process, e.g., Li_3N, $LiAl_2O_3$ are active fillers for Li^+ ion-conducting systems. Passive fillers such as Al_2O_3, SiO_2 or TiO_2 are not directly involved in the ion transport process. Such fillers have also been incorporated into gel electrolytes in order to preserve a porous structure that maximizes the adsorption of liquid electrolyte [22] and to reduce the risk of leakage [23–25].

In the present study, the effect of adding of a nanosized active filler MgO to a PVdF-HFP based Mg^{2+} ion-conducting gel polymer electrolyte is investigated by means of various physical techniques, namely, X-ray diffraction, thermal analysis, infrared spectroscopy, complex impedance analysis, cyclic voltammetry, and conductivity and transport number measurements. The gel polymer electrolyte nanocomposite is found to be a thermally and electrochemically stable material for application in power sources such as magnesium batteries.

2. Experimental

2.1. Materials

The copolymer, poly(vinylidene fluoride-hexafluoropropylene) (PVdF-HFP; average molecular weight 400 000), ethylene carbonate (EC), propylene carbonate (PC), magnesium perchlorate [$Mg(ClO_4)_2$] and the nanosized filler magnesium oxide (MgO; particle size <100 nm) were obtained from Aldrich and used without further purification. The intermediate solvent tetrahydrofuran (THF) was purchased from Merck, India. A solution cast method was used to prepare gel polymer electrolyte nanocomposite films. In this process, the liquid electrolyte was first prepared by dissolving 1 M $Mg(ClO)_4$ in a mixture of EC and PC (1:1, v/v). The host polymer PVdF-HFP was separately dissolved in THF by stirring magnetically at ∼50 °C and an appropriate amount (∼20 wt.% with respect to the liquid electrolyte for all samples) was mixed in liquid electrolyte. To prepare a gel polymer electrolyte nanocomposite, MgO nanoparticles in different weight ratios from 0 to 20 wt.% with respect to polymer weight were dispersed. The mixtures were then stirred thoroughly for ∼10 h and proper filler dispersion was ensured by keeping the mixture in an ultrasonic bath for about 30 min. Finally, the mixture was poured into glass petri dishes and allowed to evaporate the intermediate solvent, THF, to obtain solid-like, free-standing, nanocomposite films of thickness ∼300–400 μm.

Circular discs (area = 1.1 cm^2) of magnesium electrodes were obtained by palletising the magnesium powder purchased from Aldrich. These discs were polished with successive grades of emery paper to a smooth finish then washed thoroughly in acetone and dried.

2.2. Instrumentation

The thermal stability of gel polymer electrolyte nanocomposites was tested by thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA was carried out from room temperature to 475 °C under a dynamic dry nitrogen atmosphere at a heating rate of 10 °C min^{-1} using a PerkinElmer TGA system (TGA7). DSC was performed from −90 to 85 °C at a heating rate of 10 °C min^{-1} in a static Nitrogen atmosphere with the help of a DSC system of TA Instruments (Model: Q100). Morphological studies of the gel nanocomposite films were carried out with a scanning electron microscope (JEOL, JSM 5600) and an atomic force microscope (VEECO, USA, model: DI-CP-II). The SEM micrographs were taken at low vacuum after sputtering the samples with gold to prepare conductive surfaces. X-ray diffraction patterns of the films were recorded using a Philips X-ray diffractometer with Cu Kα radiation in the Bragg angle (2θ) range from 10 to 60°. The FTIR spectra were recorded with a PerkinElmer FTIR spectrophotometer.

The electrical conductivities of the gel films were evaluated by means of AC impedance spectroscopy using a LCR Hi-Tester (Model: 3522-50, HIOKI, Japan) over the frequency range from 1 Hz to 100 kHz at a signal level of 10 mV. Conductivity measurements were obtained by sandwiching the films between two stainless-steel (SS) foils over the range of 0–80 °C. Comparative cyclic voltammetric studies were performed on symmetric cells, in which the gel nanocomposite was sandwiched between SS and Mg electrodes, using an electrochemical analyzer (Model: CHI 608C, CH Instruments, USA) at a scan rate of 5 m V s^{-1}. The electrochemical stabilities of the electrolyte films were evaluated by means of linear sweep voltammetry using stainless steel as the working electrode and a Mg disc as combined counter and the reference electrodes.

The total ionic transport number (t_{ion}) was obtained by the polarization technique [26]. In this technique, a SS|gel nanocomposite|SS cell was polarized by applying a step potential of 1.0 V and the resulting potentiostatic current was monitored as a function of time. Stainless steel (SS) acted as blocking electrodes for the above cell. The 't_{ion}' was evaluated using the formula:

$$t_{ion} = \frac{i_T - i_e}{i_T} \tag{1}$$

where i_T and i_e are total and residual current, respectively. The Mg^{2+} ions transport number (t_+) of each gel electrolyte was evaluated using a combination of AC impedance spectroscopy and DC polarization studies on a Mg|gel nanocomposite|Mg cell according to the method of Evans et al. [27].

3. Results and discussion

3.1. Structural studies

The XRD patterns of the PVdF-HFP, filler-free polymer gel electrolyte and the gel polymer electrolyte nanocomposite films are shown in Fig. 1. The XRD pattern of the PVdF-HFP film shows the typical characteristic of a semi-crystalline microstructure, i.e., the co-existence of mixed crystalline and amorphous regions with predominant peaks at 2θ = 14.6, 17, 20, 26.6 and 38° (Fig. 1a). The X-ray diffractogram of the filler-free gel polymer electrolyte shows a broadened peak between 10 and 30° (Fig. 1b). The PVdF-HFP peak at ∼27° is masked in the broad peak and the intense peak at ∼38° disappears. These changes reveal clearly that the gel polymer electrolyte is predominantly amorphous and its crystallinity is depressed due to the addition of liquid electrolyte. This indicates that the liquid electrolyte solution most likely blends with the PVdF-HFP at the molecular level and functions as a plasticizer for the polymer. The diffractogram of the gel polymer electrolyte nanocomposite film shows the characteristic peaks of