BIODIESEL FUELS CONVERSION TO HYDROGEN-RICH GAS AND ELECTRICITY WITH SOLID OXIDE FUEL CELL TECHNOLOGY

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Abstract

Direct feeding of hydrocarbon fuels to Solid Oxide Fuel Cells (SOFCs) has attracted much attention in recent years. The aim of this paper is to investigate the viability of anode-supported type cells (Ni-ScSZ/ScSZ/LSM-ScSZ) operating with biodiesel fuels (BDFs) derived from Palm, Jatropha and Soybean oils, for realizing carbon-neutral power generation using fuel cells in the temperature range of 700 - 800°C. The results demonstrated that in principle direct internal reforming (DIR) of BDFs in the SOFC anode is viable, but the content of unsaturated components in BDFs should be as lower as possible to suppress performance degradation. Palm-biodiesel, containing highest amount of saturated fatty acid methyl ester (FAME) among tested BDFs, had led to most stable SOFC operation, and the amount of deposited carbon was considerably small compared to the other fuels with higher degree of unsaturation.

Keywords: Biodiesel fuel, Carbon deposition, Direct internal reforming, Hydrogen production, Solid oxide fuel cell, Steam reforming

Introduction

Nowadays, heat engines are used worldwide for transportation, manufacture, power generation, construction, and farming. However, the engines are a major contributor to environment pollution and climate change. In addition, fossil fuels could be spent only within several decades. Fuel cells are electrochemical devices that convert chemical energy directly into electrical energy without converting it to mechanical energy. Therefore, the fuel cell has potential of attaining higher electrical conversion efficiency than those of conventional technologies such as heat engines limited by Carnot efficiency. Besides, fuel cell systems can be operated with very low environmental emission levels due to their electrochemical conversion. Therefore, fuel cells are regarded as efficient and environmentally-friendly energy conversion system in the next generation. Most of fuel cells require hydrogen as a fuel, however the use of hydrocarbon fuels such as fossil fuels and biofuels is also desirable. Solid oxide fuel cell (SOFC) operated at high temperatures (600 - 900°C) which allows direct oxidation of hydrocarbon fuels without external reformer attracts much attention [1-3]. Direct internal reforming (DIR) of hydrocarbon fuels has been reported including gaseous fuels such as methane [4-5], ethane [4], and butane [4, 6], and liquid fuels such as n-decane [7], gasoline [8], synthetic diesel [7], crude and jet fuel oils [9]. In view of the exhaustion of fossil resources, the utilization of biomass sources as sustainable energy resources should be promoted more in large scale [10]. Biodiesel fuel (BDF) is an oxygenated fuel produced from biomass resources such as animal fat, plants, and waste-cooking oils. Biodiesel fuels have a high flash point, and their non-toxicity and biodegradability make their handling and storage safer compared to petro-diesel fuel. While in the past decade the share of BDF increased as an alternative fuel to petro-diesel fuel for the diesel engine, BDF is also a promising feedstock for electricity generation by solid oxide fuel cell (SOFC) [11]. However, no preceding research which systematically addressed steam reforming of practical biodiesel fuel for electricity generation has been reported. Therefore, feasibility of DIR of BDFs, produced from Palm, Jatropha and Soybean oils, to SOFC is examined in this study. In this study, in order to evaluate the potential of these fuels for SOFC applications, anodic-off gas and cell voltages of DIRSOFC running on BDFs were measured at various SOFC operating temperatures between 700 and 800^oC, at S/C = 3.5.

Experimental

Biodiesel Fuels Used in This Study

In this study, Palm-biodiesel fuel (Palm-BDF), Jatropha-biodiesel fuel (Jatropha-BDF) and Soybean-biodiesel fuel (Soybean-BDF) were produced from refined Palm, Jatropha Curcas Linn and Soybean oils, respectively, by the alkali catalysed trans-esterification reaction in a pilot scale reactor at Bandung Institute of Technology, Indonesia [12]. According to their analysis, following the ASTM methods, the fuels had almost the same physical and chemical properties as petroleum diesel fuel as shown in Table 1. The physical properties of these fuels met most of the specifications of ASTM D-6751 standard for biodiesel fuel.

Table 1. Physical Properties of the Tested BDFs

Parameter	Unit	Diesel	Palm-BDF	Jatropha-BDF	Soybean-BDF
Density, 40^oC	kg/l	0.825	0.860	0.864	0.864
Kinematic viscosity, 40^oC	cSt	3.28	4.50	4.40	4.17
Distillation, T90	^oC	330	336	347	349
Pour point	^oC	-	9	0	6
Cloud point	^oC	-	17	7	0
Sulphur content	ppm	-	1	7	<1
Phosphorus content	ppm	-	< 3	< 3	< 3
Cetane number		55-60	56.8	56.4	55.6
Acid value	mg-KOH/g	-	0.2	0.28	0.29
Ester content	%	-	99.3	94.0	97.5

The chemical compositions and impurities (Sulphur and Phosphorus) in the tested BDFs were analyzed in Shimadzu Inc., Japan. The biodiesel fuel is a complex mixture of various fatty acid methyl esters (FAME) as listed in Table 2. The main chemical compositions of the fuels were palmitic acid methyl ester (C16:0), oleic acid methyl ester (C18:1), and linoleic methyl ester (C18:2). Table 3 shows the concentrations of saturated and unsaturated components in the respective BDFs and their average structures. Palm-BDF consisted mainly of 46.4 % of saturated FAME (main component was 39.9 % of palmitic acid methyl ester) and 40.7 % of mono-unsaturated FAME (main component was 40.4 % of oleic acid methyl ester). Jatropha- and Soybean-BDF contained higher amount of unsaturated FAME compared to Palm-BDF. Jatropha-BDF consisted mainly of 41.4 % of mono-unsaturated FAME (main component was 40.5 % of oleic acid methyl ester) and 31.5 % of di-unsaturated FAME (linoleic acid methyl ester). Soybean-BDF consisted mainly of 22.5 % of mono-unsaturated FAME (main component was 22.4 % of oleic acid methyl ester) and 53.9 % of di-unsaturated FAME (linoleic acid methyl ester). Soybean-BDF not only contained higher amount of di-unsaturated FAME compared to Jatropha-BDF but also contained rather high amount of tri-unsaturated FAME (5.28 % of linolenic fatty acid methyl ester). Amount of unsaturated FAME in BDF increases in order of Palm-BDF < Jatropha-BDF < Soybean-BDF. In this study, using these fuels the influence of the chemical compositions of the biodiesel fuels on hydrogen production properties and the related SOFC performance will be discussed.

Table 2. FAME Composition of the Tested BDFs

Components	Concentration / wt%		
	Palm-BDF	Jatropha-BDF	Soybean-BDF
C8:0	0.05	0.07	0.09
C10:0	-	-	0.05
C12:0	0.41	0.06	0.31
C14:0	1.08	0.07	0.17
C15:0	0.05	-	-
C16:0	39.9	13.7	10.7
C17:0	0.08	0.09	0.09
C18:0	4.35	0.09	3.19
C20:0	0.36	6.65	0.33
C22:0	0.08	0.07	0.41
C23:0	-	-	0.07
C24:0	0.05	-	0.11
C16:1	0.19	0.86	0.09
C18:1	40.4	40.5	22.4
C18:2	12.0	31.5	53.9
C18:3	0.21	0.17	5.28
C20:1	0.15	0.07	0.31

Table 3. Composition of Saturated and Unsaturated Components in the Tested BDFs

	Concentration / wt%		
	Palm-BDF	Jatropha-BDF	Soybean-BDF
Saturated	46.4	20.9	15.5
Mono-unsaturated	40.7	41.4	22.5
Di-unsaturated	12.0	31.5	53.9
Tri-unsaturated	0.21	0.17	5.28
Average structure	$C_{18.0}H_{34.8}O_2$	$C_{18.7}H_{35.0}O_2$	$C_{18.8}H_{34.5}O_2$

Fabrication of Single Cell of Solid Oxide Fuel Cell

Anode-supported half cells with a diameter of 20 mm (purchased from Japan Fine Ceramics, Japan) in which 10 mol% Sc_2O_3-1 mol% CeO_2-89 mol% ZrO_2 (scandia-stabilized zirconia abbreviated by ScSZ) electrolyte with a thickness of 30 μm was sintered on a porous anode support (mixture of NiO and ScSZ (NiO:ScSZ = 5.6:4.4)) with a thickness of 800 μm were used to fabricate single cells. A mixture of NiO (> 99.9 %, Kanto Chemical, Japan) and ScSZ (Daiichi Kigenso Kagaku Kogyo, Japan) powders with a weight ratio of 8:2 was screen-printed and subsequently sintered on the anode support at 1200 °C for 3 h as an anode current collector with the area of 8 x 8 mm^2. A mixture of $(La_{0.8}Sr_{0.2})_{0.98}MnO_3$ (> 99.9 %, Praxair, USA, abbreviated by LSM) and ScSZ with a weight ratio of 1:1 was adopted as a cathode functional layer and coarse LSM was applied as a cathode current collector layer. The pastes are deposited on the ScSZ electrolyte of half-cell via screen printing. A porous cathode with the area of 8 x 8 mm^2 was obtained by sintering the deposited pastes at 1200 ^{o}C for 5 h. Pt mesh with Pt wire was attached to the each surface of the anode and cathode as the current collectors using a Pt paste. Schematic view of the single cell was shown in Figure 1.

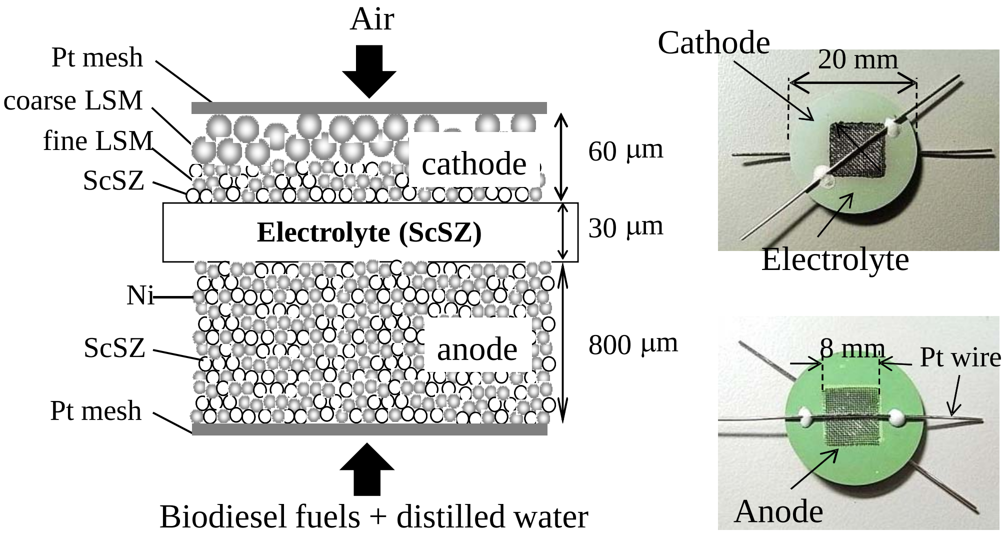

Figure 1. Schematic view and optical images of anode-supported SOFC single cell used in this study

Electrochemical Measurements

The electrochemical measurement setup for biodiesel-fueled SOFC is shown in Figure 2. The button cell was heated from room temperature to 900 ^{o}C at 200 ^{o}C h^{-1} as a standard in our laboratory. The reduction treatment of the anode material in a flow of dry H_2 at 900 ^{o}C for 1 h, then the cell temperature was decreased to an operational temperature of 700 – 800 ^{o}C. After stopping the H_2 supply, the biodiesel fuel and distilled water were supplied by micro liquid pumps (LC-20AD, Shimadzu, Japan), with a flow rates of 6 and 21 μl min^{-1}, respectively, so that S/C became 3.5. The two liquids were mixed in the evaporator at 600 ^{o}C and then the gaseous mixture was directly supplied to the catalyst bed using 50 ml min^{-1} of N_2 carrier gas. After waiting for 1h under open circuit condition, anodic-off gas was an automatic gas chromatograph (GC-20B, Shimadzu, Japan), and then a current-voltage curve of the direct internal reforming (DIR) SOFC running on BDF was measured in the current density range between 0 and 0.4 A cm^{-2}. After the I-V measurement, again, the current load was increased up to 128 mA (corresponding to 0.2 A cm^{-2}), and subsequently the terminal voltage was galvanostatically measured for 50 h. After testing, the cell temperature was decreased to room temperature under thorough N_2 purging of the anode compartment. The surface and cross-section of the tested anode were observed by a field emission scanning electron microscope with EDS (FESEM 5200, Hitachi High-Technologies, Japan).

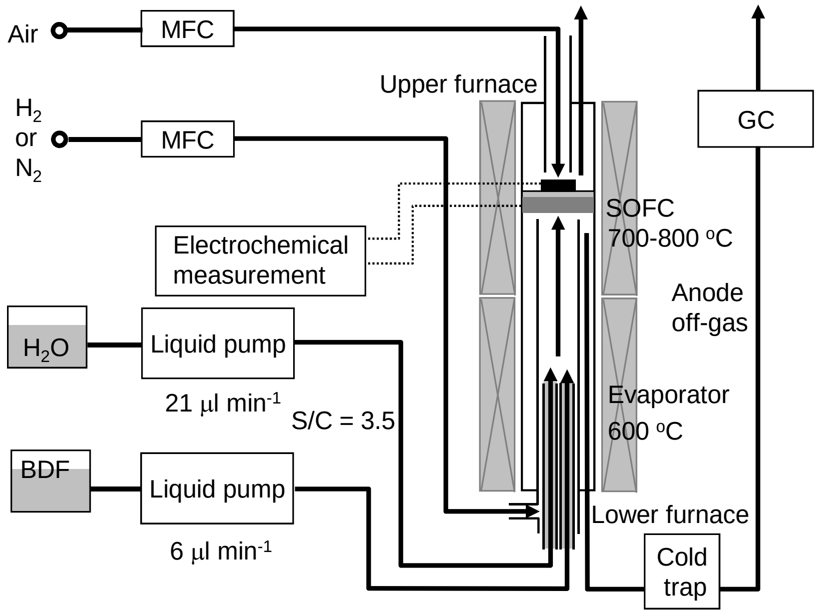

Figure 2. Experimental setup for testing DIRSOFC running on BDF

Results and Discussion

Direct Internal Reforming of Biodiesel Fuels

Direct internal reforming of BDF in SOFC for electricity generation is complex reactions as shown in Figure 3. Many reactions occur simultaneously on the anode SOFC including many side reactions. Biodiesel fuels are steam reforming within the porous Ni-based anode at high temperature, producing hydrogen, carbon monoxide, water, carbon dioxide, light hydrocarbons (C_xH_y) and coke. Then the electrochemically active H_2 and CO are only oxidized at the triple phase boundary to generate electricity and heat through electrochemical oxidation [1-2].

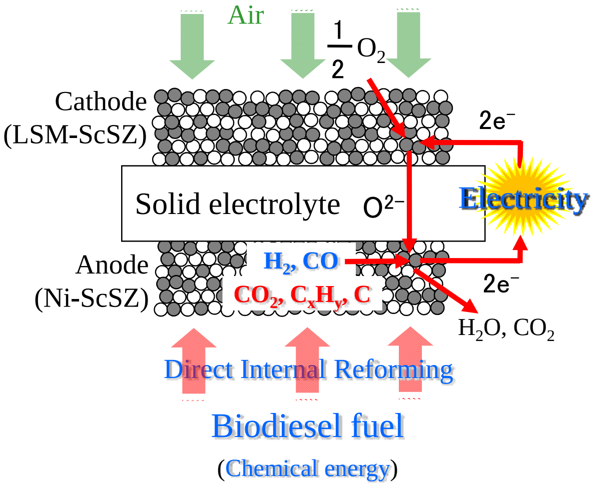

Figure 3. Principle of DIRSOFC running on BDF

The main reactions inferred in the steam reforming of BDF are listed in Table 4 [11]. Steam reforming (reaction 1) producing H_2 and CO, and pyrolysis (reaction 2) producing C_xH_y (CH_4 and C_2H_4) and coke, as well as H_2 and CO, may occur as competing reactions. Both reactions are endothermic reactions, promoted at higher temperatures. Steam reforming is a heterogeneous reaction catalysed by Ni, whereas pyrolysis, a non-catalytic gas phase reaction, tends to occur at water-lean regions or at deactivated surface regions of catalyst. Excess H_2O reacts not only with C_xH_y (reaction 3), but also with the produced CO (reaction 4), to form further H_2. Reactions 5 and 6 are exothermic hydrogenation reactions which consume H_2 and produce CH_4. Reactions 7 and 8 are endothermic gasification reactions of coke. While S/C = 3.5 is thermodynamically out of the carbon deposition region [9-10], the contributions of reactions 5, 7, and 8 are not negligible, when carbon is deposited on the catalyst surface.

Table 4. Main Reactions Involved in Steam Reforming of BDFs

1	$C_nH_mO_2 + (n-2)H_2O \Leftrightarrow (n+m/2-2)H_2 + nCO$	Steam reforming
2	$C_nH_mO_2 \Leftrightarrow$ gases (H_2, CO, C_xH_y) + coke	Pyrolysis
3	$C_xH_y + xH_2O \Leftrightarrow xCO + (x+y/2)H_2$	Steam reforming
4	$CO + H_2O \Leftrightarrow H_2 + CO_2$	Water-gas shift
5	$C + 2H_2 \Leftrightarrow CH_4$	Hydrogenation
6	$CO + 3H_2 \Leftrightarrow CH_4 + H_2O$	Hydrogenation
7	$C + H_2O \Leftrightarrow CO + H_2$	Coke gasification
8	$C + CO_2 \Leftrightarrow 2CO$	Boudouard-reaction

Figure 4 shows the temperature dependence of fuel conversion and gas concentrations in anodic-off gas for DIR of BDFs on SOFC anode. The performance of BDF reforming increased with increasing the operational temperature because of the enhancement of the steam reforming reaction rate. At lower operational temperatures, exothermic hydrogenation reactions of coke (reaction 5) and carbon monoxide (reaction 6) are promoted, therefore H_2 decreased and CH_4 increased with decreasing temperature. At higher operational temperatures, endothermic steam gasification of coke (reaction 7) and the Boudouard reaction (reaction 8) are promoted, therefore the relative amount of CO against CO_2 in reformate increased with increasing temperature. Total concentrations of electrochemically active H_2 and CO were around 70-80 vol. % for all tested BDFs, which are suited to SOFC operation. The steam reforming of Palm-BDF, having highest amount of saturated component among the tested fuels, resulting in highest electrochemical performance (see Figure 5 and 6). The performance of steam reforming decreased in the order of Palm-BDF > Jatropha-BDF > Soybean-BDF, indicating that higher content of saturated components led to highest quality of anodic-off gas for SOFC operation. In addition to H_2, CO and CO_2, significant amount of CH_4 and C_2H_4 were detected especially for internal reforming on SOFC anode. The existence of CH_4 and C_2H_4 indicates that the internal reforming reaction did not reach equilibrium. Ethylene is well known as a precursor of carbon deposition [13]. At the sites covered with the deposited carbon, the steam reforming reactions (reactions 1, and 3) and shift reaction (reaction 4) may be retarded. Reactions 5, 7 and 8 in which carbon is one of the reactant selectively may proceed.

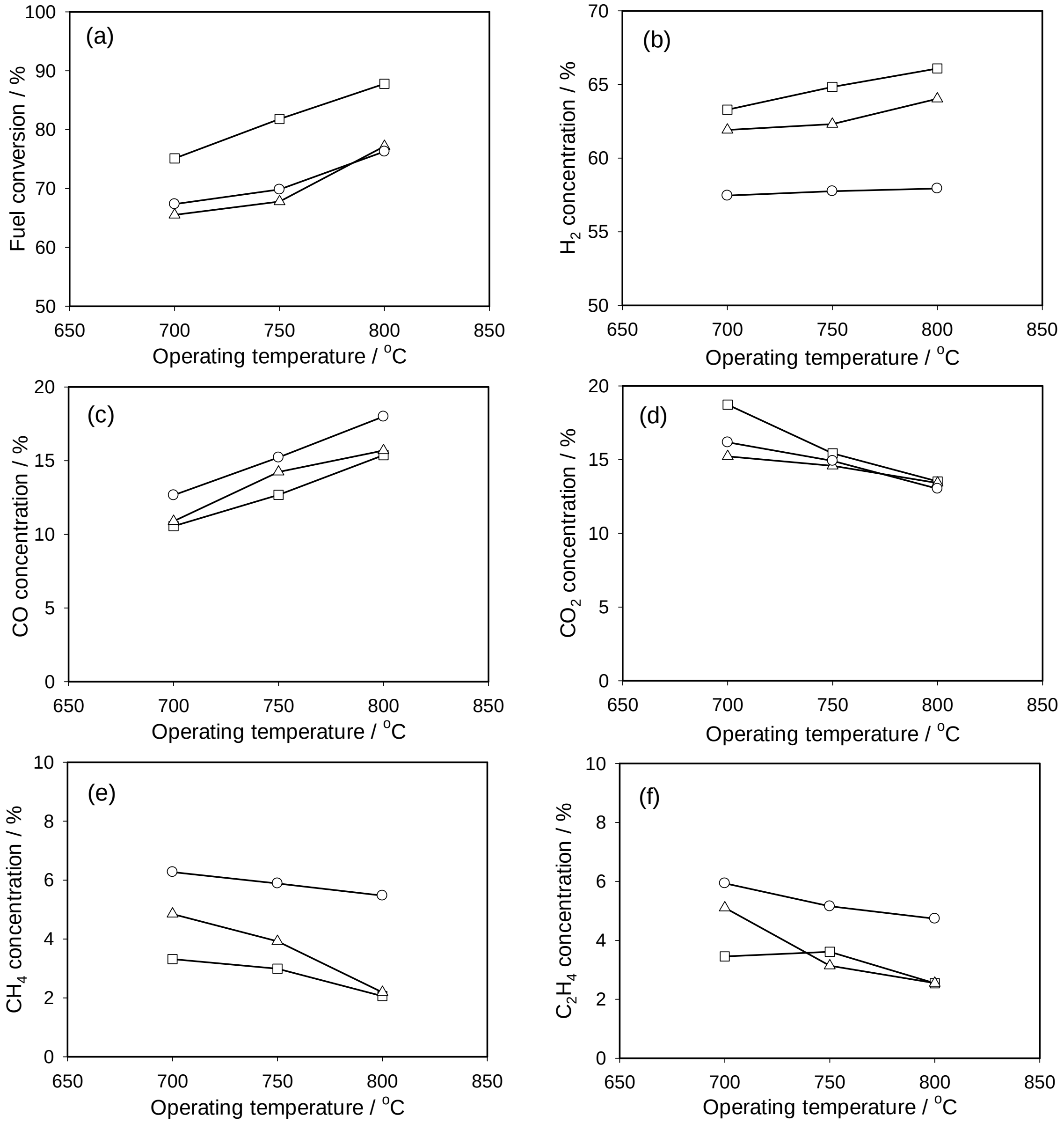

Figure 4. Fuel conversion and gas concentrations in anodic-off gas for the steam reforming of Palm-BDF (□), Jatropha-BDF (Δ), and Soybean-BDF (O) on anode material of SOFC

Electrochemical Performance of DIRSOFC Running on BDFs

Figure 5 shows the current-voltage curves in the temperature range of 700–800 °C when practical BDFs were fed to SOFC. Cell performance increased with increasing the operational temperature because of the enhancement of the steam reforming reaction rate (see Figure 4) as well as electrochemical reaction rate. The cell voltage at the same conditions decreased in the order of Palm-BDF > Jatropha-BDF > Soybean-BDF. Palm-BDF fuelled SOFC had led to power density of 294 mW cm^{-2} for DIRSOFC running on Palm-BDF at 0.4 A cm^{-2} and 800 °C, which is comparable to the performance for H_2-fueled SOFC operation [14].

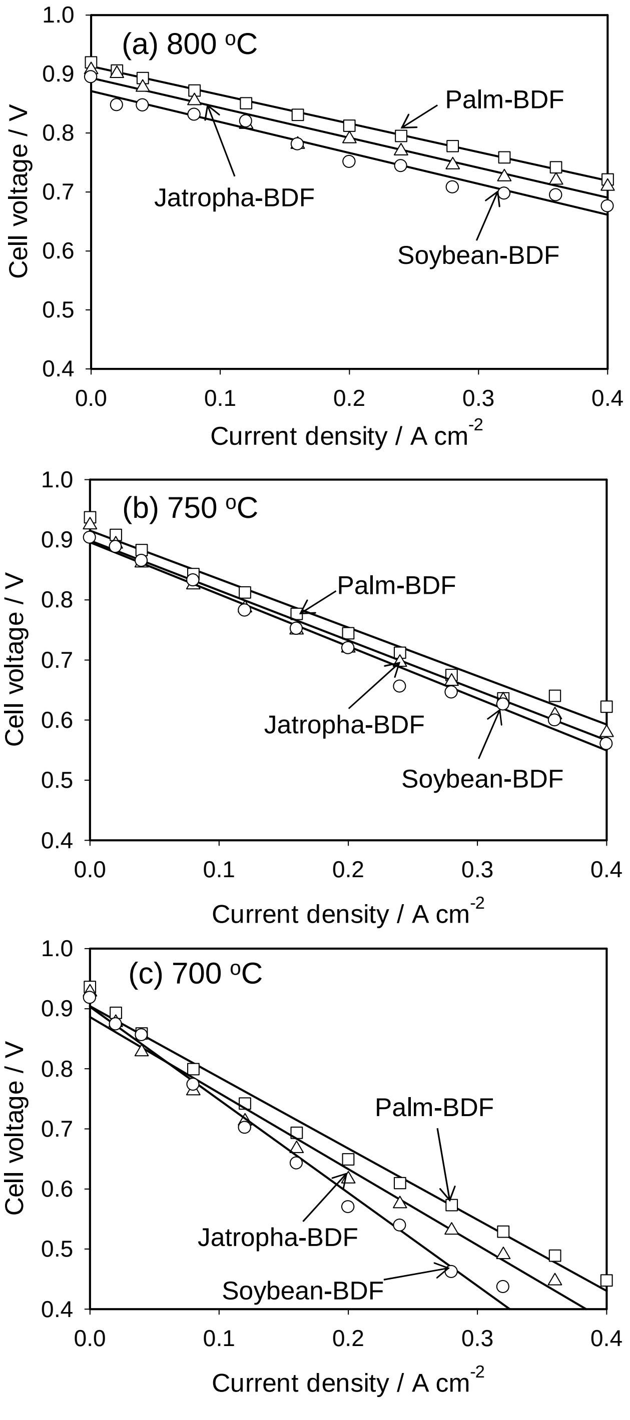

Figure 5. Cell voltage versus current density for DIRSOFCs running on Palm-BDF (□), Jatropha-BDF (Δ), and Soybean-BDF (O) at (a) 800 °C, (b) 750 °C, and (c) 700 °C under S/C = 3.5

Figure 6 shows the results of galvanostatic measurements of DIRSOFC at different operating temperatures for the BDFs under the condition of 0.2 A cm^{-2} and S/C = 3.5. Stable voltage without outstanding oscillation was obtained only for palm-BDF in the temperature range of 700-800 °C. In contrast Jatropha- and Soybean-BDF resulted in unstable cell voltage with remarkable voltage oscillation. Especially, at 700 °C cell voltage for DIRSOFC running on Jatropha-, and Soybean-BDF dropped abruptly within 40 h and 47 h, respectively. The result show that the electrochemical performance of DIRSOFC increased with increasing the content of saturated components in the BDFs.

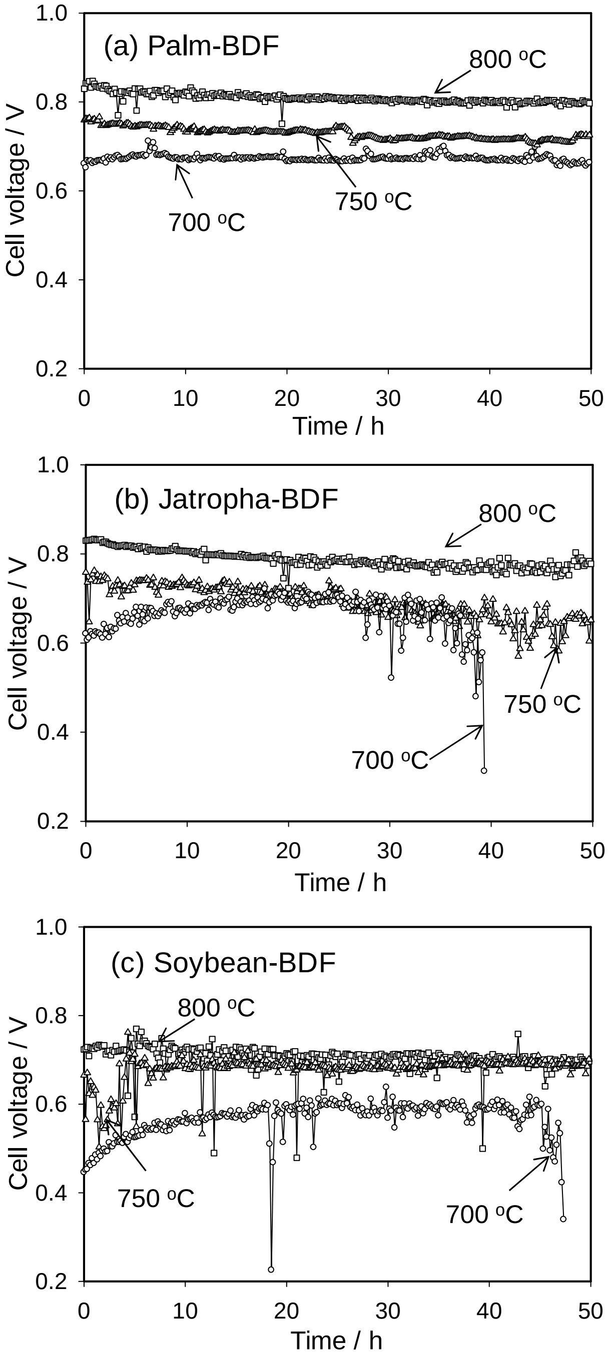

Figure 6. Cell voltage of DIRSOFCs running on (a) Palm-BDF, (b) Jatropha-BDF, and (c) Soybean-BDF in the temperature range of 700-800 °C under S/C = 3.5 and 0.2 Acm^{-2} for 50 h

After stopping the supply of BDFs, the cell temperature was decreased to room temperature under thorough N_2 purging of the anode compartment. Optical images of the SOFCs after 50h feeding BDFs are shown in Figure 7. Nearly no carbon was observed at 800 °C in the case of Palm-BDF, whereas the other BDFs had led to significant amount of carbon on the anode surface. Carbon deposition tended to be more significant at lower operational temperatures and at higher content of unsaturated FAMEs in BDFs [10]. Severe carbon deposition occurred only on the surface of the anode, where it is most susceptible to coking, due to high concentration of long chain hydrocarbons or low S/C [14]. Inside of the porous SOFC anode was quite clean. The occurrence of electrochemical consumption of H_2 leading to an increase in local S/C and direct electrochemical consumption of carbon may prevent coking inside of the anode.

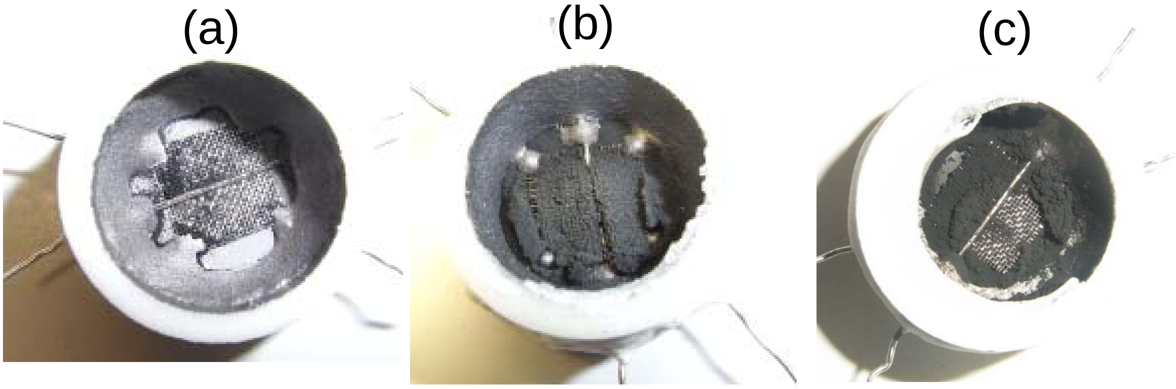

Figure 7. Pictures of the anode side after 50h galvanostatic measurements of DIRSOFCs running on BDFs at 800 °C shown in Figure 6; (a), (b), and (c) are for Palm-, Jatropha-, Soybean-BDF, respectively

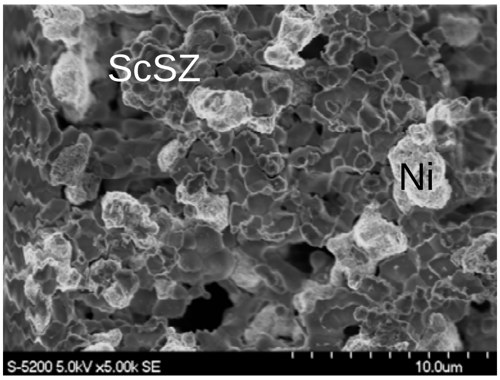

Figure 8. FESEM images of inside of the porous anode support shown in Figure 7c

Conclusions

In this study, DIRSOFC was evaluated in the temperature range of 700-800 °C by feeding the practical BDFs. Three different biodiesel fuels and two different pure chemicals having different degree of unsaturation of C-C bond were fed directly to anode substrate. The results demonstrated that in principle direct-feeding of biodiesel fuels into SOFC is viable, but the degree of unsaturation of liquid hydrocarbon fuels should be as lower as possible. Direct feeding of practical BDFs caused carbon deposition which was more significant at lower temperature and at higher degree of unsaturation. Carbon deposition was not observed on the SOFC anode only when Palm-BDF was supplied at the operational temperature of 800 °C. The results indicated that the degree of unsaturation is quite important factor to control electrochemical performance of DIRSOFC running on biodiesel fuels.

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