



Preparation of polyethylene oxide composite electrolytes containing imidazolium cation salt-attached titanium oxides and their conducting behavior



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ABSTRACT

We report an addition effect of imidazolium salt modified filler (IS-TiO₂), which is successfully prepared by sol-gel process and incorporated in poly(ethylene oxide) (PEO) based nanocomposite polymer electrolytes (NCPE). In order to ascertain the thermal and crystalline properties of NCPE with maximum conductivity, films were subjected to differential scanning calorimeter (DSC) analysis. The crystallinity of the NCPE was evaluated using X-ray diffraction (XRD) and the ionic conductivity was measured by AC impedance method. Ionic conductivities of NCPE containing TiO₂ or IS-TiO₂ are examined as a function of temperature. FT-IR spectroscopy is used to study polymer structure and interactions between PEO chain and filler, which can make changes in the force constant of C–O groups. The morphology of CPE was analyzed by SEM method. Owing to the presence of imidazolium salt attached on titanium oxide, the beneficial effects were obtained such as the better dispersion and lower interfacial resistance of polymer electrolytes. In accordance with these reasons, the NCPE containing the imidazolium salt modified filler shows slightly higher ionic conductivity than the NCPE containing the pure TiO₂.

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Introduction

In recent years, the development of nanocomposite polymer electrolytes (NCPE) for a wide variety of application was driven by the intrinsic properties of polymer electrolytes, such as relative ease in fabrication compact, thin-film forming ability, lightweight devices, high energy density, and wide electrochemical window [1,2]. NCPE comprising of a polar polymer matrix, lithium salt, plasticizer, and inorganic nano filler, has been proposed to replace liquid electrolytes and to decrease dendrite growth forming barriers. Among these kinds of composites, the most popular and conventional candidate was the poly(ethylene oxide) (PEO)-based polymer composite [3]. The Li⁺ ion motion in NCPE is coupled with the local segmental relaxation, where the relaxation time for the segmental motion of PEO chain is coupled with the conduction relaxation time, and a proper environmental state can only be obtained when PEO is in its amorphous conditions. However, PEO generally crystallize below 70 °C which also roughly

corresponds to the melting point. The crystallization of PEO chains may hamper the ionic motion and become the cause of decay of ionic conductivity.

To overcome this shortcoming of PEO, one promising approach is the introduction of an inorganic particles, organic acid and ceramic powder into the polymer electrolyte due to its large surface area, resulting the promoted salt dissociation and the suppression of local chain re-organization. The addition of the fillers has been extensively examined to improve higher degree of amorphous phase of the host polymer at room temperature [4]. It was found that the increase of room temperature conductivities could bring improved interfacial as well as mechanical properties. It has been observed that the nano-sized particle play a significant role in the NCPE systems. From this view point, these effects of the fillers would influence on the dispersion and nature of individual material system, resulting the control of ionic conductivity and the structural properties in PEO-based electrolytes. Furthermore, thermal transitions and morphology of NCPE depends on the size, surface areas and surface feature of ceramic fillers. Due to the presence of this unique characteristic of nano filler, several attempts to improve the ionic conductivity of NCPE have been reported, which include Al₂O₃ [5,6], TiO₂ [7], MgO [8] and related

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oxides. However, these nano ceramic fillers tend to form large agglomerates.

One strategy to resolve the shortcomings of polymer electrolytes and to improve the dispersion of filler. From this kind of perspective, a preparation of imidazolium-salt (IS) and nano ceramic filler is a beneficial step toward enhancing filler performances in NCPE. Imidazolium-salt (IS) has been attracting much attention in various applications especially in the field of organic synthesis, catalysis, separation, and good solvent for many electrochemical devices. This continuously growing interest is motivated by their unique properties such as high thermal stability, no combustion, wide electrochemical window, and unusual dissolving capability. In the past decade, there has been increasing use of imidazolium-salt (IS) in many research fields such as Li battery [9], dye-sensitized solar cell [10], separation technology, and material synthesis [11].

Here, as part of a continuing effort to develop advanced composite polymer electrolytes, we implement a preparation of new imidazolium-salt attached TiO₂ (IS-TiO₂). In the present study, we endeavor to overcome the aforementioned limitations of NCPE and dispersion behavior of the filler, we develop a new modified filler with imidazolium salt, which was based on sol-gel process. Common sol-gel method is chemical method to make nanostructured particles by a compositional and microstructural tailoring through controlling metal alkoxides as a precursor. In sol-gel synthesis, it occurs rapid hydrolysis and polycondensation reactions between highly reactive alkoxide titanium precursors and water. These two reactions have a strong influence on the structure and properties of final product. Factors affecting the sol-gel process include the water/alkoxide ratio, amount of water, varied temperature, solvent and additive. With a various these parameters, materials of different structure and surface chemistry can be obtained. As a result, the obtained imidazolium-salt attached TiO₂ (IS-TiO₂) was used as a new filler to prepare a series PEO-based NCPE with LiClO₄. It was anticipated that the mesoporous structure of new filler and PEO matrix would provide shorter ion transport paths, resulting in higher conductivity and better electrochemical stability. From this view point, features of the new filler is further discussed by scrutinizing Li⁺ ion behavior of the NCPE and its specific interaction with PEO matrix.

Experiment details

Materials

Poly(ethylene oxide) with average molecular weights of 1×10^6 (Aldrich) was used respectively without further purification. Lithium perchlorate (LiClO₄) was obtained from Wako and dried under vacuum ($<10^{-1}$ Torr) for overnight at 50 °C before use. Acetonitrile (AN) and propylene carbonate (PC) were purchased from Junsei, respectively, stored under glove box with dry argon atmosphere before use. Isopropoxide titanium (TTIP), isopropyl alcohol and imidazolium salt (IS) also were acquired from Sigma-Aldrich.

Synthesis of IS-TiO₂

The nanostructured IS-TiO₂ was synthesized as follows: titanium tetraisopropoxide (TTIP) was first mixed with isopropanol at room temperature. After the translucent mixture stirred for 30 min, the imidazolium salt (IS) was added into mixed solution to various IS/TTIP molar ratio 1:3. After stirring for 10 min, the deionized water slowly was added for providing enough time of hydrolysis and condensation reaction at room temperature. The mixed solution was stirred vigorously for 30 min. The resulting suspension was washed thoroughly several times with distilled

water and dried at 100 °C. The resulting products were included with residual of IS and organics. In order to remove, above powder was mixed with acetonitrile in a Teflon-lined autoclave at 50 °C. The final product was also recovered by filtration, washed and dried at 100 °C for overnight [12,13].

Fabrication of composite polymer electrolytes

To prepare the nanocomposite polymer electrolytes, the conventional solution technique was used to prepare PEO polymer matrix, PEO and LiClO₄ salt in molar ratio 16:1, PEO:PC plasticizer in a molar ratio 1:0.5, with different weigh ratio IS-TiO₂ and TiO₂. The preparation of NCPE films involved first the dissolution of the PEO in acetonitrile. The polymer matrix solution was agitated for 6 h at 40 °C. After stirring, LiClO₄ and PC added to the PEO-based polymer matrix solution. After a completely homogenous solution was obtained, various IS-TiO₂, TiO₂ were added to polymer matrix solution, after which another agitation was sustained for 3 h. Finally, the precursor mixture was subject to sonication for 1 h, in order to attain a uniform dispersion of nanoparticles. Subsequently, the resulting suspension and any residual solvent were poured into Teflon Petri dish and evaporated slowly at 60 °C for overnight in vacuum oven. Consequently, the solid polymer electrolyte was peeled from the laboratory dish and stored inside the glove box.

Characterization methods

The X-ray diffraction (XRD) patterns of NCPE films were obtained with a PHILIPS (Netherlands), X'Pert-MPD System equipped with a rotation anode and using line focus 3 kW Cu-K α X-ray tub radiation. The thermal behaviors of the films with a typical weight of 10 mg were studied using differential scanning calorimetry (DSC 6 series, Perkin Elmer Co. Ltd.) under N₂ atmosphere and the measurements were taken from 0 to 100 °C with a heating of 5 °C/min. The morphology of NCPE films was investigated by SEM (HITACHI S53500N). The FT-IR spectra were obtained by Spectrum GX. Spectra were recorded in KBr powder at ratio of sample: KBr = 1:10 and scanned 16 times in transmission mode with a KBr background.

Electrochemical characterization

Stainless steel/PEO based composite polymer electrolytes/stainless steel cell was assembled to determine the ionic conductivity by using a Galvanostat/Potentiostat with impedance analyzer (Iviumstat, Netherlands). Two electrodes carried out by means of AC impedance spectroscopy over the frequency range from 200 MHz to 10 Hz with amplitude of 0.1 V. The film thickness varied from 0.007 to 0.02 cm and the sample controlled oven for 1 h before measurement. The ionic conductivity values (σ) were calculated from the bulk resistance (R_b), which was determined by equivalent circuit analysis software by using following equation [14]:

$$\frac{1}{\sigma} = \frac{R_b A}{t} \quad (1)$$

where R_b is the bulk resistance, and t and A are the thickness of the electrolytes film and the areas of film.

Results and discussion

Structure of modified fillers

Imidazolium salt attached TiO₂ (IS-TiO₂) was immobilized on the surface of titanium. The resulting heterogeneous filler and pure

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