

The single cell of low temperature solid oxide fuel cell with sodium carbonate-SDC (samarium-doped ceria) as electrolyte and biodiesel as fuel

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Abstract. In this research NSDC (composite of Na_2CO_3 -SDC) was prepared by the sol-gel method to produce NSDC1 and also by the ceramic method to produce NSDC2. The prepared NSDC then were analyzed by XRD embedded with Le Bail refinement to study the change of characteristic peaks, their crystal structure, and their cell parameters. Meanwhile, the measurement of impedance was conducted to study the electrical conductivity of the prepared materials. A single cell was prepared by coating NSDC-L (a composite of NSDC with $\text{Li}_{0.2}\text{Ni}_{0.7}\text{Cu}_{0.1}\text{O}_2$) on both surfaces of NSDC. The NSDC-L was used as anode and cathode. The ionic conductivity of NSDC1 and NSDC2 at 400 °C are $4.1109 \times 10^{-2} \text{ S.cm}^{-1}$ and $1.6231 \times 10^{-2} \text{ S.cm}^{-1}$, respectively. Both electrolytes have ionic conductivity higher than $1 \times 10^{-4} \text{ S.cm}^{-1}$, therefore, can be categorized as good electrolyte [1]. However, the NSDC1 shows electrode-electrolyte conduction. It indicates the existence of electronic migration from electrolyte-electrode or vice versa. Those may cause a short circuit during fuel cell operation and will reduce the fuel cell performance fastly. The single cell tests were conducted at 300, 400, 500 and 600 °C. The single fuel cell with NSDC1 and NSDC2 as electrolyte show maximum power density at 400 °C with the power density of $3.736 \times 10^{-2} \text{ mW.cm}^{-2}$ and $2.245 \times 10^{-2} \text{ mW.cm}^{-2}$, respectively.

1. Introduction

Over decades, the fossil fuel combustion occurs to produce energy for life. Meanwhile, the combustion process releases carbon as pollution to the environmental and allows the global warming effect. Therefore, a clean technology in energy conversion is required. A fuel cell is a promising device for energy conversion due to its flexibility of fuel options and low carbon emission. The fuel cell convert fuel into electrical energy through reduction and oxidation reaction [2]. Solid oxide fuel cell, SOFC, has high efficiency of converting energy, i.e. 65%. The SOFC also can use many fuels whether fossil fuels or new and renewable fuels. The SOFC design also simple. However, it operates at a high temperature of 800 – 1000 °C [3]. In order to reduce the operational temperature of SOFC, some efforts have been conducted to find the electrolyte material that has high ionic conductivity at low temperature. Samarium-doped ceria, SDC, has been known as a promising one. SDC has ionic conductivity at around 0.1 S.cm^{-1} at low temperature ($< 600 \text{ °C}$) [4]. Unfortunately, doped-ceria features mixed ionic-electronic conductivity that leads to reducing fuel cell performance due to a short circuit of anode-cathode that cause electronic conduction [5].



Recently, dual phase- materials are known to have a higher efficiency for Intermediate-Low Temperature Solid Oxide Fuel Cell, ILT-SOFC [6]. The composite of ceria-carbonate, NSDC, which was used as electrolyte provide ionic conductivity at around 10^{-1} S.cm⁻¹ at 600 °C, and it was developed for an intermediate-SOFC [7]. A nano core-shell samarium-doped ceria with amorphous Na₂CO₃ has an ionic conductivity of 0.1 S.cm⁻¹ at above 300 °C [8]. Meanwhile, the SDC-Li₂CO₃-Na₂CO₃ shows ionic conductivity of 0.02 S.cm⁻¹ to 0.9 S.cm⁻¹ at 400 – 600 °C [9]. The carbonate can inhibit the electronic conduction of doped- ceria. The electronic conduction occurs due to a reduction of Ce⁴⁺ into Ce³⁺ during fuel cell running [10]. The sodium carbonate addition also does not change the crystal structure of SDC due to the amorphous properties of carbonate [8].

The composite of sodium carbonate-SDC (NSDC) with Li_{0.2}Ni_{0.7}Cu_{0.1}O (LNC) may become a potential material for electrode due to it's mixed ionic-electronic conduction and also the catalytic properties of nickel and copper [11]. The composite of NSDC with LNC (NSDC-L) has been used as an electrode for low temperature-SOFC with glycerol and bioethanol as fuels. The maximum power density with glycerol fuel is 215 mW.cm⁻² at 580 °C. It may have a great impact on sustainable energy and environmentally friendly energy [11]. However, the hygroscopic property of the sodium carbonate, Na₂CO₃, might become a problem. The sodium carbonate is a hygroscopic molecule, in which it will spontaneously absorb water molecules when it is exposed to air [12]. In addition, its diffraction pattern does not confirm the presence of carbonate phase [13, 14]. Even, the presence of the sodium carbonate phase only interpreted from the presence of Na peak in the EDX spectrum [14]. Meanwhile, the Na peak might come from sodium oxide.

In this research, the NSDC was prepared through two methods i.e. sol-gel preparation with pre-heating treatment on Na₂CO₃ producing NSDC2 and without pre-heating treatment on Na₂CO₃ producing NSDC1. The different method of preparation objects to find the less hygroscopic NSDC. This paper also discusses the crystal structure change after composite formation. The Le Bail refinement was conducted to analyze the phase content in the composite. This paper also analyzes the change of ionic conductivity. A single cell was constructed with the prepared NSDC as electrolyte and NSDC-L as an electrode. The single cell performance was tested with biodiesel as fuel.

2. Experiment

The samarium-doped ceria, Ce_{0.8}Sm_{0.2}O_{1.9}, was synthesized through sol-gel method. The precursors were cerium nitrate hexahydrate (Ce(NO₃)₃.6H₂O, 99%, Sigma-Aldrich) and samarium nitrate hexahydrate (Sm(NO₃)₃.6H₂O, 99.9%, Sigma-Aldrich). The precursors were mixed stoichiometrically in deionized- water. The citric acid and Polyethylene Glycol, PEG were added as a chelating agent. The mixing process was conducted under continuous stirring at 50 °C until forming a gel. Then followed by heating treatment at 400 °C that produced a yellow powder. The yellow powder then to be heated at 800 °C for 10 hours.

The composite of SDC with sodium carbonate (Na₂CO₃) was prepared by dissolving Ce(NO₃)₃.6H₂O (99.99%) and Sm(NO₃)₃.6H₂O (99.9%) in deionized water with a molar ratio of Ce³⁺: Sm³⁺ = 4:1 to produce a 100 mL of synthesis solution. The 200 mL of carbonate solution (1.0 M) was added gradually with addition rate of 10 mL.min⁻¹ under continuous stirring for 2 hours at 100 °C. The mixture then was heated at 800 °C for 2 hours to produce NSDC1. The second type of NSDC, i.e., NSDC2 was prepared with similar method. However, the Na₂CO₃ was heated at 800 °C before used.

Synthesis of Li_{0.2}Ni_{0.7}Cu_{0.1}O was conducted by sol-gel method. A stoichiometric weight of Li₂CO₃ (99.9 %), Cu(OH)₂ (95 %) and NiCO₃.2Ni(OH)₂.4H₂O (46%, Ni-based) were dissolved in deionized-water to produce 1.0 M of the synthetic solution. Citric acid solution (99.5 %) was added at the ratio of total ions to the cations of citric acid at 1:2. The addition was conducted under high rate stirring to produce a homogeneous solution, and the continued with heating at 100 °C for 2 hours under stirring condition and followed with heating at 800 °C for two hours.

The anode and cathode were prepared by mixing NSDC with LNC-271 at a ratio of 1:1. The mixture was then mixed with α-terpineol at ratio of 1:1 to form a slurry. A pellet of the electrolyte with a diameter of 1 cm and thickness of 1.5 cm was prepared by pressing NSDC with a hydraulic

press and then sintered at 800 °C. The NSDC pellet was coated with NSDC-L at both surfaces by screen printing method and then heated at 600 °C for 2 hours. Silver paste and Ag mesh were applied on both surfaces of NSDC-L |NSDC|NSDC-L. Meanwhile, silver wire was attached to the single cell and connected to the measurement device. The scheme of single cell measurement is described in Figure 1(b). A micrometer (mA) was connected in series with the single cell. Meanwhile, a voltmeter was connected in parallel to the anode-cathode. A potentiometer was used to discard current by switching the resistance. Biodiesel vapor flowed into the single cell as fuel, and oxygen in the air was used oxidator. The single cell test was conducted at 300, 400, 500 and 600 °C.

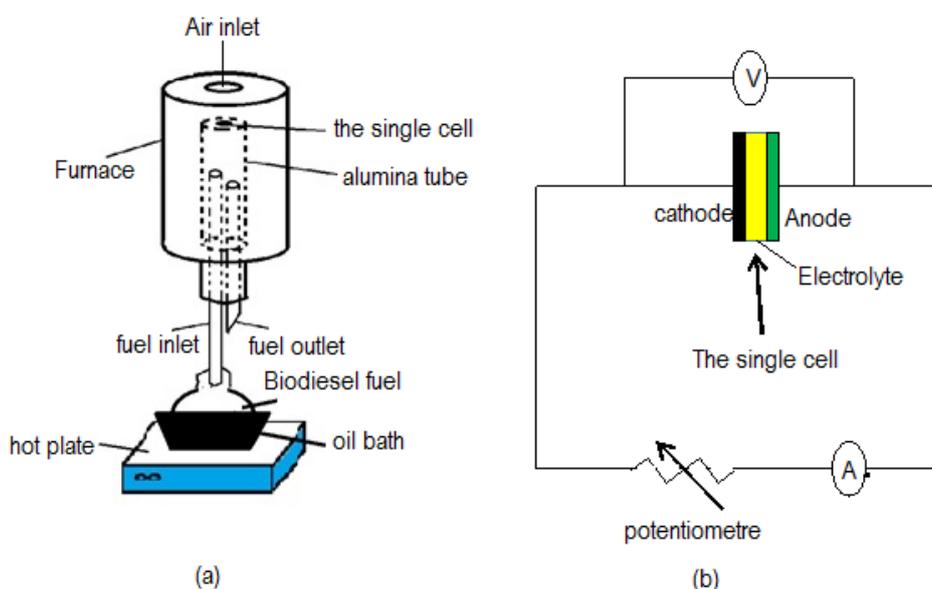


Figure 1. The scheme of single cell testing (a) and the electronic network on the power density measurement (b)

3. Result and Discussion

The samarium-doped ceria, SDC that was synthesized in this research has a diffraction pattern that is in agreement with the standard diffraction of SDC #28791 from ICSD (Figure 1). The result of Le Bail refinement shows that SDC was crystallized in cubic structure with a space group of $FM3M$ and the cell parameter 5.437909(2) Å. The refinement result was depicted in Table 1.

The two types NSDCs have been synthesized which were defined as NSDC1 and NSDC2. The NSDC1 was synthesized without heating treatment on sodium carbonate. Meanwhile, in NSDC2 synthesis, the sodium carbonate was pre-heated at 800 °C. The diffraction patterns of each in comparison to the SDC pattern are depicted in Figure 2. The diffraction pattern does not show any peaks of Na_2CO_3 . The amorphous phase might allow the sodium carbonate peaks did not presence in the patterns [9]. The amorphous structure might occur due to thermal treatment would fuse the sodium carbonate and then layered the SDC particles [10]. However, Le Bail refinement only proceed well when the Na_2CO_3 phase was included in the calculation. The refinement also detects the presence of sodium oxide, Na_2O . The results of refinement are listed in Table 1 in which the prepared NSDCs consist of three phases of SDC, Na_2CO_3 , and Na_2O .

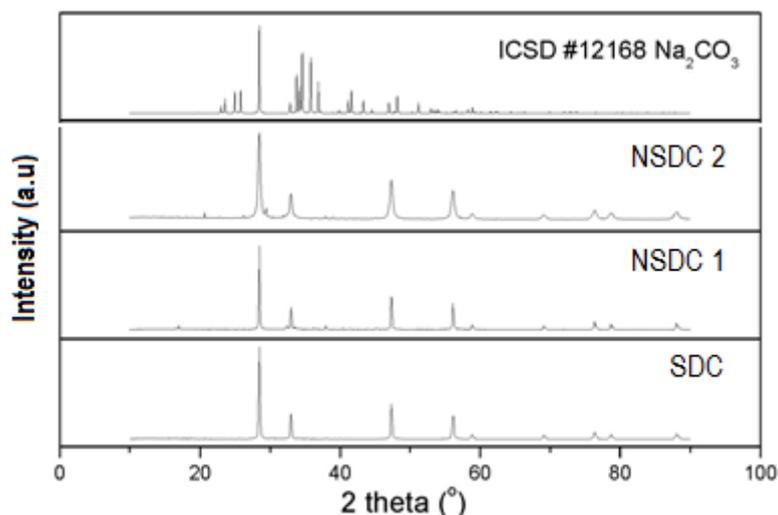


Figure 2. The diffraction patterns of NSDC1 and NSDC2 in comparison with SDC pattern dan standard diffraction of Na_2CO_3 #12168

Table 1. The cell parameters of SDC, NSDC1 and NSDC2 as resulted from Le Bail refinement

Cell parameters	SDC		NSDC1		NSDC2		
	<i>Cubic FM3M</i>	<i>Cubic FM3M</i>	Na_2CO_3 <i>Monoclinic C12/M1</i>	Na_2O <i>Cubic FM3M</i>	<i>Cubic, FM3M</i>	Na_2CO_3 <i>Monoclinic C12/M1</i>	Na_2O <i>Cubic FM3M</i>
a (Å)	5.433000(0)	5.433000(0)	9.013000(0)	5.550000(0)	5.433000(0)	9.013000(0)	5.550000(0)
b (Å)			5.237000(0)			5.237000(0)	
c (Å)			6.312000(0)			6.312000(0)	
V (Å ³)	160.36853(0)	160.36853(0)	295.818878(0)	166.374954(0)	160.36853(0)	295.818878(0)	166.374954(0)
Rp (%)			6.92			6.92	
Rwp (%)			6.85			6.85	

The impedance analysis on the prepared NSDCs found that the materials show different Nyquist plot as described in Figure 3 and Figure 4. Fitting on the impedance data found that the SDC consist of only ionic conductivity at 300 – 500 °C and the electrode-electrolyte conductivity present at 600 °C (Table 2). Meanwhile, the ionic conductivity of NSDC1 is on the order of 10^{-6} . The ionic conductivity values are not sufficient for the electrolyte. Also, the NSDC1 is very hygroscopic then it was not proper for single cell test. The NSDC1 was prepared by mixing the sodium carbonate solution with the solution of SDC precursors. The aqueous phase of sodium carbonate might become the reason of the hygroscopic property of the NSDC1. Meanwhile; the NSDC2 was prepared by mixing the pre- heated sodium carbonate powder with the solution of SDC precursors. Then, the NSDC2 is not hygroscopic like the NSDC1. Also, the NSDC2 shows higher ionic conductivity than SDC at various temperature. However NSDC2 also shows the electrode-electrolyte conduction at 300 – 600 °C. The electrode-electrolyte conduction may indicate the presence of electronic migration that even started since 300 °C. The conduction might cause cell performance degradation due to short circuit.

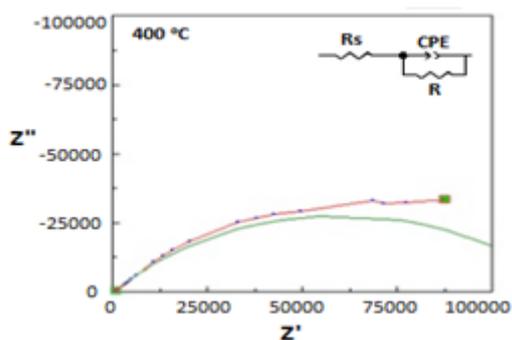


Figure 3. The Bode plot of impedance data of NSDC1 at 400 °C

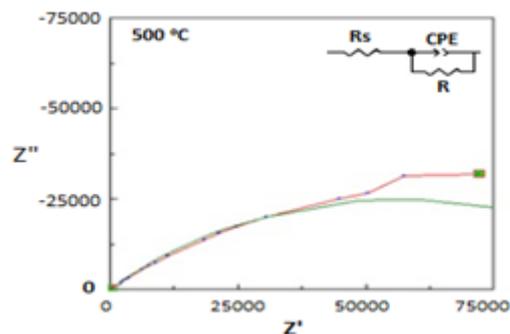


Figure 4. The Bode plot of impedance data of NSDC1 at 500 °C

Table 2. The electrical conductivity of SDC, NSDC1, and NSDC2.

Materials	Temperature (°C)	Ionic conductivity (S.cm ⁻¹)	Electrode-electrolyte conductivity (S.cm ⁻¹)	Capacitance (Farad)	
				CPE*_1	CPE*_2
SDC	300	3.0233x10 ⁻⁶	-	2.012x10 ⁻¹⁰	-
	400	3.9237x10 ⁻⁵	-	6.701x10 ⁻¹⁰	-
	500	6.3901x10 ⁻⁴	-	8.066x10 ⁻⁸	-
	600	3.6439x10 ⁻³	2.15x10 ⁻²	5.556x10 ⁻⁸	3.931x10 ⁻⁵
NSDC1	400	1.8743x10 ⁻⁶	-	1.515x10 ⁻⁷	-
	500	1.9448x10 ⁻⁶	-	3.928x10 ⁻⁷	-
	600	4.5302x10 ⁻⁶	-	3.464x10 ⁻⁷	-
NSDC2	300	9.0440x10 ⁻³	2.0667x10 ⁻²	2.371x10 ⁻¹¹	5.621x10 ⁻⁴
	400	4.1109x10 ⁻²	2.6318x10 ⁻³	3.102x10 ⁻¹⁵	1.544x10 ⁻³
	500	6.4600x10 ⁻²	6.3280x10 ⁻³	9.511x10 ⁻¹⁵	1.381x10 ⁻³
	600	1.5073x10 ⁻¹	1.4184x10 ⁻²	3.062x10 ⁻¹²	2.168x10 ⁻³

The single cell testing on NSDC2 as electrolyte found that the optimum power density occurred at 400 °C with a value of $3.736 \times 10^{-1} \text{ mW.cm}^{-2}$, as described in Figure 5. The open circuit voltage is 0.760 Volt. Meanwhile, the power density at 300 °C is $3.138 \times 10^{-1} \text{ mW.cm}^{-1}$, and the open circuit voltage is 0.97 Volt. The power density is still too low compare to the single cell with glycerol as fuel i.e. 215 mW.cm^{-2} at 580 °C [11]. The high molecular weight of biodiesel might cause low gas phase diffusion in the functional materials. The low grade of biodiesel may also cause less conversion of liquid phase into the gas phase. The power density dropped at a high operational temperature of 500 °C and 600 °C. Those might occur due to at high temperature the reduction reaction of Ce^{4+} into Ce^{3+} occurred and allowed a short circuit that reduce the fuel cell performance. The conductivity measurement of NSDC2, as it was calculated from impedance data, confirms that NSDC2 provide the

electronic-ionic conductivity even at 300 °C. It might occur due to the transportation of electrons from the electrode cross to the electrolyte. It also confirms that the composite electrolyte can be provided as a medium for electronic migration.

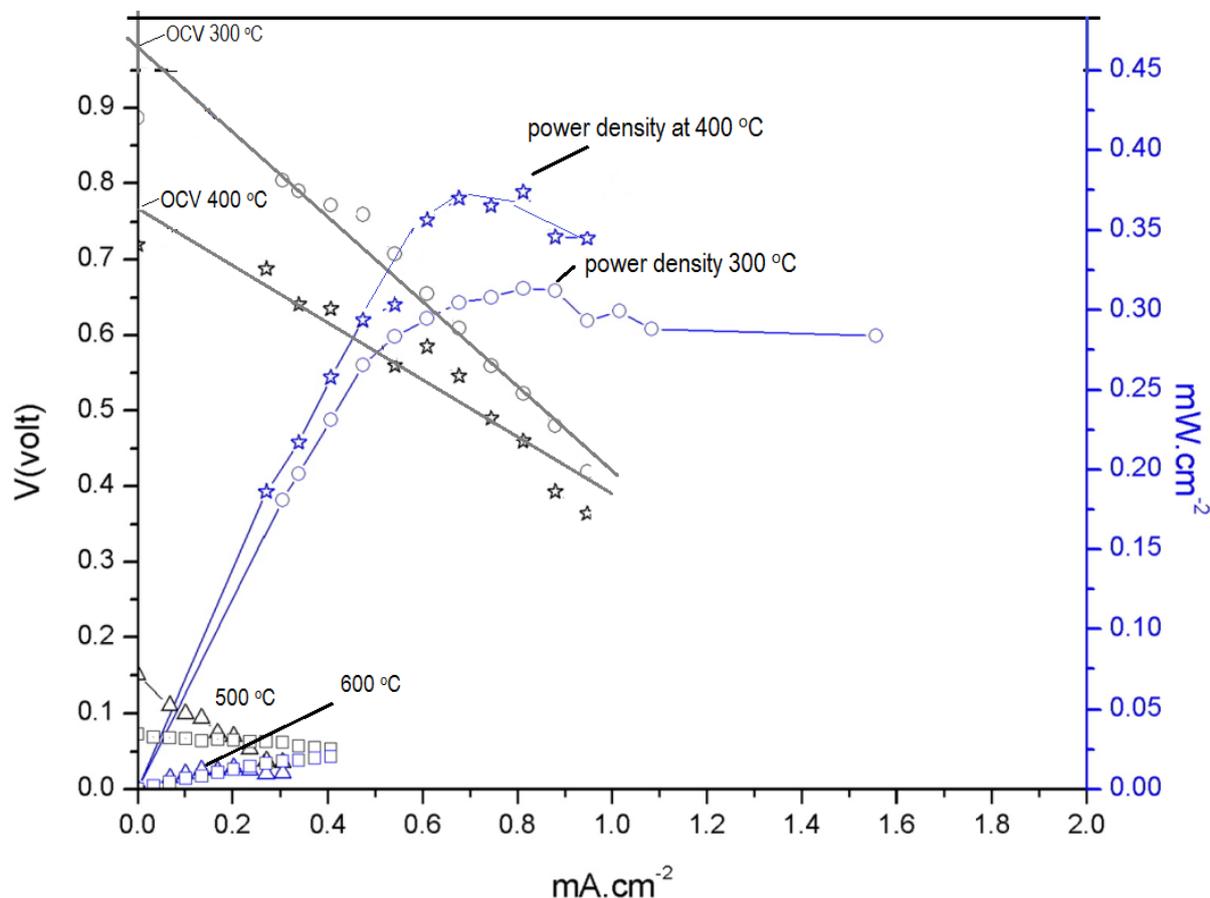


Figure 4. The power density ($\text{mW}\cdot\text{cm}^{-1}$) and *open circuit voltage* (volt) NSDC2 at various temperature.

4. Conclusion

The composite of sodium carbonate with samarium-doped ceria was successfully synthesized by sol-gel method with pre-heating treatment or without pre-heating treatment on sodium carbonate. The composites consist of three phases of SDC, Na_2CO_3 and Na_2O . The presence of sodium carbonate and sodium oxide did not change the crystal structure of SDC. The ionic conductivity of composite with the pre-heating treatment of sodium carbonate i.e. NSDC shows higher ionic conductivity than the composite prepared without pre-heating treatment, i.e. NSDC1. The ionic conductivity is also higher than SDC at various temperatures. NSDC1 is very hygroscopic, and it is not proper for single cell fabrication. The power density of single cell with NSDC2 as electrolyte and NSDC-L as electrodes is $3.736 \times 10^{-1} \text{ mW}\cdot\text{cm}^{-2}$ at 400 °C with biodiesel as fuel.

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