

Pyrolysis result of polyethylene waste as fuel for solid oxide fuel cell with samarium doped-ceria (SDC)-carbonate as electrolyte

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Abstract. In this research, the result of pyrolysis on polyethylene was used as fuel for a solid oxide fuel cell (SOFC). The pyrolysis result is a liquid which consists of hydrocarbon chains. According to GC-MS analysis, the hydrocarbons mainly consist of C7 to C20 hydrocarbon chain. Then, the liquid was applied to a single cell of NSDC-L | NSDC | NSDC-L. NSDC is a composite SDC (samarium doped-ceria) with sodium carbonate. Meanwhile, NSDC-L is a composite of NSDC with LiNiCuO (LNC). NSDC and LNC were analyzed by X-ray diffraction to understand their crystal structure. The result shows that presence of carbonate did not change the crystal structure of SDC. SEM EDX analysis for fuel cell before and after being loaded with polyethylene oil to get information of element diffusion to the electrolyte. Meanwhile, the conductivity properties were investigated through impedance measurement. The presence of carbonate even increases the electrical conductivity. The single cell test with the pyrolysis result of polyethylene at 300 – 600 °C, found that the highest power density is at 600 °C with the maximum power density of 0.14 mW/cm² and open circuit voltage of 0.4 Volt. Elemental analysis at three point spots of single cell NDSC-L |NSDC|NSDC-L found that a migration of ions was occurred during fuel operation at 300 – 600 °C.

1. Introduction

Increasing on energy consumption in this world became a problem that should be solved. It sparks many efforts to find alternatives solution to the problems. Such as converting some plants to fuel, animal wastes to become biogas, and also converting plastic waste to fuel. Research on polyethylene conversion through pyrolysis found that the polyethylene could be converted into gas for fuel, and continued to be condensed into oil [1]. Pyrolysis or thermal cracking offers suitable methods for long chain decomposition [2], to produce a chemical utilization of energy. The advantage of this method over combustion is a reduction in the volume of gas products by a factor of 5 to 20 which leads to considerable savings in the gas conditioning [3]. Many investigators have studied the pyrolysis of polyethylene. The observed similarity in the distribution and yields of volatile products from standard polymers and plastic wastes based on polyethylene suggests that the pyrolysis over the temperature range 500-800 °C can be used to convert these plastic wastes into corresponding monomers and hydrocarbons [4]. High-density Polyethylene (HDPE), the highest liquid yield is at 450 °C, highly



volatile products are obtained at low temperature, and the products obtained at 500 °C and 550 °C are viscous liquid and wax [5]. Decomposition of low-density polyethylene by pyrolysis method found that the oil consists of 60% of alkane and 32% of alkene compounds, which are the typical compounds found in fuel [6].

It is known that plastic waste can not be decomposed naturally, and it becomes a huge problem for the environment [7]. Polyethylene is a kind of polymer that usually used for industrial and everyday life purposes. Therefore, the polyethylene waste is one of a major component of household waste. Meanwhile, it is known that pyrolysis on polyethylene could produce oil that consists of the hydrocarbon chain. The hydrocarbon chain is actually a potential liquid fuel. However, the technology that uses those liquid fuel has still not established yet. Therefore, a pessimistic statement might raise as the pyrolysis of polyethylene into fuel does not impact the increasing of energy production or become an alternative way for energy production, because the technology that uses the waste plastic oil is not ready [8]. The fuel cell can become a potential technology for energy conversion that may use those waste plastic oil. Due to as an electrochemical cell, the fuel cell has wide options of fuel, i.e. hydrogen fuel, methane, butane and also hydrocarbons. Those fuels could be converted into electrical energy in the fuel cell system [9].

In this research, an effort to convert the polyethylene waste into a liquid fuel was conducted. Then, the research continues to apply that liquid fuel as a fuel for a solid oxide fuel cell that consists of NSDC as electrolyte and NSDC-L as an electrode.

2. Experimental

2.1. Procedure of research

2.1.1. Pyrolysis of polyethylene the oil as the result

The polyethylene waste from a plastic bottle was cut into pieces and then was placed into the pyrolysis reactor. The pyrolysis process was conducted under 400-500 °C. The reactor setup was described in the previous paper [1]. The vapor formed was condensed by cooling water system and then collected in a container, as the polyethylene oil. The Oil was analyzed by Gas Chromatography-Mass Spectroscopy (GCMS): GC17A MSQP 5000 Shimadzu to identify the type of the produced hydrocarbon molecules and also the main component of the oil.

2.1.2. Preparation of single cell and fuel cell test

Samarium Doped-Ceria, $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SDC), was synthesized by sol-gel method [10]. The precursors were cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99 %, Sigma-Aldrich), $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9 %, Sigma-Aldrich). The precursors were mixed stoichiometrically and dissolved with deionized water. Citric acid and polyethylene glycol as chelating agents were added under continuous stirring at 50°C until a transparent gel was formed, then the temperature was increased until 400 °C until a yellowish powder formed. The powder then was heated at 800 °C for 10 hours.

NSDC was prepared through the sol-gel method [10], in which the Cerium Nitrate Hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and Samarium Nitrate Hexahydrate ($\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) blend with the molar ratio of $\text{Ce}^{3+} : \text{Sm}^{3+} = 4:1$ in 100 mL of solution. The Na_2CO_3 powder was firstly heated at 800 °C before it was dissolved in water to form 1.0 M of the solution. The mixed solution was heated at 100 °C and stirred for 2 h. The heating was continued to 800 °C for 2 hours to produce pure powder [11].

Synthesis of LiNiCuO catalyst by Sol-Gel method where ratio molar of $\text{Li}^+ : \text{Ni}^{2+} : \text{Cu}^{2+} = 2:7:1$ from material $\text{Li}_2\text{CO}_3 : \text{CuCO}_3 : \text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ in 1,0 Mol deionized water. Citric acid is added and stirred until homogeneous. The solution was heated at 100 °C to form sol then sintered at 800 °C for 2 hours.

The pellet of SDC and NSDC were prepared by pressing with a hydraulic press. Then it was sintered at 800 °C for 2 hours. The 1:1 weight ratio of NSDC and LiNiCuO was mixed with α -terpineol to form a homogeneous slurry. The slurry then applied to the both surface of NSDC and SDC by screen printing method and then heated at 600 °C for 2 hours to produce a single cell of NSDC - L | NSDC | NSDC - L. Ag mesh, as the current collector, was attached on both side with Ag paste as a

sealer. Ag wire was attached to that Ag mesh and connect the cell with I-V meter (microvoltmeter, 89 Constant), a potentiometer up to 20k Ω . Scheme of the single cell with the electrical network is described in Figure 1(a). Meanwhile, the scheme of single cell performance measurement is described in Figure 1(b). The fuel cell test was conducted at 300 °C, 400 °C, 500 °C and 600 °C with polyethylene liquid as fuel and oxygen in the air as oxidator. The polyethylene liquid was converted into gas by heating at 150 °C. In this research, the gas reforming was conducted by evaporating polyethylene liquid and the polyethylene gas would be reformed inside the fuel cell reactor.

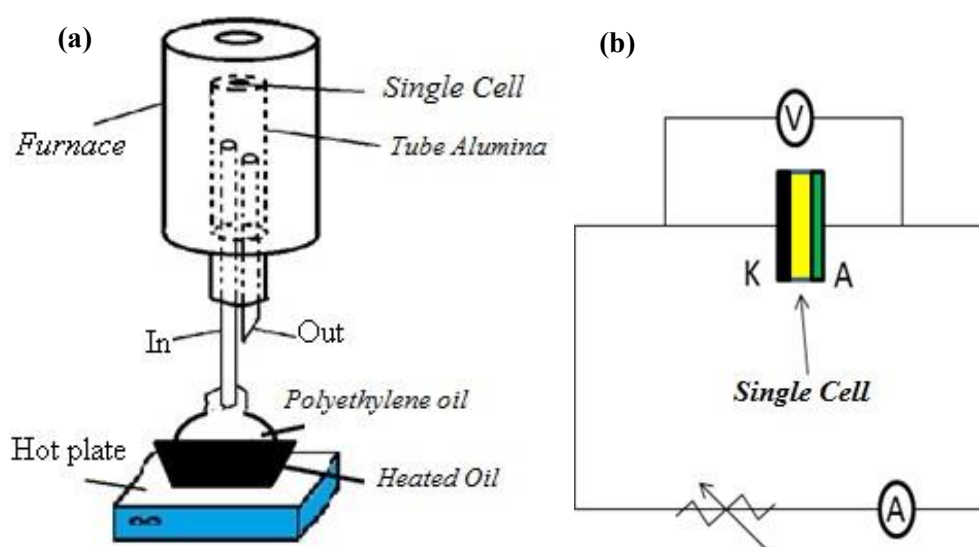


Figure 1. Scheme of single cell and the single cell test measurement

3. Result

The polyethylene liquid as produced from pyrolysis shows a yellow color liquid with physical properties as listed in Table 1.

Table 1. Physical Properties of the liquid polyethylene

No.	Properties	Identification
1	Color	Yellow
2	Density (g.cm ⁻³)	0.760
3	Viscosity (Poise)	0.58
4	Ph	4

Meanwhile, molecular identification by GC-MS analysis results in a spectrum as depicted in Figure 2.

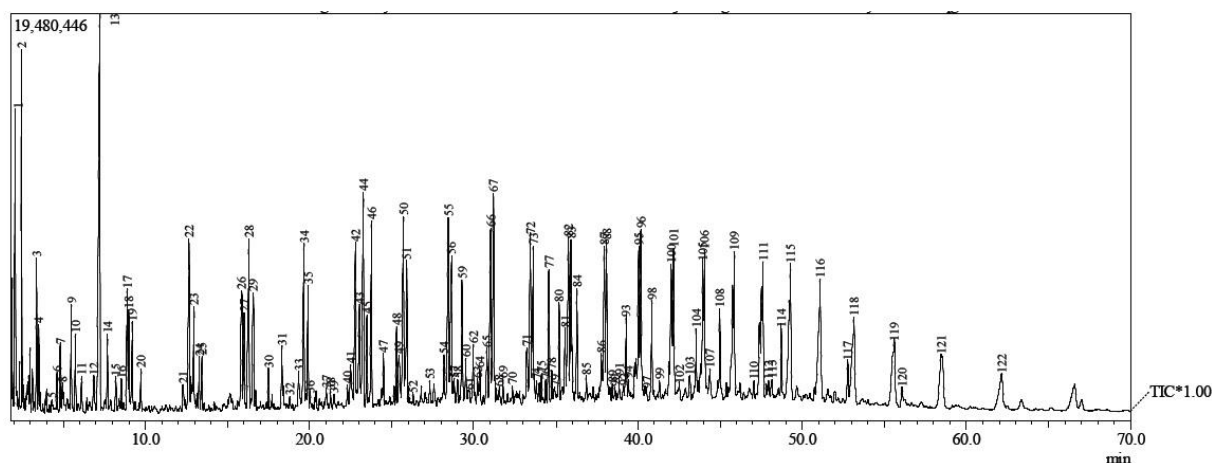


Figure 2. Chromatogram of the liquid polyethylene as produced by pyrolysis process

GC spectrum shows many peaks present in the liquid. It indicates that the liquid consist of some hydrocarbon with a various number of carbon chains. The Mass spectroscopy might identify some major peaks that present on the GC spectra. Some MS spectrums are depicted in Figure 3-6.

SE:90 Formula: C₉H₁₈ CAS: 19549-87-2 MolWeight: 126 RetIndex: 0

CompName: 2,4-Dimethyl-1-heptene

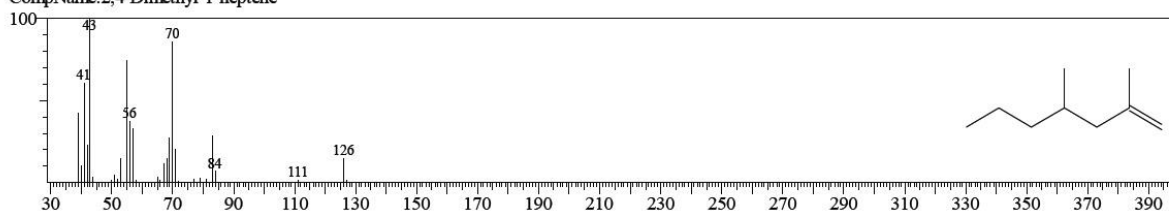


Figure 3. Mass-Spectroscopy of peak 13 from polyethylene oil chromatogram

SI:92 Formula: C₁₂H₂₄ CAS: 74630-42-5 MolWeight: 168 RetIndex: 0

CompName: 1-Undecene, 7-methyl- (CAS)

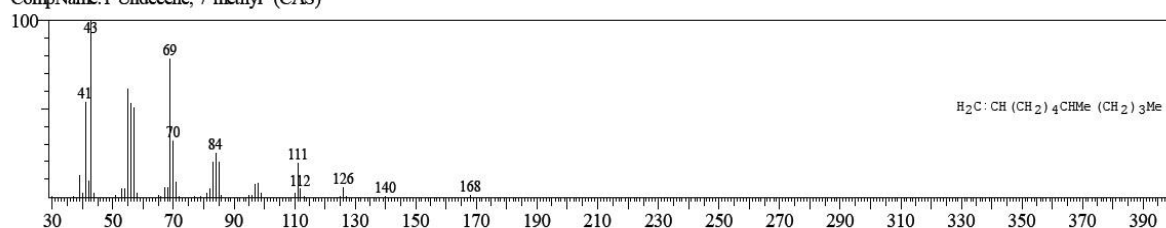


Figure 4. Mass-Spectroscopy of peak 44 from polyethylene oil chromatogram

SI:96 Formula: C₁₅H₃₀ CAS: 13360-61-7 MolWeight: 210 RetIndex: 0

CompName: 1-Pentadecene

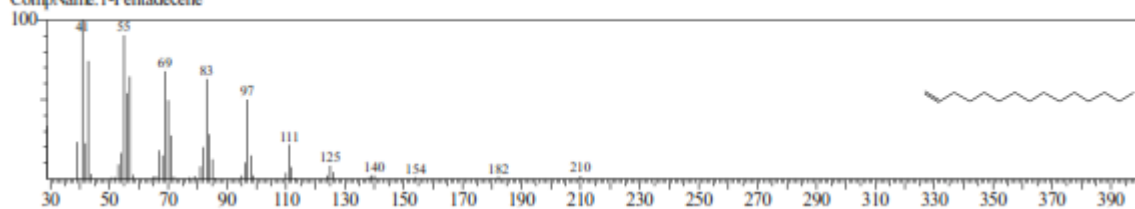


Figure 5. Mass-Spectroscopy of peak 55 from polyethylene oil chromatogram

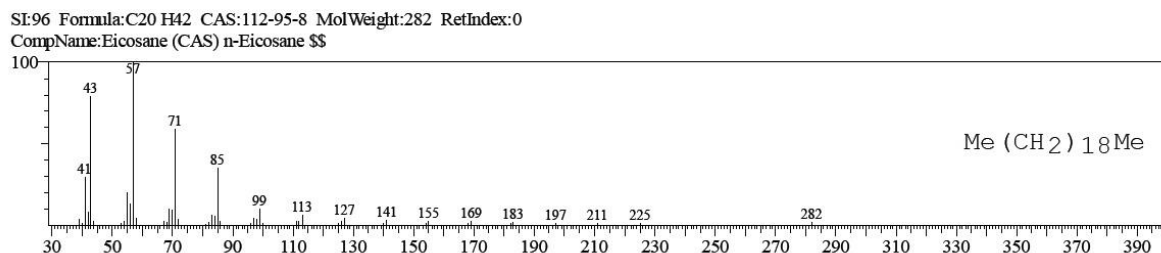


Figure 6. Mass-Spectroscopy of peak 101 from polyethylene oil chromatogram

The GC-MS analysis shows that the liquid polyethylene contains hydrocarbon compound with the carbon chain ranging from C₇ until C₂₀. The analysis was conducted at a column temperature of 60°C with split injection mode and electron ionization system, and also helium gas as the gas carrier. The analysis shows that the main compounds of the liquid polyethylene as detected by chromatogram are C₉H₁₈ with a molecular weight of 126, C₁₂H₂₄ with a molecular weight of 168, C₁₅H₃₀ with a molecular weight of 210, and C₂₀H₄₂ with a molecular weight of 282. The result shows that some long-chain hydrocarbon molecules dominate the composition of the liquid polyethylene as the pyrolysis product. The long chain hydrocarbon molecules usually provide high boiling point temperature to convert the liquid into the gas phase. Therefore, that kind of liquid fuel actually needs to a posttreatment by catalytic cracking to reduce the carbon chain at least into C₇ until C₁₅. Short chain hydrocarbon will convert into gas easier than the long chain hydrocarbon, and it may increase its performance as fuel for the solid oxide fuel cell.

Table 2. Hydrocarbon compound of polyethylene pyrolysis oil

No	Compound of Hydrocarbon	Amount of Hydrocarbon (%)
1	C ₅ H ₁₀	1.49
2	C ₆ H ₁₂	1.69
3	C ₇ H ₁₄	2.04
4	C ₈ H ₁₆	2.18
5	C ₉ H ₁₈	10.44
6	C ₁₀ H ₂₀	3.8
7	C ₁₁ H ₂₂	2.71
8	C ₁₂ H ₂₄	14.11
9	C ₁₃ H ₂₆	2.72
10	C ₁₄ H ₂₈	9.06
11	C ₁₅ H ₃₀	2.4
12	C ₁₆ H ₃₂	9.61
13	C ₁₇ H ₃₄	3.35
14	≥C ₁₈ H ₃₈	34.4

From this research, SDC and NSDC have been synthesized by the sol-gel method. Analysis of SDC powder was done by XRD to determine the crystal structure. The diffraction pattern of SDC compared to SDC diffraction standard from ICSD #28791 is shown in Figure 7. It can be seen that the peaks are in good agreement with the standard peaks, confirming that the SDC was successfully synthesized.

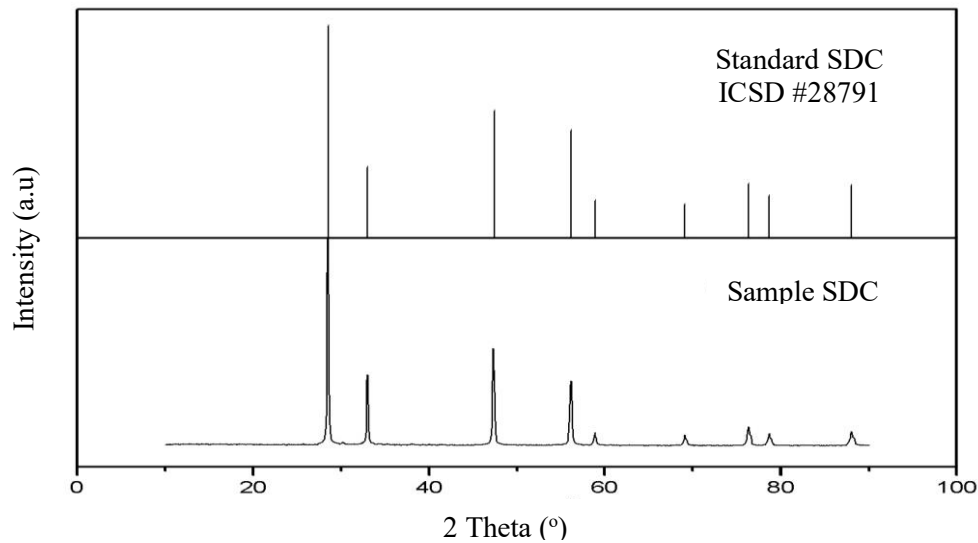


Figure 7. Diffractogram of Composite SDC and SDC standard

Meanwhile, NSDC is a mixture of SDC with Na_2CO_3 at a molar ratio of 1: 1. Before being mixed, Na_2CO_3 was calcinated at 800°C to release the H_2O molecules. The diffractogram (Figure 7) does not show any characteristic peaks of Na_2CO_3 . It indicates that the Na_2CO_3 is in an amorphous structure [10, 12]. The amorphous Na_2CO_3 might coat the SDC particles [14] (Zhu et al., 2006). Le Bail refinement on NSDC diffraction data found that the NSDC has two phases, i.e SDC and Na_2O . The SDC is cubic with a space group of $FM\ 3\ M$. Meanwhile, Na_2O also in a cubic structure with space group $FM\ 3\ M$. The cell parameters are listed in Table 2. The cell parameter of SDC is $5.437909(2)\ \text{\AA}$, and it becomes $5.433043(2)\ \text{\AA}$ after combined with Na_2CO_3 . It indicates that the sodium ions, Na^+ , or did not enter into the SDC structure. Both are combined as a composite which still carries they own properties.

Table 3. The cell parameters of SDC and NSDC as the result of Le Bail refinement with cubic structure and space group of $FM3M$

Parameter cell	SDC	NSDC	
	SDC cubic $FM\ 3\ M$	SDC cubic $FM\ 3\ M$	Na_2O $FM\ 3\ M$
a(\AA)	5.437909(2)	5.433043(2)	5.550000(0)
b(\AA)			
c(\AA)			
Volume (\AA^3)	160.803619(1)	160.36852(9)	170.953888
Rp %	7.828	3.87	
Rwp %	7.926	3.80	

The single cell test of NSDC-L [NSDC] NSDC-L was conducted at 300, 400, 500, and 600 °C. The I-V curve is described in Figure 9. The result shows that the power density increases as the temperature increases. Meanwhile, the open circuit voltage, OCV reached the highest value on 500°C of temperature and was measured at 0.475 V. The values are listed in **Table 4**. The highest power density was found at 600 °C of operational temperature on 0.14 mW.cm⁻². However, the power density which is 0.14 mW.cm⁻² is still too low for commercial purpose. GC-MS analysis shows that the polyethylene liquid mainly consists of C7-C20. Heating at 150 °C apparently only vaporize C7 and C8 which are the only small amount of the liquid fuel. Therefore, only small amount of fuel that would reform into hydrogen and carbon monoxide.

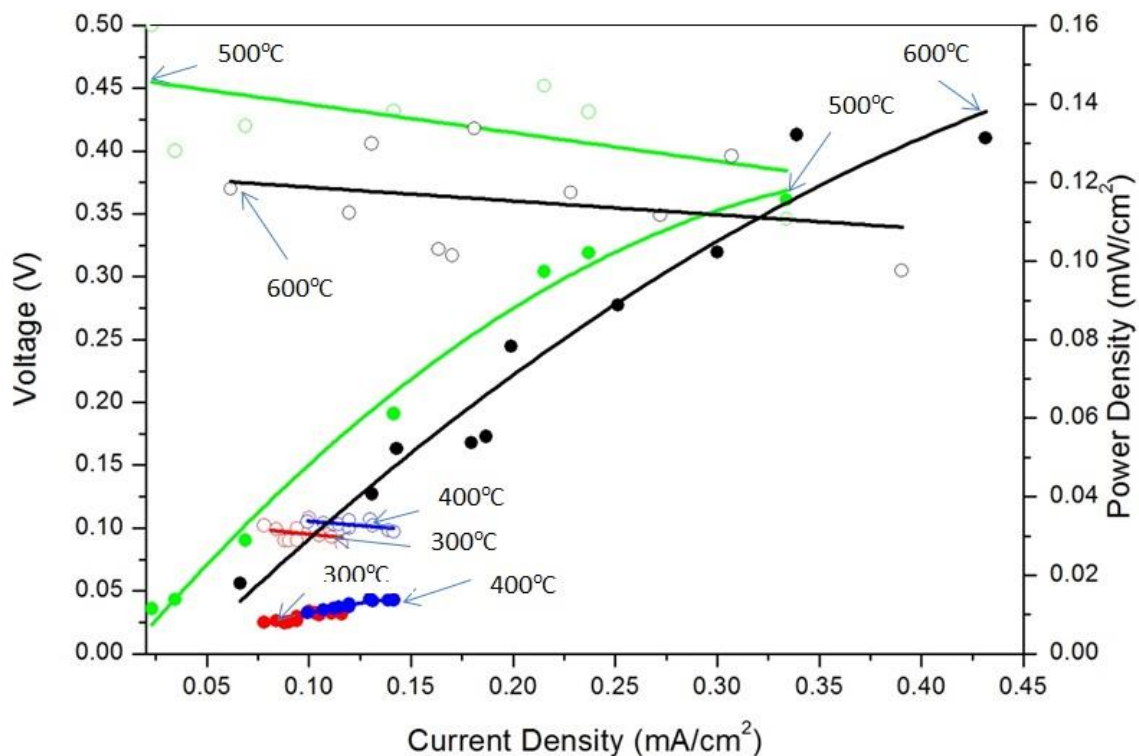


Figure 9. Effect of operation temperature on NSDC application loaded by polyethylene oil.

Table 4. The Open circuit voltage (volt) and power density (mW.cm⁻²) at various temperature

Temperature (°C)	Open circuit voltage (volt)	Capacity (mW.cm ⁻²)
300	0.10	0.0105
400	0.11	0.0140
500	0.475	0.1200
600	0.400	0.1400

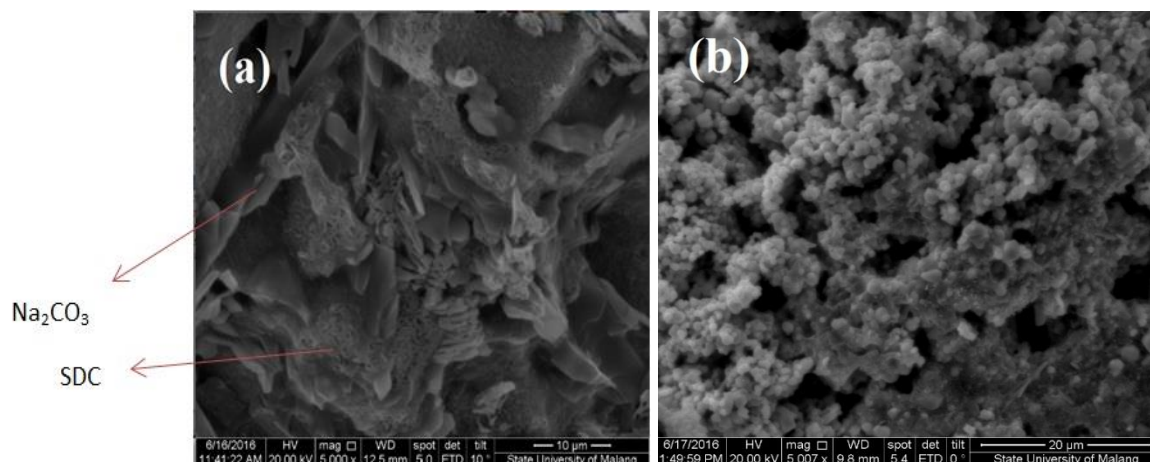


Figure 8. NSDC Image by SEM (a) before and after (b) being loaded with polyethylene oil

SEM analysis shows that there is a different morphology of NSDC electrolyte at before and after being loaded with polyethylene oil. Na_2CO_3 showed as an irregular chunk (**Figure 8a**) due to the preheating treatment changed sodium carbonate to sodium oxide. This is in accordance with the Le Bail refinement which confirms the presence of Na_2O instead of Na_2CO_3 . The morphology after being loaded with polyethylene oil has a different form (**Figure 8b**). Heat treatment during fuel cell operation seemed to melt Na_2O chunks and the melted form layered the SDC particles.

Elemental analysis by EDX on three positions of the cathode-NSDC interface, in the middle of NSDC, and at the anode-NSDC interface shows that during fuel cell operation at 300 – 600 °C there was a migration of ions whether from the electrolyte, NSDC, to electrode, NSDC-L or vice versa. It can be seen in Table 5. That the Cerium content in electrolyte part (in the middle) increased from 08.03 % to 25.82 %, indicating the Cerium ions transport from the electrode to electrolyte. However, cerium ions content also increased on cathode and anode part. It might because of the decreasing of carbon content that caused the cerium part to be increased and also the migration from electrolyte part. Table 5 shows that the increasing of Ce content is highest among others. It confirms that the increasing was not only coming from rational effect but also because of ionic migration. Meanwhile, Cu ions are detected at the cathode and anode part, but those are not detected in the electrolyte part. It indicates that there was no migration of Cu ions from the electrode to the electrolyte.

Table 5. Elemental content of single cell NSDC-L(cathode)|NSDC|NSDC-L(anode) at before and after fuel cell test. The EDX analysis was conducted at three points.

Element	% Weight at Point					
	Cathode-NSDC interface		Middle (NSDC)		NSDC-anode interface	
	Before	After	Before	After	Before	After
C	18.50	07.80	13.56	06.39	13.32	05.64
O	42.00	35.92	33.33	31.91	35.83	24.00
Na	33.25	32.86	41.45	28.88	34.74	16.83
Ce	02.54	19.05	08.03	25.81	10.40	37.75
Sm	01.21	03.79	02.66	06.84	02.95	12.06
Ni	01.90	00.42	00.96	00.17	01.86	02.32
Cu	00.60	00.17	-	-	00.90	00.41

4. Conclusions

Polyethylene liquid that was produced through pyrolysis method contains hydrocarbon chain ranging $C_5 - C_{20}$. A single fuel cell of NSDC-L [NSDC|NSDC-L can convert polyethylene liquid into electricity and produce a maximum power density of 0.14 mW/cm^2 and open circuit voltage of 0.4 Volt at 600°C . Gas reforming needs to be increased by heating treatment method and fuel cell design. SEM/EDX analysis of the three spots confirm that there was an ionic migration between electrode-electrolyte part.

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