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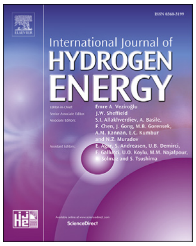

Engineering mesoporosity promoting high-performance polymer electrolyte fuel cells

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ABSTRACT

Proton exchange membranes (PEMs) are a vital component in fuel cells (FCs) that attract significant research interest for the present hydrogen energy use. High proton conductivity of PEMs under various operation conditions highly influences the integrated performance of FCs that determines their commercial applications. Hence mesoporous superacidic sulfated zirconia (S-ZrO_2) is fabricated and introduced into Nafion matrix to construct hybrid PEMs. The mesoporosity of S-ZrO_2 is demonstrated highly controllable. High mesoporosity leads to increased amount of sulfonic groups (–SO_3H) aggregating on S-ZrO_2 surface. When introduced in PEMs, the highly mesoporous S-ZrO_2 chemically enhances the amount of proton-containing groups, structurally improves the density of ion channels, and reserves water as effective reservoirs, which resultantly maintains high proton conductivity under variable conditions, and thus the performance of assembled FCs. The S-ZrO_2 exhibits the highest surface area of 181 $m^2\ g^{-1}$. The hybrid PEMs loaded with 10 wt% such S-ZrO_2 achieve a highest proton conductivity of 0.83 S cm^{-1} that is ~7 time of that for pristine Nafion® membranes. The power density at 0.6 V of FCs with the hybrid PEMs is 786 mW cm^{-2}, much higher than that for commercial Nafion 211.

Introduction

Beneficial characteristics of mesoporous materials, such as tunable pore sizes and large surface areas, widely spread their applications in various energy-related technologies, such as rechargeable lithium batteries, fuel cells, supercapacitors, water splitting catalysis, etc [1,2]. Although major research of mesoporous materials focuses on their electrode use [3–6], their intrinsic properties make them highly potential to reserve and transport liquids and ions, functionalizing in electrolytes, yet rarely reported [7].

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Proton exchange membranes (PEMs) are one of the key components used in PEM fuel cells (PEMFCs), a state-of-the-art energy conversion device for hydrogen energy use. And Nafion® is presently one of the most commercialized PEMs. However, Nafion [8] has a low functional group content, relatively poor conductivity, and high environmental sensitivity, resulting in underperformance of PEMFCs that hinders the hydrogen energy industrialization [9–11]. For the purpose of improving the properties of Nafion, various filler materials were incorporated, including oxides [12], heteropolyacides [13], functional carbon nanotubes [14], solid acids [15], etc. Several properties of the Nafion-based PEMs are improved, such as mechanical strength, thermal stability, selective permeability, and so forth. However, most of these fillers cannot effectively promote the ionic conductivity of Nafion membranes. The reason is that the fillers are chemically inert that cannot offer extra protonic groups to enhance the mass density, i.e. ionic exchange capacity (IEC), of protons in the PEMs. Furthermore, these fillers are dimensionally in micron size with very low surface area in several square meters per gram ($m^2\ g^{-1}$), that cannot construct effective ionic nanochannels for fast proton transport [16]. By increasing the surfacial protonic groups and internal mesopores of the fillers, promising fillers can be predicted to highly improve the IEC with efficient proton transport, which leads to high proton conductivity of the PEMs [17].

Among the reported filler materials, sulfated zirconia (S-ZrO_2) is considered to be one solid superacidic oxide that can successfully offer plenty of surfacial sulfonic acid groups to improve the density of proton in the PEMs [18]. Several techniques have been applied to fabricate ZrO_2 so far (Table 1). However, these methods can seldom offer high surface areas with a large number of mesopores [19–35]. Herein we report a new synthetic method to produce S-ZrO_2 with controllable surface area and mesoporosity, the highest of which is 181 $m^2\ g^{-1}$. Such a high mesoporosity enhances both the number of surface protonic groups and the ionic nanochannels for proton transport. When the S-ZrO_2 is introduced in Nafion matrix, a great amount of sulfonic groups aggregate onto the S-ZrO_2/Nafion interfaces, effectively constructing continuous ionic pathways [36]. And the hybrid PEMs can achieve high proton conductivity of 0.83 S cm^{-1}, with highly enhanced single fuel cell performance of 786 mW cm^{-2} at 0.6 V.

Table 1 – Reported zirconia with different surface areas.

No.	Specific surface area ($m^2\ g^{-1}$)	Zr-containing precursor	Ref
1	181	Zirconyl chloride	This work
2	38	Zirconium ethoxide	[19]
3	114	Tungstated zirconia hydroxide	[20]
4	119	Hydrous zirconium oxide	[21]
5	15	Zirconium acetate	[22]
6	132.2	Zirconyl nitrate	[23]
7	53	Ceria-zirconia mixed oxides	[24]
8	6.87	Zirconia solid acid	[25]
9	65	Zirconyl nitrate	[26]
10	31	Zirconyl nitrate	[27]
11	100	Zirconium chloride	[28]
12	13.2	Yttria stabilised zirconia powders	[29]
13	17.8	Zirconium nitrate	[30]
14	153.9	Zirconium hydroxide	[31]
15	52.55	Zirconyl nitrate monohydrate	[32]
16	19.0	Zirconyl nitrate	[33]
17	27.3	Zirconia hydroxide	[34]
18	28	Zirconium oxychloride	[35]

Experimental

Materials

Sulfuric acid (H_2SO_4, AR) was purchased from Shanghai Chemical Reagent Co. (China). Zirconyl chloride ($ZrOCl_2$, 99.0 wt%) and ammonium sulfate ($(NH_4)_2SO_4$, 99.0 wt%) were purchased from Sinopharm Group Chemical Reagent Co. (China). Black Pearls 2000 (BP2000, carbon material with high surface area of about 1500 $m^2\ g^{-1}$) carbon was received from Cabot Corp. All the above chemicals were used as received.

Preparation of S-ZrO_2

$ZrOCl_2$ and $(NH_4)_2SO_4$ with the molar ratio of 2:1 was first mixed as the precursor. This precursor was then blended with BP2000, an effective dispersing agent, with various weight ratios. The mixtures were grinded for about 30 min in a corundum mortar, and aged for 24 h (h) under 30 °C. Then they were treated in air at 280 °C for 6 h with a ramping rate of 5 °C min^{-1}. After that the temperature was increased to 600–650 °C for 4 h with a ramping rate of 5 °C min^{-1} in air. The resulting white samples were rinsed in 1 M H_2SO_4 for 24 h, and washed with deionized water for thorough protonation. After filtration and drying for several hours, the final samples were obtained.

Recasting of S-ZrO_2/Nafion membranes

10 wt% Nafion/dimethyl sulfoxide (DMSO) solution with mass ratio of 1:9 was obtained via reflux of the blend of commercial 5 wt% Nafion/isopropanol solution and refluxed DMSO. Then as-prepared zirconia-containing samples were incorporated into the 10 wt% Nafion/DMSO solution with different weight ratio, followed by thorough stirring for overnight. The mixed solutions were then casted on a flat substrate. The substrate was adjusted to horizontal to make sure the recast solution reaching even thickness. The recast solution was vacuum dried at the temperature of 70 °C for 12 h and crystallized at 150 °C for 4 h [37]. The obtained recast S-ZrO_2/Nafion membranes were then peeled off and soaked in 1 M hot H_2SO_4 at 80 °C for 1 h, then thoroughly rinsed and restored in deionized water for the following tests.

Membrane electrode assembly (MEA) preparation

An MEA was fabricated by a common method [38]. Typically 70% Pt/C catalysts were mixed with Nafion to obtain catalyst

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