Synthesis of Tetragonal ZrO_2 Nanocrystals with a High Proton Conductivity

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Pure tetragonal ZrO_2 nanocrystals were prepared at low temperature (85 °C). Their proton conductivity measured at 80 °C in N_2 is 5.63×10^{-5} S/cm which is one order of magnitude higher than that of 1.72×10^{-6} S/cm for the sulfated counterpart or of 4.17×10^{-6} S/cm reported in the literature for 3-nm crystals of $ZrO_2{\cdot}nH_2O$.

Zirconia has attracted much attention for its technological applications in various fields including heterogeneous catalysis and polymer electrolyte fuel cells.[1,2] For example, introduction of ZrO_2 in polymer matrix can overcome the main problem that polymer electrolyte fuel cells meet when it works at the medium temperatures (80–130 °C), namely, the proton conductivity loss due to not full hydration of the membrane. ZrO_2 has characteristic proton conduction which could improve the performance of the polymers at high temperatures. Consequently, it is very important to enhance the proton conductivity of ZrO_2. As is popular in many catalytic reactions,[3] tetragonal ZrO_2 nanostructure with a high surface area can give rise to high chemical activities, which allow the creation of pronounced hydration terminations favourable for high proton conductivity. However, it remains a great challenge to fabricate phase-pure tetragonal zirconia of large surface hydration (or large surface areas) without loss of sample crystallinity and phase purity.

The widely used methods to prepare zirconia often require annealings at high temperatures >500 °C, which results in mixed phases of tetragonal and monoclinic structures with low surface areas.[4] Recently, Chen and Qin reported the preparation of pure ZrO_2(*tetr*) by hydrothermal methods at 180 °C using alcohol as additives.[5] Nevertheless, the relatively high temperatures and pressures make it unbeneficial to achieve large surface areas. Sol–gel technique is a common method to obtain ZrO_2(*tetr*) with comparatively high accessible area, while zirconium alkoxides were often used as the starting materials and high-temperature annealing is generally needed.[6] Supporting zirconia into pores of ordered mesostructured silica has also been developed to stabilize tetragonal structure for large surface area.[7] Nevertheless, these preparative processes are usually very complicated and the highly expensive zirconium alkoxides or the surfactant are required, which strongly limits the production of zirconia with desirable features of hydration and proton conductivity for medium temperature polymer electrolyte fuel cell uses.

In this letter, we prepared pure tetragonal ZrO_2 with a large surface area. The obtained samples were terminated with hydration layers which produced a surprisingly high proton conductivity in comparison with those reported in literature. Since sulfated zirconia has indicated capable for increasing water uptake by the Nafion membrane for high proton conductivity at high temperatures,[8] we also initiated a control study on the sulfated ZrO_2 nanocrystals and the relevent structure, hydration, and proton conductivity at 80 °C.

Firstly, 0.5 mol/L $ZrOCl_2$ solution was dropped into ammonia solution (5 wt %) under continuously stirring till pH is 10–10.5. A white precipitate was then filtered and sufficiently washed with deionized water till no chloride anions were detected by $AgNO_3$ solution. This precipitate along with 3 mol/L NaOH solution was heated in a water bath at 85 °C for 4.5 h. The products were collected after washing with distilled water until pH 7 and dried at 60 °C for 3 h. Sulfated zirconia was prepared by immersing one gram of as-prepared zirconia into 2.5 mol/L H_2SO_4 solution at room temperature for 2 h. The obtained samples were filtered off and then dried at 110 °C for 12 h in an oven.

Conductivities of the samples were measured at 80 °C using AC impedance technique. All samples were pressed uniaxially into pellets with a diameter of 7 mm and a thickness of 1.7–1.9 mm under a pressure of 300 MPa. Silver paste was coated onto the opposite sides of the pellets and dried at room temperature to form the electrodes. All conductivity measurements were performed in a frequency range of 20 Hz to 1 MHz in a dry N_2 atmosphere.

Phase purity and particle sizes of the as-prepared samples were characterized by X-ray powder diffraction (XRD) on a Rigaku D/MAX 2500 diffractometer with Cu Kα radiation. XRD patterns of the samples are shown in Figure 1. All diffraction peaks matched well the standard diffraction data of tetragonal ZrO_2 (JCPDS No. 42-1164). No traces of monoclinic phase or amorphous phases were observed. The obvious broadening of diffraction peaks indicated that the as-prepared zirconia had a small particle size. The mean particle size estimated by the Scherrer formula for the most intense peak (101) was about 4.4 nm. Sulfated zirconia has the similar XRD pattern (Figure 1b) to that of as-prepared zirconia, which means that sulfated process did not change the crystal structure and particle sizes. This finding is clearly different from that reported for sulfated TiO_2 in which particle size was decreased upon sulfation.[9]

The hydration and sulfation of the samples were quantitatively examined by thermogravity (TG) coupled with quadru-

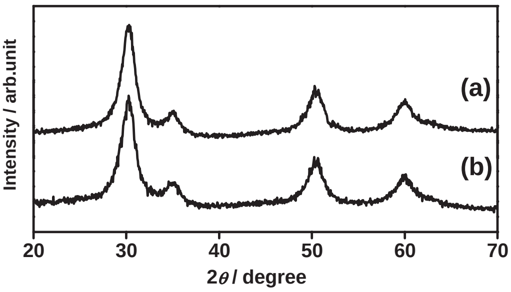

Figure 1. XRD patterns of (a) as-prepared and (b) sulfated zirconia.

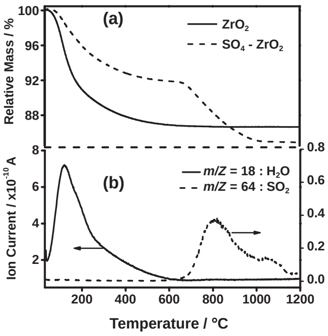

Figure 2. (a) TG curves of as-prepared and sulfated zirconia and (b) QMS curves of sulfated zirconia.

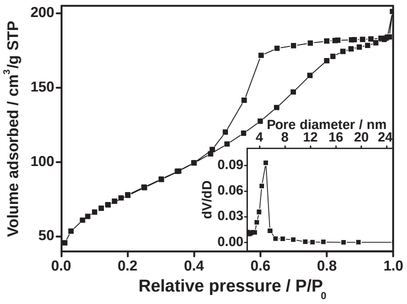

Figure 3. N_2 adsorption/desorption isotherms of as-prepared zirconia. Inset is the pore size distribution.

pole mass spectrometry (QMS). As indicated in Figure 2a, a continuous mass loss was observed for the as-prepared ZrO_2 in a wide temperature range from 30 to 800 °C. The total amount of absorbed water was determined to be 13.3 wt %. For sulfated zirconia, there are two obvious mass losses detected. The first mass loss is observed from 30 to 400 °C, which is amounted at 8.26 wt % associated with the water evaporation from the surface of sulfated zirconia, as confirmed by the signal at $m/z = 18$ in Figure 2b. The second mass loss is about 7.0 wt %, which is associated with the decomposition of sulfated species as is indicated by the occurrence of $m/z = 64$ signal in the range 650–1200 °C (Figure 2b).[10] From these results, the formula for as-prepared and sulfated zirconia could be written as $ZrO_2{\cdot}1.05H_2O$ and $ZrO_2{\cdot}0.13SO_3{\cdot}0.67H_2O$, respectively.

Surface areas of as-prepared and sulfated zirconia were measured by N_2 adsorption and desorption at 77 K. Both samples showed similar hysteresis loops at relatively high pressures, indicating a mesopore structure (Figure 3). The pore size was distributed in the range of 3.2–6.5 nm (insert of Figure 3). The surface area for as-prepared zirconia was 282 m^2/g, which is much closer to that of 270 m^2/g for sulfated zirconia. It should be noted that the surface areas of present samples are significantly larger than that (<200 m^2/g) prepared by sol–gel method or precipitation.[3]

To verify if surface hydration of ZrO_2 nanoparticles plays a dominant role in promoting the proton conductivity of polymer fuel cells at a working temperature of 80 °C, we did a control study on AC impedance spectra of the samples at 80 °C.

As indicated in Figure 4, a semicircle and a spike were observed in the whole frequency range, which is associated with the total resistance of proton conduction and electrode polarization.[12] It is surprising that the proton conductivity for the as-prepared ZrO_2 is 5.63×10^{-5} S/cm, which is one order of magnitude larger than that of 1.72×10^{-6} S/cm for the sulfated counterpart or that of 4.17×10^{-6} S/cm reported for 3-nm crystals of $ZrO_2{\cdot}nH_2O$ in ref 12. Phase purity, surface hydration, and amorphous state are three primary factors[11,12] that determine the proton conductivity since (1) different phases of ZrO_2 may have distinct surface structure, bond strength, surface acidity, which cause uncertain variations in actived sites and hydration degree for proton conductivity; (2) crystalline/amorphous state is associated with the surface defects that might contribute to the proton motion. For the present work, however, all samples have a pure cubic phase, while no trace of amophous state was observed. Therefore, surface hydration could be a primary factor that is responsible for the proton conductivity. This is also confirmed by the fact that the decreased hydration upon surface sulfation has led to a lower proton conductivity, contrary to what is expected for superacidic sulfated ZrO_2.[10,12]

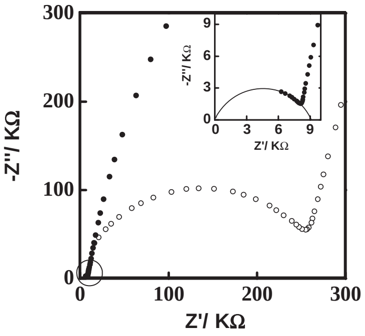

Figure 4. AC impedance spectra for as-prepared (solid circle) and sulfated ZrO_2 (open circle) measured at 80 °C in air.

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