

Fabrication and Fuel Cells Performance of Lanthanum-Doped Cerium Diphosphate Electrolyte

Thanh-Hao Nguyen, Minh-Vien Le*

Faculty of Chemical Engineering, Ho Chi Minh City University of Technology, VNU, 268 Ly Thuong Kiet Street, Distric 10, Ho Chi Minh City, Vietnam
 lmvien@hcmut.edu.vn

Proton conductivity of indium-doped cerium diphosphate (CeP_2O_7) was investigated to explore its potential for application as an electrolyte in intermediate temperature fuel cells. The La^{3+} -doped CeP_2O_7 powder was synthesized by the digestion of metal oxide in a phosphoric acid solution. The structure and ion conductivity of La^{3+} doped CeP_2O_7 were analysed using X-ray diffraction, scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS). Under humidified conditions, the La^{3+} -doped CeP_2O_7 exhibited sufficient conductivity in the intermediate temperature range. The maximum ionic conductivity of $\text{Ce}_{0.95}\text{La}_{0.05}\text{P}_2\text{O}_7$ was $2.00 \times 10^{-2} \text{ Scm}^{-1}$ at 180°C . The maximum power density of the fabricated H_2/air fuel cells using the $\text{Ce}_{0.95}\text{La}_{0.05}\text{P}_2\text{O}_7$ as electrolyte (0.44 mm thickness) was 49.0 mW cm^{-2} at 240°C . The results indicate that $\text{Ce}_{0.95}\text{In}_{0.05}\text{P}_2\text{O}_7$ is a promising material for the fabrication of intermediate temperature fuel cells.

1. Introduction

Many attempts on proton conductor based on inorganic materials have been reported. A number of tetravalent metal diphosphate salts, $\text{M}^{\text{IV}}\text{P}_2\text{O}_7$ ($\text{M} = \text{Sn}, \text{Ti}, \text{Zr}, \text{Ce}$), have been proved the superior conductive properties in the intermediate temperature range of $100 - 350^\circ\text{C}$. This particular temperature range is of interest since it covers most of operating temperatures ranges for energy conversions and chemical processes, and a few solid proton conductors offer viable conductivity and stability for practical applications (Jin et al. 2010). Cerium diphosphate, a class of $\text{M}^{\text{IV}}\text{P}_2\text{O}_7$ compounds, has been demonstrated as a high proton conductor in the intermediate temperature range (Le and Tsai, 2017).

Ion conductivity of CeP_2O_7 was reported of 0.018 Scm^{-1} at 200°C under humidified conditions (Sun et al., 2009). Singh et al. (2012) reported that a maximum conductivity value of CeP_2O_7 was $2.1 \times 10^{-4} \text{ Scm}^{-1}$ at 175°C in air with 6 % H_2O . Most researches have proven that CeP_2O_7 family is necessary for humidified electrolyte to support the number of jump sites in the CeP_2O_7 matrix which lead to increasing proton conductivity.

A partial substitution of foreign elements on the cerium site may enhance the proton conductivity and broaden the temperature window for electrolyte applications (Le et al., 2011). Mg-doped CeP_2O_7 ($\text{Ce}_{0.9}\text{Mg}_{0.1}\text{P}_2\text{O}_7$) exhibited sufficient conductivity in the intermediate temperature range, with the ion conductivity of $4.0 \times 10^{-2} \text{ Scm}^{-1}$ at 200°C in humidified air with 11.4 % H_2O (Le et al., 2011). The Mg doped- CeP_2O_7 widened the temperature range from 160 to 280°C . Sr-doped cerium diphosphate, $\text{Ce}_{0.9}\text{Sr}_{0.1}\text{P}_2\text{O}_7$, has been proved to possess a maximum conductivity of $6.3 \times 10^{-3} \text{ Scm}^{-1}$ at 90°C in air with 12 % H_2O (Singh et al. 2013a); $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{P}_2\text{O}_7$ (Singh et al. 2014a) reached $2.91 \times 10^{-2} \text{ Scm}^{-1}$ at 190°C , in humidified air ($p_{\text{H}_2\text{O}} = 16.2 \text{ kPa}$); $\text{Ce}_{0.9}\text{Mn}_{0.1}\text{P}_2\text{O}_7$ (Singh et al. 2014b) reached $2.24 \times 10^{-2} \text{ Scm}^{-1}$ at 170°C ($p_{\text{H}_2\text{O}} = 16.2 \text{ kPa}$) and $1.4 \times 10^{-3} \text{ Scm}^{-1}$ at 100°C in a wet air atmosphere ($p_{\text{H}_2\text{O}} = 7.4 \text{ kPa}$) for $\text{Ce}_{0.95}\text{Eu}_{0.05}\text{P}_2\text{O}_7$ (Wang et al. 2014). It has been shown in the literatures that acceptor-doped cerium diphosphates exhibit random variations in electrical conductivity, without showing any dependence on nature of the dopants (Singh et al. 2013b).

Lanthanum, the rare earth element, which is located in same group of cerium in the periodic table has the similar chemical and physical properties to those of Cerium. In addition, La^{3+} cation has a lower valance state to Ce^{4+} , which make more interesting in the investigation of La^{3+} -doped CeP_2O_7 , which has not been investigated. In present work, we have synthesised the $\text{Ce}_{1-x}\text{La}_x\text{P}_2\text{O}_7$ and investigated its proton conductivities

at various temperatures by electrochemical impedance spectroscopy (EIS). The phase composition and microstructure of La^{3+} -doped cerium diphosphate were also explored. Fuel cells using La^{3+} -doped cerium diphosphate were fabricated and tested the fuel cell performance under intermediate temperature and humidified conditions.

2. Experiments

2.1 Preparation of La^{3+} -doped CeP_2O_7 samples

La^{3+} -doped CeP_2O_7 powder was obtained in the same manner as reported previously (Le et al., 2011). The molar ratio of phosphoric acid (85 %, Acros) to metal was controlled to be 2.3 : 1. The resultant yellow paste after refluxing was calcined at 300 °C for 8 h. The calcined sample was ground in agate pestle and mortar. Disk samples ($\text{Ce}_{1-x}\text{La}_x\text{P}_2\text{O}_7$, $x = 0, 0.05, 0.1, 0.2$) were prepared by uniaxially pressing the ground powder into a stainless steel mould (diameter 14 mm and thickness 0.5 - 1.2 mm) at hydrostatic pressure of 300 MPa, then sintered at 400 °C for 8 h.

2.2 Characterisation of La^{3+} -doped CeP_2O_7

The X-ray powder diffraction (XRD) patterns of the samples were obtained at ambient temperature on D2 Phaser, Bruker diffractometer using a $\text{CuK}\alpha$ radiation source (1.5418 Å) and nickel filter operating at 50 kV and 200 mA. Diffraction patterns were recorded in the 2θ range of 15 – 70° with the step size of 0.03°. The infrared (IR) spectra were collected between 400 – 4,000 cm^{-1} using a Fourier-transform infrared spectrometer, FTIR, (Digilab FTS-3500, Biorad). The IR sample was pelletised into a powdered mixture that contained 3 wt% cerium phosphate (400 °C calcined) and 97 % KBr. The reported spectra are the average over 64 scans.

2.3 Impedance measurement

It has been proved that the migration of protons in CeP_2O_7 -based material occurs by hopping from oxygen vacancy site and water molecule Singh et al. (2012). The CeP_2O_7 membrane should be humidified to increase the number of vehicle sites which lead to the facilitated conductivity of CeP_2O_7 . In this research, the La^{3+} -doped CeP_2O_7 samples were measured in a sealed stainless steel chamber with tight humidity and temperature control. The chamber humidity was manipulated by the air flow passing a humidifier, pre-calibrated to supply nearly saturated humidified air at a specific temperature (~93 % relative humidity, <60 °C). The phosphate disk was polished and printed with a silver layer on both sides. The silver electrodes were pressed against two 0.2 mm gold wires, then connected to the electrical feedthroughs and then placed in the chamber. Impedance data were collected with a S1260 A frequency response analyser. The steady impedance data were fitted with an equivalent circuit to get R_{gi} and R_{gb} , the resistance of bulk and grain boundary contribution, respectively. The value of the proton conductivity σ is calculated as Eq(1), where t is the thickness of the disk and A is the disk area.

$$\sigma = tA^{-1}(R_{gi} + R_{gb})^{-1} \quad (1)$$

2.4 Fuel cell fabrication and evaluation

The membrane-electrode assembly (MEA) was prepared by compressing a polished $\text{Ce}_{1-x}\text{La}_x\text{P}_2\text{O}_7$ pellet (Figure 1), which had been sintered at 400 °C for 8 h, against two circular area of 1.05 cm^2 gas diffusion layers of carbon paper (GDL-10BC, SIGRACET). One side of these two carbon papers was coated with a catalyst ink which was made by mixing 50.0 wt% of Pt/C catalyst powder (20 wt% Pt supported by Vulcan, BASF), 35.0 wt% of $\text{Ce}_{0.95}\text{La}_{0.05}\text{P}_2\text{O}_7$ powder (5CLaP) and 15 wt% of polytetrafluoroethylene (PTFE, 60 wt%, Aldrich). In order to obtain homogeneous ink, an appropriate amount of glycerol solvent was added to the above mixture and mixed using mortar and pestle. The cathode and anode were dried at 150 °C to remove the glycerol solvent. The Pt loading for both anode and cathode was calculated to be 0.6 mg cm^{-2} . The fuel was humidified hydrogen, 50 % H_2 and 50 % N_2 , while the oxidant was humidified air. The performance of the hydrogen/air fuel cell was measured by using a Keithley238 source-measure unit.

3. Result and discussion

Figure 2 shows the XRD patterns of $\text{Ce}_{1-x}\text{La}_x\text{P}_2\text{O}_7$ powder ($x = 0, 0.05, 0.1, 0.2$) calcined at 300 °C for 12 h. All detected peaks of $\text{Ce}_{1-x}\text{La}_x\text{P}_2\text{O}_7$ samples ($x = 0, 0.05$) at 2θ 17.91°, 20.72°, 23.16°, 25.44°, 29.49°, 34.71°, 47.49 and 55.68° were well indexed to the cubic CeP_2O_7 structure (Pa-3) by comparison with the JCPDS Card file No. 16-0584. The impurity phase of CeO_2 and other unidentified signals were detected in $\text{Ce}_{0.9}\text{La}_{0.1}\text{P}_2\text{O}_7$ and $\text{Ce}_{0.8}\text{La}_{0.2}\text{P}_2\text{O}_7$ samples. Peaks of CeO_2 were detected at 2θ of 28.7° and 33.3°, whereas peaks of

unidentified phases were detected at 22.8° , 25.1° , 27.2° , 31.4° . The peaks of the CeO_2 residue intensified as the La^{3+} concentration increased. According to the X-ray diffraction patterns, it is clearly shown in Figure 2b that the peaks shift to low diffraction angle due to the larger ionic size of La^{3+} 0.113 nm (Ali et al., 2013) than that of Ce^{4+} . These results indicated that 5 mol% La^{3+} was the substitutable limiting concentration for Ce^{4+} .

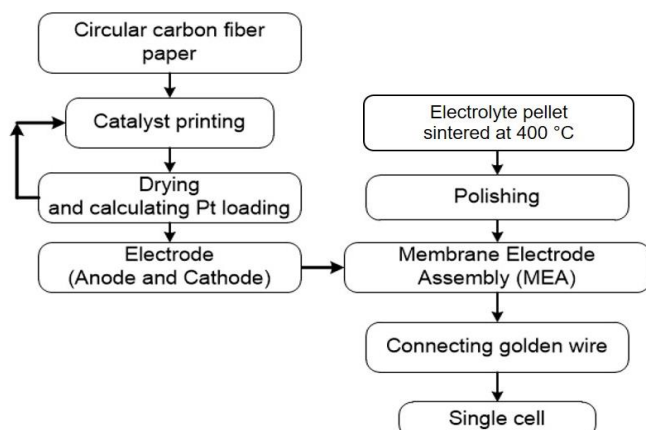


Figure 1: Schematic of single cell assembly

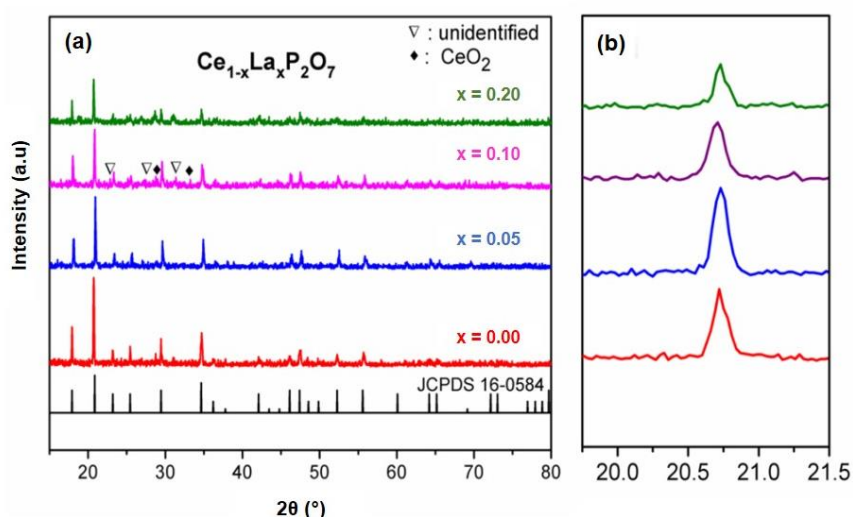


Figure 2: X-ray diffraction patterns of the synthesised $\text{Ce}_{1-x}\text{La}_x\text{P}_2\text{O}_7$ powder

Similar to 300°C calcined samples, the XRD patterns of 400°C calcined samples as shown in Figure 3a indicate identical peaks of CeP_2O_7 structure. Peak intensities of 400°C annealed pellets were higher than that of 300°C . This implied that the CeP_2O_7 based material is thermally stable up to 400°C . All further samples, therefore, were treated at a maximum of 400°C for 8 h.

To evaluate the utilisation of La-doped cerium diphosphate for fuel cell application, the synthesised powder was dry pressed into circular-shape plate with 14 mm in diameter and 0.40 – 1.0 mm in thickness, sintered at 400°C for 8h before polished both sides to the designed thickness and dried in electric oven. The 400°C sintered pellet was microstructure analysed using a field-emission scanning electron microscope (FE-SEM, JSM6500F, JEOL). Figure 3b to 3e show the top-view image of four pellets ($x = 0, 0.05, 0.1, 0.2$) with the least densification, indicating that a number of micron sized pores dispersed in small cubic grains still remained in the sample. This is similar to the observation of the Mg-doped CeP_2O_7 (Le et al., 2011). The relative density of the $\text{Ce}_{0.95}\text{La}_{0.05}\text{P}_2\text{O}_7$ pellet prepared in this study was estimated to be $\sim 74.7\%$, whereas, the $\text{Ce}_{0.90}\text{La}_{0.1}\text{P}_2\text{O}_7$ pellet (10CLaP) was measured to be 66.1% , being lower than that reported for Mg^{2+} -doped CeP_2O_7 (Le et al., 2011) or In^{3+} -doped CeP_2O_7 (Le et al., 2017) prepared in a similar heating treatment temperature.

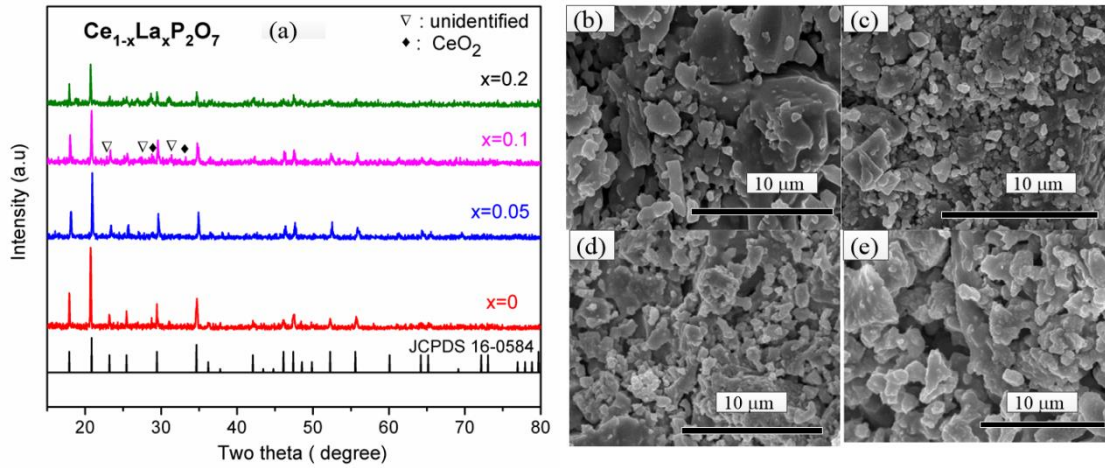


Figure 3: (a) X-ray diffraction patterns and microstructure of the $Ce_{1-x}La_xP_2O_7$ pellets calcined at 400 °C for 8 h (b) $x = 0$, (c) $x = 0.05$, (d) $x = 0.10$, (e) $x = 0.20$

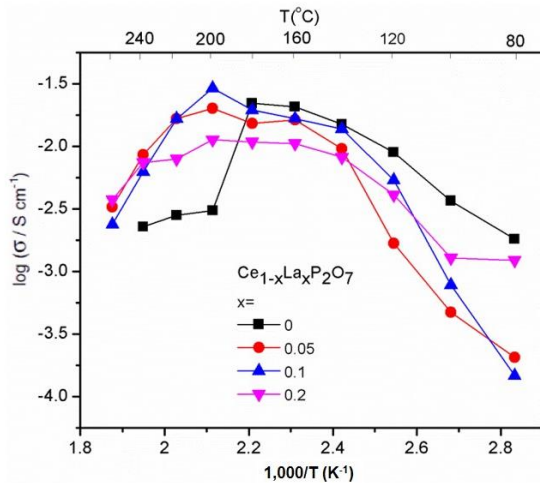


Figure 4: Variation in conductivity of 400 °C-sintered $Ce_{1-x}La_xP_2O_7$ vs. temperature under humidified conditions

Another material's characteristic is proton conductivity property. Humidification is critical to the proton conductivity in the cerium pyrophosphate by the hopping mechanism (Le et al., 2011). The samples were needed to obtain a steady-state humidified sintered disk at 80 °C, and the time it took to reach the steady-state value was shorter as the measurement temperature increased. The conductivity as a function of temperature at 80 – 260 °C was performed. As shown in Figure 4 the conductivity values of $Ce_{1-x}La_xP_2O_7$ ($x = 0, 0.05, 0.1$) samples are higher than 10^{-2} Scm^{-1} , a required conductivity for electrolyte applications and higher than that of $Ce_{0.8}La_{0.2}P_2O_7$ sample due to impurity phases, as mentioned in Figure 3a. When the temperature became higher than 180 °C, the temperature dependence of the samples began to differ from each other. Conductivity of the undoped sample dropped from $1.71 \times 10^{-2} \text{ Scm}^{-1}$ to $2.51 \times 10^{-3} \text{ Scm}^{-1}$, whereas, the conductivities of other samples $Ce_{1-x}La_xP_2O_7$ ($x = 0.05, 0.1$) were still nearly constant when temperature increase up to 220 °C. As a result, the undoped CeP_2O_7 would be more suitable for low-temperature applications, in the range of 120 – 180 °C. Figure 4 shows that the maximum proton conductivities of $Ce_{0.95}La_{0.05}P_2O_7$ and $Ce_{0.90}La_{0.10}P_2O_7$ were measured to be $2.00 \times 10^{-2} \text{ Scm}^{-1}$ at 180 °C and $2.29 \times 10^{-2} \text{ Scm}^{-1}$ at 200 °C. The applicable temperature range of the $Ce_{0.95}La_{0.05}P_2O_7$ and $Ce_{0.90}La_{0.10}P_2O_7$ samples ($\sigma \geq 1.0 \times 10^{-2} \text{ Scm}^{-1}$) was 120 – 250 °C, wider than that of the un-doped sample. It can be concluded that the 400 °C-sintered $Ce_{1-x}La_xP_2O_7$ ($x = 0.05, 0.1$) samples had the most conductive composition in this investigation.

The performance of fuel cell Pt/C| 10CLaP |Pt/C using a 0.43 mm thick electrolyte was evaluated at various temperatures under humidified H_2 /air fuel cell conditions as shown in Figure 5a. The open-circuit voltages (OCVs) at the tested temperatures were between 0.50 V and 0.65 V, considerably lower than the theoretical

value of ~ 1.1 V. The low OCVs of this cell were due to the lesser densification of electrolyte, resulting in the physical leakage of hydrogen gas through the electrolyte, as our sensor detected the low of hydrogen concentration at the cathode side. The peak power density of this cell reaches low value of 28.9 mW cm^{-2} at 140°C .

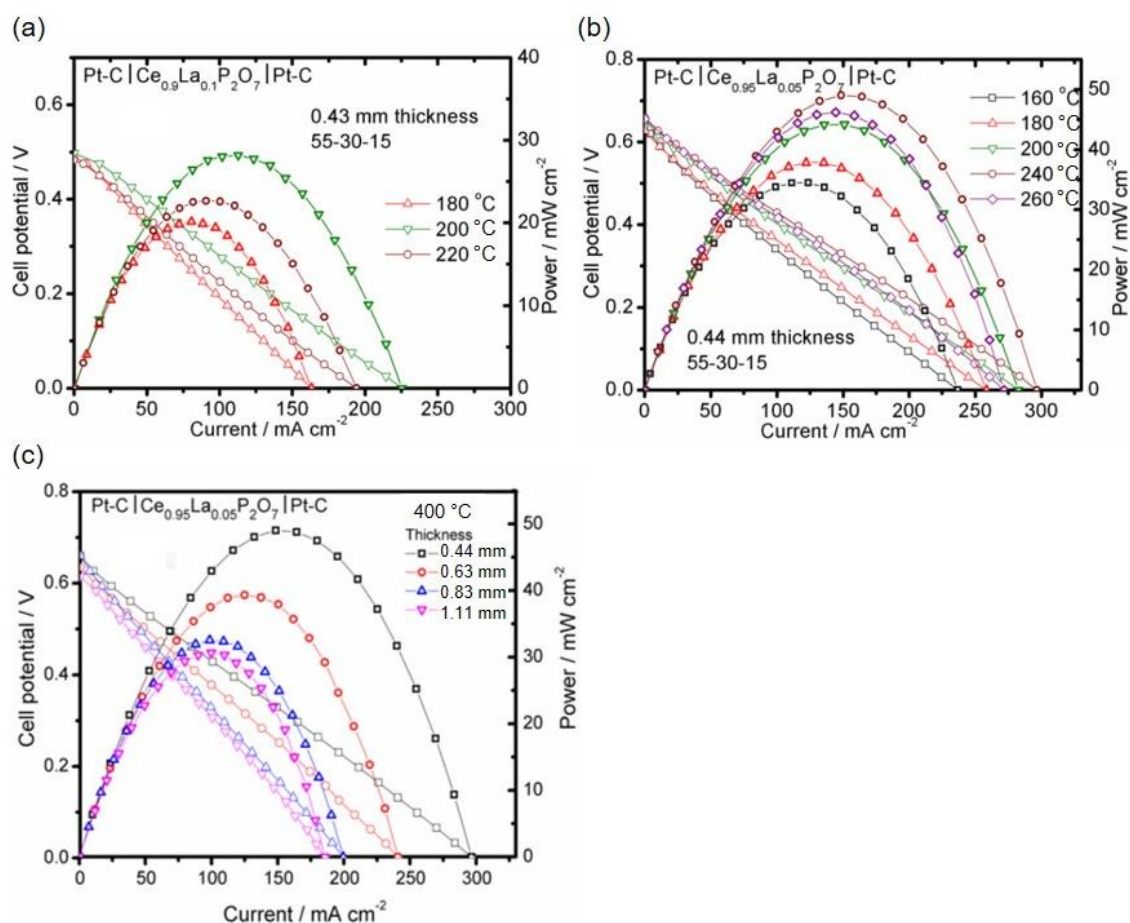


Figure 5: Cell voltage and power density of fuel cells vs. temperature under humidified conditions using electrolytes, (a) $\text{Ce}_{0.9}\text{La}_{0.1}\text{P}_2\text{O}_7$ (b) $\text{Ce}_{0.95}\text{La}_{0.05}\text{P}_2\text{O}_7$ and (c) $\text{Ce}_{0.95}\text{La}_{0.05}\text{P}_2\text{O}_7$ with different thickness

The higher densification of electrolyte ($x = 0.05$) measured of 74.7 %, the OCVs value increase, a range from 6.5 to 6.8 V as illustrated in Figure 5b. The Pt/C | 5CLaP | Pt/C cell performance was strongly dependent on the operating temperature. The peak power density increased in value with the increasing operating temperature, reaching the maximum value of 49.0 mW cm^{-2} at 240°C , and then decreased to 46.2 mW cm^{-2} at 260°C . Deducing from this, the power density of this intermediate temperature fuel cell was strongly influenced by the conductivity of the electrolyte, which followed the same trend as the proton conductivity. It is concluded that this fuel cell is suitable for operating at around 220°C . Figure 5c shows the cell voltage and power density curve of the Pt/C | 5CLaP | Pt/C fuel cells in relation to the differences in the thickness of the electrolyte, from 0.44 to 1.11 mm. Cell performance decrease with increasing thickness of electrolyte due to increasing ohmic resistance. The performance of this cell Pt/C | 5CLaP | Pt/C using $\text{Ce}_{0.95}\text{La}_{0.05}\text{P}_2\text{O}_7$ electrolyte thickness of 0.44 mm was 49.0 mW cm^{-2} at 240°C , which was higher than those of the CeP_2O_7 cell, reported by Sun et al. (2009), (48.9 mW cm^{-2} at 140°C), the H_3PO_4 doping PTFE/ $\text{Sn}_{0.95}\text{Mg}_{0.05}\text{P}_2\text{O}_7$ cell reported by Wang et al. (2015). These peak power values were much lower than that of the $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$ cell (264 mW cm^{-2} at 250°C) (Heo et al., 2006), and that of the cell fabricated using a composite electrolyte of H_3PO_4 -doped PBI/SAPO, which was 439.6 mW cm^{-2} at 200°C (Jin et al., 2011). The low power of cell could have resulted from the less-ideal cell potential and thick electrolyte membrane. The result indicates that $\text{Ce}_{0.95}\text{La}_{0.05}\text{P}_2\text{O}_7$ is a promising electrolyte for intermediate temperature fuel cells.

4. Conclusions

In this study, La-doped CeP_2O_7 were synthesised with varying lanthanum doping levels, and the proton conductivity in the intermediate temperature range was investigated. The result of XRD indicates that single phase $\text{Ce}_{0.95}\text{La}_{0.05}\text{P}_2\text{O}_7$ was successfully synthesised. The higher value and wider range of conductivities were found in $\text{Ce}_{0.95}\text{La}_{0.05}\text{P}_2\text{O}_7$ sample. The maximum power density of 49.0 mW cm^{-2} at $240 \text{ }^\circ\text{C}$ was generated by fuel cells fabricated using the $\text{Ce}_{0.95}\text{La}_{0.05}\text{P}_2\text{O}_7$ electrolyte. The fuel cell can be improved by increasing densification and decreasing the thickness of 5CLaP electrolyte.

References

- Ali A.I., Ahmed M.A., Okasha N., Hammam M., Son J.Y., 2013, Effect of the La^{3+} ions substitution on the magnetic properties of spinal Li-Zn-ferrites at low temperature, *Journal of Materials Research and Technology*, 2, 356-361.
- Heo P., Shibata H., Nagao M., Hibino T., Sano M., 2006, Performance of an intermediate temperature fuel cell using a proton conducting $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$ electrolyte, *Journal of the Electrochemical Society*, 153, 897-901.
- Jin Y.C., Lee B., Hibino T., 2010, Development and application of SnP_2O_7 -based proton conductors to intermediate temperature fuel cells, *Journal of the Japan Petroleum Institute*, 53, 12-23.
- Jin Y.C., Nishida M., Kanematsu W., Hibino T., 2011, An H_3PO_4 -doped polybenzimidazole/ $\text{Sn}_{0.95}\text{Al}_{0.05}\text{P}_2\text{O}_7$ composite membrane for high-temperature proton exchange membrane fuel cells, *Journal of Power Sources*, 196, 6042-6047.
- Le M.V, Tsai D.S., Yang C.Y., Chung W.H., Lee H.Y., 2011, Proton conductors of cerium pyrophosphate for intermediate temperature fuel cell, *Electrochimica Acta*, 56, 6654-6660.
- Le M.V, Tsai D.S., 2017, Proton conducting fuel cells using the indium-doped cerium diphosphate electrolyte, *Chemical Engineering Transactions*, 56, 361-366.
- Singh B., Im H., Park J., Song S., 2012, Electrical behavior of CeP_2O_7 electrolyte for the application in low-temperature proton-conducting ceramic electrolyte fuel cells, *Journal of the Electrochemical Society*, 159, 819-825.
- Singh B., Im H., Park J.Y, Song S., 2013a, Studies on ionic conductivity of Sr^{2+} -doped CeP_2O_7 electrolyte in humid atmosphere, *The Journal of Physical Chemistry C*, 117, 2653-2661.
- Singh B., Jeon S.Y., Im H.N., Park J.Y., Song S.J., 2013b, Electrical conductivity of M^{2+} -doped ($\text{M} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$) cerium pyrophosphate-based composite electrolytes for low-temperature proton conducting electrolyte fuel cells, *Journal of Alloys and Compounds*, 578, 279-285.
- Singh B., Jeon S.Y., Kim J.H., Park J.Y, Bae C., Song S.J., 2014a, Ionic Conductivity of Gd^{3+} doped cerium pyrophosphate electrolytes with core-shell structure, *Journal of the Electrochemical Society*, 161, 464-472.
- Singh B., Kim J.H., Jeon S.Y., Park J.Y., Song S.J., 2014b, Mn^{2+} -doped CeP_2O_7 composite electrolytes for application in low temperature proton-conducting ceramic electrolyte fuel cells, *Journal of the Electrochemical Society*, 161, 133-138.
- Sun X., Wang S., Wang Z., Ye X., Wen T., Huang F., 2009, Proton conductivity of CeP_2O_7 for intermediate temperature fuel cells, *Solid State Ionics*, 179, 1138-1141.
- Wang H., Sun L., Luo C., Fan S., 2014, Studies on ionic conduction in $\text{Ce}_{0.95}\text{Eu}_{0.05}\text{P}_2\text{O}_7$ at intermediate temperatures, *Bulletin of the Korean Chemical Society*, 35, 1465-1468.
- Wang H., He X., Shi Y., Sun L., Luo C., Cui Y., 2015, A H_3PO_4 -doped polytetrafluoroethylene/ $\text{Sn}_{0.95}\text{Mg}_{0.05}\text{P}_2\text{O}_7$ proton-conducting inorganic-organic composite electrolyte, *Materials Letters*, 145, 1-3.