

PERFORMANCE STUDY ON THE USE OF BIOMASS CARBON IN A DIRECT CARBON FUEL CELL

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ABSTRACT: The main fossil fuel energy sources continue to present challenges for CO₂ emission reduction, and carbon neutral biomass options like miscanthus will make an increasing contribution to the energy mix in decades ahead. The use of carbons for electricity production in carbon fuel cells have been shown to provide conversion efficiencies up to 80%, and the work presented will report on the performance of a range of biomass materials used as fuel sources with a molten carbonate fuel cell. The materials are first converted to char by pyrolysis at around 800 °C, yielding between 20 – 30% carbon by weight. Disordered graphitic structures are known to provide the greatest reactivities in fuel cells, and some structural analysis is reported for the materials investigated. The results reported will focus on current/voltage behaviour for the biomass materials examined, which will include miscanthus and willow.

INTRODUCTION

The direct carbon fuel cell (DCFC) is a special kind of high temperature fuel cell that directly uses carbon as anode and fuel. The DCFC has a higher achievable efficiency (80%) as an electrical power generator for power plants than other fuel cells. The raw material for powering DCFC is solid carbon-rich fuels, such as biomass, coal, and organic waste, which are abundant in nature [1]. Most conventional fuel cells operate on gaseous fuels. These fuels (natural gas, propane, or alcohol) are reformed to hydrogen syngas and then fed into the fuel cell stack. The DCFC on the other hand can operate on solid carbon fuel. At high temperatures (> 600 °C), these fuel are electro-oxidised to CO₂ at the anode compartment creating electricity [2]. The overall cell reaction is given by Equation 1 [1];



The DCFC is becoming more important because of the various advantages that it offers. Because no heat engines or reformers are needed in the DCFC system it is mechanically simple to build and can be located in biomass sites, thus reducing cost of transportation, and reducing environmental pollution. The production of tiny carbon particles through pyrolysis used in the DCFC requires less energy and capital than the production of hydrogen-rich fuels used in other fuel cells such as the MCFC and SOFC [1].

Carbon oxidation in a DCFC is done electrochemically at the anode unit without direct mixing with air and CO₂ is created as a pure gas which can be captured and stored as part of carbon capture and storage (CCS) strategy. Thus the emissions released from a DCFC can be very low when compared to power plants. DCFC operation can cut carbon emission from coal by 50% and reduce off-gas volume by 10 times when compared to coal-burning power plants. Also there are no particulates (fly ash) released by DCFC operations, and this is good for the environment [1, 3-5]. A DCFC gives a higher thermodynamic advantage over other types of fuel cell, because going by Equation (1) its theoretical electrochemical conversion is about 102%. The chemical potentials of the reactants (carbon) and product (CO₂) are fixed and are not dependent on the position or the extent of fuel conversion in the cell, thus the reactant and product exist in their pure state [1, 5-11].

Pyrolysis of biomass is used in the production of solid (charcoal), liquid (tar and other organics) and gas products. Research in the area of pyrolysis is becoming more and more

important, because of its many advantages. Several researches have been carried out on biomass pyrolysis, and for the purpose of the DCFC, the char is of paramount concern [12-25]. As an example, Onay and Kockar [13] obtained 24.5 – 31% char yield from rapeseed, while Şensöz obtained between 30 – 59 wt.% char from pine barks pyrolysis. This paper focuses on the pyrolysis of carbon rich particles from miscanthus straw and willow wood chips to power the direct carbon fuel cell.

MOLTEN CARBONATE ELECTROLYTE IN DCFC

The use of mixed molten carbonates ($\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$) for DCFC is recommended because of their high conductivity, good stability in the presence of CO_2 (carbon electrooxidation product) and suitable melting temperature [1, 7]. Equations 2 and 3 represent the anode and cathode reactions in molten carbonate electrolytes and Equation 4 gives the cell voltage. CO_2 is formed at the anode side and partially recycled to the cathode side, therefore, its partial pressure has an influence on the cell voltage [1].



$$E_{\text{cell}} = E^{\circ} - (RT/4F)\ln[\text{CO}_2]_{\text{anode}}^3 + (RT/4F)\ln([\text{O}_2][\text{CO}_2]_{\text{cathode}}^2) \quad (4)$$

EXPERIMENTAL

Design of the Direct Carbon Fuel Cell (DCFC)

The electrochemical section of the DCFC consists of mica seals, gold wire, a porous nickel disc (1.5 mm thickness, 25 mm diameter, 40% void), a zirconia cloth impregnated with $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$, and a gold mesh on the cathode side, which provided the conductive surface as current collector. The electrolyte absorbed within the zirconia cloth is a mixture of Li_2CO_3 and K_2CO_3 , mixed in the ratio of 46.6 wt.% Li_2CO_3 and 53.4 wt.% K_2CO_3 [24]. Gold wires were used as electrical contacts on the electrode (anode and cathode). The construction of the fuel cell was done after the various preparations of the anode, cathode and electrolyte ensuring that the components were flat and made good electrical contact. The wire contacts were added to both the anode and cathode. Figure 1 shows the components of the DCFC. The fuel cell was located between two ceramic cylinders 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. Another mica seal was placed at the base to tolerate any expansion of material when the DCFC was placed in the furnace. Flattened gold wire contacts were passed across the anode and the cathode seals. The DCFC system was tightened and secured by using springs, nuts and bolts, these maintained the tension during heating and provided the support needed to hold the electrode system in the furnace. The wire connectors were insulated using ceramic beads.

The ratio of the carbon fuel to the carbonate used in the fuel mixture is 1:7 and 1.5 g of the carbon/carbonate mixture was supplied to the anode side of the DCFC system. A thermocouple was connected through the cathode side of the DCFC to monitor the temperature in the region of the electrode. Nitrogen gas was connected to the inlet to the anode (to purge the system from CO_2 produced) while air/ CO_2 was connected to the cathode chamber to maintain adequate oxidant for the half-cell electrochemical reaction. The gases were monitored by rota-meter, to regulate the flow rates. The furnace was heated up gradually at a rate of 5 °C/min. When the fuel cell temperature was at 250 °C, nitrogen gas was introduced through the anode at a rate of 200 cm^3/min . At a temperature of 400 °C the air/ CO_2 mixture was released through the cathode at a rate of 1500 cm^3/min for air, and 600 cm^3/min for CO_2 and the DCFC was then heated up to an operating temperature. After the measurement the furnace was shut down while nitrogen gas was allowed to purge the system during cooling.

The electrolyte system consisted of 0.5 mm thick zirconia cloth (ZYW 30A supplied by Zircar Zirconia Inc.) of 25 mm diameter, which was prepared by contacting with a molten carbonate mixture at around 600 °C.

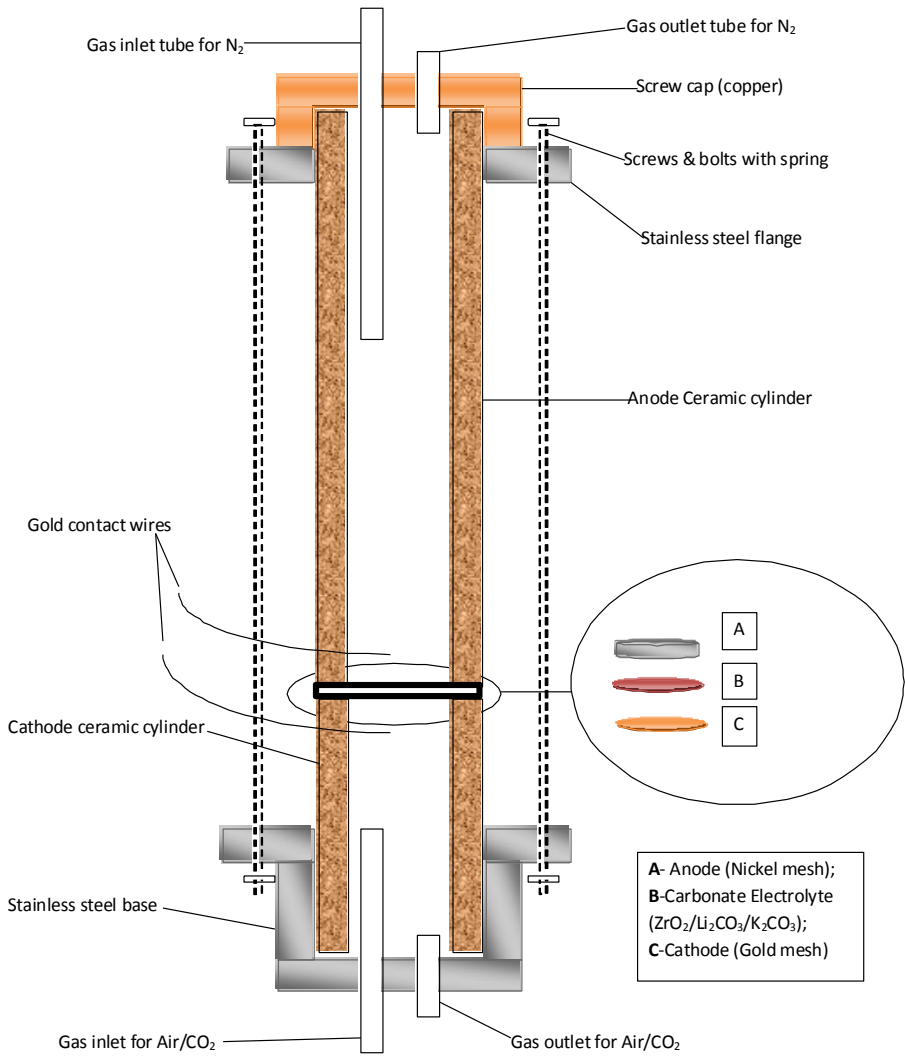


Figure 1. Schematic of the direct carbon fuel cell (DCFC). Overall height is 280 mm.

Preparation and Analysis of Biomass

The miscanthus samples were supplied by Bical (Swindon) and willow by Coppice Resources Ltd (Retford). The samples were chopped into smaller pieces before grinding. The grinding was carried out using the Cross Beater Mill (Model 16-150, Glen Creston Ltd.) with a sieve size of

2.0 mm. The chopped biomass was added to the mill in stages for effective grinding and the process was repeated three times to obtain the effective particle size. Figure 2 shows the chopped and ground miscanthus.



Figure 2. Miscanthus straws chopped and ground

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 °C and 950 °C respectively. The moisture content was estimated using the Memmert oven operated at a temperature of 105 °C for an hour. The fixed carbon was calculated by difference. The carbon and hydrogen contents were analysed using Carbolite furnace operated at 1350 °C. The Bomb calorimeter (PARR 1261) was used to obtain the calorific value of the biomass.

The biomass samples of particle size of 0.5 to 2.0 mm, were dried at 100 °C before pyrolysing in a cylindrical Lenton furnace, which was electrically heated and where the pyrolysis was monitored locally by thermocouple. In each run of the experiment 7.0 g of sample was fed into the reactor, which was heated at a rate of 7 °C/min up to the operating temperature of 800 °C, which was then held for 30 min. [14, 19]. Nitrogen gas was used to purge the system at a rate of 4000 cm³/min, during and after the pyrolysis process until it cooled down to 200 °C.

Preparation of Carbon Fuel Particles

The carbon/carbonate fuel mixture was prepared consisting of the char (15 wt. %), with the balance being the lithium and potassium carbonates [24, 25]. The carbonate mixture components (Li₂CO₃/K₂CO₃) were prepared by dissolving in 25 ml of water to ensure proper mixing and the mixture dried in an oven at 100 °C for 4 hours. The carbonate was then finely ground and mixed with the biomass carbon to form the fuel mixture for the cell.

RESULTS AND DISCUSSION

Table 1 and 2 gives the result of the proximate and ultimate analyses carried out on miscanthus straw and willow wood chip after size reduction. The results show a lot of similarity for the biomass under study. Table 3 and 4 gives the result of the analyses carried out on the carbon produced from miscanthus and willow after pyrolysis. Table 5 shows the results of pyrolysis on miscanthus and willow.

Table 1 shows that the measured CVs of dry miscanthus (18.83 MJ/kg) and willow (19.29 MJ/kg) are at the upper end of the normal range for biomass materials, and the values for the derived chars, 29.11 and 29.56 MJ/kg respectively, can be compared with the value for pure carbon black of 33.84 MJ/kg. These char values are consistent with the measured carbon contents of 82.46 wt.% for miscanthus and 81.00 wt.% for willow and are in agreement with the findings from other researchers [12-20]. In general, the percentage carbon obtained from the pyrolysis of biomass is in the range of 20-25%. It was observed that the biomass carbon readily absorbed

moisture during storage with 5.61 wt.% and 4.20 wt.% for miscanthus and willow carbon respectively (Tables 3 and 4).

Table 1. Proximate, Ultimate and Calorific Value analyses for ground miscanthus straw.

Analysis sample	Proximate Analysis				Calorific Value MJ/kg	Ultimate analysis	
	Moisture Contents wt. %	Ash wt. %	Volatiles wt. %	Fixed carbon wt. % (by diff.)		Carbon wt. %	Hydrogen wt. %
1	6.24	2.12	78.95	12.69	19.08	45.88	4.68
2	7.97	1.85	73.88	16.30	19.69	45.50	5.37
3	7.93	2.02	74.70	15.35	17.72	45.88	5.22
Average	7.38	2.00	75.84	14.78	18.83	45.75	5.09

Table 2. Proximate, Ultimate and Calorific Value analyses for ground willow wood chip.

Analysis sample	Proximate Analysis				Calorific Value MJ/kg	Ultimate analysis	
	Moisture Contents wt. %	Ash wt. %	Volatiles wt. %	Fixed carbon wt. % (by diff.)		Carbon wt. %	Hydrogen wt. %
1	7.30	1.63	75.10	15.97	19.47	45.77	3.71
2	7.33	1.48	75.49	15.70	19.48	43.98	3.26
3	7.36	1.72	75.31	15.61	18.91	40.39	3.57
Average	7.33	1.61	75.30	15.76	19.29	43.38	3.51

Table 3. Moisture, Calorific Value and Ultimate analyses for Miscanthus carbon.

Analysis sample	Moisture Contents wt. %	Calorific Value MJ/kg	Ultimate analysis	
			Carbon wt. %	Hydrogen wt. %
1	5.78	28.93	83.50	1.47
2	5.50	29.27	80.39	0.71
3	5.55	29.14	83.50	0.73
Average	5.61	29.11	82.46	0.97

Table 4. Moisture, Calorific Value and Ultimate analyses for Willow carbon.

Analysis sample	Moisture Contents wt. %	Calorific Value MJ/kg	Ultimate analysis	
			Carbon wt. %	Hydrogen wt. %
1	4.22	29.81	75.41	1.03
2	4.21	29.44	83.60	1.65
3	4.18	29.43	83.98	1.25
Average	4.20	29.56	81.00	1.31

Table 5. Pyrolysis results for miscanthus and willow at 800 °C.

Biomass	Heating rate (°C/min)	Moisture content (wt.%)	Biomass mass (g)	Carbon mass (g)	Percent of carbon (wt.%)
Miscanthus	7	6.81	6.76	1.53	22.67
Willow	7	7.54	7.53	1.81	24.05

X-Ray Diffraction (XRD) Analyses

X-ray diffraction (XRD) analyses were carried out on industrial carbon black (Alfa Aesar, USA), willow and miscanthus carbons. The results from the XRD are presented in Figures 3 to 5. The XRD patterns were generated using the software (STOE WinX^{POW} 2.10) that runs with the Siemens D500 X-Ray Diffractometer System. Figure 3 shows the pattern for carbon black, which is a pure carbon with a disordered graphitic structure. This disordered nature is noted as being important in its application in the DCFC where research has shown that the chemical reactivity of carbons to oxidation is strongly dependent on structure, particularly the extent of graphitisation [7,27,28]. Pure graphite demonstrates a strong and sharp 2 θ peak at 26.554°, corresponding to the graphite layer spacing of 3.3541. The broader peak in Figure 3 is consistent with a distributed range of layer spacing characteristic of turbostratic carbon and associated with greater reactivity.

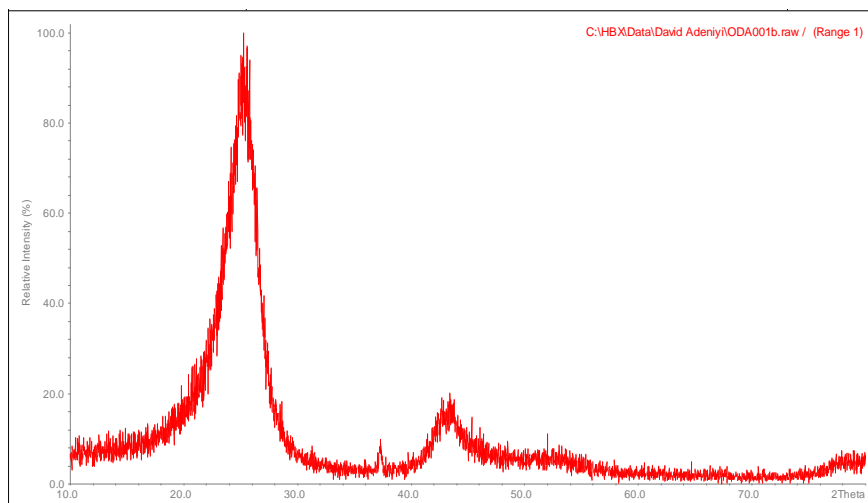


Figure 3. X-ray diffraction (XRD) pattern on carbon black.

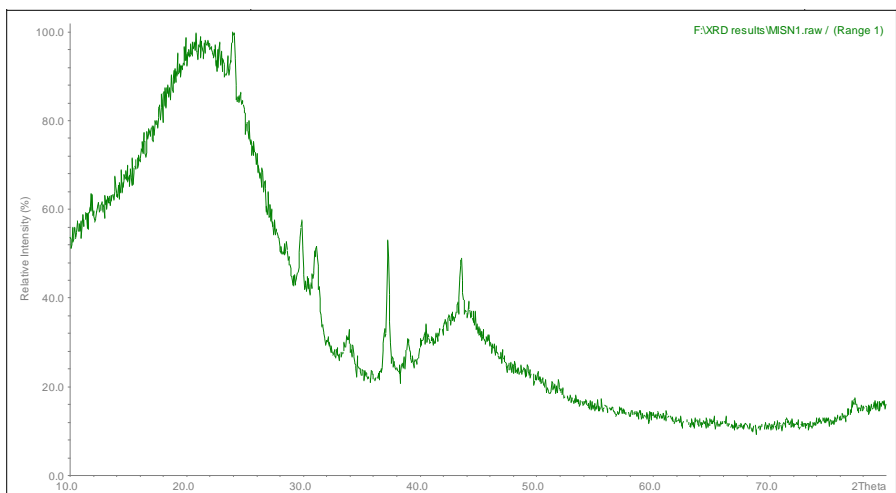


Figure 4. X-ray diffraction (XRD) pattern on miscanthus carbon.

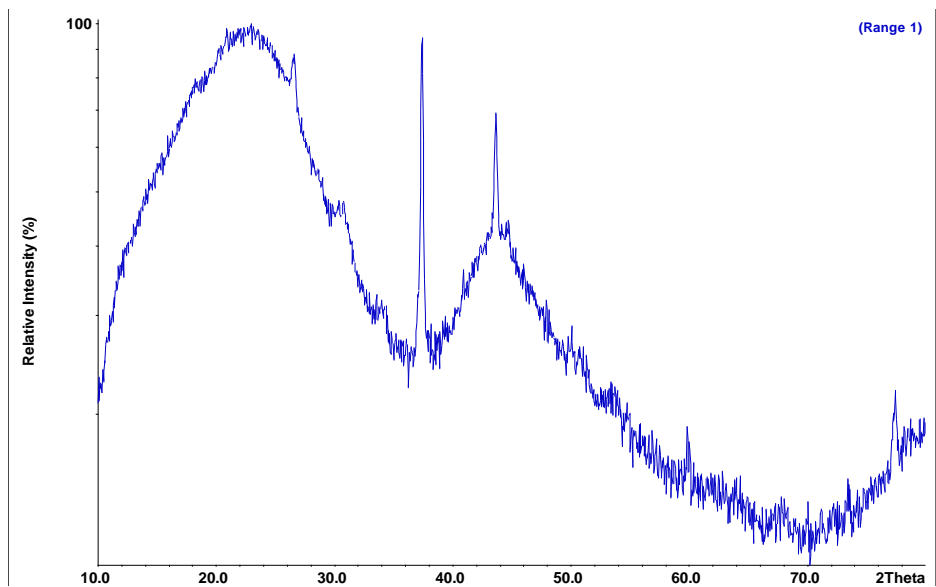


Figure 5. X-ray diffraction (XRD) pattern for willow carbon.

Figure 4 and 5 show some similarity with that of carbon black indicating that the char has a degree of disordered graphite content. In evidence also are the sharp peaks corresponding to contributions from silica in the ash, identified from the STOE databank spectra.

DCFC Performance Using Miscanthus and Willow Char Fuel

Figures 6 to 11 give the performance of the DCFC using miscanthus carbon fuel particles for three different temperatures. The flow rates of N_2 , CO_2 and air used in this operation were 200

cm³/min, 600 cm³/min and 1500 cm³/min respectively. The N₂ gas was connected to the anode of the cell and this help to purge the cell from any CO₂ produce at the half cell reaction of the anode. CO₂ and air were introduced through the cathode side of the fuel cell to permit oxygen transport through the cell.

In assessing the voltage/current behaviour of the fuel cell, a range of load resistances were used ranging from 1.16 MΩ to 1.2 Ω. For each load resistance chosen at a particular temperature condition, the cell voltage was allowed to stabilise to its new value before recording.

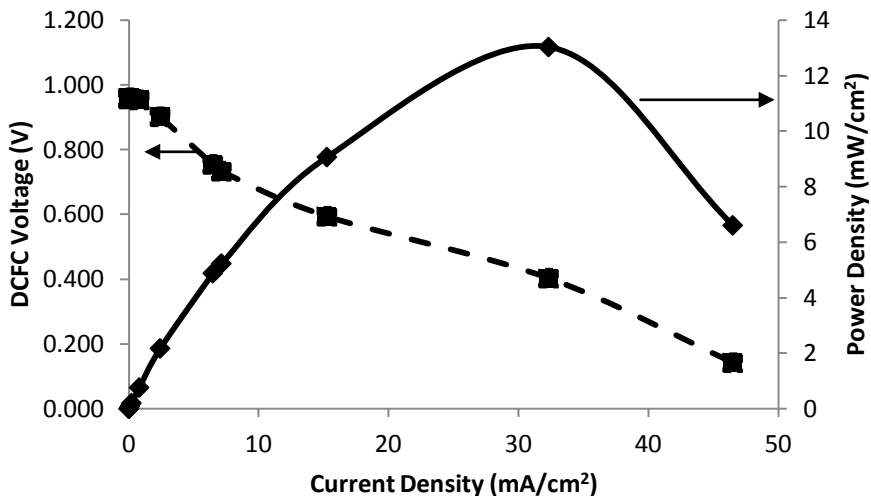


Figure 6. DCFC performance using miscanthus carbon fuel at 700°C.

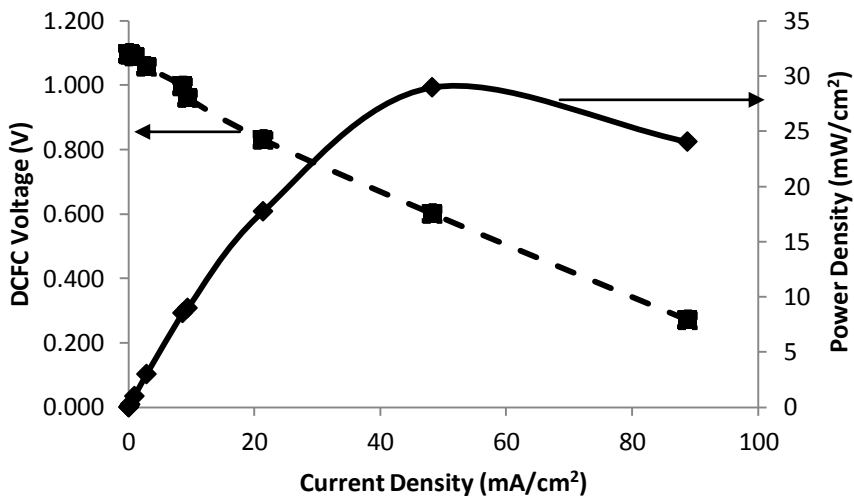


Figure 7. DCFC performance using miscanthus carbon fuel at 850°C.

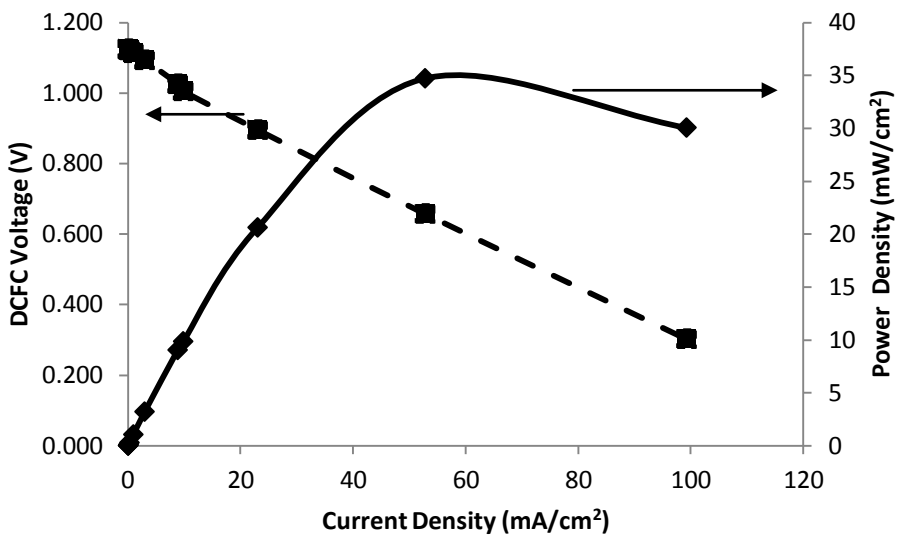


Figure 8. DCFC performance using miscanthus carbon fuel at 900°C.

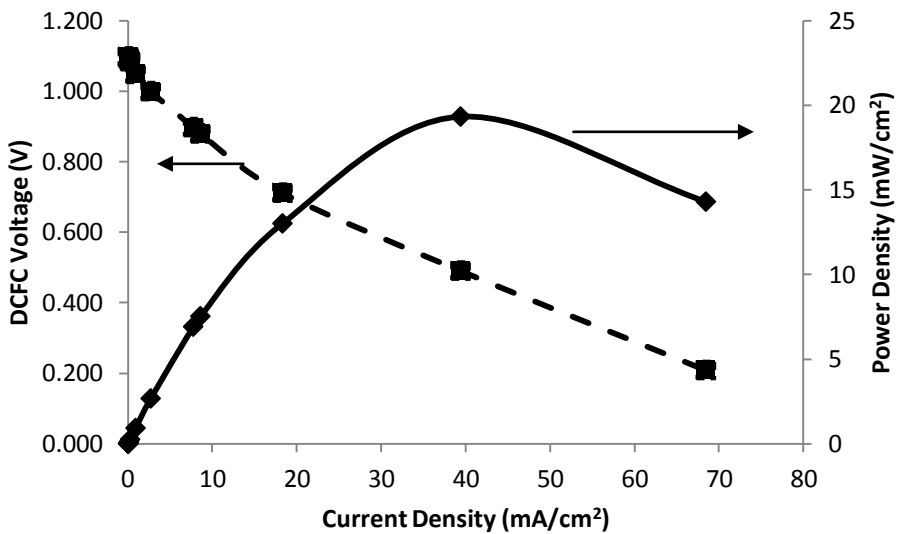


Figure 9. DCFC performance using willow carbon fuel at 700°C.

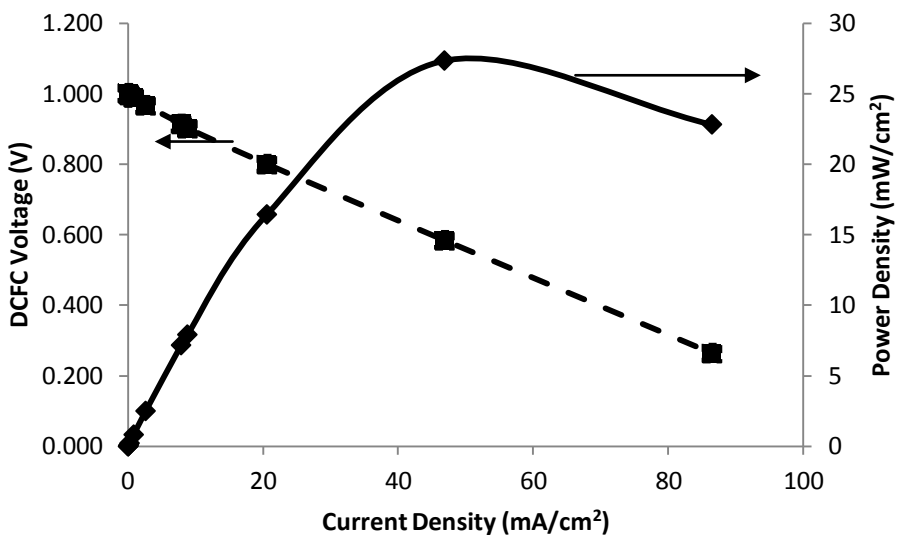


Figure 10. DCFC performance using willow carbon fuel at 850°C.

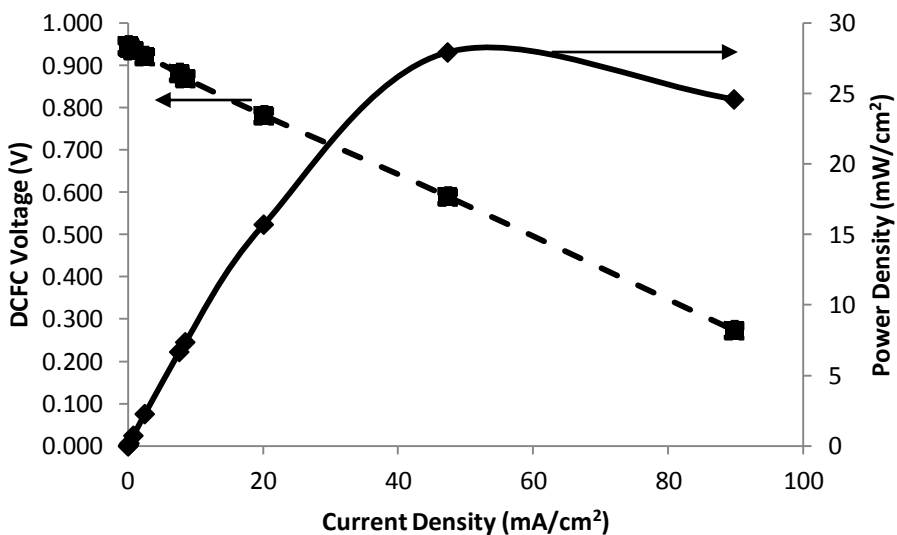


Figure 11. DCFC performance using willow carbon fuel at 900°C.

Results Summary

The power and voltage curves show characteristic behaviour for fuel cells, and of particular interest are the effective open circuit voltage, peak power and current density behaviour. A number of characteristic operating parameters are presented in Table 6.

Table 6. Measured cell parameters for miscanthus and willow.

DCFC operating Parameter	Miscanthus			Willow		
	Temperature °C			Temperature °C		
	700	850	900	700	850	900
Open circuit voltage (V)	0.97	1.10	1.13	1.1	1.0	0.95
Peak power density (mW/cm ²)	13.0	28.9	34.7	19.3	27.5	28.3
Maximum current density (mA/cm ²)	46.5	88.7	99.2	68.4	87.0	89.7
Current density at 0.8 V (mA/cm ²)	12.0	25.0	33.0	12.0	20.0	17.5
Efficiency at peak power (%)	40.0	55.8	59.7	46.0	55.8	53.8

Both materials show an increasing trend in performance with increasing temperature, with the peak power density for miscanthus at 900 °C being slightly higher than for the willow. Also shown are thermal efficiency values for conversion to electricity. The enthalpy of oxidation of pure carbon to carbon dioxide at the operating temperatures is 394 kJ/mol, whereas the available work from the cell is represented by the measure ΔG value based on $\Delta G = -n F E$. The thermal conversion efficiency can then be represented by $-\Delta G / -\Delta H$.

At 0.8 V, this efficiency corresponds to 78%, and the current densities available from the cell at this operating condition are shown in the table. Efficiency values are also calculated for the cells operating at the maximum power condition, and it can be seen that these approach 60% for the miscanthus material at the highest temperature. These values emphasise the efficiency benefits achievable for electricity generation from biomass materials and compare with around 35% for generation from conventional combustion and steam cycle plant.

CONCLUSIONS

As a result of the major conventional energy resources coming to a verge of extinction there is a need to look at a more promising option and also one that is environmentally friendly. Biomasses, like miscanthus and willow, supply the needed option along with other several biomasses available globally. We have presented a performance study on the use of biomass carbon for the operation of the direct carbon fuel cell (DCFC). The DCFC allow the chemical energy of carbon to be directly converted into electrical energy and heat which can be of great benefit in this present time in which there is a greater demand for more energy to power the growing world population. The pyrolysis experiment conducted was at a temperature of 800 °C with a heating rate of 7 °C/min, giving 25% carbon with a CV of 30 MJ/kg. The XRD analysis carried out on the biomass carbons show some similarity to disordered carbon black suggesting crystallographic disorder of the carbon structure and associated chemical reactivity which can power the DCFC. Results from the miscanthus and willow carbon fuel show that there is improvement in the performance of the DCFC as the temperature is increased, as indicated by the increment in the current and power densities. The performance efficiency based on power also shows the same trend with 59.7% for miscanthus and 55.8% for willow.

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