

博士論文（要約）

**Studies on Cesium Phosphates-based
Composite Electrolytes for
Intermediate Temperature Fuel Cells**

（中温作動型燃料電池のためのリン酸
セシウムを用いた複合体電解質の研究）

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Introduction

Fuel cells are electrochemical energy conversion devices that convert chemical energy in fuel directly into electrical energy (and heat) with high efficiency and low emission of pollutants [1]. In addition, when supplied with hydrogen derived from renewable energy sources (wind, solar, and biomass), fuel cells have the potential to substantially and positively impact many areas, including environmental, economic, and energy security [2]. Intermediate-temperature fuel cells (ITFCs), operating at 200-600 °C, have been drawing considerable attention due to their inherent advantages over both low-temperature and high-temperature fuel cells [3,4]. ITFCs not only decrease electrode catalyst poisoning by carbon monoxide and simplify water management compared to low-temperature polymer electrolyte membrane fuel cells, but also broaden the material options compared to high-temperature solid oxide fuel cells, which operate at > 600 °C to have acceptable oxygen ion conductivity [4,5]. However, ITFCs have not seen practical applications because key component materials are not available yet, especially the electrolyte. Cesium phosphates such as CsH_2PO_4 and $\text{CsH}_5(\text{PO}_4)_2$ exhibit high anhydrous proton conductivity ($> 10 \text{ mS cm}^{-1}$) and thermal stability (up to 300 °C) [6,7]. CsH_2PO_4 undergoes a “superprotonic” phase transition at ca. 230 °C from monoclinic (low-temperature phase) to cubic (high-temperature phase) with a drastic increase in its proton conductivity, exceeding 10 mS cm^{-1} . Despite its attractive electrochemical properties, CsH_2PO_4 has poor mechanical integrity due to superplastic behavior of superprotonic solid acids [8]. $\text{CsH}_5(\text{PO}_4)_2$ exhibited extremely high proton conductivity of $\sim 200 \text{ mS cm}^{-1}$ above 160 °C under 30% $\text{H}_2\text{O}/\text{Ar}$ atmosphere, and this was attributed to its melting at $\sim 154 \text{ °C}$ [7]. Various oxides (e.g., SiO_2) and pyrophosphates (e.g., SiP_2O_7) were developed as matrices for CsH_2PO_4 and $\text{CsH}_5(\text{PO}_4)_2$ [9,10]. However, the present cesium phosphates-based composite electrolytes are prepared by mixing and pressing the corresponding powders, there are no chemical bonds between the matrix particles, resulting in a low mechanical strength and stability.

The present work focuses on the development of new matrix materials with interconnected-network structure for CsH_2PO_4 and $\text{CsH}_5(\text{PO}_4)_2$. Both organic and inorganic matrices were investigated. In addition, a special focus was given to the interface interaction between $\text{CsH}_5(\text{PO}_4)_2$ and silica, and the correlation between the interface interaction and electrolyte property was investigated. The reason for the performance degradation in $\text{CsH}_5(\text{PO}_4)_2/\text{SiO}_2$ composites was clarified, which is very important for the stability enhancement of $\text{CsH}_5(\text{PO}_4)_2$ -based composites for ITFCs.

Experimental

Poly(vinylidene fluoride) and heat-resistant epoxy were developed as polymer matrices, and silica with an interconnected network structure was developed as an inorganic matrix. (a) The $\text{CsH}_2\text{PO}_4/\text{PVDF}$ composite electrolytes were prepared by a slurry casting method. Certain amounts of CsH_2PO_4 and PVDF were blended and mixed with dimethylformamide, which served as a solvent, to form a suspension. The suspension was ball-milled for 4 days to homogeneously disperse the CsH_2PO_4 particles. After ball-milling, the resulting slurry was poured onto a glass plate and dried at 80 °C for 12 h to remove the

solvent. Finally, the obtained thin electrolyte was peeled off from the glass plate. (b) The CsH_2PO_4 /epoxy composite electrolytes were prepared by curing a slurry composed of CsH_2PO_4 particles and epoxy. CsH_2PO_4 particles, which had sizes smaller than 10 μm , and epoxy were mixed and ground with a mortar and pestle to form a slurry. The obtained slurry was sequentially 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 . (c) The $\text{CsH}_5(\text{PO}_4)_2$ doped glass membranes were prepared by an optimized sol-gel method. Briefly, certain amounts of TEOS and phosphoric acid were dissolved in a mixture of ethanol and water and hydrolyzed by stirring for 24 h at room temperature. Then, a certain amount of $\text{CsH}_5(\text{PO}_4)_2$ was added to the mixture with a further stirring for 2 h at room temperature. The resultant clear transparent solution was gelled at room temperature for ~ 15 days. Gel films obtained were then annealed at 150 °C for 12 h under saturated water vapor to facilitate the condensation reaction between silanol groups.

Mesoporous and microporous silica were chosen as the matrices for $\text{CsH}_5(\text{PO}_4)_2$, and the thermal property and crystalline structure of $\text{CsH}_5(\text{PO}_4)_2$ in the $\text{CsH}_5(\text{PO}_4)_2/\text{SiO}_2$ composites were investigated. The composites were prepared by mixing and pressing the corresponding powders. In order to clarify the real interface interaction between SiO_2 and $\text{CsH}_5(\text{PO}_4)_2$, the X-ray diffraction and differential thermal analysis (DTA) were conducted on the as prepared pellets. In addition, conductivity measurements at fixed temperatures (158 and 210 °C) as well as during repeated heating and cooling (106 °C \rightarrow 158 °C \rightarrow 106 °C) were conducted to examine the stability of $\text{CsH}_5(\text{PO}_4)_2$ -based composites.

Results and discussion

The CsH_2PO_4 /PVDF composite electrolytes consisted of a physical dispersion of CsH_2PO_4 particles in the PVDF polymer network and were thin and flexible. The crystalline structure and thermal behavior of CsH_2PO_4 were not influenced by the PVDF. There is a dramatic increase of the electrolyte conductivity as the temperature increases from 210 to 230 °C due to the phase transition of CsH_2PO_4 from the low conductive phase to the high conductive phase at 230 °C. The electrolyte conductivity also increases with increase of CsH_2PO_4 content in the composite electrolytes. The composite electrolyte with 70 wt% CsH_2PO_4 showed a high conductivity of 10 mS cm^{-1} at 270 °C under 30% $\text{H}_2\text{O}/\text{Ar}$ atmosphere as well as a tensile strength of 7 MPa at room temperature. The composite electrolyte with 70 wt% CsH_2PO_4 showed stable conductivity at 259 °C under 30% $\text{H}_2\text{O}/\text{Ar}$ atmosphere for 48 h. A fuel cell assembled with this electrolyte exhibited an open circuit voltage of 0.92 V and a peak power density of 86 mW cm^{-2} .

The CsH_2PO_4 /epoxy composite electrolytes consisted of a physical dispersion of CsH_2PO_4 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 electrolyte conductivity gradually increased as the CsH_2PO_4 content increased from 70 wt% to 80 wt%. However, as the CsH_2PO_4 content increased from 80 wt% to 85 wt%, the electrolyte conductivity decreased, which was attributed to of the formation of voids

in the composite. The composite electrolyte with 80 wt% CsH_2PO_4 showed a high conductivity of 11 mS cm^{-1} at $259 \text{ }^\circ\text{C}$ under 30% $\text{H}_2\text{O}/\text{Ar}$ atmosphere as well as a flexural strength of 7.3 MPa at room temperature. The composite electrolyte with 80 wt% CsH_2PO_4 showed a stable conductivity at $259 \text{ }^\circ\text{C}$ under 30% $\text{H}_2\text{O}/\text{Ar}$ 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} .

The $\text{CsH}_5(\text{PO}_4)_2$ doped glass membranes were prepared by an optimized sol-gel method using phosphoric acid as a catalyst for tetraethylorthosilicate hydrolysis. Infrared spectroscopy showed the formation of Si-O-P bonds and scanning electron microscopy showed that the glass membranes have smooth cross-sectional structures. Domains of $\text{CsH}_5(\text{PO}_4)_2$ with sizes of 5-12 nm were uniformly distributed over the membrane cross section. The melting point of $\text{CsH}_5(\text{PO}_4)_2$ in the glass membrane was lower by $20\text{-}40 \text{ }^\circ\text{C}$ than that for pure $\text{CsH}_5(\text{PO}_4)_2$. For a glass membrane with a molar ratio of $\text{SiO}_2 : \text{CsH}_5(\text{PO}_4)_2 : \text{H}_3\text{PO}_4 = 4 : 1 : 0.36$, 62 % of the pore volume was filled with $\text{CsH}_5(\text{PO}_4)_2$ and showed the best electrochemical performance. The glass membrane showed high conductivity of 22 mS cm^{-1} at $219 \text{ }^\circ\text{C}$. The membrane was novel because the silica support formed an interconnected matrix that provided stability, as shown by continuous operation at $210 \text{ }^\circ\text{C}$ for at least 50 h. A fuel cell assembled with the glass membrane exhibited an open circuit voltage of 0.94 V and a peak power density of 85 mW cm^{-2} . The fuel cell produced a stable output voltage of 0.53 V for at least 50 h under a current density of 100 mA cm^{-2} .

Comparing mesoporous silica and microporous silica, the mesoporous silica had a strong interface interaction with $\text{CsH}_5(\text{PO}_4)_2$, resulting in the partial disordering of $\text{CsH}_5(\text{PO}_4)_2$ in the close vicinity of the silica particles. In addition, the melting point and enthalpy change of $\text{CsH}_5(\text{PO}_4)_2$ decreased significantly in the $\text{CsH}_5(\text{PO}_4)_2/\text{mesoporous silica}$ composites. On the contrary, the microporous silica had a weak interaction with $\text{CsH}_5(\text{PO}_4)_2$, and the melting point of $\text{CsH}_5(\text{PO}_4)_2$ decreased by a few degrees in the $\text{CsH}_5(\text{PO}_4)_2/\text{microporous silica}$ composites. As a result, the $\text{CsH}_5(\text{PO}_4)_2/\text{mesoporous silica}$ composite exhibited conductivity higher than that of the $\text{CsH}_5(\text{PO}_4)_2/\text{microporous silica}$ composite by two orders of magnitude at $< 140 \text{ }^\circ\text{C}$. In addition, it was found that the grinding time had a significant influence on the thermal behavior and crystalline structure of $\text{CsH}_5(\text{PO}_4)_2$ in the $\text{CsH}_5(\text{PO}_4)_2/\text{mesoporous silica}$ composites, but the pressing pressure had little effect on them. Differently, the grinding time and pressing pressure had negligible effect on the thermal behavior and crystalline structure of $\text{CsH}_5(\text{PO}_4)_2$ in the $\text{CsH}_5(\text{PO}_4)_2/\text{microporous silica}$ composites, and this was attributed to the weak interaction between them.

Results from the stability test indicated that the $\text{CsH}_5(\text{PO}_4)_2/\text{SiO}_2$ composites were not stable during repeated heating and cooling processes due to the structural damages or existence of $\text{CsH}_5(\text{PO}_4)_2$ particles that were not highly dispersed into the silica matrix. However, the $\text{CsH}_5(\text{PO}_4)_2$ doped glass membrane exhibited extremely stable conductivity. From these findings, we identified two criteria for the preparation of $\text{CsH}_5(\text{PO}_4)_2$ -based composites with high stability. First, a strong interaction between the

matrix and $\text{CsH}_5(\text{PO}_4)_2$ is crucial to the disordering of $\text{CsH}_5(\text{PO}_4)_2$. The disordered state of $\text{CsH}_5(\text{PO}_4)_2$ mitigates the damage caused by the repeated melting and crystallization of $\text{CsH}_5(\text{PO}_4)_2$. Second, matrices with an interconnected structure are advantageous to prevent the structural damages caused by the phase transition of $\text{CsH}_5(\text{PO}_4)_2$.

Conclusions

This work focused on the preparation of cesium phosphates-based composite electrolytes for intermediate temperature fuel cells. Both organic and inorganic materials with an interconnected network structure were developed as supporting matrices for CsH_2PO_4 and $\text{CsH}_5(\text{PO}_4)_2$, and promising results were obtained. In addition, study on the interface interaction between $\text{CsH}_5(\text{PO}_4)_2$ and silica matrices provided a fundamental knowledge about the characteristics of adding oxides into solid acids.

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