

A Ternary Composite $\text{Ti}_{0.95}\text{Fe}_{0.05}\text{P}_2\text{O}_7/\text{NaPO}_3/\text{NaTi}_2(\text{PO}_4)_3$ Electrolyte with Enhanced Electrochemical Performance for Solid Oxide Fuel Cells

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A novel ternary composite $\text{Ti}_{0.95}\text{Fe}_{0.05}\text{P}_2\text{O}_7/\text{NaPO}_3/\text{NaTi}_2(\text{PO}_4)_3$ electrolyte was successfully fabricated by a simple solid-phase method at 700 °C. The phase composition, morphology and electrochemical properties of the ternary composite electrolyte were characterized by means of X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS). The results indicated that the electrochemical performance of the ternary composite electrolyte was better than that of single-phase Mg- or Fe-doped TiP_2O_7 and a conductivity of $3.9 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$ was obtained at 800 °C in a dry nitrogen atmosphere. H_2/O_2 fuel cell performance using the ternary composite $\text{Ti}_{0.95}\text{Fe}_{0.05}\text{P}_2\text{O}_7/\text{NaPO}_3/\text{NaTi}_2(\text{PO}_4)_3$ as the electrolyte was examined. An open circuit voltage of approximately 1.04 V and a maximum power output density of $167.1 \text{ mW} \cdot \text{cm}^{-2}$ were achieved at 800 °C. This work offers a new alternative for the design of ternary composite metal pyrophosphates electrolyte.

Keywords: Composite electrolyte; Conductivity; Fuel cell; XRD

1. INTRODUCTION

Consumption of non-renewable fossil fuels not only leads to an increase of greenhouse gas emissions, but also does not conform to the concept of sustainable development. Over the past decades, fuel cells (FCs) have attracted extensive attention as next-generation energy sources, especially considering environment preservation and sustainable development [1-4]. The performance and operating temperature of fuel cells depend significantly on the properties of the electrolyte material used. Well-studied solid oxide fuel cells (SOFCs) with yttria-stabilized zirconia electrolyte often work at high operating temperatures above 800°C, but due to the low conductivity at low temperatures, more expensive interconnects and sealing materials are necessary. However, proton exchange membrane fuel cells (PEMFCs) require operating temperatures below 100 °C, which often means the poisoning of the

platinum catalyst by carbon monoxide and water management issues. Therefore, proton conductor electrolytes operating in an intermediate-temperature range are the most promising candidates for SOFCs compared with those operated in low- and high-temperature ranges [5-8].

Tetravalent metal pyrophosphates (MP_2O_7 , $M = Ti, Sn, Si, Ce,$ and Zr) are known for their remarkably high protonic conductivities, providing a potential practical application for intermediate-temperature fuel cells [9-13]. And it is known that partial substitution of low valence or tetravalent cation for M^{4+} can increase the conductivity of MP_2O_7 in humid and dry atmospheres. However, it is difficult to fabricate a fully dense electrolyte membrane, even when sintered at 1400 °C and above, due to the poor sinterability of single phase MP_2O_7 . Furthermore, sintering at high temperatures results in the vaporization of phosphate phase, which seriously deteriorates the electrical conductivity of MP_2O_7 [6-8]. Therefore, there is an increasing demand for novel pyrophosphate conductors with high thermal stability, excellent mechanical properties, and good proton conductivity.

Sodium titanium phosphate ($NaTi_2(PO_4)_3$), a NASICON-type material with high ionic conductivity, could be used in the fabrication of sodium-ion batteries, gas sensors and fuel cells due to its open channels, which facilitate ion transportation [14,15]. Our publications have shown that $Ti_{0.95}Mg_{0.05}P_2O_7$ composited with $(K/Na)Ti_2(PO_4)_3$ acts as an efficient electrolyte material, and good electrical performance is obtained under intermediate-temperature conditions [16]. In addition, many investigations have reported that ammonium metaphosphate (NH_4PO_3) shows great potential in intermediate-temperature fuel cell application as a proton-conducting electrolyte as a result of its relatively high ionic conductivity [17-20]. It is clear that the partial decomposition of NH_4PO_3 to HPO_3 at operating temperature is the reason for the high conductivity of NH_4PO_3 . On the other hand, NH_4PO_3 -based composite electrolytes comprised of NH_4PO_3 and a crystallized supporting matrix, such as $(NH_4)_2MnP_4O_{13}$ [18], $(NH_4)_2SiP_4O_{13}$ [19], and TiP_2O_7 [20], have been proposed to overcome the instability of NH_4PO_3 and in turn to enhance the conductivity.

Accordingly, the combination of these properties to develop a new electrolyte material with high conductivity, good stability and a wide application temperature range is essential for practical application of the intermediate-temperature fuel cell. In the present work, a novel ternary composite $Ti_{0.95}Fe_{0.05}P_2O_7/NaPO_3/NaTi_2(PO_4)_3$ was prepared by the conventional solid-state reaction method and its structural, morphological and electrical properties were investigated by powder X-ray diffraction, scanning electron microscopy and impedance spectroscopy techniques.

2. EXPERIMENTAL SECTION

Sodium oxalate and appropriate amounts of Fe_2O_3 , TiO_2 were added to 85% H_3PO_4 aqueous solution to form a homogeneous slurry. The weight ratio of sodium oxalate to metal pyrophosphate was kept at 4:1, according to the formula of $Ti_{0.9}Fe_{0.1}P_2O_7$. This slurry was preheated at 350 °C for 1 h in air until the reaction was completed. The resulting powder was ground and pressed under the pressure of 200 MPa into pellets, and these were calcined at 700 °C for 4 h to yield a ternary $Ti_{0.95}Fe_{0.05}P_2O_7/NaPO_3/NaTi_2(PO_4)_3$ composite material.

The structure determination of the composite material powder was characterized by X-ray diffraction (XRD) using an X' Pert Pro MPD diffractometer in the 2θ range $20-70^\circ$ using Cu K α radiation ($\lambda = 0.15406$ nm). The morphology and porosity of the composite material pellet were investigated using a JEOL JSM 6460A scanning electron microscope (SEM).

The ionic conductivity measurements of the ternary $\text{Ti}_{0.95}\text{Fe}_{0.05}\text{P}_2\text{O}_7/\text{NaPO}_3/\text{NaTi}_2(\text{PO}_4)_3$ composite electrolyte were conducted in a three-electrode system on an electrochemical analyzer (CHI660E) and performed in the temperature range $400-800^\circ\text{C}$ in a dry nitrogen atmosphere. The as-sintered ceramic pellets were polished, then 20%Pd-80%Ag electrodes were attached to each side of the ternary composite electrolyte by painting on one layer of conducting paste, and Ag wires were used as current collectors. EIS measurement was performed to provide the resistance information of bulk, grain boundaries, and electrodes by applying an AC voltage with an amplitude of 10 mV and the frequency range of 1 Hz to 1 MHz. The effect of oxygen partial pressure ($p\text{O}_2$) on the ionic conductivity of the ternary composite electrolyte was measured over the range of 10^{-20} to 1 atm by using mixed O_2 , N_2 and H_2 at 700°C . An H_2/O_2 fuel cell was fabricated with the ternary $\text{Ti}_{0.95}\text{Fe}_{0.05}\text{P}_2\text{O}_7/\text{NaPO}_3/\text{NaTi}_2(\text{PO}_4)_3$ composite pellet as electrolyte and the fuel cell performance was measured at 800°C .

3. RESULTS AND DISCUSSION

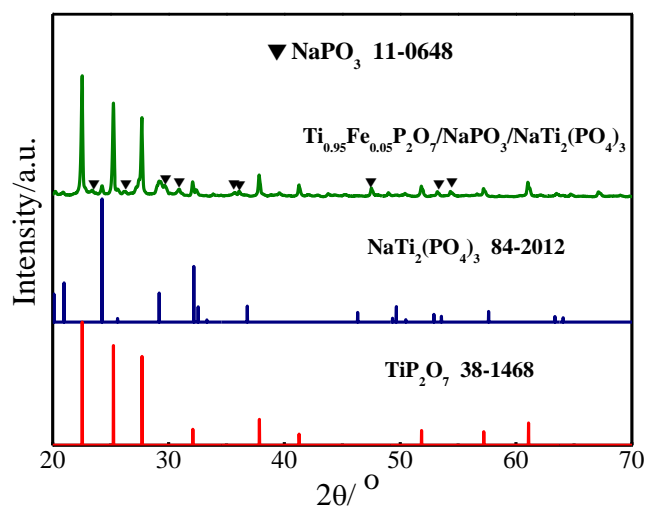


Figure 1. XRD pattern of the $\text{Ti}_{0.95}\text{Fe}_{0.05}\text{P}_2\text{O}_7/\text{NaPO}_3/\text{NaTi}_2(\text{PO}_4)_3$ ternary composite powder.

The phase composition of the Fe doped titanium pyrophosphate composite powder was recognized through the XRD pattern, which is shown in Fig. 1. Diffraction peaks assigned to $\text{NaTi}_2(\text{PO}_4)_3$ (JCPDS 84-2012) and NaPO_3 (JCPDS 11-0648) were observed in addition to the peaks of cubic TiP_2O_7 (JCPDS 38-1468). The ionic radius of Fe^{3+} (0.64 \AA) with coordination number 6 is close to that of Ti^{4+} (0.68 \AA) ion, which indicates that Fe^{3+} can substitute for Ti^{4+} in the lattice of cubic TiP_2O_7 without any significant alteration of the crystalline structure [21-23]. Our study revealed that ternary

Ti_{0.95}Fe_{0.05}P₂O₇/NaPO₃/NaTi₂(PO₄)₃ composite material was successfully obtained after full reaction at 700 °C, with no other impurity phase.

The SEM morphologies of the sintered Ti_{0.95}Fe_{0.05}P₂O₇/NaPO₃/NaTi₂(PO₄)₃ electrolyte disk are shown in Fig.2. It can be seen that the sintered composite electrolyte is fully dense and a microcrack-free membrane formed. However, few pores are observed in Fig. 2(a). This might be due to the volatilization of trace PO₃⁻ in the synthesis process. NaPO₃ is in a molten state at 700 °C, it fills the gaps between Ti_{0.95}Fe_{0.05}P₂O₇ and NaTi₂(PO₄)₃ grains after cooling. This helps to form a compact composite electrolyte.

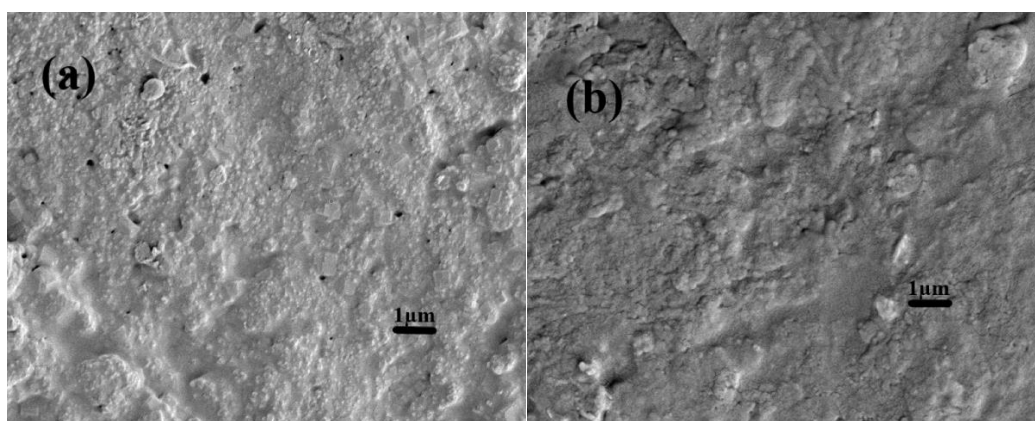


Figure 2. (a)External and (b)cross-sectional SEM images of the Ti_{0.95}Fe_{0.05}P₂O₇/NaPO₃/NaTi₂(PO₄)₃ ternary composite electrolyte.

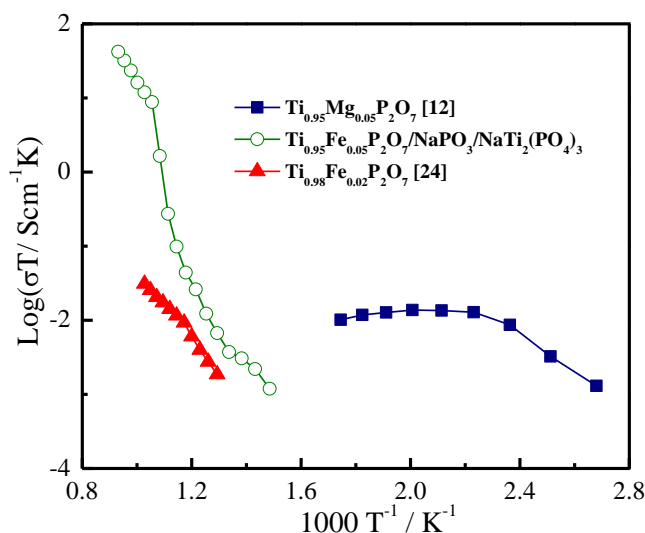


Figure 3. Temperature dependence of conductivity of Ti_{0.95}Fe_{0.05}P₂O₇/NaPO₃/NaTi₂(PO₄)₃ (400–800 °C), Ti_{0.95}Mg_{0.05}P₂O₇ [12] (100–300 °C) and Ti_{0.98}Fe_{0.02}P₂O₇ [24] (500–700 °C).

The total conductivity of the $\text{Ti}_{0.95}\text{Fe}_{0.05}\text{P}_2\text{O}_7/\text{NaPO}_3/\text{NaTi}_2(\text{PO}_4)_3$ ternary composite electrolyte between 400 °C and 800 °C in a dry N_2 atmosphere was studied and compared with single phase electrolyte $\text{Ti}_{0.98}\text{Fe}_{0.02}\text{P}_2\text{O}_7$ [24] and $\text{Ti}_{0.95}\text{Mg}_{0.05}\text{P}_2\text{O}_7$ [12], as illustrated in Fig.3. It can be seen that the ternary composite exhibited one or two orders of magnitude higher conductivity than $\text{Ti}_{0.98}\text{Fe}_{0.02}\text{P}_2\text{O}_7$ in the same temperature range and the highest value of $3.9 \times 10^{-2} \text{ S}\cdot\text{cm}^{-1}$ was obtained at 800 °C. Although $\text{Ti}_{0.95}\text{Mg}_{0.05}\text{P}_2\text{O}_7$ showed relatively high conductivity of $1.4 \times 10^{-2} \text{ S}\cdot\text{cm}^{-1}$ in a dry air atmosphere at the relatively low temperature of 225 °C, its electrical conductivity decreased with the increasing of operating temperature as the thermal stability of single titanium pyrophosphate is poor, which indicates that it can only be used within a range of 100-300 °C. In addition, it can be observed that there is a bend at approximately 675 °C in the conductivity plot, which is indicative of the melting of NaPO_3 . It is possible that NaPO_3 provides the additional ion transport pathways and results in an increase of ionic conductivity, which might be similar to the role of alkali carbonate salts in the ceria-based carbonate composite systems [25,26] and alkaline halides in our previous reports [27] in the ionic transport process. The ternary composite electrolyte has higher conductivity, better stability and a wider application temperature range than that of $\text{Ti}_{0.95}\text{Mg}_{0.05}\text{P}_2\text{O}_7$ [12]. It is presumed that this result may be due to the formation of a three-dimensional network structure from $\text{P}_2\text{O}_7^{4-}$, PO_3^- and PO_4^{3-} in the $\text{Ti}_{0.95}\text{Fe}_{0.05}\text{P}_2\text{O}_7/\text{NaPO}_3/\text{NaTi}_2(\text{PO}_4)_3$ ternary composite, which makes a long-range order tunneling for ion transportation, improves the efficiency of ion transfer and further enhances the conductivity.

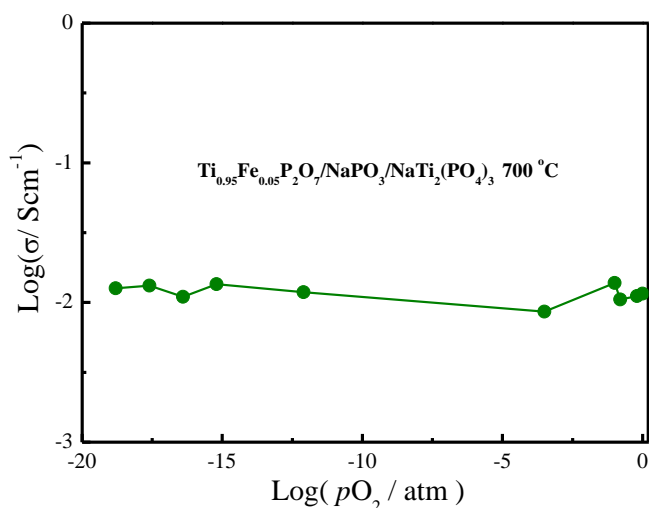


Figure 4. Dependence of conductivity of $\text{Ti}_{0.95}\text{Fe}_{0.05}\text{P}_2\text{O}_7/\text{NaPO}_3/\text{NaTi}_2(\text{PO}_4)_3$ on $p\text{O}_2$.

Fig.4 shows the dependence of the conductivity of the $\text{Ti}_{0.95}\text{Fe}_{0.05}\text{P}_2\text{O}_7/\text{NaPO}_3/\text{NaTi}_2(\text{PO}_4)_3$ ternary composite on partial pressure of oxygen at 700 °C. The plot indicates that at low oxygen partial pressures the conductivity of $\text{Ti}_{0.95}\text{Fe}_{0.05}\text{P}_2\text{O}_7/\text{NaPO}_3/\text{NaTi}_2(\text{PO}_4)_3$ almost remains constant, suggesting that ionic conduction is dominating, and the conductivity decreases at first and then increases along with the partial pressure of oxygen increases. The discrepancy in conductivities between the low and high oxygen partial pressures is attributed to the presence of some degree of electron hole conduction [28].

Fig. 5 is the Nyquist curve of the $\text{Ti}_{0.95}\text{Fe}_{0.05}\text{P}_2\text{O}_7/\text{NaPO}_3/\text{NaTi}_2(\text{PO}_4)_3$ ternary composite electrolyte under open circuit condition at $800\text{ }^\circ\text{C}$. It can be seen that a depressed semicircle in the high-middle frequency region and a tail with a slope of approximately 45° in the low frequency region were obtained. The high frequency intercept of the curve with the real axis gives the ohmic resistance and the value of the ohmic resistance is $2.53\ \Omega\cdot\text{cm}^2$.

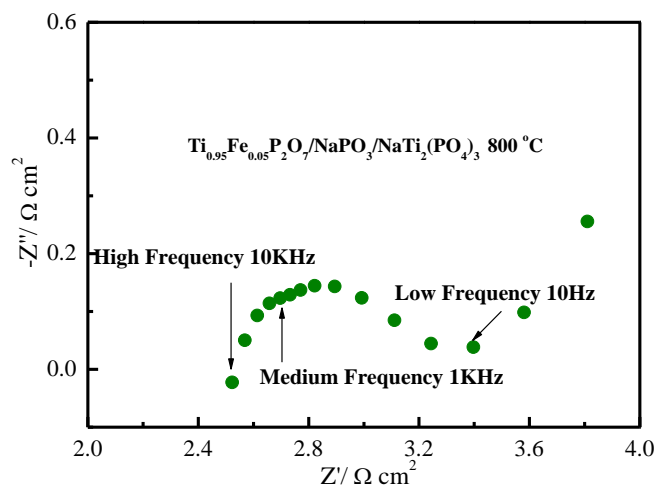


Figure 5. Nyquist curve of $\text{Ti}_{0.95}\text{Fe}_{0.05}\text{P}_2\text{O}_7/\text{NaPO}_3/\text{NaTi}_2(\text{PO}_4)_3$ under open circuit condition measured at $800\text{ }^\circ\text{C}$.

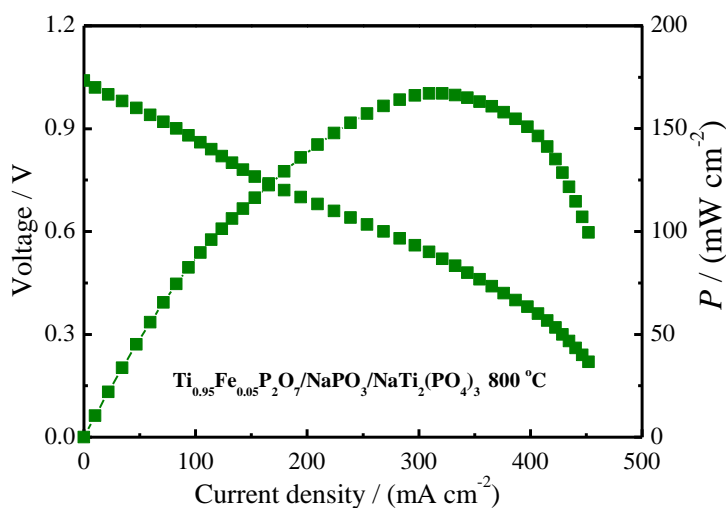


Figure 6. The H_2/O_2 fuel cell performance using $\text{Ti}_{0.95}\text{Fe}_{0.05}\text{P}_2\text{O}_7/\text{NaPO}_3/\text{NaTi}_2(\text{PO}_4)_3$ as electrolyte at $800\text{ }^\circ\text{C}$.

The low frequency intercept of the semicircle with the real axis represents the electrode polarization resistance and the total resistance of the cell was calculated to be $3.36\ \Omega\cdot\text{cm}^2$. The tail in the low frequency region can be interpreted as the high polarization resistance, which could be related to the significant change of the conductive mechanism of the electrolyte-electrode interface or the resistance of ion or electron diffusion. The ohmic resistance value of the ternary composite electrolyte is below the resistance value of $3.65\ \Omega\cdot\text{cm}^2$, measured in a dry N_2 atmosphere at $800\text{ }^\circ\text{C}$. It might be that

the composition of electrolyte resulted in more ion transport pathways for ion transfer, minimizing the resistance of ion transport, improving the efficiency of ion transfer, and finally enhancing the ionic conductivity.

Fig. 6 shows the H₂/O₂ fuel cell performance (*I-V* and *I-P* curves) using Ti_{0.95}Fe_{0.05}P₂O₇/NaPO₃/NaTi₂(PO₄)₃ ternary composite as the electrolyte at 800 °C with H₂ and O₂ as fuel and oxidant, respectively. The thickness and the area of the electrolyte are 1.41 mm and 0.5 cm², respectively. The open circuit voltage of the cell is approximately 1.04 V, which proved the density of the ternary composite electrolyte, and there is no short circuit and no crossover of H₂ or O₂; the electronic conduction is negligible. Although the thickness of electrolyte layer is 1.41 mm, a power density of the cell as high as 167.1 mW·cm⁻² is obtained at 800 °C with the current density of 309.4 mA·cm⁻² and the circuit voltage of 0.54 V. This suggests that the ternary composite electrolyte with relatively low ohmic resistance and polarization resistance leads to better ionic conductivity and cell performance [16]. The performance of FCs largely depends on the design and preparation of the electrolyte and the configuration of the cell. Reducing the thickness of electrolyte and enhancing the catalytic activity of the electrodes will improve the performance of FCs and higher power density will be achieved.

4. CONCLUSIONS

In this work, we successfully synthesized a novel ternary composite Ti_{0.95}Fe_{0.05}P₂O₇/NaPO₃/NaTi₂(PO₄)₃ electrolyte for ITFCs. The ternary composite electrolyte exhibits enhanced electrochemical performance compared with single-phase Mg- or Fe-doped TiP₂O₇ and a conductivity of 3.9×10⁻² S·cm⁻¹ was achieved at 800 °C in a dry nitrogen atmosphere. The operation tests of a H₂/O₂ fuel cell with the ternary composite electrolyte showed an open circuit voltage of approximately 1.04 V and a maximum power output density of 167.1 mW·cm⁻² at 800 °C. The ohmic and total resistance were 2.53 Ω·cm² and 3.36 Ω·cm² under open circuit condition at 800 °C, respectively. Thus, ternary Ti_{0.95}Fe_{0.05}P₂O₇/NaPO₃/NaTi₂(PO₄)₃ composite electrolyte is a promising electrolyte candidate for solid oxide fuel cells.

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CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

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