International Journal of Nanoelectronics and Materials
IJNeaM
ISSN 1985-5761 | E-ISSN 2232-1535

Synthesis and Electrical Properties of Fe/Sm Co Doped CeO_2

Nur Fathin Syuhada Samsudin[a,*], Salmie Suhana Abdullah[a,b] and Norzarul Asri Kamis[c]

[a]*Faculty of Chemical Engineering & Technology, Universiti Malaysia Perlis, Kompleks Pusat Pengajian Jejawi 2, 02600 Arau Perlis, Malaysia*
[b]*Centre of Excellent for Frontier Materials Research (Frontmate), Universiti Malaysia Perlis, Jalan Kangar-Alor Setar, Kampung Seriab 01000 Kangar Perlis, Malaysia*
[c]*Faculty of Mechanical Engineering & Technology, Universiti Malaysia Perlis, Kampus Tetap Pauh Putra, 02600 Arau, Perlis, Malaysia*
**Corresponding author. Tel.: +6-019-989-1406; e-mail: salmie@unimap.edu.my*

ABSTRACT

High productivity and environmental consciousness have made the environmentally friendly features of solid oxide fuel cells (SOFC) an alternative energy source that has attracted attention as a potential solution to problems such as pollution, global warming, and lack of fuel availability. In the field of SOFC, extensive research has been focused on the development of cells that exhibit good electrochemical performances and are highly durable. Samarium doped ceria (SDC) has become the material that is frequently investigated as a potential electrolyte for SOFC. Compositional modification of SDC doped with Fe as second dopant was investigated in this project. The samples were synthesized using a solid state reaction method from raw materials, which are cerium oxide, samarium oxide, and iron oxide, then sintered at temperatures of 1480 ^{o}C. Different concentrations of Fe (0-10 mol%) were doped in SDC. To assess the effects of double dopants on the crystal structure and electrical characteristics, X-ray diffraction (XRD) analysis was employed for phase confirmation, and impedance was measured to determine electrical conductivity. All samples were sintered at 1480 ^{o}C and have a relative density more than 95%. It was discovered that, in the lower temperature range of 300-600 ^{o}C, significant improvement can be seen when Fe was doped in SDC, where 5 mol% Fe doped SDC shows the highest conductivity with a value of 1.09 S/m at 600 ^{o}C, which is more than 3 times higher than SDC, showing that Fe is a potential candidate as second dopant in SDC.

Keywords: *Solid oxide fuel cell, Solid electrolyte, Samarium doped Ceria, Solid state reaction method*

1. INTRODUCTION

In recent research on renewable energy sources, fuel cells have been singled out as one of the most promising potential energy sources for the future. Fuel cells have various advantages including high efficiency, mobility in the use of the essential fuels and the flexibility to be manufactured for a wide variety of operating temperatures. Because of such features, fuel cells have become a competitive power source in recent years. These features allow fuel cells to be applied in a variety of applications, which has led to their development in demand [1]. Solid oxide fuel cell (SOFC) is the one type of example of fuel cell [2] where can generate electricity by converting chemical energy like oxygen and hydrogen as a fuel at high efficiency [3-7]. SOFC has been attracting a lot attention since it has good dominance like affordability, high efficiency and green credentials [2,8,9]. Due to the excellent electrical characteristic along with high ionic conductivity, ceria based solid electrolyte has been identified as an attractive candidate for electrolyte of SOFC [10-15].

CeO_2 is a highly stable oxide material that may be doped with a variety of elements in order to increase its ionic conductivity [5,12,16,17]. This is possible since pure ceria has a low ionic conductivity. Samarium doped ceria, often known as samarium doped ceria (SDC), is a common solid electrolyte that is based on ceria and is typically utilized in SOFC. This is due to the fact that SDC have low activation energy, making it easier for vacancies to move across the lattice, as well as also make it simple to produce oxygen vacancies. However, in order to improve the performance of SOFCs, a co-doping ceria-based method that increases the conductivity of solid electrolytes used in SOFCs is utilized. This method was reported to be effective in a prior study [10]. Due to the fact that Fe_2O_3 is an excellent dopant for increasing ionic conductivity and acts as a sintering aid for CeO_2-based electrolytes, it was decided to use it as the dopant in this investigation [18,19]. In addition to this, it acts as an impurity degreaser at grain boundaries, and the oxidation state of Fe^{3+} has the ability to increase the number of oxygen vacancies and the ionic conductivity of the material. During the course of this research, Fe_2O_3 doped SDC was synthesized, and the correlation between the structural and electrical properties of such doping was investigated.

2. MATERIALS AND METHOD

CeO_2 (99.9% purity, Acros Organics), Sm_2O_3 (99.95% purity, Sigma Aldrich), and Fe_2O_3 (96% purity, Sigma Aldrich) were used as raw materials. Samarium doped ceria (SDC) was used as the reference sample throughout the research, and various concentration of dopant, Fe was substituted in Sm. Samples were synthesized using the conventional solid state reaction method. Raw materials were measured out in a stoichiometric ratio and mixed in an agate mortar with

ethanol for an hour to ensure homogeneity. The solid solution of $Ce_{0.8}Sm_{0.2}O_{1.9}$, $Ce_{0.8}Sm_{0.175}Fe_{0.025}O_{1.9}$, $Ce_{0.8}Sm_{0.15}Fe_{0.05}O_{1.9}$, $Ce_{0.8}Sm_{0.125}Fe_{0.075}O_{1.9}$, $Ce_{0.8}Sm_{0.1}Fe_{0.1}O_{1.9}$, are abbreviated as SDC, SDC-Fe0.025, SDC-Fe0.05, SDC-Fe0.075 and SDC-Fe0.1. The uniformly dry powder was pressed into pellets using a manual hand press and subjected to pressure of 3000 psi before being sintered at temperatures of 1480 °C for five hours. The green bodies were 15 mm in diameter and 2-3 mm in diameter in thickness.

The density of the sintered pellet was measured using Archimedes' method for three times replication. Meanwhile, to perform an X-ray diffraction (XRD) analysis by using Bruker D2 Phaser, the sintered pellet was crushed to a powder. XRD was performed using Cu Kα radiation and scan range was between 20° and 90°. An XRD analysis was performed to verify the phase.

After applying silver paste to both sides of the pellet and heating it for one hour at 700 °C, impedance measurement was done at temperatures from 300 °C to 800 °C with frequencies from 0.1 Hz to 1 MHz [20]. Impedance spectroscopy was used to investigate the sintered pellet's electrical conductivity. Additionally, by comparing the diameter and thickness of the sample before and after sintering, the volume shrinkage that occurs during the process was measured by five time replication.

3. RESULT AND DISCUSSION

3.1. Phase Confirmation and Crystal Structure Analysis

The XRD pattern of SDC-Fe with various Fe concentrations has been sintered at 1480 °C for five hours is shown in figure 1. All samples exhibit all of the main peaks that are characteristic of the flourite structure. However, SDC-Fe0.05 and SDC-Fe0.075 sample have secondary phase meanwhile, other samples have single that can be identified. The samples display all main reflections conforming to the references listed on the PDF card 01-075-0157, which is suggestive of the complete development of a CeO_2-based solid solution with a characteristic cubic flourite structure. In addition, the peak of the XRD pattern obtained by a sample with Fe doping is narrow than the peak obtained by a sample with no Fe added especially at 2θ, 27-28°. Therefore, the crystal structure of the sample might be improved with Fe doped into SDC in comparison to the sample that was not doped. Due to this, Fe doping can produce major alterations of the original crystalline structure, such as covalent imbalance and lattice distortion, which could result in a rise in the concentration of oxygen vacancy and boost the migration of lattice oxygen, in other words, an increase in the number of applications for which the material is suitable [21,22].

The lattice parameter of the sample was derived from the XRD analysis, which is displayed in figure 2. The values of each sample's lattice parameter were calculated by using the HighScores Plus software to the peak data of the XRD. Compared to CeO_2 without any dopant which has a lattice parameter of 0.5411 nm [23], synthesized has a slightly larger lattice parameter of 0.5444 nm. In the meantime, the lattice parameter of SDC-Fe decreases with an increase in the concentration of Fe. At 10 mol% of Fe, the lattice parameter is 0.5422 nm, but it slightly increases to 0.5428 nm when doped with 2.5 mol% of Fe. Changes in the crystal lattice and the way charges are distributed affect its chemical and physical properties [21]. Changes to the lattice parameters can occur when dopant atoms made of Fe are introduced into a crystal lattice. One of the most evident mechanisms occurs due to a size mismatch between the dopant impurity and the host atom that it substitutes for [24]. Because the sizes of individual atoms can vary, the process of incorporating additional atoms might result in the lattice being stretched or distorted in order to accommodate the new atom's dimensions. In this case, Fe^{3+} with ionic radius of 0.0645nm [25] was doped in Sm^{3+} with ionic radius of 0.0964 nm [26].

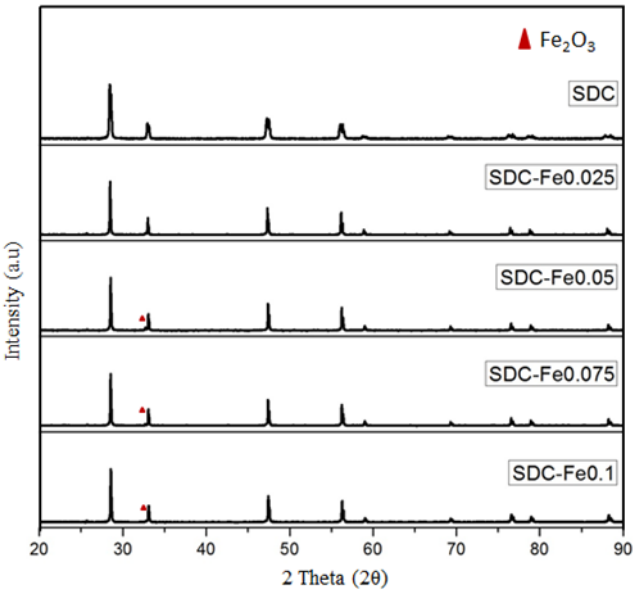

Figure 1. The diffractions peaks position with 2 theta degree.

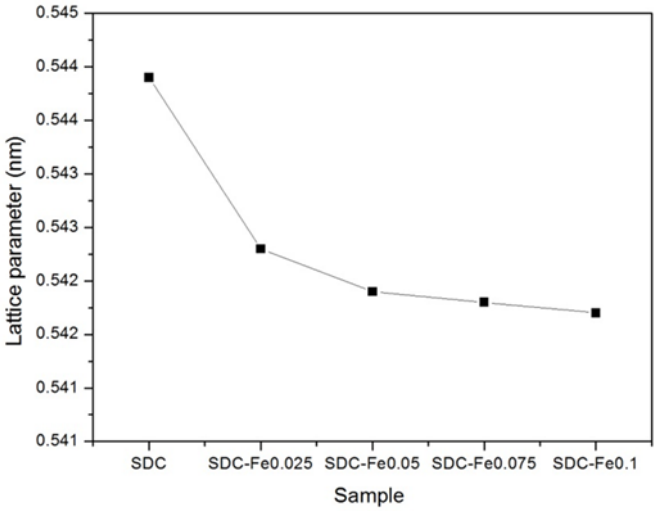

Figure 2. Lattice parameter of sample derived from XRD pattern.

3.2. Physical Properties

The density measurement of SDC sample as well as SDC-Fe with varying concentrations is displayed in Figure 3. The density of the sample is greatly increased by the addition of a little amount of Fe (0-10 mol %), which indicates that the addition has a beneficial impact in promoting the formation of dense solid electrolyte. However, the density of all samples are increase when compared to SDC samples that have not been doped with any Fe at all. For a SOFC, the relative density of a suitable solid electrolyte must be greater than 90% for the device to operate as intended. This is to prevent cross-diffusion during operation in SOFC, which could lead to a short circuit in the device. The incorporation of Fe into SDC has the potential to result in a high density, which in turn can serve as a sintering aid [27]. Sintering additives are commonly included to enhance the process of densification. The use of metallic additives such as Fe is employed to enhance the sinterability of materials. This improvement primarily relies on the formation of liquid phase, which facilitates particle rearrangement and mass transfer throughout the sintering process [28]. So that, by adding Fe greatly promotes the densification of SDC. This is most likely because viscous flow sintering happened in Fe-doped SDC prior to the addition of Fe [28].

Figure 4 depicts the volume reduction that occurred in the sample as a result of the sintering process, which was measured both before and after the process. The trend percentage of shrinkage gradually increases from 29.99% to 38.48% for SDC and SDC-Fe0.025, and the trend percentage of shrinkage increases similarly for SDC-Fe0.075 and SDC-Fe0.1, which are respectively 38.57% and 38.98%. The sample with SDC-Fe0.05 had a shrinkage percentage of 40.07%, making it the winner in this category. In a nutshell, the addition of Fe into SDC resulted in shrinkage in all of the samples following the sintering process.

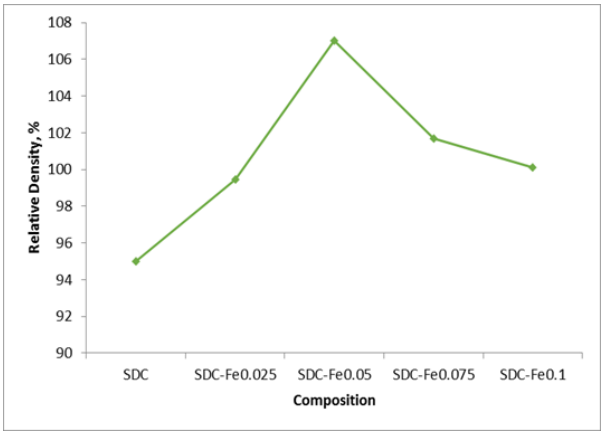

Figure 3. Density value sintered at 1480 °C.

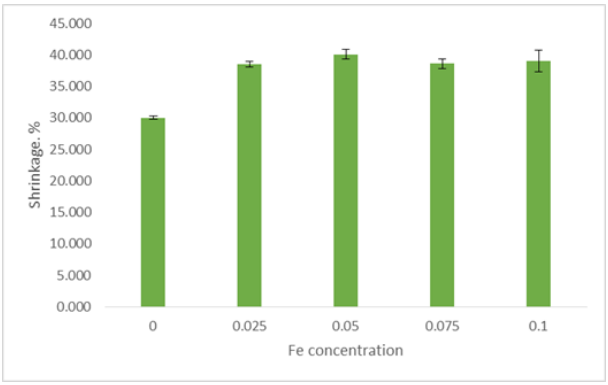

Figure 4. Volume shrinkage of sample sintered at 1480 °C.

3.3. Electrical Properties

The correlation between the total conductivity value of samples with varied concentrations of Fe and temperatures ranging from 300 °C to 800 °C is depicted in Figure 5. By applying Equation 1, one can determine the total conductivity of the sample.

$$\sigma = L/SR \quad (1)$$

Where, L and S represent the sample thickness and area of the surface respectively while R represents as resistances. The measured conductivity data at different temperature are analysed with the Arrhenius equation in Equation 2.

$$\sigma = A/T \exp(-E/kT) \quad (2)$$

The presence of Fe has a positive effect on the conductivity of the samples where we can see from Figure 5, all SDC-Fe samples show higher conductivity compared to SDC. Noticeable enhancements are observable within the low temperature range 300 °C to 600 °C, as opposed to the higher-temperature range of 700 °C to 800 °C. At 300 °C, SDC-Fe0.05 managed to attain the highest conductivity, in comparison to all the samples which is 0.024 S/m and more than one order compared to SDC. This sample maintained its ability to attain the highest conductivity at temperatures ranging from 300 °C to 600 °C.

As the temperatures increase, the disparity in conductivity becomes reduced. At high temperatures between 700 °C – 800 °C, the conductivity of SDC-Fe sample is comparable. Nevertheless, SDC-Fe0.075 shows slightly higher conductivity than that of other samples. At 800 °C, SDC-Fe0.075 attained highest conductivity, which is 3.402 S/m and 8 times higher compared to SDC. Another study found that adding 5 mol% of Fe led to greater conductivity at temperatures ranging from 600 °C to 800 °C [9]. However, the ionic conductivity can be influenced by the lattice parameter due to its impact on the ionic radius of the ions present in the crystal lattice. As can be seen in Figure 2, the lattice parameter become slightly smaller after the mol% of Fe was added. So, when the lattice parameter is reduced, it might impose limitations on the mobility of ions, resulting in a decrease in ionic conductivity. Comparing the conductivity of all samples at 600 °C in Figure 6, conductivity of SDC-Fe increase when Fe concentration is

up to 5 mol%, and further doping resulted in decreasing conductivity. Aside from that, the conductivity of the SDC-Fe0.10 sample is just marginally higher than that of the reference sample SDC.

Figure 7 shows the activation energy obtained from the Arrhenius plot. As can be seen generally from this figure, single doped SDC has higher activation energy compared to SDC-Fe samples. This indicates the agreement on correlation between activation energy and conductivity value. The activation energy of SDC is 0.828 eV, meanwhile SDC-Fe0.025, SDC-Fe0.05, SDC-Fe0.075 and SDC-Fe0.1 has 0.658 eV, 0.577 eV, 0.657 eV and 0.638 eV respectively. SDC-Fe0.05 sample has the lowest activation energy. The increase in ionic conductivity can be related to a decrease in the activation energy required for ionic conduction [24].

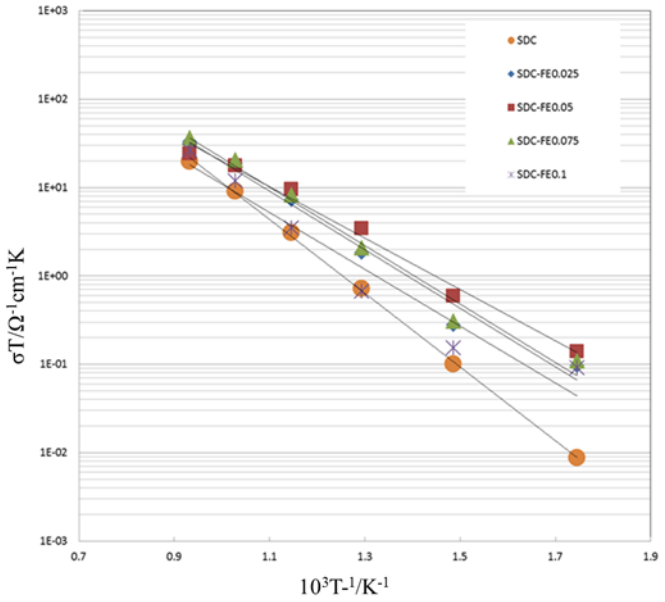

Figure 5. Arrhenius plot of different sample at 300 °C to 800 °C.

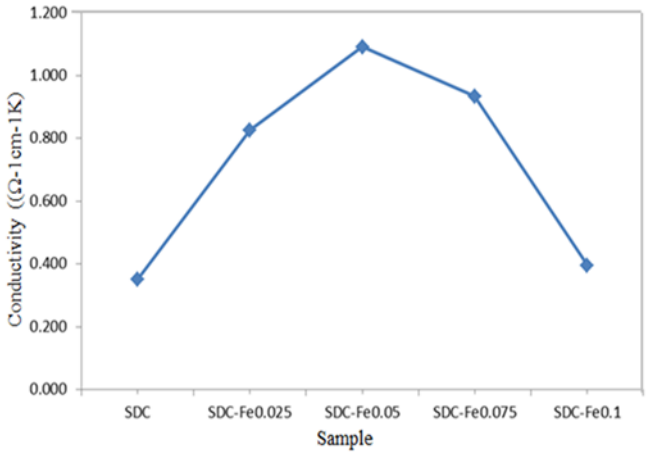

Figure 6. Total conductivity represent at 600 °C.

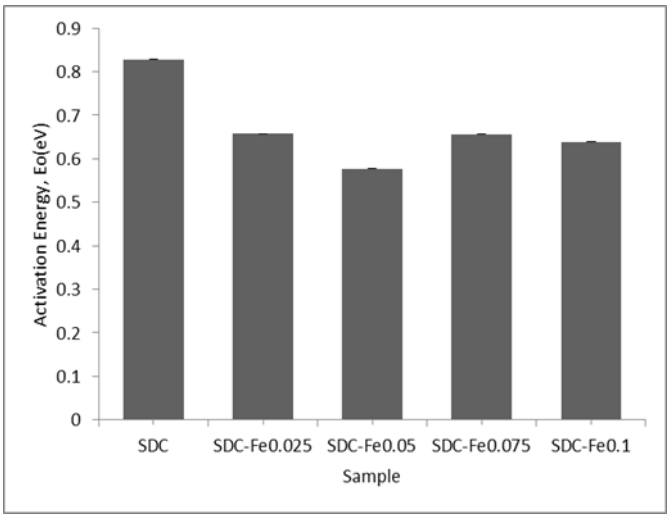

Figure 7. Activation energy of the samples.

4. CONCLUSION

The crystal structure of each of the produced Fe_2O_3 doped SDC samples as well as their ionic conductivity was analyzed. At a sintering temperature of 1480 °C, SDC and SDC-Fe0.025 samples successfully achieved a single phase meanwhile SDC-Fe0.05, SDC-Fe0.075 and SDC-Fe0.1 samples have secondary phase and agreed very well with the PDF card 01-075-0157. Fe doping has the potential to improve the density of the material. Doping with Fe can result in an increase in the conductivity of SDC, which results in an obvious increase at temperature of 300 °C for all samples but only a slight increase compared to SDC whenever it is heated between 700 °C and 800 °C. The results of this analysis showed that every sample obtained more than 95% densification, SDC-Fe0.05 shows the most significant improvement at lower temperature region meanwhile SDC-Fe0.075 sample achieving the highest conductivity at 800 °C which is 3.402 S/m. However, these candidates material need to be explored more to improve the conductivity and other properties most for application of electrolyte for SOFC.

ACKNOWLEDGMENTS

The author would like to acknowledge the support from the Fundamental Research Grant Scheme (FRGS) under a grant number of FRGS/1//2020/STG05/UNIMAP/02/4 form the ministry of Higher Education (MoHE) Malaysia.

REFERENCES

[1] Agbede, O. O., Hellgardt, K., & Kelsall, G. H. (2020). Electrical conductivities and microstructures of LSM, LSM-YSZ and LSM-YSZ/LSM cathodes fabricated on YSZ electrolyte hollow fibres by dip-coating. Materials Today Chemistry, 16, 100252.

[2] Ahamer, C., Opitz, A. K., Rupp, G. M., & Fleig, J. (2017). Revisiting the Temperature Dependent Ionic Conductivity of Yttria Stabilized Zirconia (YSZ). Journal of The Electrochemical Society, 164(7), F790.

[3] Singh, M., & Singh, A. K. (2020). Studies on structural, morphological, and electrical properties of Ga3+ and Cu2+ co-doped ceria ceramics as solid electrolyte for IT-SOFCs. International Journal of Hydrogen Energy, 45(44), 24014–24025.

[4] Istomin, S. Ya., Lyskov, N. V., Mazo, G. N., & Antipov, E. V. (2021). Electrode materials based on complex d-metal oxides for symmetrical solid oxide fuel cells. Russian Chemical Reviews, 90(6), 644–676.

[5] Cheng, J., Tian, C., & Yang, J. (2019). Effects of Fe2O3 addition on the electrical properties of SDC solid electrolyte ceramics. Journal of Materials Science: Materials in Electronics, 30(17), 16613–16620l-.

[6] Kasaeian, A., Javidmehr, M., Mirzaie, M. R., & Fereidooni, L. (2023). Integration of solid oxide fuel cells with solar energy systems: A review. Applied Thermal Engineering, 224, 120117.

[7] Guan, L., Le, S., Zhu, X., He, S., & Sun, K. (2015). Densification and grain growth behavior study of trivalent MO1.5 (M=Gd, Bi) doped ceria systems. Journal of the European Ceramic Society, 35(10), 2815–2821.

[8] Zakaria, Z., Abu Hassan, S. H., Shaari, N., Yahaya, A. Z., & Boon Kar, Y. (2020). A review on recent status and challenges of yttria stabilized zirconia modification to lowering the temperature of solid oxide fuel cells operation. International Journal of Energy Research, 44(2), 631–650.

[9] R Hua, G., Ding, X., Zhu, W., & Li, J. (2015). Enhanced ionic conductivity of Sm0.2Ce0.8O2−δ electrolyte for solid oxide fuel cells through doping transition metals. Journal of Materials Science: Materials in Electronics, 26(6), 3664–366.

[10] Jaiswal, N., Tanwar, K., Suman, R., Kumar, D., Upadhyay, S., & Parkash, O. (2019). A brief review on ceria based solid electrolytes for solid oxide fuel cells. Journal of Alloys and Compounds, 781, 984–1005.

[11] Lapa, C. M., de Souza, D. P. F., Figueiredo, F. M. L., & Marques, F. M. B. (2010). Two-step sintering ceria-based electrolytes. International Journal of Hydrogen Energy, 35(7), 2737–2741.

[12] Wang, B., Zhu, B., Yun, S., Zhang, W., Xia, C., Afzal, M., Cai, Y., Liu, Y., Wang, Y., & Wang, H. (2019). Fast ionic conduction in semiconductor CeO2-δ electrolyte fuel cells. NPG Asia Materials, 11(1), Article 1.

[13] Mekhilef, S., Saidur, R., & Safari, A. (2012). Comparative study of different fuel cell technologies. Renewable and Sustainable Energy Reviews, 16(1), 981–989.

[14] Okkay, H., Bayramoglu, M., & Faruk Öksüzömer, M. (2013). Ce¬0.8Sm0.2O1.9 synthesis for solid oxide fuel cell electrolyte by ultrasound assisted co-precipitation method. Ultrasonics Sonochemistry, 20(3), 978–983.

[15] Pawar, M. J. (2010). Effect of Co Co-Doping on the Densification and Electrical Conductivity of Ce0.9Sm0.1O2-δ; Solid Electrolytes. 01, 27–31.

[16] Tao, S. W., Irvine, J. T. S., & Kilner, J. A. (2005). An Efficient Solid Oxide Fuel Cell Based upon Single-Phase Perovskites. Advanced Materials, 17(14), 1734–1737.

[17] Melchionna, M.; Bevilacqua, M.; Fornasiero, P. (2020). The Electrifying Effects of Carbon-CeO2 Interfaces In (Electro) Catalysis. Materials Today Advances, 6, 100050–.

[18] J. Zolhafizia, M. Azham Azmia, H.A. Rahman a, H. Zakariaa, S. Hassana, S. Mahzana, A. Ismaila, A.M.T. Ariffina, Tukimon M.F.a, U.A. Yusofa & N. A. Baharuddin. (2022). Samarium Doped Ceria (SDC) Electrolyte Modification by Sintering Aids Addition to Reducing Sintering Temperature: A Review Jurnal Kejuruteraan 35(1) 2023: 65-76.

[19] Ahamer, C., Opitz, A. K., Rupp, G. M., & Fleig, J. (2017). Revisiting the Temperature Dependent Ionic Conductivity of Yttria Stabilized Zirconia (YSZ). Journal of the Electrochemical Society, 164(7), F790.

[20] Yin, S., Li, M., Zeng, Y., Li, C., Chen, X., & Ye, Z. (2014). Study of Sm0.2Ce0.8O1.9 (SDC) electrolyte prepared by a simple modified solid-state method. Journal of Rare Earths, 32(8), 767–771.

[21] Li, Qingqing; Huang, Zhen; Guan, Pengfei; Su, Rui; Cao, Qi; Chao, Yimin; Shen, Wei; Guo, Junjie; Xu, Hualong; Che, Renchao (2017). Simultaneous Ni Doping at Atom Scale in Ceria and Assembling into Well-defined Lotus-like Structure for Enhanced Catalytic Performance. ACS Applied Materials & Interfaces, acsami.7b03394-.

[22] Li, Shuna; Zhu, Huaqing; Qin, Zhangfeng; Zhang, Yagang; Wang, Guofu; Wu, Zhiwei; Fan, Weibin; Wang, Jianguo (2018). Catalytic Performance of Gold Supported on Mn, Fe and Ni Doped Ceria in the Preferential Oxidation of CO in H2-Rich Stream. Catalysts, 8(10), 469–.

[23] A. Younis, D. Chu, and S. Li, 'Cerium Oxide Nanostructures and their Applications', Functionalized Nanomaterials. InTech,, (2016).

[24] Hark B. Lee; Friedrich B. Prinz; Wei Cai (2010). Atomistic simulations of surface segregation of defects in solid oxide electrolytes, Acta Materialia, Science Direct, 58(6), 2197–2206.

[25] Neeraj Kumar; H. Kishan; A. Rao; V.P.S. Awana (2010). Fe ion doping effect on electrical and magnetic properties of La0.7Ca0.3Mn1−xFexO3 ((0 ≤ x ≤ 1)). Journal of Alloys and Compounds, 502(2), 0–288.

[26] Yang, Yong; Pan, Heng; Guan, Li; Wang, Dawei; Zhao, Jinxin; Yang, Jingfa; Yang, Zhiping; Li, Xu (2020). Electronic structure and luminescent properties of Sr3Al2O6:Sm3+ orange phosphor prepared by hydrothermal method. Journal of Materials Research and Technology, S2238785419321039–.

[27] Anirban, Sk., & Dutta, A. (2020). Revisiting ionic conductivity of rare earth doped ceria: Dependency on different factors. International Journal of Hydrogen Energy, 45(46), 25139–25166.

[28] Zheng, Y., Zhou, M., Ge, L., Li, S., Chen, H., & Guo, L. (2011). Effect of Fe2O3 on Sm-doped ceria system solid electrolyte for IT-SOFCs. Journal of Alloys and Compounds, 509(2), 546–550.