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Short communication

Improved surface proton conduction of yttrium-stabilized zirconia via acidic modifications

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Abstract

This work studied the acidic surface modifications on the conduction properties of yttrium-stabilized zirconia (YSZ) nanocrystals using sulfuric and phosphoric acid protonation techniques with an aim to discover suitable additives of the proton-conducting membranes for intermediate temperature operation. All YSZ nanostructures were hydrothermally prepared and the sample surfaces were modified with sulfate or phosphate groups by subsequently immersing the as-prepared samples into sulfuric or phosphoric acid. The obtained samples were characterized by X-ray diffraction, high-resolution transmission electron microscope, element analysis, infrared spectra, N_2 adsorption/desorption, and impedance spectroscopy. It was found that the samples exhibited a cubic fluorite structure with a grain size of 4.5 nm and a high surface area of 205 $m^2\,g^{-1}$. Proton conduction measurements showed that sulfate-modified samples had an apparently low proton conductivity, while the phosphate-modified ones exhibited a significant proton conductivity and improved thermal stability. These observations were explained by taking into account the grafted species and the amount of hydrated water.

Keywords: Yttrium-stabilized zirconia; Surface modification; Proton conductivity

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are one of the most promising clean energy technologies for transportation and stationary applications [1,2]. Polyperfluorosulfonic acid (PFSA) membranes such as Nafion are currently widely used as the key proton-conducting electrolyte for low-temperature PEMFCs. To possess advantages such as faster electrode kinetics, greater tolerance to impurities in the fuel stream, and easier water-thermal management, PEMFCs have to be operated at intermediate temperatures between 100 and 300 °C [3,4]. Unfortunately, such PFSA membranes are unavailable because of the low thermal stability and decreased conductivity that occur at high temperatures. There have been considerable efforts to modify the PFSA membranes to achieve high-temperature operation. One promising route is to add inorganic additives to PFSA to form composites. Previous literature work has shown that PFSA membranes modified by silica and H_3PO_4 additives can retain water for high conductivity even at higher temperatures [5,6]. However, since silica is amorphous in nature, its chemical/hydrolytic stability during the fuel cell operation is still questionable [7]. Furthermore, the existence of free phosphoric acid will degrade the mechanical properties of the membranes [8]. An alterative solution is to anchor acid onto insoluble species such as hydrous zirconia, since hydrous zirconia has an intrinsic proton conduction, higher thermal stability, and therefore is an ideal candidate for acidic modification [2,9]. Hara and Miyayama [10] studied the proton conduction of zirconia and found that the surface sulfation gave rise to a high conductivity of 5×10^{-2} S cm^{-1} at 60–150 °C which is promising for higher temperature composite PEMFC. Nevertheless, the applications of sulfated zirconia are still limited by high dependence on the relative humidity [1,11]. Comparatively, phosphorized zirconia nanoparticles (40–60 nm) were reported to exhibit proton conductivity of the order of 10^{-3} S cm^{-1} and show a better stability against relative humidity [8,12]. Nevertheless, the proton conductivity as a function of temperatures was previously popularly ignored and the nature of relationships between grafted

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species and proton conductivity is still unclear, putting huge uncertainties in property optimization of phosphorized zirconia nanoparticles as additives of PFSA membranes.

In this work, we addressed the thermal stability and temperature dependent proton conductivity of YSZ nanoparticles. First, we successfully prepared YSZ nanoparticles with high surface area by hydrothermal process. Second, we grafted different acid groups onto the sample surfaces with an aim to enhance the proton conduction in terms of a better grain-to-grain transfer and larger concentrations of ionizable OH groups on surfaces. Finally, the effects of grafted species, microstructure, and surface hydration on proton conductivity were investigated.

2. Experimental

Eight moles percent of yttrium-stabilized zirconia nanocrystals were prepared by a hydrothermal method according to the following procedure: given amounts of Y_2O_3 were dissolved in diluted HNO_3 and then the obtained clear solution was mixed with 0.5 M $ZrOCl_2$ solution. Amorphous hydrated ZrO_2 was precipitated by adding the obtained mixed solution into ammonia solution (5 wt%) under continuous stirring. The mixed solution was adjusted to pH 10.5, which was then filtered and washed with deionized water till the filtrate did not become turbid when 3 M $AgNO_3$ was added. Then, this precipitate along with 4 M NaOH solution was transferred to 25 mL vessels sealed by stainless steel, which was placed in an oven at 130 °C for 12 h. The products were collected after washing with distilled water till the pH of the filtrate was about 7, and then dried at 60 °C for 3 h.

Sulfated and phosphated YSZ were obtained by immersing one gram of the as-prepared zirconia into 2.5 M H_2SO_4 and H_3PO_4 solution at room temperature for 2 h, respectively. The obtained samples were filtered off and then dried at 110 °C for 12 h in an oven.

The structures of the samples were characterized by X-ray diffraction (XRD) on Rigaku D/MAX 2500 X-ray diffractometer using a copper target. The grain size was calculated with Scherrer formula: $D = 0.9\lambda/(\beta \cos\theta)$, where λ is the X-ray wavelength, β is the half-width at half maximum, and θ is the diffraction angle. The particle sizes and morphologies of samples were determined using transmission electron microscope (TEM) on a JEM-2010 apparatus with an acceleration voltage of 200 kV. Surface areas of the samples were measured using Brunauer–Emmett–Teller (BET) method by N_2 adsorption and desorption at 77 K in a Micromeritics ASAP 2020 system. Chemical compositions of the samples were investigated by elemental analysis on Vario EL III and Inductive Coupled Plasma Emission (ICP) spectrometer on Ultima 2. Infrared spectra of the samples were measured on a Perkin–Elmer IR spectrophotometer using a KBr pellet technique.

The samples were pressed uni-axially into pellets with 7 mm in diameter and 1–2 mm in thickness under a pressure of 300 MPa. Silver paste was painted onto the opposite sides of the pellets and dried at room temperature to form the electrodes. Conductivity was determined by the AC impedance method on Agilent 4284 A apparatus in the frequency range of 20 Hz to 1 MHz with an applied voltage of 1 V and 30–150 °C under dry N_2 atmosphere.

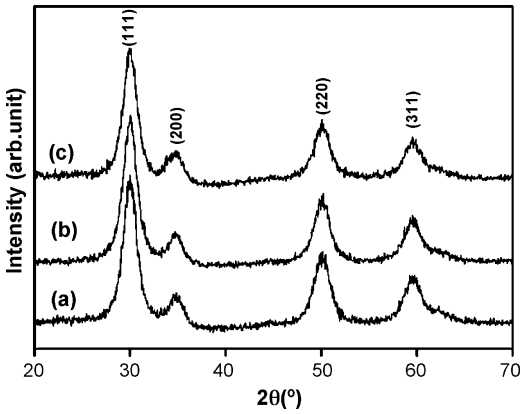

Fig. 1. XRD patterns of (a) as-prepared, (b) sulfate-modified YSZ, and (c) phosphate-modified YSZ.

3. Results and discussion

3.1. Synthesis of YSZ nanocrystals

XRD pattern of the as-prepared YSZ sample is shown in Fig. 1a. All diffraction peaks are indexed to the standard cubic fluorite structure (JCPDS. No. 89–6687). The diffraction peaks are obviously broadened, which indicates small particle size for the as-prepared YSZ. The mean particle size estimated by Scherrer formula for the most intense peak (1 1 1) is about 4.5 nm, which is confirmed by TEM micrographs (Fig. 2). It is also seen from Fig. 2 that the particles are homogeneously distributed in spherical shape and loosely agglomerated. The corresponding HRTEM image (inset of Fig. 2) clearly shows that the samples are highly crystalline. The interplanar spacing for (1 1 1) plane measured is 0.2882 nm, which is close to that obtained by XRD calculations.

The surface areas of the as-prepared YSZ nanocrystals were measured using BET method. The as-prepared samples show hysteresis loops at relatively high pressures, indicating a mesopore structure (Fig. 3). The pore size is distributed in the range

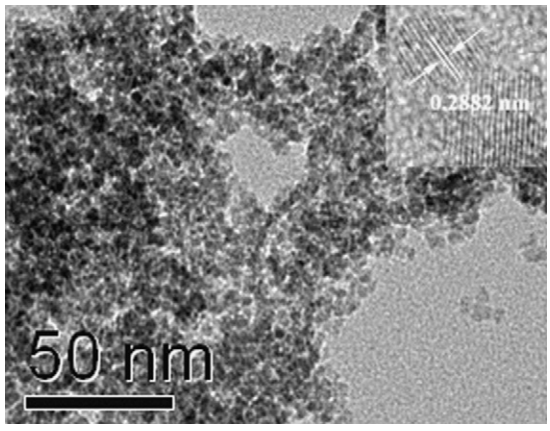

Fig. 2. TEM photo of the as-prepared YSZ nanoparticles. Inset: corresponding HRTEM image.