



Dense composite electrolytes of Gd^{3+} -doped cerium phosphates for low-temperature proton-conducting ceramic-electrolyte fuel cells

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Received 3 November 2014; received in revised form 4 December 2014; accepted 5 December 2014

Available online 12 December 2014

Abstract

Dense Gd^{3+} -doped cerium pyrophosphate–phosphate (CGP–P) composites are prepared by infiltrating H_3PO_4 into partially sintered CGP substrates and then heat-treating at 375–400 °C. The phase composition and microstructure of CGP–P composites are studied by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM), which shows that the H_3PO_4 reacts with CGP to form phosphate phases in the pores and results in a dense CGP–P composite. The ionic conductivity of CGP–P composite is studied by electrochemical impedance spectroscopy (EIS) in dry and humid atmosphere in 90–230 °C range for its application as electrolyte in proton-conducting ceramic-electrolyte fuel cells (PCFCs). It is observed that the ionic conductivity of the composite GCP–P-1h/375, formed by 1 h acid-treatment followed by heat-treatment at 375 °C, is $2.73 \times 10^{-6} \text{ S cm}^{-1}$ at 230 °C in unhumidified air but in humidified air (water vapor pressure, $p\text{H}_2\text{O}=0.12 \text{ atm}$) it shows a maximum of 0.051 S cm^{-1} at 170 °C, which is significant for its application as electrolyte in PCFCs.

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Keywords: B. Composites; C. Ionic conductivity; Proton-conducting ceramic-electrolyte fuel cells; Gd^{3+} -doped cerium pyrophosphate

1. Introduction

Over the years, oxygen-ion conducting electrolyte based solid oxide fuel cells (SOFCs) have been one of the most widely explored fuel cell configurations. However, the normal operating temperature of SOFCs ranges above 800 °C and though such a high temperature is advantageous for ensuring faster ion-transport and electrode kinetics, it also poses some operational and economic constraints in the form of slower start-up and shut-down, and the issues with the thermo-mechanical stability and compatibility of various components [1]. In recent decades, the development of proton-conducting perovskite-type oxide based SOFCs has enabled the lowering of the operating temperature of SOFCs to 600–800 °C range.

However, this temperature range is still considered as high enough and there have been requirements for developing new solid state electrolytes for the protonic-conducting ceramic-electrolyte fuel cells operating in 100–500 °C range [2,3].

The PCFCs operating in 100–500 °C range envisage the idea of designing a new fuel cell configuration by doing away with the disadvantages associated with the low temperature operation of polymeric electrolyte membrane fuel cells and the high temperature operation of SOFCs. However, in order to realize this idea, one of the basic requirements is to look for new electrolyte materials having high ionic conductivity in aforesaid temperature range [2]. Due to the lower energy of activation for protonic conduction, in comparison to that for oxygen-ion conduction, proton conducting materials are expected to be the potential candidates as electrolyte in 100–500 °C range. Currently, the important materials which have been under consideration as solid state electrolyte in the low-temperature PCFCs include heteropolyacids and polyphosphates (such as $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, $\text{H}_4\text{GeW}_{12}\text{O}_{40}$ and $(\text{NH}_4)_2\text{MP}_4\text{O}_{13}$; M = Si, Ti, Sn, and Mn) [4–6], and tetrahedral oxyanion based oxyacids

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(such as CsHSO₄, Rb₃H(SeO₄)₂, and (NH₄)₃H(SO₄)₂ [7–9], metal phosphates and pyrophosphates (such as LaPO₄, LaP₃O₉, SnP₂O₇, and CeP₂O₇) [10–14].

Among the above mentioned materials, tetravalent metal pyrophosphates (TMPs) have shown considerably high proton conductivity (10^{-4} – 10^{-1} S cm⁻¹) in 100–400 °C range and are being considered as promising electrolyte for PCFCs [14]. However, due to the poor thermal stability and sinterability of many of these materials, the fabrication of dense electrolyte samples has been one of the major challenges towards their application as electrolytes in PCFCs [14–18]. Often, it requires sintering at ≥ 1400 °C to get fairly dense tin pyrophosphate samples [19]. However, sintering at such a high temperature leads to the evaporation of excess phosphate phase at high temperatures, which severely lowers their proton conductivity, as the presence of excess phosphate phase has been found to be key to high proton conductivity of TMPs [14,16,20–23]. In an attempt to develop TMP based dense electrolytes, Sato et al. [24,25] have fabricated dense binary metal oxide–pyrophosphate composites containing excess amorphous phosphate phases (collectively denoted as P_mO_n) by reacting porous metal oxide substrate with excess phosphoric acid solution at ~ 600 °C, which confirms that the decomposition of H₃PO₄ can be used for pore-filling of pre-fabricated substrates.

Considering the poor sinterability of TMPs, there have been attempts to utilize their potential of highly proton-conducting electrolytes by forming the composites of these materials with H₃PO₄-loaded organic polymers such as polybenzimidazole, polytetrafluoroethylene [26–28], other phosphate-based proton-conductors such as LaP₃O₉, CsH₂PO₄ [29,30] and solid acids [31]. The objective of this work is to explore the possibility of low-temperature (≤ 300 °C) fabrication of dense proton-conducting composite electrolytes using partially sintered cerium phosphates as substrate. We have explored the densification of porous substrate of 10% Gd³⁺-doped CeP₂O₇ (CGP) by the formation of amorphous P_mO_n phases into its pores. The CGP densification was performed by H₃PO₄ loading on CGP substrate and GDC infiltrated CGP substrate, followed by heat-treatment at different temperatures.

2. Experimental

2.1. Fabrication of dense composites

Gd³⁺-doped CeP₂O₇ was synthesized by digesting GDC powder with H₃PO₄ following the procedure mentioned elsewhere [32]. Briefly, the 10% Gd³⁺-doped cerium oxide powder (GDC-F, Kceracell, BET = 10–15 m²/g, PSD (d₅₀) = 0.3–0.6 μm) and H₃PO₄ (85%, Dae Jung) were mixed in P/(Ce+Gd) molar ratio of 2.7 in a covered alumina crucible with constant stirring using a magnetic stirrer at ~ 95 °C for ~ 8 h to get a highly viscous paste. The temperature was then raised to ~ 150 °C to form a dry yellow solid. The solid was ground with mortar and pestle, and then calcined at 300 °C for 8 h in a covered alumina crucible. The calcined powder was grinded with a mortar and a pestle, sieved by a 76 μm mesh test sieve, and the obtained powder was used for further

characterization. For the pellet preparation, the calcined powder was molded into disks (thickness ≈ 2.0 mm; diameter = 9 mm). The disks were isostatically cold pressed at 150 MPa and then sintered at 375 °C in covered alumina crucible for 12 h to get partially sintered CGP disks.

For the fabrication of GDC infiltrated CGP (CGP–GDC) substrates, CGP substrate was infiltrated with a GDC dispersion. The GDC dispersion was prepared by adding 10 g GDC in 60 ml ethanol solution, along with Solspers 24000 (Lubrizol, USA) as a dispersant, by ball-milling for 24 h. The CGP substrate was dipped into GDC dispersion under vacuum for 30 min and then removed from the dispersion and heated at 300 °C for 5 h.

Furthermore, the CGP–GDC disks were dipped in 85% H₃PO₄ solution at 100 °C for 1–5 h to load H₃PO₄ into its pores. The H₃PO₄ loaded CGP–GDC disks were removed from the H₃PO₄ solution and their surfaces were wiped with Kimwipes (Yuhan-Kimberly, Korea) disposable wipers. The acid-loaded CGP–GDC disks were then heat-treated at different temperatures for 5 h to get CGP–GDC–phosphate (CGP–GDC–P) composites.

On the other hand, for the fabrication of CGP–P composites, the CGP disks were directly dipped (without GDC infiltration) in 85% H₃PO₄ solution at 100 °C for 1–5 h to load H₃PO₄ into its pores. The H₃PO₄ loaded CGP disks were removed from the H₃PO₄ solution and their surfaces were wiped with Kimwipes disposable wipers. The acid-loaded CGP disks were then heat-treated at different temperatures for 5 h to get 10% Gd³⁺-doped cerium phosphate–phosphate (CGP–P) composites.

The surface of the heat-treated CGP–GDC–P composites and CGP–P composites was cleaned by polishing the outer surface with sand paper, followed by ultrasonication in isopropanol to remove loosely attached materials onto the surface. The detail about the acid-treatment time and heat-treatment temperature for various CGP–P composites is presented in Table 1.

2.2. Physical characterization

The crystalline phases in as-calcined powders and the powders from crushed heat-treated disks were examined using an X-ray diffractometer (XRD-7000, Shimadzu) equipped with a Cu-K α radiation source (1.5406 Å) and operated at 40 kV and 30 mA at a scan rate of 2°/min between scanning angles (2θ) of 10° and 80°. The microstructure of the fractured section

Table 1

Details about phosphoric acid-treatment time and heat-treatment temperature for the fabrication of various CGP–P composites.

CGP–P composite	Acid-treatment time (h)	Heat-treatment temperature (°C)
CGP–P-1h/375	1	375
CGP–P-5h/375	5	375
CGP–P-1h/400	1	400
CGP–P-5h/400	5	400

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