

# Interfacial conduction mechanism of cesium hydrogen phosphate and silicon pyrophosphate composite electrolytes for intermediate-temperature fuel cells



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## ABSTRACT

As an electrolyte for intermediate-temperature fuel cells (ITFCs), which are operative at 200 °C to 300 °C, a composite electrolyte  $\text{CsH}_5(\text{PO}_4)_2/\text{SiP}_2\text{O}_7$  has been investigated. The  $\text{CsH}_5(\text{PO}_4)_2/\text{SiP}_2\text{O}_7$  composite is reported to exhibit higher conductivity than pure  $\text{CsH}_5(\text{PO}_4)_2$ , possibly by forming a highly-conductive new phase at the interface between  $\text{CsH}_5(\text{PO}_4)_2$  and  $\text{SiP}_2\text{O}_7$ . In this study, we have prepared several  $\text{SiP}_2\text{O}_7$  matrices of different surface properties, and studied the effect of the surface properties on the total conductivity as well as on the formation mechanism of the interfacial conductive phase. An effective medium approximation method was applied to the measured conductivity to analyze the interfacial conductive phase. Several  $\text{SiP}_2\text{O}_7$  matrices of different acid properties and crystalline properties were fabricated, and the conductivity of the  $\text{CsH}_5(\text{PO}_4)_2/\text{SiP}_2\text{O}_7$  composite electrolyte was measured by AC impedance method. The acidity and crystallinity of the  $\text{SiP}_2\text{O}_7$  matrices were found to be important properties for the formation of the interfacial conductive phase. The highest conductivity of the interfacial conductive phase was estimated to be  $500 \text{ mS cm}^{-1}$ , which is almost three times larger than that of the pure  $\text{CsH}_5(\text{PO}_4)_2$ ,  $160 \text{ mS cm}^{-1}$ .

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## 1. Introduction

Fuel cells convert chemical energy directly to electrical energy with high efficiency and at low pollution levels. High energy conversion efficiency can be expected for fuel cells, since the efficiency is not confined by Carnot cycle as in the case of internal combustion engines. Fuel cells are classified according to the types of electrolytes and operating temperatures. Low-temperature types operated below 200 °C and high-temperature types operated above 600 °C have been actively investigated. Particularly, polymer electrolyte fuel cells (PEFCs) and solid oxide fuel cells (SOFCs) have already been commercially available in Japan. On the other hand, intermediate-temperature fuel cells (ITFCs) operative at 200–600 °C are not fully developed because ionic conductors used as the electrolytes for ITFCs are under investigation to improve conductivity as well as thermal stability [1,2]. ITFCs are attractive energy conversion systems since they offer various advantages over low- and high-temperature fuel cells as follows: rapid start-up and shutdown can be possible and various kinds of materials can be used in the assembly when they are compared to the high-temperature types [2–4], while improvements in energy conversion efficiency and superior tolerance to CO poisoning of the

Pt electrodes are expected in comparison with low-temperature types [5,6].

Phosphate-based electrolytes are promising in the intermediate temperature range, and recently relatively high proton conductivity of  $1 \times 10^{-4} \text{ S cm}^{-1}$  at ca. 350 °C is reported for thin membranes of phosphate glasses [7,8]. Among phosphate-based electrolytes, cesium dihydrogen phosphate,  $\text{CsH}_2\text{PO}_4$ , is known as a proton conductor to show high conductivity applicable to an intermediate temperature fuel cell [9,10]. The proton conductivity drastically increases from ca.  $1 \times 10^{-5} \text{ S cm}^{-1}$  to  $1 \times 10^{-2} \text{ S cm}^{-1}$  at ca. 230 °C due to the phase transition from the low-temperature to the high-temperature phase. Furthermore, an intermediate-temperature fuel cell employing this material as an electrolyte was successfully demonstrated [11,12]. Since  $\text{CsH}_2\text{PO}_4$  possesses low thermal stability and mechanical strength due to the phase change, a matrix material is mixed with the conductive phase to form composite electrolytes [13]. Such matrix materials have mostly quite low conductivity and dilute the proton concentration in the form of composites, leading to the decrease in the conductivity of the composite electrolytes, especially in a high-temperature phase after the phase transition [14]. Unexpectedly, composite electrolytes based on  $\text{CsH}_2\text{PO}_4/\text{SiP}_2\text{O}_7$  are reported to exhibit higher proton conductivity than the pure  $\text{CsH}_2\text{PO}_4$  conductive phase in the entire temperature range from 100 to 250 °C [15–17]. This is because  $\text{CsH}_5(\text{PO}_4)_2$  phase is formed via chemical reaction between  $\text{CsH}_2\text{PO}_4$  and  $\text{SiP}_2\text{O}_7$ ,

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and the interaction between  $\text{CsH}_5(\text{PO}_4)_2$  and  $\text{SiP}_2\text{O}_7$  contributes to the high proton conductivity [18,19]. It is also indicated that an interfacial phase of high conductivity is formed at the interface of  $\text{CsH}_5(\text{PO}_4)_2$  and  $\text{SiP}_2\text{O}_7$  [18]. The precise mechanism for the high proton conduction in the interfacial phase has not been investigated systematically yet, but understanding of this interfacial layer is needed to develop effective electrolytes in the intermediate temperature range. In this study, several  $\text{SiP}_2\text{O}_7$  matrices of different surface properties have been fabricated to investigate the effect of the surface properties on the total conductivity as well as on the formation mechanism of the interfacial conductive phase. An effective medium approximation method was applied to the measured conductivity to analyze the interfacial conductive phase.

## 2. Experimental

### 2.1. $\text{CsH}_5(\text{PO}_4)_2$ and $\text{SiP}_2\text{O}_7$ preparation

$\text{CsH}_5(\text{PO}_4)_2$  was prepared by drying an aqueous solution of  $\text{H}_3\text{PO}_4$  (Sigma-Aldrich Inc.) and  $\text{Cs}_2\text{CO}_3$  (Sigma-Aldrich Inc.) at a molar ratio of 4:1 at 100 °C overnight. The  $\text{SiP}_2\text{O}_7$  matrices were synthesized in the following manner: tetraethyl orthosilicate (TEOS, TCI) and  $(\text{NH}_4)_2\text{HPO}_4$  (Sigma-Aldrich Inc.) were mixed in water-ethanol solution, so as to have a molar ratio,  $\text{SiO}_2:\text{H}_2\text{O}:(\text{NH}_4)_2\text{HPO}_4:\text{CH}_3\text{CH}_2\text{OH} = 1:46:2:58$ . The mixture was stirred at 70 °C to 90 °C in an oil bath and evaporated to dryness. The resultant samples were calcined at 300 °C, 500 °C, or 700 °C to obtain  $\text{SiP}_2\text{O}_7$  matrices. The calcination temperature and calcination procedure were varied to prepare  $\text{SiP}_2\text{O}_7$  matrices with different crystal and acidic properties. The formation of  $\text{SiP}_2\text{O}_7$  phase was confirmed by XRD measurements.

### 2.2. Electrochemical measurements

For electrochemical measurements, the prepared powders of  $\text{CsH}_5(\text{PO}_4)_2$  and  $\text{SiP}_2\text{O}_7$  were mixed in a mortar at a desired molar ratio, and then the powder mixture was pressed uniaxially with Pt/C papers (ElectroChem Inc., Pt loading  $1 \text{ mg cm}^{-2}$ ) at 250 MPa for 10 min to fabricate a  $\text{CsH}_5(\text{PO}_4)_2/\text{SiP}_2\text{O}_7$  pellet. This membrane electrode assembly (MEA) was 10 mm in diameter and the electrode area was  $0.5 \text{ cm}^2$ . The MEA was heat-treated at 220 °C under 30%  $\text{H}_2\text{O}/\text{Ar}$  for 1 h. The conductivity of  $\text{CsH}_5(\text{PO}_4)_2/\text{SiP}_2\text{O}_7$  composites was measured using AC impedance spectroscopy (Solartron 1260 frequency-response analyzer and Solartron 1287 potentiostat). The applied frequency was in the range of 0.1 Hz to 1 MHz with voltage amplitude of 30 mV. The measurement was conducted at 120–220 °C in 30%  $\text{H}_2\text{O}/\text{Ar}$  flow. At each temperature, the samples were kept for 30 min until a steady state was achieved.

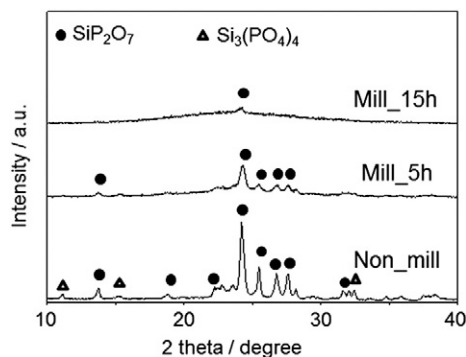


Fig. 1. XRD patterns of  $\text{SiP}_2\text{O}_7$  matrices after ball-milling treatment: milling time; 0 h (Non\_mill), 5 h (Mill\_5h), 15 h (Mill\_15h).

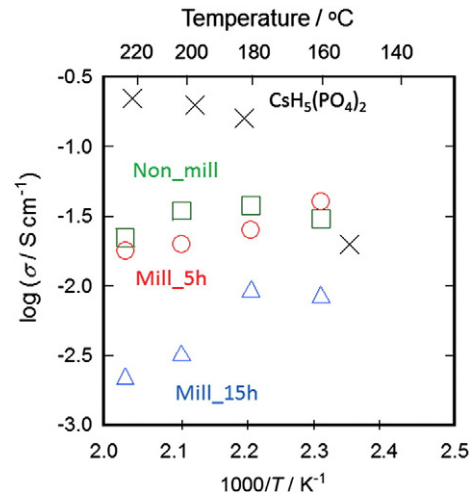


Fig. 2. The conductivity of  $\text{CsH}_5(\text{PO}_4)_2$  composites using ball-milled  $\text{SiP}_2\text{O}_7$  matrices. Milling time; 0 h (Non\_mill), 5 h (Mill\_5h), 15 h (Mill\_15h). The conductivity of pure  $\text{CsH}_5(\text{PO}_4)_2$  is after Muroyama et al. [22].

### 2.3. Effective medium approximation

Effective medium approximation (EMA) is a method to calculate conductivity of a multicomponent composite [20]. To evaluate the interfacial effect between  $\text{CsH}_5(\text{PO}_4)_2$  and  $\text{SiP}_2\text{O}_7$  matrix quantitatively, the conductivity of the composites was represented as a function of volume fraction of the matrix, and experimental data were curve-fitted with binary-phase EMA or ternary-phase EMA. For the case of binary-phase EMA where a conduction phase and a matrix phase are randomly mixed in a composite electrolyte and no interfacial effect exists between the phases, the total conductivity of the composite  $\sigma_m$  is given by the following equation:

$$2\sigma_m^2 + \{(-2\sigma_1 + \sigma_2)\varphi_1 + (-2\sigma_2 + \sigma_1)\varphi_2\}\sigma_m - \sigma_1\sigma_2 = 0 \quad (1)$$

where  $\varphi_i$  and  $\sigma_i$  represent the volume fraction and conductivity of  $i$  phase ( $i = 1, 2$ ) in the composite, respectively. When a conduction phase and a matrix phase are mixed, and an interfacial phase with a thickness of  $d$  is formed between the phases, ternary-phase EMA can be applied. When the volume fraction of matrix in a composite is  $p$ , then the probability of phase  $i$ ,  $P_i$  ( $i = 0$ : conductive phase such as  $\text{CsH}_5(\text{PO}_4)_2$ , 1: matrix phase such as  $\text{SiP}_2\text{O}_7$ , 2: interfacial phase, and  $P_0 + P_1 + P_2 = 1$ ) in the composite can be given as follows:

$$P_0 = (1-p)^m \quad (2)$$

$$P_1 = p \quad (3)$$

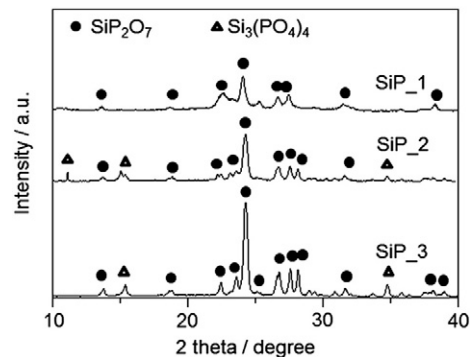


Fig. 3. XRD patterns of  $\text{SiP}_2\text{O}_7$  matrices calcined at 500 °C once (SiP\_1), twice (SiP\_2), and 3 times (SiP\_3).

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