



Short communication

An approach for restoring the proton conductivity of sintered tin pyrophosphate membranes for intermediate temperature fuel cells

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HIGHLIGHTS

- SnP₂O₇ membranes were fabricated by casting method.
- Starch was used as a pore former and binder for making porous sintered membranes.
- Proton conductivity was enhanced from 9.7×10^{-4} to 0.061 S cm^{-1} at 225 °C.
- An IT-FC (5 cm²) generated a peak power density of 78 mW cm^{-2} at 225 °C.
- An IT-FC (5 cm²) steadily ran at 100 mA cm^{-2} , 0.6 V for 45 h at 225 °C.

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ABSTRACT

Tin pyrophosphate (SnP₂O₇) membranes need a sintering process to achieve a required mechanical strength as the electrolyte of intermediate temperature fuel cells (IT-FCs) operating at temperatures of 200–300 °C at large scale. However, sintering causes a severe drop of proton conductivity due to the decomposition of SnP₂O₇ and release of residual fused phosphoric acid and/or phosphorous oxides. Here we demonstrate a route to restore the proton conductivity by introducing phosphoric acid inside a sintered SnP₂O₇ membrane to react with the degraded SnP₂O₇ for restoration. After restoration, the decomposition product SnO₂ is converted back to SnP₂O₇ and fused phosphoric acid and/or phosphorous oxides (17.7–20.0%) is regenerated. The proton conductivity is tremendously enhanced from $9.7 \times 10^{-4} \text{ S cm}^{-1}$ to 0.061 S cm^{-1} at 225 °C. A planar IT-FC (active area = 5 cm²) with a restored membrane (thickness = 0.85 mm, diameter = 40 mm) generates a peak power density of 78 mW cm^{-2} without using intermediate catalyst layers at 225 °C. It can steadily run for 45 h at 100 mA cm^{-2} with a degradation rate of 0.7 mV h^{-1} at 225 °C. The fuel and oxidant are, respectively, H₂ (50 sccm) and air (100 sccm) humidified at 30 °C.

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1. Introduction

Fuel cells are highly efficient, environmentally friendly power sources, which generate electricity by combining fuels (e.g., H₂) and oxidants (e.g., O₂) through electrochemical reactions. Intermediate temperature fuel cells (IT-FCs), operating at temperatures of 200–300 °C, have attracted great interests from fuel cell community because they offer advantages of high impurity tolerance, high

fuel flexibility, facile reaction kinetics, low-cost construction materials, etc. [1–3]. Currently, pyrophosphates of tetravalent elements (MP₂O₇ with M = Sn, Zr, Ti, and Ce) show the most promise as the proton conductive electrolytes for IT-FCs [2,3]. Among them, tin pyrophosphate (SnP₂O₇) and its doped materials have been most studied [4–10]. One major hindrance in applying them in planar IT-FCs at large scale is the challenge in developing mechanically strong, highly proton conductive, and dense membranes [2,3,11].

To date, SnP₂O₇ based electrolytes were mostly tested in a single button cell with a small active area of 1 cm² or less [5–7,9,10,12,13]. A large pressure ($1\text{--}2 \times 10^3 \text{ kgf cm}^{-2}$) was applied to press the pyrophosphate powders into a membrane [5–7,9,10,12,13]. To fabricate larger membranes, a very large press is required and that

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is impractical. Besides, the mechanical strength of such membranes is still low and not suitable for the testing under stress in a large planar cell. Therefore, the membranes should be fabricated by casting methods and a sintering process is needed to enhance the mechanical strength to realize the applications of IT-FCs at large scale. Unfortunately, it has been well recognized that the sintered pyrophosphate membranes suffer a severe drop of proton conductivity due to the decomposition of the pyrophosphates and the release of fused phosphoric acid and/or phosphorous oxides [2–4,11].

This study aims to restore the proton conductivity of the sintered SnP_2O_7 membranes. We hypothesize that the reaction of phosphoric acid (H_3PO_4) with the degraded SnP_2O_7 after sintering can regenerate SnP_2O_7 from the decomposed SnP_2O_7 and compensate the loss of phosphorous oxides and/or fused H_3PO_4 , leading to the reinstatement of proton conductivity. To approach it, we use corn starch as a pore former and binder to prepare a porous sintered SnP_2O_7 membrane. Through the pores, H_3PO_4 can be introduced inside the membrane and reacts with the degraded SnP_2O_7 to regain the composition, structure and thus the proton conductivity. The regenerated membrane will be finally tested in a planar cell to check if it can withstand the stress and exhibit restored performances.

2. Experimental

SnP_2O_7 was prepared by the reaction of H_3PO_4 and tin dioxide (SnO_2) [4,5]. The mixture of SnO_2 (99.9%, Afla Aesar), H_3PO_4 (85.6%, ACS reagent, J.T. Baker), and deionized water at a molar ratio of 1:2.2:6 was stirred in sequence at ca. 110 °C overnight (covered by aluminum foil), at 220 °C for 1 h, and at 250 °C until hard to stir. The

paste was calcined at 650 °C for 2.5 h to finally obtain SnP_2O_7 .

The as-synthesized SnP_2O_7 was dry ball-milled (agate balls and jar, SPEX 8000M Mixer/Mill) for 20 min. The obtained powders were then mixed with corn starch (Argo[®], ACH food companies) and deionized water at a mass ratio of 10:0.5:2.85. The mixture was wet ball-milled (HDPE bottle, agate balls, SPEX 8000M Mixer/Mill) for 10 min. The gained slurry was then casted in a mold ($\Phi = 25$ mm) at room temperature to get a membrane, which was further heated in a tube furnace at a ramp rate of 5 °C min^{-1} to 1050 °C for 10 h for sintering to get a porous sintered SnP_2O_7 membrane. The pores in the membrane were produced by burning off the starch during sintering [14,15]. We confirmed the starch burn-off during sintering by comparing the mass changes of two SnP_2O_7 pellet samples ($\Phi = 25$ mm) with and without starch before and after sintering. The details are presented in Supplementary Information. Non-porous sintered SnP_2O_7 membranes were also prepared without using starch. To restore the proton conductivity, the porous sintered membrane was immersed into H_3PO_4 (85.6%), heated at ca. 110 °C overnight and subsequently at ca. 180 °C for 3 h. It was then heated in a tube furnace at 500 °C for 2 h. The process and membrane are denoted as restoration process and restored SnP_2O_7 membrane, respectively. To estimate the sum content of the fused phosphoric acid and phosphorous oxides in the restored SnP_2O_7 membranes, we designed a simple route, for the first time, based on the assumption that all of the fused phosphoric acid and phosphorous oxides can combine with water back to form H_3PO_4 . The amount of H_3PO_4 determined by measuring the pH of the suspension of restored SnP_2O_7 powders in water is then used to estimate the sum content of the fused phosphoric acid and phosphorous oxides. The details are presented in Supplementary Information.

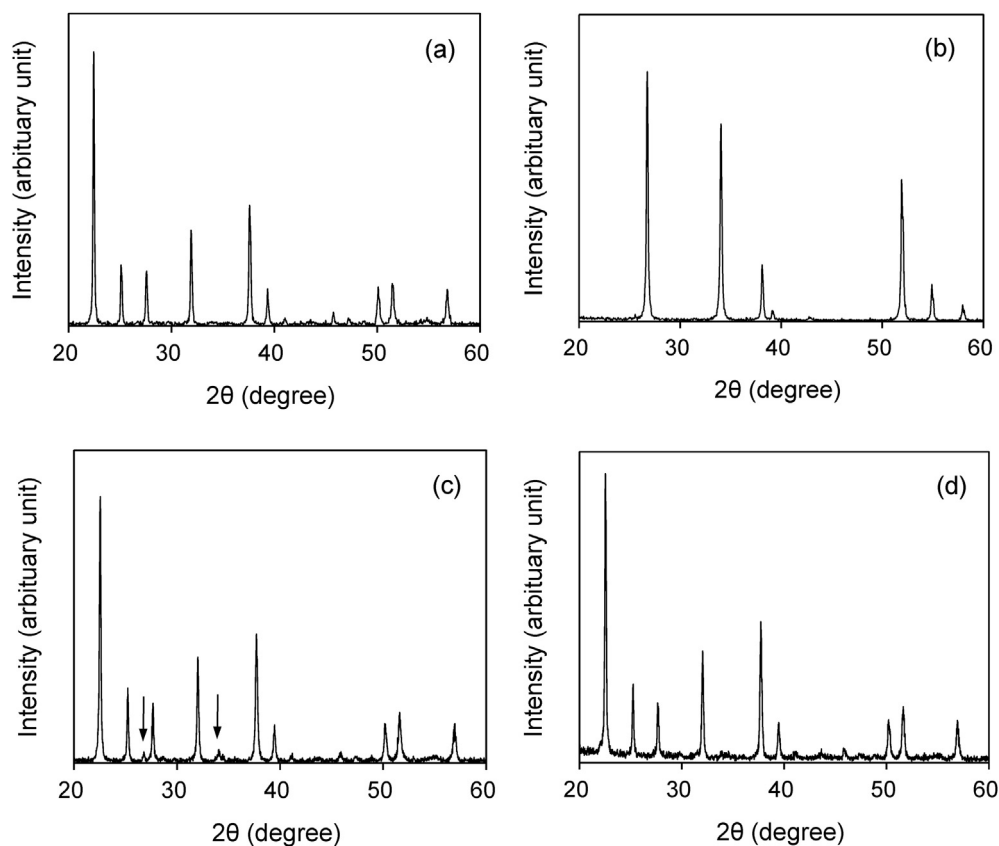


Fig. 1. XRD patterns of (a) as-synthesized SnP_2O_7 powders, (b) SnO_2 powders, (c) a sintered SnP_2O_7 membrane, and (d) a restored SnP_2O_7 membrane. The two arrows in (c) indicate the reflections of SnO_2 .

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