

Effects of $(\text{Li-Na})_2\text{CO}_3$ on The Electrical Properties of Calcia-Stabilized Zirconia/Carbonate Composite Electrolytes

Aiman Iqbal¹, Pramujo Widiatmoko¹, and Hary Devianto^{1,*}

¹ Department of Chemical Engineering, Faculty of Industrial Technology, Institut Teknologi Bandung, Jl. Ganesha No. 10, Bandung 40132, Indonesia.

Abstract. Calcia-Stabilized Zirconia (CSZ) is potential as low-cost electrolytes material for Solid oxide fuel cell (SOFC). It is fluorite structure widely known as oxygen ion conductors. Addition of carbonate salt into fluorite-based electrolyte is common to overcome low conductivity of CSZ as well as to decrease sintering temperature. Increase of ionic conductivity in the SOFC electrolyte is also influenced by presence of protons (H^+), so it is called mixed-ion electrolytes. In this study, the effect of sintering temperature and carbonate content prepared from mixture of Li_2CO_3 and Na_2CO_3 on the relative density, ionic conductivity and microstructure of electrolyte and fuel cell performance was investigated. The sintered CSZ/carbonate samples were examined physically and electrochemically by using SEM, TEM, XRD, and EIS. The unique detail of nanostructure for CSZ/carbonate was investigated by TEM. The XRD is to observed peak associating with CSZ, Li_2CO_3 , and Na_2CO_3 , as well as its crystallinity. Moreover, the electrolyte resistance was measured by EIS so that the proton conductivity and oxygen conductivity of CSZ/carbonate can be calculated. The improvement of low-cost electrolyte material such as CSZ can be realized by providing protons pathway.

1. Introduction

Fuel cell is an energy conversion device that produces electricity by electrochemical reaction. A fuel cell consist of two electrodes and electrolyte. Fuel is fed to the anode where it is oxidized and oxidant is fed to the cathode where it is reduced. Fuel cells are classified by electrolyte and temperature consist of polymer electrolyte membrane fuel cells (PEMFC), alkaline fuel cells (AFC), molten carbonate fuel cells (MCFC) and solid oxide fuel cells (SOFC). Among the types of fuel cells, SOFC offer diversified advantages such as fuel flexibility, desirable energy (chemical-to-electrical) conversion efficiency that unlimited by Carnot cycle, chemically-non pollutant, lower emission of gases, generation of heat and electricity¹.

SOFC are one of the most promising fuel cell technology. The electrolytic material, being the heart of an SOFC unit has been a topic of interest and continuous development among many researchers. Nernst, in the 1890s, recognized yttria-stabilized zirconia (YSZs) as a potential electrolyte material owing to its property of oxide ion conductivity². For high-temperature cells operating above 800°C , doped zirconia, and especially yttria-stabilized zirconia (YSZ), remains the material of choice for the electrolyte. The long-term chemical stability of YSZ and compatibility with electrode materials are well proven. The synthesis of reactive zirconia powder and thin dense electrolyte film fabrication by tape casting,

screen printing, calendaring, and chemical-electrochemical vapor deposition (EVD) processes are also well understood for implementation in large-scale manufacturing³. But the problems are caused by electrolyte material that function only a high temperature and lower ionic conductivity at lower temperature.

Stabilized-zirconia (ZrO_2), especially yttria-stabilized zirconia, is the most common electrolyte in SOFCs because the material possesses an adequate level of oxygen-ion conductivity and exhibits desirable stability in both oxidizing and reducing atmospheres. The properties of stabilized zirconia have been extensively studied. Currently applicated SOFC are based on oxides, for example YSZ and ceria with a fluorite structure. Fluorite has a simple structure group $Fm\bar{3}m$.

ZrO_2 , in its pure form, does not serve as good electrolyte, primarily because its ionic conductivity is too low. At room temperature, ZrO_2 has a monoclinic (*m*) crystal structure. The monoclinic structure changes to a tetragonal (*t*) form above 1170°C and to a cubic fluorite structure above 2370°C . The cubic phase exists up to the melting point of 2680°C . However, the addition of certain aliovalent oxides stabilizes the cubic fluorite structure of ZrO_2 from room temperature to its melting point and, at the same time, increases its oxygen vacancy concentration⁴. The most commonly used dopants are CaO , MgO , Y_2O_3 and Sc_2O_3 .

* Corresponding author: hardev@che.itb.ac.id

Yttria-stabilized zirconia material has been widely used in SOFC as electrolyte. However, yttria material is expensive and it is not widely available especially in Indonesia. Calcia can stabilize zirconia to become CSZ in cubic phase, which is the most stable phase to allow the flow of oxygen ions. Calcia has an advantage as it can be operated at a lower temperature if it is combined with other material with high ionic conductivity⁵. Therefore calcia-stabilized zirconia is potential as low-cost material for electrolytes material for SOFC.

Electrolyte conductivity has been found to be greatly influenced by the grain boundary and grain resistance that are, in turn, affected by the grain size⁶. Grain boundaries or interior contacts between particles are barriers to limit the ionic conductivity since the grain boundary conductivity is much lower than (order) that of the grain thus blocks the ionic transport. Engineering of the grain boundaries is a top option to improve and develop material ionic conductivity⁷. In single phase materials, the nanosized particles expose large surfaces leading to high surface energy⁶. Second phase material can create interfaces and surface with effective functions. Addition of carbonate salt into fluorite based given proton pathway.

Wang et al.⁸ fabricated SDC/carbonate (SDC/sodium carbonate) electrolytes based on core-shell type of particles. The particle size was < 100 nm and thickness of amorphous sodium carbonate shell varied from four to six nm. Proton conductivity (10^{-2} S cm^{-1} at 350 $^{\circ}$ C) varies from one to two orders of magnitude higher than oxygen conductivity in the temperature range 200–600 $^{\circ}$ C. Huang⁹ was investigated about the cell with SDC/(Li–Na)₂CO₃ composite electrolyte showed the best performances, and the cell with SDC/(Li–K)₂CO₃ composite electrolyte showed slightly higher performances than the cell with SDC/(Li–K)₂CO₃ composite electrolyte. It indicates that the conduction mechanism of SDC/carbonate composite electrolytes is distinct in an air atmosphere and in a H₂/air fuel cell atmosphere. The possible oxygen ion/proton conduction in SDC/carbonate composites and excellent cell performances make them a novel electrolyte for cost-effective low-temperature SOFC.

Fuel cells with such an electrolyte have delivered attractive power output at low temperature. The dual ion electrolytes can combine the advantages of proton and oxygen ion conduction. Due to the dual ion conductivity, D-SOFCs no longer require an external humidification device, which can simplify the systems. By optimizing electrode materials and stability, D-SOFCs can achieve better performance at intermediate to low temperatures¹⁰.

In this study, the effect of sintering temperature and carbonate content prepared from mixture of Li₂CO₃ and Na₂CO₃ on the relative density, ionic conductivity and microstructure of electrolyte and fuel cell performance was investigated. Li₂CO₃ and Na₂CO₃ in the molar ratio of 52Li:48Na to form a binary carbonate eutectic with a melting point temperature around 490 $^{\circ}$ C¹¹. The sintered

CSZ/carbonate samples were examined physically and electrochemically by using SEM, TEM, XRD, and EIS.

2. Methodology

The process of producing CSZ/carbonate consist of milling, dry pressing, and sintering. First step of the research was started with milling ZrO₂, CaO, PEG, PVA, Li₂CO₃ and Na₂CO₃. ZrO₂ and CaO materials were mixed with a weight ratio of 97:3. After that, PVA was added as a binder as much as 1% by weight and PEG as a plasticizer as much as 1% by weight. Li₂CO₃ and Na₂CO₃ materials were added with a molar ratio of 52:48. The composition of Li₂CO₃ and Na₂CO₃ was varied at 5,5%, 6,5% and 7,5% total weight from CSZ. Then all materials were mixed with ethanol as medium. The milling process was carried out using a ball milling for 12 hours and speed 40 rpm rotation. The process was then followed by filtration to obtain CSZ/carbonate powder. The next step was to produce electrolyte powder by drying process in oven at the temperature of 100 $^{\circ}$ C for 24 hours. The powder was dry pressed at 500 bar during 5 minutes. The last step CSZ/carbonate powder was sintered at various temperature such as 900, 1000, and 1100 $^{\circ}$ C.

Characterization was carried out on CSZ/carbonate electrolyte, including crystal structure analysis using x-ray diffractometer (XRD) along with microstructure and nanostructure analysis using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The electrolyte resistance was measured by electrochemical impedance spectroscopy (EIS) in a temperature range of 600–800 $^{\circ}$ C. Silver paste was painted on both surfaces of electrolyte. The resistivity under reducing or oxidizing atmosphere was monitored by continuously supplying anode gas (5% H₂, 95% N₂) or cathode gas (static air) to both sides of the electrolyte.

3. Result and Discussion

Through the review of CSZ electrolyte which has a single-phase material, the approach taken is to develop a material with two phases to form a strong interface. The carbonate salts bring some interesting results such as lowering sintering temperature, increasing ionic conductivity and enhancing the mechanical properties. This technology can realize superionic materials by building interfaces to form ion highways. As illustrated in Fig.1, the positive ions or protons (H⁺) pass through the interfaces of the particles while oxygen ions (O²⁻) pass through the host particles of CSZ. A Swing Model was further proposed for explaining the proton conduction in the CSZ/carbonate such as the mechanism that occurs in the Samarium-Doped Ceria/carbonate.

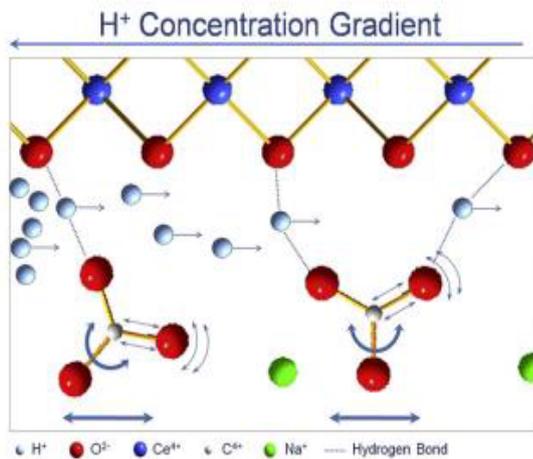


Fig. 1. Swing model pathway for SDC/carbonate ⁸.

Chen et al ¹¹ investigated that the molten carbonate contributes to the total ionic conductivity of the composite, besides the oxygen ionic conductivity. While it is worthy to point out that only the source ions (oxygen ions, here) can dedicate the effective ionic conductivity and power output. When the temperature overcomes 500°C, the solid oxide serves as a matrix with liquid carbonate phase surrounded. Continuous phase interface is consequently formed. Both the SDC and interface phase provide percolated networks for ions to pass through. Some pores existing in the electrolyte are observed in the cross-sectional images. Due to the low sintering temperature of only 700°C which is restrained by the carbonate in the electrolyte, it is hard for the electrolyte to be fully dense. However, the composite electrolyte can still be used as an electrolyte of SOFC because the carbonates melt at working temperature and serve as seals to avoid gas crossover. When the temperature lowers down, the carbonates become solid and shrank, leading to residual pores in the composite electrolyte ¹². So therefore, adding salt carbonate especially Li_2CO_3 and Na_2CO_3 can serve a matrix in the CSZ electrolyte. The performance of CSZ electrolyte, which was originally a conductor of oxygen ions, was later improved to deliver protons so that it became a mixed ion electrolyte which enhanced total ionic conductivity and mechanical properties. While still speculative, these findings are interesting, and further research is in progress

References

1. Hussain, S. & Yangping, L. Review of solid oxide fuel cell materials: cathode, anode, and electrolyte. *Energy Transitions* **4**, 113–126 (2020).
2. Nernst, W. Über die elektrolytische leitung fester körper bei sehr hohen temperaturen. *Zeitschrift für Elektro Chemie* **6**, 41–43 (1899).
3. Singh, P. & Minh, N. Q. Solid oxide fuel cells: Technology status. *Int. J. Appl. Ceram. Technol.* **1**, 5–15 (2004).
4. Minh, N. Q. Ceramic Fuel Cells. *J. Am. Ceram. Soc.* **76**, 563–588 (1993).
5. Nurbanasari, M., Syarif, D. G. & Irwan, Y. Characterization of Calcia Stabilized Zirconia as a solid Electrolyte Made through a sol gel Method in Solid Oxide Fuel Cell. 3056–3060 (2019).
6. Mahato, N., Gupta, A. & Balani, K. Doped zirconia and ceria-based electrolytes for solid oxide fuel cells: a review. *Nanomater. Energy* **1**, 27–45 (2012).
7. Zhu, B. No. *Int. J. ENERGY Res.* **33**, 1126–1137 (2009).
8. Wang, X. *et al.* Ceria-based nanocomposite with simultaneous proton and oxygen ion conductivity for low-temperature solid oxide fuel cells. *J. Power Sources* **196**, 2754–2758 (2011).
9. Huang, J., Gao, Z. & Mao, Z. Effects of salt composition on the electrical properties of samaria-doped ceria/carbonate composite electrolytes for low-temperature SOFCs. *Int. J. Hydrogen Energy* **35**, 4270–4275 (2010).
10. Shi, H., Su, C., Ran, R., Cao, J. & Shao, Z. Progress in Natural Science : Materials International Electrolyte materials for intermediate-temperature solid oxide fuel cells. *Prog. Nat. Sci. Mater. Int.* 0–1 (2020).
11. Chen, M., Zhang, H., Fan, L., Wang, C. & Zhu, B. Ceria-carbonate composite for low temperature solid oxide fuel cell: Sintering aid and composite effect. *Int. J. Hydrogen Energy* **39**, 12309–12316 (2014).
12. Di, J. *et al.* Samarium doped ceria-(Li/Na) 2CO_3 composite electrolyte and its electrochemical properties in low temperature solid oxide fuel cell. *J. Power Sources* **195**, 4695–4699 (2010).