International Journal of Ambient Energy
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/taen20

Electrochemical conversion of switchgrass and poplar in molten carbonate direct carbon fuel cell

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Accepted author version posted online: 18 Jul 2012

To cite this article: Dr. Olalekan Adeniyi PhD (2012): Electrochemical conversion of switchgrass and poplar in molten carbonate direct carbon fuel cell, International Journal of Ambient Energy, DOI:10.1080/01430750.2012.709357

To link to this article: http://dx.doi.org/10.1080/01430750.2012.709357

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Abstract

One way of sustaining fuel cell technology is using renewable and sustainable energy means provided by biomass. This paper explores switchgrass and poplar in a molten carbonate electrolyte direct carbon fuel cell. It investigates their electrochemical conversions and provides results of power density, current density, open circuit voltage and other parameters. The biomasses were pyrolysed at 800^oC to produce carbon fuels. Biomass carbon fuels were mixed with molten carbonate and subjected to different operating conditions (600^oC to 800^oC) in the fuel cell. The electrochemical performances of the poplar fuel were better than those experienced with switchgrass fuel. At 800^oC the open circuit voltage of poplar fuel (1.08 V) has higher output than switchgrass (0.87 V). The peak power density recorded for poplar fuel was 23.91 mW/cm^2 while switchgrass fuel was lower at 21.60 mW/cm^2. Poplar fuel (81.53 mA/cm^2) gave a maximum current density with switchgrass fuel lower at 74.00 mA/cm^2.

Keywords: Molten Carbonate Direct Carbon Fuel Cell, switchgrass, poplar, open circuit voltage, power density, current density, biomass, pyrolysis, carbon, fuel.

1. Introduction

Fuel cells have many benefits in terms of reduced emission, higher fuel efficiencies and smooth operations but there is a need for fuel cell to be sustainable through the use of renewable sources of energies, that is, non-fossil sources of energy that is continuously regenerated by some natural processes. Sources of renewable and sustainable energy using fuel cell technology could be applied in the following routes [1-3]:

i. The use of biomass to generate carbon, biogas, syngas (CO and H_2), methanol or hydrogen.

ii. The generation of hydrogen by water electrolysis with electricity based on renewable.

A possibility of sustainable and renewable solutions to fuel problems comes from biomass. Biomass can be burnt to generate steam for driving steam turbines (or steam engine) to make electric power or directly used in a direct carbon fuel cell (DCFC) to generate electricity and heat energy. The chemical routes could include anaerobic digestion and thermal processing of biomass to make syngas, a mixture of carbon monoxide and hydrogen. The thermal process can also be applied in conjunction with almost any carbon-containing material. Typical fuels are wood, straw, fast growing reeds and trees harvested green [4]. The focus of this paper is on the electrochemical conversion of carbon fuels from switchgrass straw and poplar wood chips to produce electricity and heat energy from the molten carbonate electrolyte direct carbon fuel cell.

2. Experimental

2.1 Design of the molten carbonate electrolyte direct carbon fuel cell

Several designs were explored for the electrochemical cell unit of the molten carbonate direct carbon fuel cell (MCDCFC). Figure 1 shows the cell arrangement that was developed. The electrolyte was zirconia cloth saturated in a mixture of 46.6 wt.% Li_2CO_3 and 53.4 wt.% K_2CO_3. Gold wires were used as electrical contacts on the anode and cathode electrodes. The fuel cell was built by placing the anode, cathode and electrolyte as shown in Figure 1 while ensuring that the components were flat and in good contact. The cell was located between two ceramic tubes and mica seals were used to give a compressive hold around the electrode components, helping to prevent the leakage of gases and fuels from the system. The DCFC system was tightened and secured by using springs, nuts and bolts, to maintain the tension during heating and provided the support needed to hold the electrode assembly in the furnace. This developed electrode assembly was further improved by introducing ceramic disc with holes, which acted as a support for the cathode side as well as keeping the electrolyte flat and in proper contact with the electrode. This cell arrangement was discovered to be stable [1, 5].

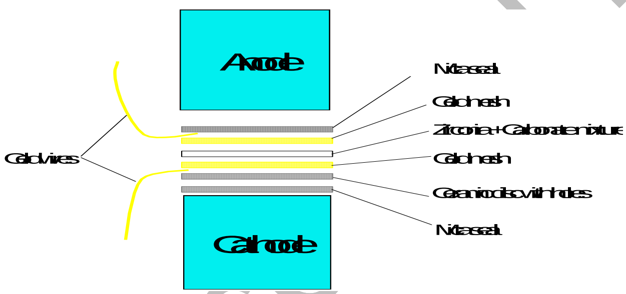

Figure 1: Gold mesh, zirconia, gold mesh electrode assembly with ceramic disc

2.2 Preparation and analysis of biomass

Swicthgrass straws and poplar wood chips were cut into smaller pieces before grinding. Grinding was carried out in the Cross Beater Mill (Model 16-150, Glen Creston Ltd.) with a sieve size of 2.0 mm. The cut biomass was added to the mill in stages for effective grinding and the process was repeated several times to obtain the effective particle size. The biomass samples of particle size of 0.5 to 2.0 mm, were dried at 100^{o}C before pyrolysing in a cylindrical Lenton furnace, which was electrically heated and the pyrolysis was monitored by thermocouple. In each run of the experiment 7.0 g of sample was fed into the reactor, which was heated at 7^{o}C/min up to the temperature of 800^{o}C. This was held for 30 min. Nitrogen gas was used to purge the system at a rate of 4000 cm^3/min, during and after the pyrolysis process until 200^{o}C. The proximate, ultimate, and calorific value analyses were carried out on the biomass. The ash and volatile content were carried out using Carbolite furnace (AAF 1100) at a temperature of 750^{o}C and 950^{o}C respectively. The moisture content was estimated using the Memmert oven operated at a temperature of 105^{o}C for an hour. The fixed carbon was calculated by difference. The carbon and hydrogen contents were analysed using Carbolite furnace operated at 1350^{o}C. The Bomb calorimeter (PARR 1261) was used to obtain the calorific value of the biomass [1].

3. Results and discussion

The results of the proximate and ultimate analyses carried out on switchgrass straw and poplar wood chip are given Table 1. The results of the analyses carried out on the carbon produced from these biomasses after pyrolysis are shown in Table 2. Table 3 gives the results of pyrolysis on the biomasses.

Table 1: Proximate, ultimate and calorific value analyses of ground biomass

Biomass	Moisture %	Ash %	Volatiles %	Fixed carbon %	CV MJ/kg	Carbon wt.%	Hydrogen wt. %
Switchgrass	7.04	7.39	71.73	13.84	17.86	41.90	4.08
Poplar	5.50	0.85	79.74	13.91	20.41	45.94	4.97

Table 2: Moisture, calorific value and ultimate analyses of biomass carbon

Biomass	Moisture (wt.%)	CV (MJ/kg)	Carbon (wt.%)	Hydrogen (wt.%)
Switchgrass	2.75	23.82	67.32	1.29
Poplar	2.64	30.90	83.74	1.70

Table 3: Pyrolysis results for switchgrass and poplar at 800^{o}C

Biomass	Heating rate (^{o}C/min)	Moisture content (wt.%)	Biomass mass (g)	Carbon mass (g)	Carbon (wt.%)
Switchgrass	7	7.73	5.9848	1.5538	25.96
Poplar	7	5.61	5.3256	1.0838	20.35

Table 1 show that the switchgrass has higher values of moisture and ash content while lower values were observed for the CV, carbon and hydrogen contents compared to poplar. The measured CV of dry switchgrass (17.86 MJ/kg) and poplar (20.41 MJ/kg) show that poplar has higher heating values than switchgrass. The values for the derived chars are 23.82 MJ/kg and 30.90 MJ/kg for switchgrass and poplar carbons, these could have effect on the electrochemical conversion of these carbon in the MCDCFC. These char values are similar with those recorded in literatures [6-9]. The percentage carbons obtained from the pyrolysis of biomass are shown in Table 3 with switchgrass having higher values than poplar.

3.1 MCDCFC Performances with gold mesh- ZrO_2-gold mesh electrode assembly

The MCDCFC electrochemical conversions recorded for the two biomass carbon fuels are presented in Figures 2- 5. Poplar fuel gave higher performances than switchgrass. The acronym PopV and PopP represent the voltages and power densities of poplar fuel and likewise for switchgrass (Swi) biomass carbon fuel. At the operating temperature of 600^{o}C, poplar fuel gave high open circuit voltage-OCV (0.85 V) while switchgrass was 0.79 V. The performances of poplar fuel could be attributed to the higher calorific values it possesses, in this work we reported 30.90 MJ/kg which is complimented with findings from other researchers [4, 10-12]. The performances of the fuels increase with increased temperature (Figure 5). Figures 2 to 4 show that the current density-voltage curves drop initially due to activation resistance. This activation resistance lead to voltage drop in the fuel cell. The curves continue to decrease linearly due to the ohmic resistance (Area Specific Resistance- ASR) of the MCDCFC. Table 4 give the calculated ASR for the MCDCFC. Eventually the voltage decreases sharply at high current density due to mass transport or concentration losses [13-18].

Other researchers have reported that woody biomass have higher values of lignin compared to the grassy biomasses, this could be responsible for the high performance experienced from poplar biomass carbons [4,12]. Lignin is also known to be amorphous due its branched and partly random structure [19], this is an added benefit for electrochemical conversion in the DCFC. Lignin has relatively low oxygen content and large energy content and very stable solid material due to its chemical structure and highly cross-linked nature [20]. At the temperature of 600°C poplar gave the higher power density (4.32 mW/cm^2) than switchgrass (2.44 mW/cm^2). At 700°C and 800°C the performances of poplar still surpass that of the switchgrass but the electrochemical performance of switchgrass increased significantly at 800°C having closer peak power density to poplar.

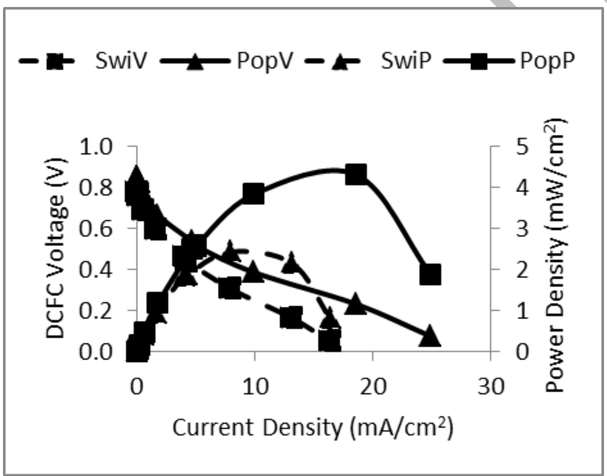

Figure 2: Electrochemical performances of the biomass carbon fuels at 600°C.

3.2 Temperature effects on MCDCFC performances with biomass carbon fuel

The effects that temperature has on the performance of the MCDCFC are shown in Figure 5.

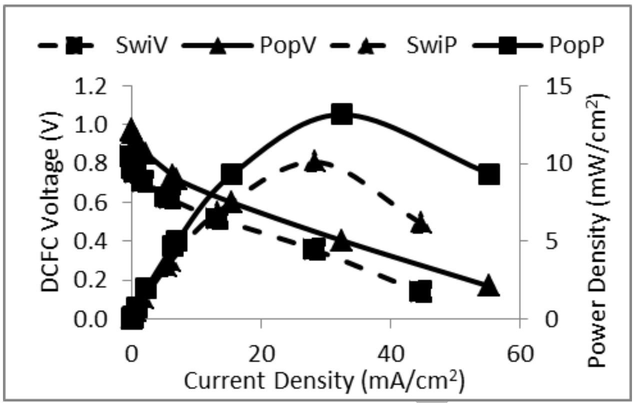

Figure 3: Electrochemical performances of the biomass carbon fuels at 700°C.

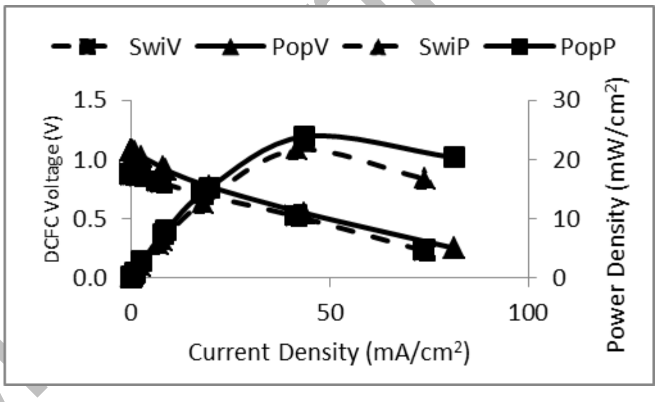

Figure 4: Electrochemical performances of the biomass carbon fuels at 800°C.

The DCFC voltages presented on these figures are the open circuit voltage (OCV) of the cell. There is a sharp rise in the OCV at 500°C, which is due to the ionic conduction in the phase of the molten carbonate and the melting of the carbonate salt mixture which is in agreement with other reports [13]. The performance of the fuel cell was greatly enhanced as the temperature increases up to 800°C, attributed to a decrease in the viscosity of the molten carbonate phase and a corresponding enhancement of the ionic conduction rate of the electrolyte and the electrochemical reactions at the two electrodes [13-17, 21].

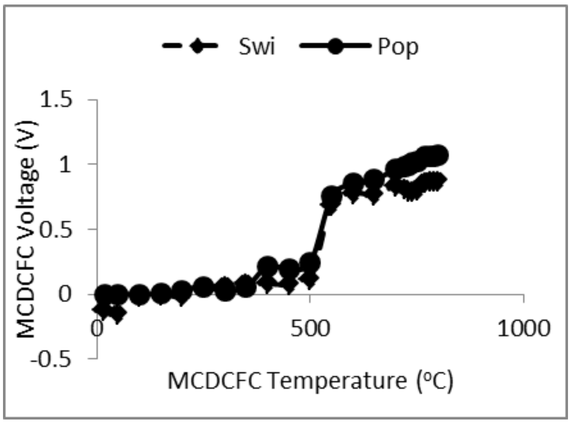

Figure 5: MCDCFC voltages of the biomass carbon fuels at different temperatures.

3.3 MCDCFC power efficiency and ASR for biomass carbon fuels

The power and voltage curves show characteristic behaviour for the single cell molten carbonate direct carbon fuel cell, and of interest are the effective peak power density, open circuit voltage (OCV), current density and the area specific resistance (ASR) behaviours. A number of characteristic electrochemical parameters are presented in Tables 4. Table 4 shows the electrochemical data for poplar and switchgrass and it shows that the OCV, power and current densities increases with the temperature rise but the ASR decreases with rise in temperature. The ASR is a measurement of the overall ohmic resistance from the biomass carbon fuels and electrolyte, the mechanical connections of the cell and the electrode materials. The ASR was calculated from the slope of the voltage versus the current density at the linear central region of the polarisation curves [15, 21]. The efficiency at peak power was calculated by dividing the voltage at peak power by the OCV and multiplying by 100%.

Table 4: MCDCFC Electrochemical data for Switchgrass and Poplar

Cell Parameter	Switchgrass			Poplar		
	Temperature ^oC			Temperature ^oC		
	600	700	800	600	700	800
Open circuit voltage (V)	0.78	0.84	0.87	0.85	0.97	1.08
Peak power density (mW/cm^2)	2.44	10.11	21.60	4.32	13.15	23.91
Maximum current density (mA/cm^2)	16.37	44.86	74.00	24.89	55.34	81.53
Current density at 0.8 V (mA/cm^2)	0.17	0.63	7.82	0.18	6.34	19.80
Voltage at peak power (V)	0.31	0.36	0.52	0.23	0.41	0.55
Area specific resistance (Ω cm^2)	36.73	13.90	9.99	26.22	13.98	12.69
Efficiency at peak power (%)	40.0	43.0	60.0	27.0	42.0	51.0

Efficiency values were calculated for the cells operating at the maximum power condition, and it can be seen that these approach 60% for the switchgrass material at the highest temperature. These values emphasise the efficiency benefits achievable for electricity generation from biomass materials when compare with around 35% for generation from conventional combustion and steam cycle plant [5, 22]. The current densities at 0.8 V corresponds to working at 80% voltage efficiency but at the expense of the current density.

4. Conclusions

The MCDCFC electrochemical performances for both switchgrass and poplar biomass carbon fuels have been investigated for different operating temperatures. The performances of the poplar biomass fuels were higher than those experienced with switchgrass fuel probably due to the facts that the woody poplar has higher heating values than the grassy switchgrass. At 800^{o}C in terms of the open circuit voltage, poplar fuel (1.08 V) had superior output than switchgrass (0.87 V). Also the peak power density recorded for poplar fuel was 23.91 mW/cm^2 while switchgrass fuel was slightly lower at 21.60 mW/cm^2. Poplar fuel (81.53 mA/cm^2) gave a maximum current density while switchgrass fuel was still lower (74.00 mA/cm^2). For the current density at 80% voltage efficiency poplar fuel (19.80 mA/cm^2) was superior to switchgrass fuel (7.82 mA/cm^2). The voltages at peak power for the biomass were close. The peak power efficiency evaluated show that switchgrass fuel (60%) gave higher value than poplar carbon fuel (51%).

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