

## **Ce<sup>3+</sup> doped CeP<sub>2</sub>O<sub>7</sub> Ceramic Electrolyte for high temperature Proton Exchange Membrane Fuel Cell**

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Proton conductors capable of operating in high temperature range (over 180°C) has attracted worldwide attention. The promising inorganic membranes candidates CeP<sub>2</sub>O<sub>7</sub> and Ce<sup>3+</sup> doped CeP<sub>2</sub>O<sub>7</sub> were used between 160 °C and 280 °C for Proton exchange membrane fuel cell (PEMFC) in this study. The structure and phase stability were analyzed by X-ray diffraction, Fourier transform infrared (FTIR), XPS (ESCALAB250Xi) and thermogravimetric analysis (TGA), and also the microstructure morphology was analyzed by scanning electron microscopy (SEM). The CeP<sub>2</sub>O<sub>7</sub> and Ce<sup>3+</sup> doped CeP<sub>2</sub>O<sub>7</sub> composite membranes exhibited high proton conductivity of 0.008 S cm<sup>-1</sup> and 0.0095 S cm<sup>-1</sup> at 200 °C, respectively. The peak power densities of Ce<sup>3+</sup> doped CeP<sub>2</sub>O<sub>7</sub> membrane were 23.5 mW cm<sup>-2</sup> at 180 °C and 26.6 mW cm<sup>-2</sup> at 200 °C, respectively.

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**Keywords:** high-temperature proton exchange membrane fuel cells; low valency cations; cerium pyrophosphate

### **1. INTRODUCTION**

During the years, proton exchange membrane fuel cells (PEMFC) at high temperature as electrochemical have attracted much attention. Operating a PEMFC at elevated temperatures could provide many advantages such as 1) lower Pt loading requirements or making it possible to use non-noble metal catalyst 2) improved CO tolerances leading to simplified fuel pre-treatment techniques, and, 3) improving the efficiency of the fuel cell [1-4]. Research on proton exchange membranes for medium temperature (120-180°C) operating under low humidity is usually focused on polybenzimidazole based membranes. PBI is typically doped with phosphoric acid (PA) to provide proton conductivity [2, 6]. PBI/PA membrane has good conductivity and acceptable mechanical strength and impermeability for PEMFC. However, the limitations of liquid PA, such as its

deactivation via phosphate anion adsorption at positive potentials, acid leaching, and degradation to pyrophosphate at temperatures over 160°C, restrict PBI/PA used in a higher temperature ranges [6-8].

Recently, a number of tetravalent metal pyrophosphates ( $MP_2O_7$ , where  $M = Sn, Ge, Zr, Si, Ce, Ti$ ) have shown significant proton conductivity ( $\sim 10^{-2} \text{ S cm}^{-1}$ ) [9-12]. Therefore, many efforts have been made to develop these kinds of materials. Hibino et al. [11] reported that the proton conductivities of  $SnP_2O_7$  materials high conductivity via doping with trivalent elements. Wang et al. reported that the fuel cell using  $Sn_{0.9}In_{0.1}P_2O_7$  as an electrolyte yields power densities of  $14.7 \text{ mW cm}^{-2}$  under  $H_2/O_2$  conditions at 443K, respectively. In the literature works, Cerium pyrophosphate has suitable protonic conductivity in 150–250°C range [14-18]. Song et al. researched  $Gd^{3+}$  Doped Cerium Pyrophosphate, which exhibited a conductivity of  $2.91 \times 10^{-2} \text{ S cm}^{-1}$  at 190°C [14]. The low proton conductivity is still the main problem for the metal pyrophosphate materials as the electrolyte. Doping with low valence cation ( $Al^{3+}, In^{3+}, Mg^{2+}, Ga^{3+}, Sc^{3+}, Mg^{2+}$  etc) [11] in  $MP_2O_7$  materials by partial substitution of  $M^{4+}$  is an usually potential way to improve the conductivity because of charge compensation for the low valency cations that provide more number of jump sites and facilitates the hopping of protons. However, doping the low valence cation are normally the different elements, this may affect the structure uniform and even thermal degradation.

In this study, we promoted 10%  $Ce^{3+}$ -doped cerium pyrophosphate ( $Ce^{4+}P_2O_7$ ) as the crystalline phase to achieve a single structure formation. The doping of lower valence cations into  $CeP_2O_7$  could provide more oxygen vacancies in the materials and would increase the basicity of the material bulk [19-20]. The 10%  $Ce^{3+}$  doped  $CeP_2O_7$  membrane proton conductivity was and fuel cell performance range from 180-250°C were studied, and the results indicated that the performance of the inorganic composite membrane was suitable for HT-PEMFC.

## 2. EXPERIMENTAL

$Ce^{3+}$  doped  $CeP_2O_7$  was prepared as follows. Briefly  $CeO_2$  and  $CeCl_3$  powder were mixed in stoichiometric proportions (9:1) and ball-milled for 8 h at 300 rpm using zirconia balls in isopropyl alcohol and then dried at 70 °C for about 20 h. The dried  $CeO_2$ - $CeCl_3$  particles were mixed with 85%  $H_3PO_4$ . This mixture was held with stirring at 90 °C until a high viscosity paste achieved. The paste was calcined in an alumina pot at 350 °C for 2.5 h in  $N_2$  gas ambience to prevent  $Ce^{3+}$  oxidized to completely  $Ce^{4+}$ . The calcined powder was pressed into pellet disks under 200 MPa. The disks (13-mm diameter) were sintered at 300 °C for 8 h in a closed alumina crucible at  $N_2$  protection and were polished with sandpaper. The thickness of the pellet membrane is 1mm. A  $CeP_2O_7$  powder was also prepared using commercially  $CeO_2$  particle.

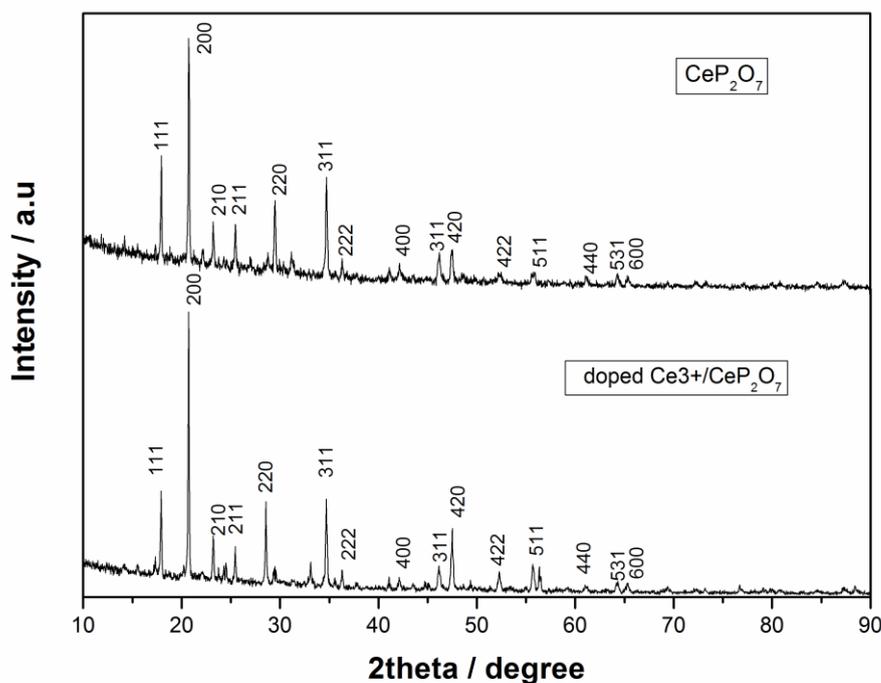
The membrane was painted with colloidal silver on both sides, and dried in an oven at 120°C for 2 hrs. The proton conductivity was measured by the two-point probe method with an AutolabPGSTAT302. The impedance measurements were carried out between frequencies of 1 and 10 kHz. The perturbation voltage was kept at 10mV. The crystal structures of different powders were analysed by X-ray diffraction (XRD, X'Pert PROMPD), with scan range of 5–80° over 2 hrs. The morphologies of the membrane were investigated by a SU-8020 Scanning Electron Microscope.

Fourier transform infrared spectroscopy (FTIR) of different samples was measured on Nicolet 67FT-IR spectrometer system between 4000 and 300  $\text{cm}^{-1}$ . The thermal behaviour was analysed by Thermogravimetric Analysis (TGA, STA449F3). XPS measurement was carried on out on a spectrometer (ESCALAB250Xi) with a Ka anticathode.

Catalyst inks were prepared by blending carbon-supported catalysts (40 wt. % Pt/C, Alfa Aesar) in a water–ethanol mixture under ultrasonic vibration for 30 mins [21, 22]. The ink was deposited on membrane for both anode and cathode directly, and then the MEA were held at 150 °C for 2 hrs. The Pt loading achieves 0.2  $\text{mg cm}^{-2}$ . The silver wires were connected to the sample by the conductive adhesive. 5vol%  $\text{H}_2/\text{Ar}$  and air were fed into anode and cathode at flow rates of 50  $\text{cm}^3 \text{min}^{-1}$  and atmospheric pressure, respectively.

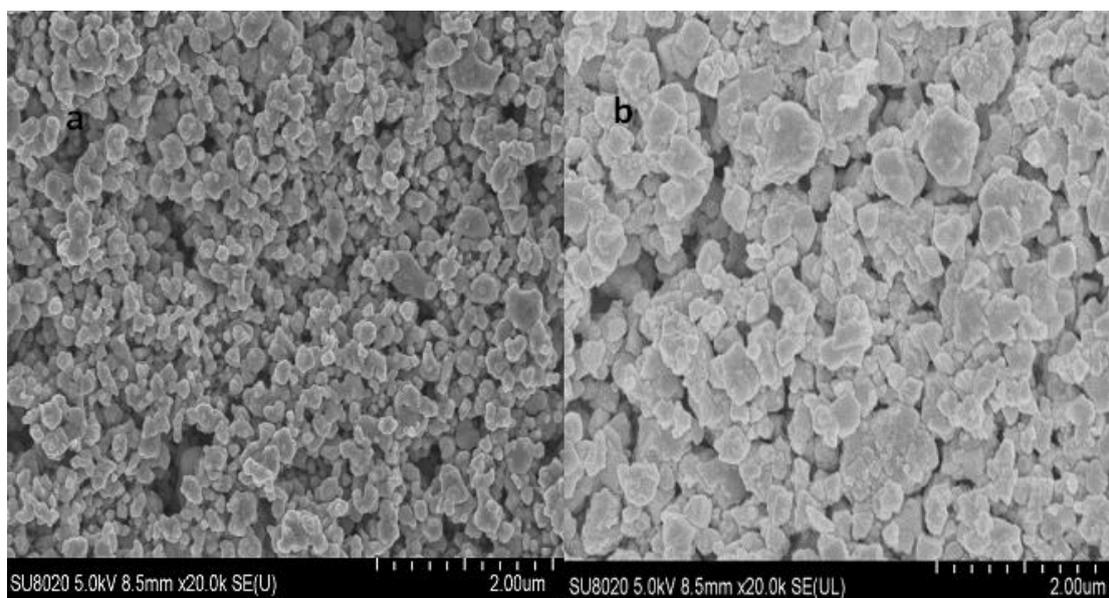
### 3. RESULTS AND DISCUSSION

Figure 1 shows the powder XRD pattern confirming diffraction peaks of  $\text{CeP}_2\text{O}_7$  (JCPDS 16-0584). The (111), (200), (210), (211), (311), (222), (400), (311), (420), (333), (422), (511), (440), (531) and (600) crystal planes of  $\text{CeP}_2\text{O}_7$  were corresponded to the XRD angles at  $17.83^\circ$ ,  $20.71^\circ$ ,  $22.19^\circ$ ,  $25.45^\circ$ ,  $27.63^\circ$ ,  $35.80^\circ$ ,  $37.11^\circ$ ,  $42.57^\circ$ ,  $46.81^\circ$ ,  $47.92^\circ$ ,  $52.36^\circ$ ,  $56.87^\circ$ ,  $62.78^\circ$ ,  $64.74^\circ$  and  $65.93^\circ$  that follows literatures reported [9]. The incorporation of  $\text{Ce}^{3+}$  into the  $\text{CeP}_2\text{O}_7$  lattice occur because the effective ionic radius of trivalent  $\text{Ce}^{3+}$  is same to  $\text{Ce}^{4+}$  (0.087 nm). The lattice parameters calculated form XRD is  $C=8.52 \text{ \AA}$  which fits well agreed with the standard pattern data.



**Figure 1.** XRD pattern of  $\text{CeP}_2\text{O}_7$  and  $\text{CeP}_2\text{O}_7$  with Cu K X-rays

SEM images (Fig. 2) depict the cross section morphologies of  $\text{CeP}_2\text{O}_7$  and  $\text{Ce}^{3+}$  doped  $\text{CeP}_2\text{O}_7$  sintered pellets. In Fig. 2a, it is observed that The pellets are not completely dense, and the presence of micrometer-size pores can be seen. Fig.2b shows that  $\text{Ce}^{3+}$ -doped  $\text{CeP}_2\text{O}_7$  particles are mostly cubic shape and size homogeneously. The particle size of  $\text{Ce}^{3+}$ -doped  $\text{CeP}_2\text{O}_7$  seems larger than the  $\text{CeP}_2\text{O}_7$  that may result a decrease proton transmit due to the small contact area between crystal grains. The densities of the  $\text{CeP}_2\text{O}_7$  and  $\text{Ce}^{3+}$ -doped  $\text{CeP}_2\text{O}_7$  pellet calculated by Archimedes' method, were  $2.09 \text{ g cm}^{-3}$  and  $2.98 \text{ g cm}^{-3}$ , respectively. This density result indicates that the less pores in the  $\text{Ce}^{3+}$ -doped  $\text{CeP}_2\text{O}_7$  membrane that benefits to inhibit the gas crossover.



**Figure 2.** SEM images of membrane cross-sections: a)  $\text{CeP}_2\text{O}_7$  and b)  $\text{Ce}^{3+}$  doped  $\text{CeP}_2\text{O}_7$

FTIR studies on  $\text{CeP}_2\text{O}_7$  and  $\text{Ce}^{3+}$ -doped  $\text{CeP}_2\text{O}_7$  are shown in Fig. 3. The appearance of the broad band at  $1290 \text{ cm}^{-1}$  can be assigned to the P-O-H in plane bending vibration of  $\text{CeP}_2\text{O}_7$ . The symmetric and asymmetric stretching frequencies of  $\text{PO}_3$  in  $\text{P}_2\text{O}_7^{4-}$  are observed at  $1090$  and  $1210 \text{ cm}^{-1}$ , respectively. The asymmetric and symmetric P-O-P bridge stretching modes are generally observed in the regions  $970\text{--}930 \text{ cm}^{-1}$  ( $960 \text{ cm}^{-1}$ ) and  $780\text{--}740 \text{ cm}^{-1}$  ( $747 \text{ cm}^{-1}$ ) regions [23-27]. There was no significant difference between two curves indicating the same chemical element in the materials.

As Fig.4 depicted, the coexistence of the  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  oxidation states are distinguishable [28]. The Ce (3d3/2) and Ce (3d5/2) XPS spectrum obtained from the fine particles are shown in Fig. 4. In addition,  $\text{Ce}^{4+}$  binding energy peaks at  $885.1\text{eV}$ ,  $898.5\text{eV}$ ,  $915.5\text{eV}$ , and also two peaks corresponding to  $\text{Ce}^{3+}$  species at  $881.7\text{eV}$  and  $903.1\text{eV}$  on the  $\text{Ce}^{3+}$  doped  $\text{CeP}_2\text{O}_7$  were clearly observed. The spectral shape shows the existence of two oxidation states  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$ , which confirmed the successful doping of  $\text{Ce}^{3+}$  in the  $\text{Ce}^{4+}\text{P}_2\text{O}_7$ .

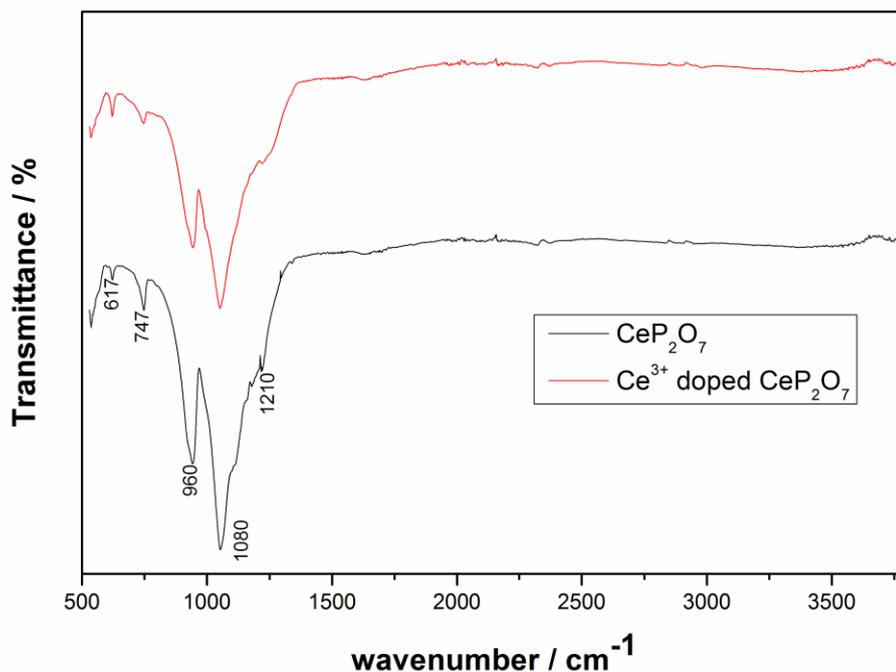


Figure 3. Infrared spectra of  $\text{CeP}_2\text{O}_7$  and  $\text{Ce}^{3+}$ -doped  $\text{CeP}_2\text{O}_7$  with the test resolution of  $4\text{ cm}^{-1}$

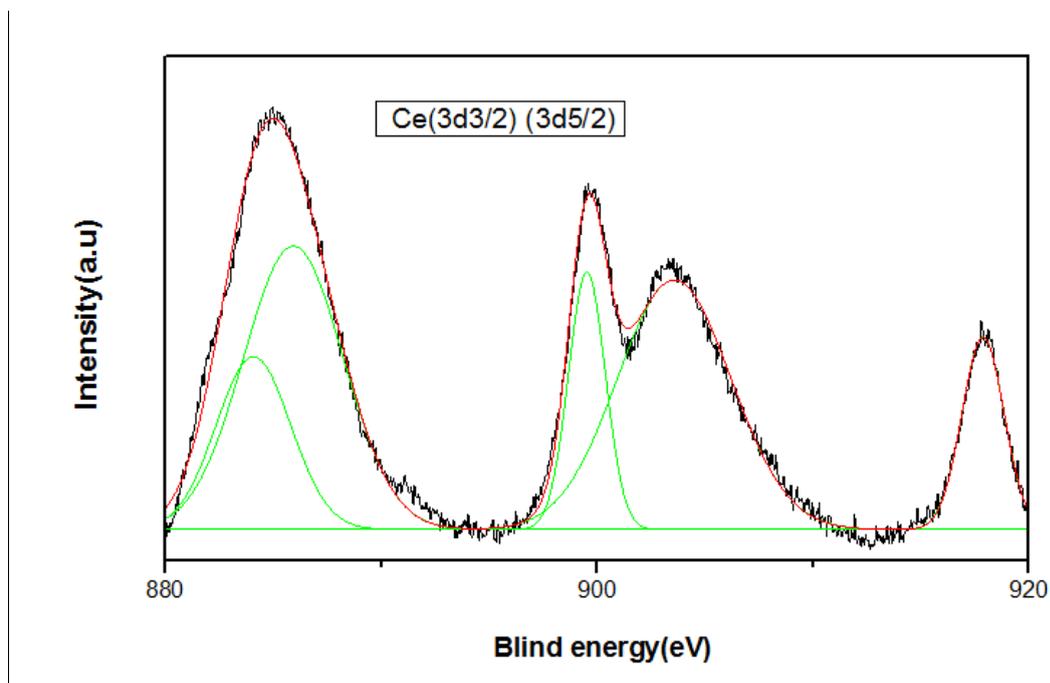
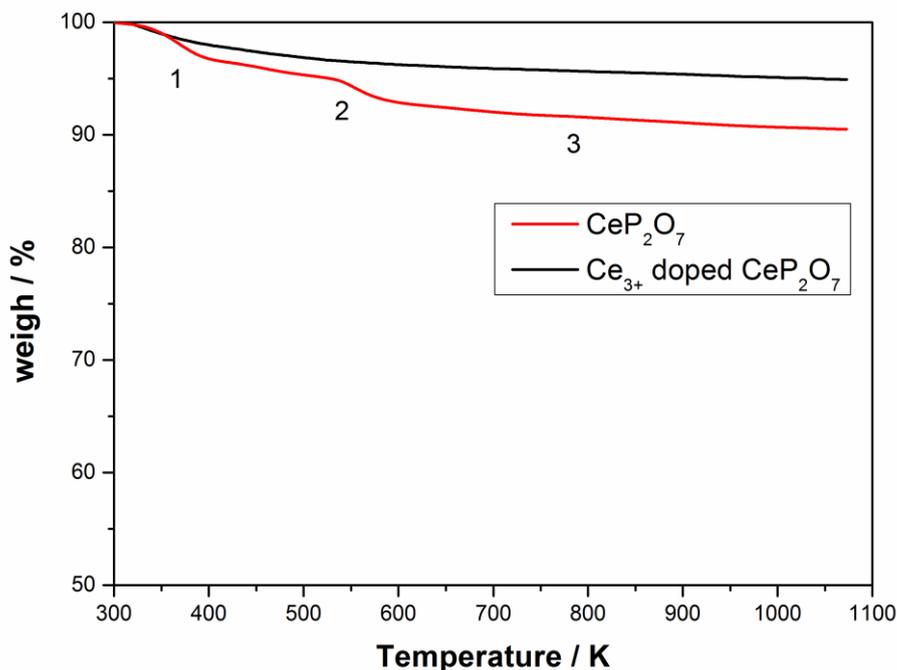


Figure 4. XPS Ce 3d photoemission spectra for Ce (3d3/2) and Ce (3d5/2)

The thermal stability of the  $\text{CeP}_2\text{O}_7$  and  $\text{Ce}^{3+}$  doped  $\text{CeP}_2\text{O}_7$  membranes is studied range from room temperature to  $800\text{ }^\circ\text{C}$  shown in Fig. 5. There are three prominent regions of  $\text{CeP}_2\text{O}_7$  weight loss in the TGA curve. The initial weight loss of about 2.5% below  $180\text{ }^\circ\text{C}$  in region 1 is caused by the water loss. The second region is mainly attributed to the partial thermal decomposition of  $\text{CeP}_2\text{O}_7$  into  $\text{CePO}_4$ ,  $\text{CeP}_3\text{O}_9$ ,  $\text{CeO}_2$  and  $\text{Ce}(\text{PO}_4)_3$  [23]. The third decrease part as shown in region 3 is appearance

of a prominent endotherm at 500°C, which is caused by the decomposition of cerium pyrophosphate into phosphate, metaphosphate and polyphosphate [30]. It was obviously seen that the Ce<sup>3+</sup> doped CeP<sub>2</sub>O<sub>7</sub> keeping stable until 800 °C. The presence of Ce<sup>3+</sup> ions is in favour of the existence of stronger hydrogen bond between the Ce-O networks [31] or weaker intermolecular forces between the P-O-P bonds [32] that may explain the reason for the stability of Ce<sup>3+</sup> doped CeP<sub>2</sub>O<sub>7</sub>.



**Figure 5.** TGA of the prepared CeP<sub>2</sub>O<sub>7</sub>, Ce<sup>3+</sup> doped CeP<sub>2</sub>O<sub>7</sub> heated from room temperature to 800 °C with a heating rate of 5 °C min<sup>-1</sup>

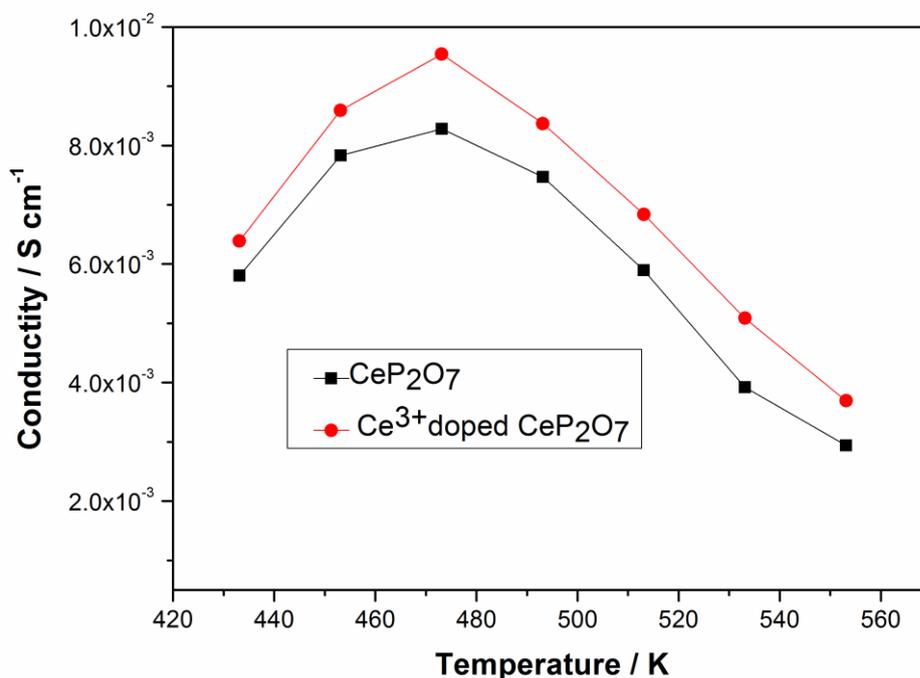
The conductivity of the CeP<sub>2</sub>O<sub>7</sub> membranes is calculated from the impedance data at 150–280°C. CeP<sub>2</sub>O<sub>7</sub> exhibits a measurable conductivity at range of 5.8×10<sup>-3</sup> S cm<sup>-1</sup> to 8.3×10<sup>-3</sup> S cm<sup>-1</sup> from 160°C to 200°C in non-humid atmosphere, and then the conductivity decreases to 2.9×10<sup>-3</sup> S cm<sup>-1</sup> while the temperature up to 280°C in Fig. 6. The conductivity is assumed that a partial disconnection of the P<sub>2</sub>O<sub>7</sub> network for proton conduction caused by the phosphate deficiency that follows the Grotthuss mechanism [34]. The protonic conduction of the solid membrane is incorporated into the CeP<sub>2</sub>O<sub>7</sub> bulk by the following reactions. [11]



Where O<sub>o</sub><sup>•</sup>, V<sub>o</sub><sup>x</sup>, OH<sub>o</sub><sup>x</sup>, PO<sub>4</sub><sub>P<sub>2</sub>O<sub>7</sub></sub><sup>x</sup> and HP<sub>2</sub>O<sub>7</sub><sub>P<sub>2</sub>O<sub>7</sub></sub><sup>x</sup> denote a lattice oxide ion, an oxygen vacancy, an interstitial proton, phosphate ions and hydrogen pyrophosphate defects at pyrophosphate sites, respectively.

The curve in Fig. 6 clearly illustrates that the Ce<sup>3+</sup> doped CeP<sub>2</sub>O<sub>7</sub> (0.01 S cm<sup>-1</sup> at 200 °C) has a higher conductivity by contrast the CeP<sub>2</sub>O<sub>7</sub> membrane in the temperature of 150-280°C. In addition to, the CeP<sub>2</sub>O<sub>7</sub> structure includes a network of MO<sub>6</sub> octahedra sharing corners with P<sub>2</sub>O<sub>7</sub> units,

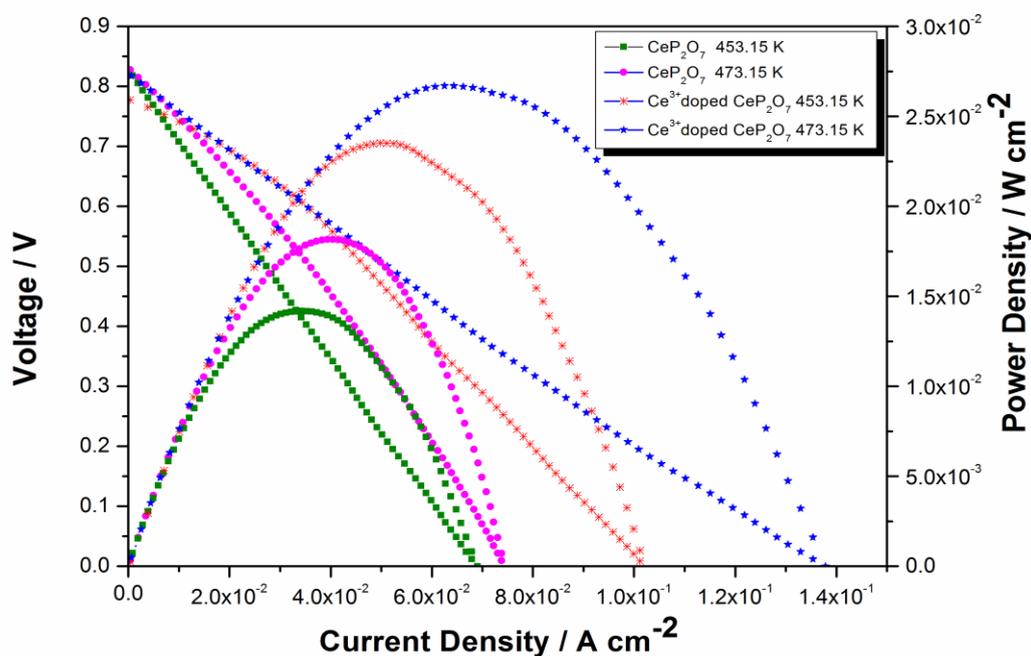
characterized by the presence of intersecting zigzag tunnels delimited by pentagonal windows [32-34]. This specific structure could provide several ion exchange sites and transport pathways which performance as the proton conductivity. Typically, the low valency cations are introduced into the bulk of  $\text{CeP}_2\text{O}_7$  by the partial substitution of  $\text{Ce}^{4+}$  cations is a suitable way to improve the proton exchange capability [38]. The substitution of  $\text{Ce}^{3+}$  for  $\text{Ce}^{4+}$ -site increases the concentration of mobile charge carriers which is expected to increase the conductivity. [34]. The long-range mobility of the proton is much greater than that of the oxygen ion and electron hole [21, 33]. The higher proton conductivity of  $\text{Ce}^{3+}$  doped  $\text{CeP}_2\text{O}_7$  is because of the presence of oxygen vacancies or holes, and also the formation of these charge carriers can be expressed, which benefits of the phosphate ions transmit. The pore size of the  $\text{Ce}^{3+}$  doped  $\text{CeP}_2\text{O}_7$  membrane is larger than the non-doped membrane as shown in SEM image, that resulting in a reduced effective electric circuit of the membrane due to the small contact area between crystal grains. This may be the other reason to affect the conductivity results which should be further explored in the next work. However, in the temperature over  $200^\circ\text{C}$  conductivity began to reduce rapidly, which could be attributed to the decomposition of  $\text{CeP}_2\text{O}_7$ , which could be attributed to the decomposition of  $\text{CeP}_2\text{O}_7$  into secondary phosphate phases, as evidenced from the TGA data. These secondary phosphates such as  $\text{CeO}_2$ ,  $\text{P}_2\text{O}_5$ , cerium orthophosphate ( $\text{CePO}_4$ ) and cerium polyphosphates ( $\text{Ce}_3(\text{PO}_4)_3$ ) [17-18] exhibit much lower ionic conductivity than that of  $\text{CeP}_2\text{O}_7$ .



**Figure 6.** Conductivities of  $\text{CeP}_2\text{O}_7$  and  $\text{Ce}^{3+}$  doped  $\text{CeP}_2\text{O}_7$  composite membranes under anhydrous conditions.

As shown in Fig.7, the polarization and power density curves are obtained at  $180^\circ\text{C}$  and  $200^\circ\text{C}$  under dry conditions for  $\text{CeP}_2\text{O}_7$  and  $\text{Ce}^{3+}$  doped  $\text{CeP}_2\text{O}_7$ . The open circuit voltages (OCVs) of  $\text{CeP}_2\text{O}_7$  and  $\text{Ce}^{3+}$ -doped  $\text{CeP}_2\text{O}_7$  membranes are over 0.8V. The performances of the cells with the

Ce<sup>3+</sup>-doped CeP<sub>2</sub>O<sub>7</sub> composite membranes are significantly better than that of the pristine CeP<sub>2</sub>O<sub>7</sub> membrane. As Fig. 7 shown, the maximum power density of CeP<sub>2</sub>O<sub>7</sub> was approximately 18 mW cm<sup>-2</sup> at the temperature of 200 °C , and the power density value of Ce<sup>3+</sup> doped CeP<sub>2</sub>O<sub>7</sub> was enhanced to 26.6 mW cm<sup>-2</sup>. This improved performance is mainly caused by the superior proton conductivity because of the much proton hopping vacancies construction while Ce<sup>3+</sup> doped. The power density of CeP<sub>2</sub>O<sub>7</sub> incersed from 14.2 to 18.4 mWcm<sup>-2</sup> by increasing the temperature range from 180 to 200°C. The results were also accordance to the variation tendency of membranes conductivity. The voltage losses of the Ce<sup>3+</sup>-doped CeP<sub>2</sub>O<sub>7</sub> membrane are 0.6 V and 0.3 V and the current losses of it from 0.033 to 0.08A cm<sup>-2</sup> at 200°C, and the result cell conductivities are approximately 0.0015 S cm<sup>-1</sup>, which is smaller than the value from the conductivity test. Because, the potential drop of the fuel cell attributed to including the ohmic loss and the cathodic polarization loss [5, 30]. The thickness of membranes reduction and the density of membranes enhancement including electrode optimization should be the other suitable ways to improve the fuel cell performance.



**Figure 7.** Polarization and power density curves of fuel cells operated at 180 °C and 200°C with 5vol% H<sub>2</sub>/Ar and air at atmospheric pressure. Pt Loading is 0.2 mg cm<sup>-2</sup> both anode and cathode.

#### 4. CONCLUSION

In this work, inorganic composite CeP<sub>2</sub>O<sub>7</sub> and Ce<sup>3+</sup> doped CeP<sub>2</sub>O<sub>7</sub> electrolytes were synthetic completely. The doping of Ce<sup>3+</sup> in CeP<sub>2</sub>O<sub>7</sub> composite membranes leads to an increase in conductivity ranging from 0.006 to 0.01 S cm<sup>-1</sup> at temperatures ranging from 160 to 200 °C, although the membrane conductivity rapidly decreased when the temperature is more than 200°C. The Ce<sup>3+</sup> doped

CeP<sub>2</sub>O<sub>7</sub> membrane also suggested better performance results (with a peak power density: 26.2 mW cm<sup>-2</sup> at 200 °C) compared with the 14.2 mW cm<sup>-2</sup> result of the un-doped CeP<sub>2</sub>O<sub>7</sub> membrane. These results conditionally suggest that this material is a potential candidate material for high temperature fuel cells.

#### ACKNOWLEDGMENTS

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