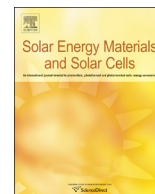




ELSEVIER

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

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

Enhanced Ionic conductivity and optical transmissivity of functionalized ZrO₂/PVdF-HFP hybrid electrolyte for energy efficient windows

John Marc C. Puguan¹, Amutha Chinnappan¹, Richard Appiah-Ntiamoah, Hern Kim*

Department of Energy Science and Technology, Energy and Environment Fusion Technology Center, Myongji University, Yongin, Kyonggi-do 449-728, Republic of Korea

ARTICLE INFO

Article history:

Received 7 October 2014

Received in revised form

6 December 2014

Accepted 17 February 2015

Available online 9 March 2015

Keywords:

ZrO₂

Composite polymer electrolyte

Electrochromic device

Nanocomposite

Smart window

ABSTRACT

A hybrid electrolyte for energy efficient windows was fabricated by incorporating functionalized zirconium oxide (ZrO₂) nanocrystals into poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) and complexed with lithium trifluoromethanesulfonate (LiCF₃SO₃). Ionic conductivity of the electrolyte increased by 4 orders of magnitude upon addition of a phase-pure cubic ZrO₂ that was synthesized by reacting zirconium (IV) isopropoxide and benzyl alcohol at 210 °C for 3 days. Functionalizing the nanocrystal with a vinyl group-containing ligand, at a ligand-to-ZrO₂ molar ratio of 0.1:1, enhanced the electrolyte's optical transmittance doubly while maintaining its high ionic conductivity of $1.78 \times 10^{-3} \text{ S cm}^{-1}$ at a loading of 3.85 ZrO₂ wt%. Further addition of the ligand significantly decreased the ionic conductivity but kept a high optical transmittance. This new nanocomposite electrolyte with further tuning has the potential to be next generation electrolyte for energy efficient windows.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Smart windows are windows which use a glazing material to control the amount of light that is allowed to pass through glass panels. One particular type is the electrochromic smart windows which are characterized by their ability to control the amount of light transmission by the application of low electrical voltage thereby providing energy efficiency and indoor comfort in buildings. This type of devices is a promising option to efficiently use a finite energy.

Electrochromic devices (ECDs) are generally composed of an electrolyte, electrochromic layer, counter electrode and electrical conductors. Electrolytes and electrochromic materials are the most vital and active components of an electrochromic device. Electrochromic materials have the ability to reversibly alter their light absorption properties within a specific range of spectral wavelength through redox reactions stimulated by low direct current (DC) potentials which result to a color change. This change is due to the generation of new absorption band in the visible region, infrared or in the microwave region [1]. For this to take place, the

electrochromic layer must be integrated with ion conducting electrolytes and some electrical contacts. The polymer electrolytes play a very essential role as the primary medium for ionic conduction in the ECD and it can be in the form of a liquid, gel or solid [2].

Two of the major functions of electrolyte in electrochemical systems are to promote mutual ionic flow and exchange between the electrodes while keeping them from direct electrical contact and to avoid electronic charge flow [2,3]. Most electrolytes are composed of solvents and salts which ionize to provide ions in the system [4]. They are generally classified into liquid electrolytes, ceramic electrolytes, solid inorganic electrolytes and polymer electrolytes [5–9]. Based on previous studies, polymer electrolytes have been preferred and were tailored for advanced electrochemical systems especially for lithium-ion batteries and electrochromic applications [10,11]. They are preferred because of their processibility, mechanical strength, stability, flexibility, and wide range of working temperature [1]. Polymer electrolytes are very vital in ECDs as they dictate the overall performance of the device [12–14]. For a polymer electrolyte to be suitable for electrochromic applications, it has to be highly ion conductive, it has a good electron donating ability, it has low bond rotation energy, thermally and electrochemically stable, it has high optical transparency, able to cover a wide range of potential, able to be confined into specific areas, and it has to be cheap but environmentally friendly [12–22]. Thus, a well-tuned formulation is very essential

* Corresponding author. Tel.: +82 313306688; fax: +82 31 336 6336.

E-mail address: hernkim@mju.ac.kr (H. Kim).¹ These authors contributed equally to this work.

for high efficiency and for longer cycle life of the device [15–19].

Composite polymer electrolytes exhibit highly improved ionic conductivity compared to the other three types. The addition of inorganic fillers like zeolites, Al_2O_3 , SiO_2 and MgO has dramatically increased the ionic conductivity of electrolytes. Furthermore, the interfacial stability and the mechanical strength of the composites were also enhanced. The polymer matrices that were investigated in the recent years are polyethylene oxide (PEO), polyacrylonitrile (PAN), polymethyl methacrylate (PMMA), and polyvinylidene fluoride (PVdF) [5–10,23–27]. PVdF has gained attention and been used recently as electrolyte for electrochromic systems due to its many advantages like high mechanical strength and its high dielectric constant which aids in the ionization of the salt giving a higher charge density. However, PVdF does not work well with lithium ions because of its semi-crystalline property [1]. To favor the ease of flow of the ions, copolymers of PVdF like poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) and poly(vinylidene fluoride-co-trifluoroethylene) (PVdF-TrFE) must be considered as these have amorphous parts in them. Moreover, incorporation of nanofiller further inhibits the formation of crystallites in the polymer, thus, enhancing its amorphicity. However, the nanofillers used in the previous studies exhibit low dielectric constants. In order to enhance the ionization of the salt in the electrolyte, filler with high dielectric constant must be incorporated. As shown in Table 1, ZrO_2 is one of the few dielectric oxides which have a high dielectric constant and at the same time high band gap energy [28]. Unlike the other oxides, TiO_2 and SiO_2 which are widely used as nanofillers, they do not possess both properties. This makes ZrO_2 unique among all other oxide nanomaterials as electrolyte nanofiller for electrochromic device applications. To enhance its dispersibility in the polymeric substrate, ZrO_2 was functionalized by attaching a vinyl-containing ligand via simple chemical reaction. A new organic-inorganic hybrid electrolyte was found to have enhanced ionic conductivity and improved optical transmittance necessary for such application.

2. Experimental

2.1. Synthesis of ZrO_2 nanocrystals

Synthesis of ZrO_2 nanocrystals was described elsewhere [29] with some modification (Fig. 1). Zirconium (IV) isopropoxide (99.9%, Aldrich), 5 g, and benzyl alcohol (> 98%, Showa), 75 ml, were put in a 150 ml stainless steel reactor. The reactor vessel was placed in a bench top supercritical reactor system, sealed and heated to 210 °C for 3 days under continuous stirring (200 rpm). The reactor was cooled to room temperature and a white turbid dispersion was obtained. Using a high speed centrifuge (Supra 21 K), the dispersion was centrifuged at 15,000 rpm for 30 min to

Table 1
Comparison of relevant properties among inorganic oxide dielectrics.

Material	Dielectric constant, K	Band gap E_g (eV)	Crystal structure (s)
SiO_2	3.9	8.9	Amorphous
Si_3N_4	7	5.1	Amorphous
Al_2O_3	9	8.7	Amorphous
Y_2O_3	15	5.6	Cubic
La_2O_3	30	4.3	Hexagonal, Cubic
Ta_2O_5	26	4.5	Orthorhombic
TiO_2	80	3.5	Tetragonal (rutile, anatase)
HfO_2	25	5.7	Monoclinic, tetragonal, cubic
ZrO_2	25	7.8	Monoclinic, tetragonal, cubic

remove benzyl alcohol. The precipitate was further washed by two repeated cycles of sonication and centrifugation with absolute ethanol (Merck) to remove excess solvent. The nanoparticles were dried at 80 °C in vacuum for 24 h and then were kept in desiccator until use.

2.2. Synthesis of composite polymer electrolyte

Appropriate amounts of propylene carbonate (PC, 99.7%, Aldrich) and lithium trifluoromethanesulfonate (LiCF_3SO_3 , 98%, Acros Organics) were dissolved in N,N-dimethylformamide (DMF, 99.8%, Showa) (Table 2). The mixture was stirred for 15 min to dissolve solids. PVdF-HFP (1:1 polymer ratio, Sigma-Aldrich) was gradually added and was stirred until a clear and homogeneous solution was obtained. Different amounts of as synthesized ZrO_2 nanocrystals were added into the solution and the solution was stirred for 2 h. The solution was subjected to ultra-sonication for 15 min to achieve homogeneous suspension. Composite polymer electrolytes were synthesized by casting method and were air dried for 12 h. They were pre-dried at 60 °C for 1 h before drying under vacuum at 90 °C for 24 h to ensure complete removal of solvent and moisture.

In order to enhance the dispersion of the ZrO_2 nanoparticles in the polymer matrix, 3-(trimethoxysilyl)propyl methacrylate (MPS, 98%, Acros Organics) was added to a fresh sample containing a certain amount of ZrO_2 prior to ultrasonication. The solution was allowed to complete reaction for 3 days with continuous stirring. It was casted on glass, dried and kept in desiccator prior to ionic conductivity measurements. Compositions of the samples are described in Table 3.

2.3. Characterization techniques

2.3.1. Electrochemical impedance spectroscopy (EIS)

Ionic conductivities of the composite polymer electrolytes were measured by AC impedance spectroscopy (Zahner, IM6eX) unit coupled with a 4-point probe conductivity cell in 50 mHz to 100 kHz frequency range. The impedance studies were carried out by sandwiching the electrolyte film (4 cm × 1 cm) into the conductivity cell having 4 Pt-electrodes (Fig. 2). Thickness of each sample (~15 μm) was measured by a screw gauge micrometer. The ionic conductivity, σ , of each electrolyte was calculated from $\sigma = l/R_b A$; where, l is the distance between the working and the sensing electrodes which is 1 cm, R_b is the bulk resistance and A is the cross sectional area of the membrane perpendicular to ion flow. The real impedance (Z') was plotted against the imaginary impedance (Z'') and the bulk resistance was obtained from the intercept with the real axis.

2.3.2. X-ray diffraction (XRD) and dynamic light scattering (DLS)

X-Ray diffraction spectra of the samples were generated using the PANalytical (X'pert-Pro) with operating voltage of 40 kV and current of 40 mA at X-ray wavelength of 1.5406 Å. The samples were scanned at 2θ angles between 10° and 80° with a step size of 0.03°.

Particle size distribution of synthesized ZrO_2 was obtained by dynamic light scattering technique using Zetasizer Nano ZS (Malvern Instruments Ltd.). Dispersions of 1.48 wt% ZrO_2 in DMF was prepared.

2.3.3. UV-vis spectroscopy

Optical transmittances of the composite polymer electrolytes, which were spin coated on ITO-PET substrate, with ~5 μm thickness were determined using UV-vis Spectrophotometer (Varian, Cary 100) from 300 nm to 800 nm wavelength range at room temperature and under controlled humidity (40 ± 2%). The samples were placed perpendicular to the light beam of the spectrophotometer.

Download English Version:

<https://daneshyari.com/en/article/77876>

Download Persian Version:

<https://daneshyari.com/article/77876>

[Daneshyari.com](https://daneshyari.com)