



CsH₂PO₄/Epoxy Composite Electrolytes for Intermediate Temperature Fuel Cells



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ABSTRACT

In this study CsH₂PO₄/epoxy composite electrolytes were prepared by dispersing CsH₂PO₄ particles, whose sizes were smaller than 10 μm, in a low-viscosity heat-resistant epoxy resin. The epoxy polymerization was promoted by thermal curing. The composite electrolyte consisted of a physical dispersion of CsH₂PO₄ particles in the cross-linked epoxy matrix. The polymerized epoxy showed a high thermal stability with no weight loss or phase transformation up to 290 °C. The composite electrolyte with 80 wt% CsH₂PO₄ showed a high conductivity of 11 mS cm⁻¹ at 259 °C under 30% H₂O/Ar atmosphere as well as a flexural strength of 7.3 MPa at room temperature. The composite electrolyte with 80 wt% CsH₂PO₄ showed a stable conductivity at 259 °C under 30% H₂O/Ar atmosphere for 50 h. A fuel cell assembled with this electrolyte exhibited an open circuit voltage of 0.95 V and a peak power density of 38 mW cm⁻². In addition, the fuel cell produced an output voltage higher than 0.44 V during a 6 h test under an output current density of 70 mA cm⁻² with humidified H₂ as the fuel and humidified O₂ as the oxidant.

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1. Introduction

Fuel cells are electrochemical devices that directly convert chemical energy in fuels (e.g., hydrogen and methanol) into electrical energy [1,2]. Most systems that have been commercialized so far are based on a proton exchange membrane-type electrolyte [3]. However, these membranes require cumbersome water management systems to maintain humid operating conditions, which limit the temperature of operation to less than 100 °C, and they are also permeable to hydrogen and methanol, which lowers fuel efficiency [4,5]. Intermediate temperature fuel cells (ITFCs) that operate at 200–600 °C have been drawing considerable attention due to advantages over proton exchange membrane fuel cells such as simplified water management, low electrode catalyst poisoning by carbon monoxide, and fast reaction kinetics and diffusion rates [4–12]. Polymer electrolytes are not applicable in ITFCs due to their dehydration or chemical degradation at temperatures higher than 100 °C [10,11]. Proton conductors with conductivities of above 10 mS cm⁻¹, especially

under low water content in the atmosphere, are key materials to achieve intermediate temperature operation of fuel cells [4,12].

Cesium dihydrogen phosphate, CsH₂PO₄, is a solid acid compound that facilitates anhydrous proton transport with proton conductivities in the order of 10 mS cm⁻¹ at temperatures near 250 °C [5,13–16]. The phase transition of this material at ca. 230 °C from monoclinic (low-temperature phase) to cubic (high-temperature phase) brings about a drastic increase in its protonic conductivity by several orders of magnitude [13–16], making this material very promising for applications in fuel cells operating at intermediate temperatures (~250 °C). The first successful preparation of a solid acid fuel cell using a humidity-stabilized CsH₂PO₄ electrolyte was reported in 2004 [5], and it was proved that a humidity with an equivalent *P*(H₂O) of ~0.3 atmospheric pressure is sufficient to prevent CsH₂PO₄ dehydration up to a temperature of ~270 °C. However, pure CsH₂PO₄ has poor mechanical integrity due to superplastic behavior of superprotonic solid acids, and the material is easily deformed by even a slight mechanical force [15,16], causing physical leaks through the electrolyte. The addition of oxides (e.g., SiO₂) or pyrophosphates (e.g., SiP₂O₇) as matrices for CsH₂PO₄ has been studied as an effective method for improvement of not only mechanical integrity but also protonic conductivity [17–23]. However, in these composite electrolytes obtained by pressing the corresponding powders of CsH₂PO₄ and the matrix, there are no chemical bonds between the matrix particles. Thus, the composite

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electrolytes are low in mechanical strength, requiring thicknesses larger than 1 mm [24]. It is important to develop new matrix materials with an interconnected network that is thermally stable at intermediate temperatures.

The combination of inorganic and organic materials is the usual practice in preparation of electrolyte materials with enhanced electrochemical and mechanical properties for fuel cells operating at temperatures higher than 100 °C [25]. There are many reports on the application in ITFCs of inorganic/organic composite electrolytes [6,26–31], such as NH_4PO_3 /polytetrafluoroethylene [26], $\text{Sn}_{0.95}\text{Al}_{0.05}\text{P}_2\text{O}_7$ /polystyrene-*b*-poly(ethylene/propylene)-*b*-polystyrene [30], and $\text{Fe}_{0.4}\text{Ta}_{0.5}\text{P}_2\text{O}_7$ /sulfonated polystyrene-*b*-poly(ethylene/butylene)-*b*-polystyrene [31]. In the previous work [6], we reported the preparation of CsH_2PO_4 /polyvinylidene fluoride composite electrolytes with a conductivity of 10 mS cm^{-1} at 270 °C under 30% $\text{H}_2\text{O}/\text{Ar}$ atmosphere. However, polyvinylidene fluoride was under a molten state at 270 °C, causing the composite electrolyte to be mechanically weak. Thus, it is important to develop new matrix materials with high mechanical stability at the application temperature of ~250 °C for CsH_2PO_4 -based composite electrolytes.

In this work a low-viscosity heat-resistant epoxy resin was chosen as the polymer supporting matrix due to its high thermal stability as well as high mechanical strength [32]. The polymerization of epoxy monomers was promoted by thermal curing. The electrolyte structure and composition were investigated with scanning electron microscopy (SEM), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and differential thermal analysis (DTA). The flexural strength was determined by 3-point flexural testing. The electrolyte conductivity was measured at temperatures from 117 to 270 °C under 30% $\text{H}_2\text{O}/\text{Ar}$ atmosphere. In addition, the performance of the fuel cell assembled with the composite electrolyte was examined at 259 °C with humidified H_2 as the fuel and humidified O_2 as the oxidant.

2. Experimental

2.1. Materials

Cs_2CO_3 (99.995% trace metals basis, Sigma–Aldrich), H_3PO_4 (85 wt% in water, Sigma–Aldrich), dimethylformamide (DMF, 99.8%, Sigma–Aldrich), low-viscosity heat-resistant epoxy resin (Duralco™ 4460, Cotronics Corp.), and commercial silica (AY-200, Tosoh Silica Corporation, specific surface area: $253 \text{ m}^2 \text{ g}^{-1}$, pore size distribution: 1–40 nm), which is denoted as $\text{SiO}_2\text{-C}$ in this paper, were used as supplied. Distilled water prepared with an auto still (WG203, Yamato Scientific Co., Ltd.) was used for the experiments.

2.2. Preparation

Cesium dihydrogen phosphate, CsH_2PO_4 , was prepared by dissolving stoichiometric quantities of Cs_2CO_3 and H_3PO_4 in distilled water and drying overnight at 120 °C. The CsH_2PO_4 /epoxy composite electrolytes were prepared by curing a slurry composed of CsH_2PO_4 particles and epoxy, as illustrated in Fig. 1. First, CsH_2PO_4 particles were prepared as follows. A certain amount of CsH_2PO_4 was mixed with DMF, which served as a dispersing agent, to form a suspension that was then ball-milled (Fig. S1) for 4 days to reduce the particle size of CsH_2PO_4 . After ball-milling, the resulting slurry was dried at 120 °C for 24 h to remove the solvent. Optical images showed that the as-prepared CsH_2PO_4 particles had sizes smaller than $10 \mu\text{m}$ (Fig. 1(a)). Second, certain amounts of CsH_2PO_4 particles and epoxy were mixed and ground with a mortar and pestle to form a slurry. The obtained slurry was transferred to a perfluoroalkoxy alkane (PFA) vial and sequentially

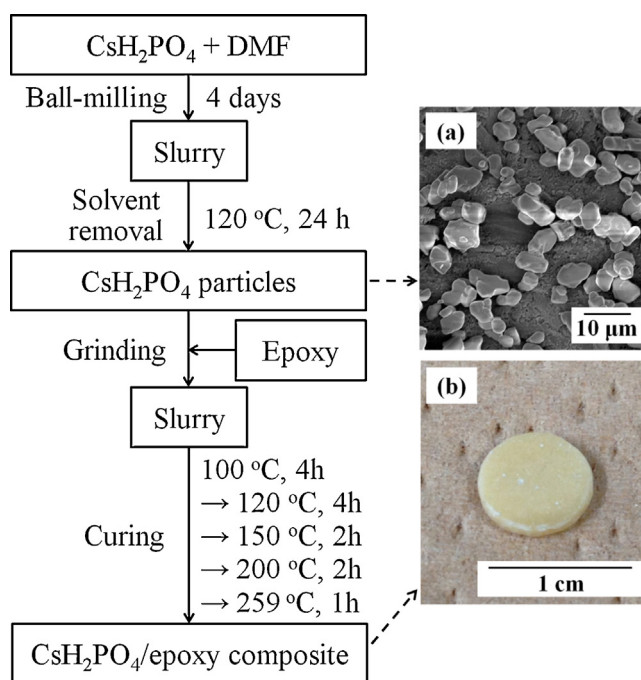


Fig. 1. Synthetic procedure for obtaining the CsH_2PO_4 /epoxy composite electrolytes. Optical images at different preparation stages are given on the right.

cured at 100 °C for 4 h, 120 °C for 4 h, 150 °C for 2 h, 200 °C for 2 h, and 259 °C for 1 h to polymerize the epoxy. The first four steps were conducted under atmospheric conditions, and the last step was conducted under 30% $\text{H}_2\text{O}/\text{Ar}$ atmosphere to prevent dehydration of CsH_2PO_4 . Finally, the obtained composite was removed from the PFA vial and polished with sandpaper (800 grit) to make a pellet (Fig. 1(b)), which was used for characterization measurements. For comparison, a sample composed of pure epoxy was prepared following the same curing procedure as in Fig. 1 without addition of CsH_2PO_4 particles.

2.3. Characterization

The cross-sectional morphology was determined by scanning electron microscopy (SEM, Hitachi S-900). A cross section of the composite electrolyte was obtained by mechanical cracking. The crystalline structure of the composite electrolyte, which was ground into powder with a mortar and pestle, was determined by X-ray diffraction (XRD, Rigaku RINT2400). Thermogravimetric analysis (TGA, Shimadzu TGA-51) and differential thermal analysis (DTA, Shimadzu DTA-50) were performed from room temperature to 500 °C at a heating rate of 10 °C min^{-1} under atmospheric conditions. The composite electrolytes were cut into small pieces, and a single piece (~5 mg) was used for each TGA or DTA measurement. The flexural strength was determined by 3-point flexural testing (Instron 5848), as illustrated in the inset figure in Fig. 4. All samples were tested at a testing speed of 1.0 mm min^{-1} under atmospheric conditions. For each test, five measurements were conducted and the average value was calculated. The flexural strength (τ) was calculated according to the following equation:

$$\tau = 1.5 P L W^{-1} t^{-2} \quad (1)$$

where P is the maximum load in the load-crosshead displacement plot, L is the distance between the two lower anvils, W is the sample width, and t is the sample thickness.

The porous structure of $\text{SiO}_2\text{-C}$ was analyzed by nitrogen adsorption/desorption isotherm analysis (Belsorp-miniII, BEL Japan, Inc.) after degassing under vacuum at 100 °C for 8 h. The

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