Solid State Ionics 289 (2016) 133–142

Contents lists available at ScienceDirect

Solid State Ionics

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

Interfacial interaction and melting point depression of $CsH_5(PO_4)_2$ in $CsH_5(PO_4)_2/SiO_2$ composites

Geletu Qing, Ryuji Kikuchi *

[a] Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
[b] CREST, Japan Science and Technology Agency (JST), Japan

ARTICLE INFO

Article history:
Received 1 February 2016
Received in revised form 10 March 2016
Accepted 12 March 2016
Available online 18 March 2016

Keywords:
Intermediate temperature fuel cells
$CsH_5(PO_4)_2$
SiO_2
Composite electrolyte
Interfacial interaction
Melting point depression

ABSTRACT

This work reports the interfacial interaction in composites composed of $CsH_5(PO_4)_2$ and SiO_2. The composites were prepared by grinding and pressing the mixture of corresponding powders. Two kinds of silica with different pore sizes (SiO_2-meso: 2–100 nm; SiO_2-micro: 0.4–1.6 nm) were used as the supporting matrices, and the composites were characterized by various methods. Differential thermal analyses showed that the composite composed of $CsH_5(PO_4)_2$ and SiO_2-meso possessed three phases of $CsH_5(PO_4)_2$ that changed to a molten state at ~120, ~140, and above 150 °C, respectively. Infrared spectroscopy indicated that the absorption bands between 800 and 1400 cm^{-1}, which were assigned to the stretching vibrations of PO_4 tetrahedra in $CsH_5(PO_4)_2$, transformed into a plateau in the spectrum of the composite composed of $CsH_5(PO_4)_2$ and SiO_2-meso, and this phenomenon was attributed to the interfacial interaction between $CsH_5(PO_4)_2$ and SiO_2-meso by forming a hydrogen bond net. Differently, the composite composed of $CsH_5(PO_4)_2$ and SiO_2-micro was predominated by the bulk phase of $CsH_5(PO_4)_2$ with a melting point above 150 °C, and the absorption bands arising from the stretching vibrations of PO_4 tetrahedra in $CsH_5(PO_4)_2$ were not affected by the addition of SiO_2-micro. When the molar ratio of $CsH_5(PO_4)_2$ and SiO_2-meso was 1:4, 71% of $CsH_5(PO_4)_2$ in the composite was incorporated into the pores of SiO_2-meso, while, for the composite composed of $CsH_5(PO_4)_2$ and SiO_2-micro, this value was 16%. Thus, it was speculated that the large pores of SiO_2-meso were readily accessible for the $CsH_5(PO_4)_2$ to enter, and the interfacial interaction between these two components at a large contacting interface resulted in the disordering of $CsH_5(PO_4)_2$, while the small pores of SiO_2-micro were not available for the $CsH_5(PO_4)_2$ and there was a weak interaction between them due to the small contact area. As a result, at temperatures below 140 °C, the composite composed of $CsH_5(PO_4)_2$ and SiO_2-meso exhibited conductivity higher than that of the composite composed of $CsH_5(PO_4)_2$ and SiO_2-micro by two orders of magnitude. In addition, the interaction between $CsH_5(PO_4)_2$ and SiO_2-meso became stronger with the increase of the grinding time from 15 to 45 min, while changed little with the increase of the pressing pressure from 150 to 450 MPa.

1. Introduction

Solid acids are inorganic acid compounds with anhydrous proton conductivity [1–3] and high-temperature stability (up to 300 °C) [4–6]. Fuel cells employing solid acids as electrolytes are operable at intermediate temperatures (100–300 °C) [6–8], and offer many advantages over polymer electrolyte membrane fuel cells, *i.e.*, low electrode catalyst poisoning by carbon monoxide [9–11], fast reaction kinetics [12–14], and simplified water management [15–17].

Candidate solid acids for applications in intermediate temperature fuel cells (ITFCs) include $MHSO_4$ [18–20], MH_2PO_4 [21–23] and $MH_5(PO_4)_2$ [24–27], where M represents alkaline metals of K, Rb and Cs. $MHSO_4$ and MH_2PO_4 underwent a "superprotonic" phase transition [28–30]. On passing through the transition the conductivity increased by several orders of magnitude to a value of 1 to 10 mS cm^{-1} [31–33]. In addition, cesium pentahydrogen diphosphate, $CsH_5(PO_4)_2$, exhibited extremely high conductivity of ~200 mS cm^{-1} above 160 °C under 30% H_2O/Ar atmosphere [34,35], and this was attributed to the melting of $CsH_5(PO_4)_2$ at ~154 °C. Humidified conditions were required to prevent $CsH_5(PO_4)_2$ from dehydrating as well as to maintain the high proton conductivity [35]. $CsH_5(PO_4)_2$-based composites were prepared by adding oxides (for example, SiO_2) or pyrophosphates (for example, SiP_2O_7) as matrices [35,36], and the resulting composites were in the solid states at elevated temperatures despite the melting of $CsH_5(PO_4)_2$ [34]. It was reported that the matrices had a significant influence on the thermal property and protonic conductivity of $CsH_5(PO_4)_2$-based composites [16,35,36]. In the composites composed of $CsH_5(PO_4)_2$ and SiO_2 with the specific surface area of SiO_2 varying from 120 to 520 $m^2\ g^{-1}$, the addition of SiO_2 resulted in a partial amorphization of

---

* Corresponding author at: Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan.
E-mail addresses: qglt09@chemsys.t.u-tokyo.ac.jp (G. Qing), rkikuchi@chemsys.t.u-tokyo.ac.jp (R. Kikuchi).

http://dx.doi.org/10.1016/j.ssi.2016.03.013
0167-2738/© 2016 Elsevier B.V. All rights reserved.

$CsH_5(PO_4)_2$, and the maximal degree of amorphization took place in the composite with the highest specific surface area of SiO_2, resulting in a conductivity increase by up to 1–2 orders of magnitude compared to that of the polycrystalline $CsH_5(PO_4)_2$ at 140 °C [16]. In addition, comparing the composites of $CsH_5(PO_4)_2/SiP_2O_7$ and $CsH_5(PO_4)_2/SiO_2$ with the same $CsH_5(PO_4)_2$ concentration, the previous one exhibited one order of magnitude higher conductivity than the latter one, and this was because SiP_2O_7 had much better compatibility (or much smaller contact angle) with $CsH_5(PO_4)_2$ than SiO_2 [35,36]. Due to the complicated nature of the interfacial interaction between $CsH_5(PO_4)_2$ and the matrices, the detailed interaction mechanism is not clear yet. The matrix properties as well as the sample preparation and measuring conditions can have effects on the interfacial interaction. However, according to our knowledge, a systematic study on this topic has not been reported in the literature.

In this work the composites composed of $CsH_5(PO_4)_2$ and SiO_2 were synthesized using two kinds of silica with different pore sizes as the supporting matrices. The interfacial interaction between $CsH_5(PO_4)_2$ and SiO_2 was studied by differential thermal analysis and Fourier-transform infrared spectroscopy. The volume fraction of $CsH_5(PO_4)_2$ that was incorporated into the pores of SiO_2 was evaluated by nitrogen adsorption/desorption isotherm analysis. In addition, the influence of the preparation parameters, including the grinding time and pressing pressure, on the thermal behavior of the composites was investigated in detail. A schematic illustration of the interface structure in the composite was proposed according to the experimental results.

2. Experimental

2.1. Materials

Cs_2CO_3 (99.995% trace metals basis, Sigma-Aldrich), H_3PO_4 (85 wt.% in water, Sigma-Aldrich), $Si(OC_2H_5)_4$ (TEOS, ≥99.0%, Sigma-Aldrich), C_2H_5OH (99.5%, Wako Pure Chemical Industries, Ltd.), HCl (6 mol L^{-1}, Wako Pure Chemical Industries, Ltd.) and mesoporous silica (AY-200, Tosoh Silica Corporation), which is denoted as SiO_2-meso in this work, were used as supplied. Distilled water prepared with an auto still (SA-2100A, Tokyo Rikakikai Co., Ltd.) was used for the experiments.

2.2. Preparation

Cesium pentahydrogen diphosphate, $CsH_5(PO_4)_2$, was prepared by dissolving stoichiometric quantities of Cs_2CO_3 and H_3PO_4 in distilled water and drying overnight at 100 °C [25]. As a comparison to SiO_2-meso (specific surface area: 262 $m^2\ g^{-1}$; pore size distribution: 2–100 nm), a new kind of microporous silica was prepared from TEOS as reported previously [26]. Briefly, a mixture of TEOS, ethanol, water and hydrochloric acid in a molar ratio of 1:10.3:16.7:0.09 was prepared and hydrolyzed for 24 h at room temperature. The resulting sol was dried at 80 °C for 48 h. Then the sample was annealed at 400 °C for 2 h. The obtained silica was denoted as SiO_2-micro (specific surface area: 420 $m^2\ g^{-1}$; pore size distribution: 0.4–1.6 nm). The $CsH_5(PO_4)_2/SiO_2$-meso (or SiO_2-micro) composites were prepared according to the following procedure. First, certain amounts of $CsH_5(PO_4)_2$ and SiO_2-meso (or SiO_2-micro) were mixed together and ground for t min to form a mixture. The molar ratio of $CsH_5(PO_4)_2$ and SiO_2-meso (or SiO_2-micro) in the mixture was r: 4. Second, the obtained mixture was uniaxially pressed for 10 min under P MPa to form pellets. The values of r, t, and P are listed in Table 1.

2.3. Characterization

The cross-sectional morphology was determined by scanning electron microscopy (SEM, Hitachi S-900). A cross section of the composite was obtained by mechanical cracking. The crystalline structure of the composite was determined by X-ray diffraction (XRD, Rigaku RINT2400). The XRD measurements were conducted on as-prepared pellets according to the following procedure. First, the pellet was stuck to the middle position of the well in a sample plate using a double-sided bonding tape. Second, the sample plate carrying the pellet was polished with sandpaper (800 grit) to make the height of the pellet the same as that for the sample plate. Finally, the sample plate carrying the pellet was used for XRD measurements. Differential thermal analyses (DTA, Shimadzu DTA-50) were performed from room temperature to 300 °C at different heating rates from 1 to 10 °C min^{-1}, under atmospheric conditions or 30% H_2O/Ar atmosphere. The composites were cut into small pieces, and a single piece (~5 mg) was used for each DTA measurement. Fourier transform infrared (FTIR) spectra were recorded by infrared spectroscopy (FTIR-4600, JASCO Corporation) with a spectral resolution of 4 cm^{-1}. The FTIR spectra were recorded within the spectral range 4000–400 cm^{-1} using the KBr squash method.

Table 1
Lists of composite electrolytes prepared in this study.

(a) The molar ratio of $CsH_5(PO_4)_2$ and SiO_2-meso (or SiO_2-micro) is r: 4. t = 25 min. P = 250 MPa

r	0.50	0.75	1.0	1.5	2.0

(b) The grinding time is t. r = 1.0. P = 250 MPa

t/min	15	25	35	45

(c) The pressing pressure is P. r = 1.0. t = 25 min

P/MPa	150	250	350	450

The volume concentration of $CsH_5(PO_4)_2$ in the composite (φ_{CHP}, CHP represented $CsH_5(PO_4)_2$) was evaluated by the following equation:

$$\varphi_{CHP} = m_{CHP}{\rho_{CHP}}^{-1}V^{-1} \tag{1}$$

where m_{CHP} is the weight of $CsH_5(PO_4)_2$ in the composite, ρ_{CHP} is the density of pure $CsH_5(PO_4)_2$, and V is the volume of the composite. The value of ρ_{CHP} was determined from the weight and volume of a pure $CsH_5(PO_4)_2$ pellet, which was prepared according to the same procedure as that for the $CsH_5(PO_4)_2/SiO_2$-meso (or SiO_2-micro) composite, and the obtained value was 2.667 g cm^{-3} (theoretical value: 2.713 g cm^{-3} [37]). Similarly, the volume concentration of SiO_2-meso (or SiO_2-micro) in the composite (φ_{silica}) was evaluated by the following equation:

$$\varphi_{silica} = m_{silica}{\rho_{silica}}^{-1}V^{-1} \tag{2}$$

where m_{silica} is the weight of SiO_2-meso (or SiO_2-micro) in the composite, and ρ_{silica} is the true density of SiO_2-meso (or SiO_2-micro). The true density of SiO_2-meso and SiO_2-micro was assumed to be the same, and was approximated by the density of fused silica, which was 2.2 g cm^{-3}. With the values of φ_{CHP} and φ_{silica}, the volume concentration of pores in the composite (φ_{pore}) was calculated by the following equation:

$$\varphi_{pore} = 1 - \varphi_{CHP} - \varphi_{silica}. \tag{3}$$

The volume fraction of $CsH_5(PO_4)_2$ (ψ_{CHP}) that was incorporated into the pores of SiO_2-meso (or SiO_2-micro) was evaluated by the following equation based on the assumption that all the pores in the $CsH_5(PO_4)_2/SiO_2$-meso (or SiO_2-micro) composites came from the inner pores of SiO_2-meso (or SiO_2-micro).

$$\psi_{CHP} = \left(m_{silica}\nu_{silica} - V\varphi_{pore}\right)\left(m_{CHP}{\rho_{CHP}}^{-1}\right)^{-1} \tag{4}$$

where ν_{silica} is the pore volume (per unit mass) of SiO_2-meso (or SiO_2-micro). The value of ν_{silica} was determined for each composite according to the following procedure. First, $CsH_5(PO_4)_2$ in the $CsH_5(PO_4)_2/SiO_2$-meso (or SiO_2-micro) composite was removed by washing with