The behaviour of biomass char in two direct carbon fuel cell designs

两个直接碳燃料电池设计中生物质炭的行为

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Abstract - **The performances of two fuel cell designs are reported using carbon fuel arising from the pyrolysis of a number of common biomass materials. In the first, a simple design based on carbonate saturated zirconia cloth is used whilst in the second, a proprietary prototyping button cell based on solid oxide technology is investigated. Gold mesh current collectors are used in both cases. Results are presented for the power density and cell voltage versus current density at 800ºC and show that peak powers of 70 mW/cm^2 at current densities of 100 mA/cm^2 are achievable and that the more highly engineered solid oxide design will perform better by a factor of around 5 on both measures. The results demonstrate that, with only moderate processing, power generation from biomass using more advanced electrochemical technologies, with higher thermal efficiencies, can make a useful contribution to the overall effort to reduce CO$_2$ emissions.**

Keywords – **fuel cell, biomass, carbon, current, power, pyrolysis, voltage**

I. INTRODUCTION

The direct carbon fuel cell (DCFC) is a special kind of high temperature fuel cell that directly uses carbon as fuel supplied to the anode and has the potential to reduce the complexities of reforming hydrocarbon raw materials to fuels such as hydrogen. The DCFC has been shown to offer significantly higher thermal efficiencies [1] for electrical power generation compared to combustion routes and even for other fuel cell types using different fuels. The raw materials for powering a DCFC are solid, carbon-rich fuels, and much of the effort in recent years has been devoted to fossil fuel carbon sources, such as coal and petroleum coke. The benefits arising from the use of these fuels in DCFCs are equally available to biomass derived carbon and the overall cycle efficiencies when DCFCs are incorporated into appropriate combined cycles are likely to be higher than those associated with current gasification processes due to the intrinsically higher efficiency of the carbon fuel cell stage of such cycles.

At the higher temperatures normally used for DCFCs (> 600ºC), carbon fuel is electro-oxidised to CO$_2$ at the anode compartment creating electricity [2]. 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 around biomass sites, thus reducing the cost of transportation, and reducing environmental pollution. The production of tiny carbon particles produced by pyrolysis and used in the DCFC requires less energy and capital than the production of hydrogen-rich fuels used in other fuel cell types. Since carbon oxidation is achieved electrochemically at the anode without direct mixing with air, the CO$_2$ is created as a pure gas which can be captured and stored as part of a carbon capture and storage (CCS) strategy. This aspect, combined with the potential 50% reduction in CO$_2$ emissions due to improved thermal efficiency, indicates that low emissions may be achieved at lower energy costs when compared to conventional power plants.

Additional operational benefits include the avoidance of fly ash emissions and the associated capture technologies [1, 3-6]. A DCFC has certain efficiency advantages over other types of fuel cell arising from the nature of the reactants and products and due to the small entropy change (~ 2 J/mol K). The transport of oxygen to a fuel cell anode is conventionally achieved by three routes, using molten carbonates, molten alkali metal hydroxides or using solid electrolytes such as stabilised zirconia. In the present work, the designs use the molten carbonate and solid zirconia electrolyte systems.

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. Many researches have been carried out on biomass pyrolysis, and for the purpose of the DCFC, the char is of particular relevance [7-9]. The relative proportions of pyrolysis products depends on the properties of the source material such as fixed carbon and volatiles content as well as process employed, which includes heating rates and soak temperature. As an example, Onay and Kockar [8] obtained 24 – 31wt% char yield from rapeseed, while Şensöz obtained between 30 – 59wt.% char from pine barks pyrolysis. This paper focuses on the char produced from the pyrolysis of miscanthus straw (M. giganteus), and wood chips from willow (salix) and spruce (picea) and the primary interest is in the behaviour of these chars in a fuel cell device.

II. BIOMASS MATERIALS AND PREPARATION

The biomass samples were chopped into smaller pieces before grinding, which was carried out using a Cross Beater Mill 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 before carrying out proximate, ultimate, and calorific value analyses.

The ash and volatile content were measured using a furnace operating at temperature of 750°C and 950°C respectively. The moisture content was determined using an oven operated at 105°C for an hour and the fixed carbon was calculated by difference. The total carbon and hydrogen contents were measured by sample oxidation in a furnace operated at 1350°C and calorific values for the dry samples were determined using a bomb calorimeter.

The biomass samples of particle size of 0.5 to 1.0 mm, were dried at 100°C before pyrolysing in a cylindrical, electrically heated furnace (70 mm diameter). In each pyrolysis cycle, the sample was heated at a rate of 7 °C/min up to the operating temperature of 800°C, and held for 30 min. [9]. Nitrogen gas was used to purge the system at a rate of 4 litre/min, during and after the pyrolysis process until it cooled down to 200°C. The proportion of char produced in each case was in the range 22 - 24wt%, which compares with other reported results for the conditions used. Table 1 summarise the biomass pyrolysed char properties.

TABLE I, PROPERTIES OF BIOMASS CHAR.

Material	Fixed carbon wt.%	Hydrogen wt.%	Calorific Value MJ/kg
Miscanthus	87.37	1.03	29.11
Willow	84.55	1.37	29.56
Spruce	92.96	1.14	32.53

Evidence of graphitic structure in the chars was examined by application of XRD (Cu, Kα) to the powders. These showed broad peaks with maxima in range $2\theta = 22 - 28°$, which indicates some disordered graphite layers but also a high degree of amorphous carbon and are similar to patterns reported by others for coal samples.

III. PREPARATION OF CARBON FUEL PARTICLES

Each biomass char was ground by ball milling following the same procedure for each material. Size analysis on the samples was carried using laser diffraction sizing and showed that 50% of the weight fell within the particle size range 2.2 -8.1 μm. At the operating temperature of the fuel cell, the fuel is presented as a slurry dispersed in a molten carbonate mixture.

The fuel particles were dispersed in a Li_2CO_3/K_2CO_3 mixture at a concentration of 15 wt.% and the carbonate components were mixed in the ratio of 46.6 wt.% Li_2CO_3 and 53.4 wt.% K_2CO_3, giving a melting point close to 500°C. The carbonates were prepared by initially dissolving in water followed by drying at 100°C and, following fine grinding, were mixed with the biomass carbon to form the fuel mixture for the cell.

IV. FUEL CELLS CONSTRUCTION AND OPERATION

The two fuel cell types employed are identified as molten carbonate (MCFC) and solid oxide (SOFC). For the MCFC the electrolyte consists of the same molten carbonate mixture as was used for the char fuel dispersion, whilst the SOFC consisted of a button cell of yttria stabilised zirconia [11]. For both systems the same overall cell containment was used.

The electrode assembly for each type was held between two open alumina tubes of 24 mm internal diameter, 3 mm wall, and oriented vertically. The end of each tube was held within a closed metal chamber, which included built-in flanges and allowed steel, spring loaded tie bars to be fixed between each end of the system to hold the electrode assemblies in place. The overall length of the tubular assembly was 280 mm.

The lower 80% of the tubular system could then be located within a furnace and the cell operating temperature was monitored locally using a sheathed K-type thermocouple which entered through the upper metal chamber. Inlet and outlet tubes were provided through the upper and lower metal chambers to allow some purging on the anode side and the oxidant gas on the cathode side.

For the MCFC, the electrolyte system consisted of 0.5 mm thick zirconia cloth (ZYW 30A supplied by Zircar Zirconia Inc.) of 25 mm diameter, which was saturated with the molten carbonate mixture at around 600°C. Current collectors in the form of gold mesh, (99.9%, 0.06 mm wire diameter, 65% open area, supplied by Goodfellow) were placed in contact with this electrolyte on both sides, and on the lower cathode side, a ceramic support was provided in the form of a perforated disc of 1.5 mm diameter to maintain good contact between the mesh and the electrolyte disc, and which at the same time allowed air contact. Annular mica rings formed the boundary between the electrode assembly and the upper and lower alumina tubes.

For the SOFC, the central element was a button cell of 25 mm diameter (supplied by Fuel Cell Materials) consisting of

an yttria stabilised zirconia electrolyte (150 μm in thickness) and central 12.5 mm diameter anode layer (50 μm thickness) consisting of nickel/zirconia cermet and corresponding cathode layer (50 μm thickness) composed of lanthanum strontium manganite (LSM). The anode side of the button cell as supplied, is in the oxidised form and this was subjected to a reducing atmosphere consisting of 5% hydrogen in nitrogen for 1 hour at 900°C prior to use. Any subsequent processing steps which required elevated temperatures ensured that the same protective reducing atmosphere was provided. This cell element was further processed with the addition of gold mesh current collectors on anode and cathode sides, which were attached using silver ink to the edges and a further heat cycle at 900°C for 20 minutes. The silver ink consists of a suspension of fine silver particles in a terpene oil and is available from Fuel Cell Materials. Both nickel and LSM inks are available in a similar form from the same supplier.

In order to ensure good continuity between the electrode surfaces and their respective gold meshes, nickel ink and LSM ink were then applied sparingly to their respective mesh surfaces, with any excess removed. The electrode assembly was then dried ready for use.
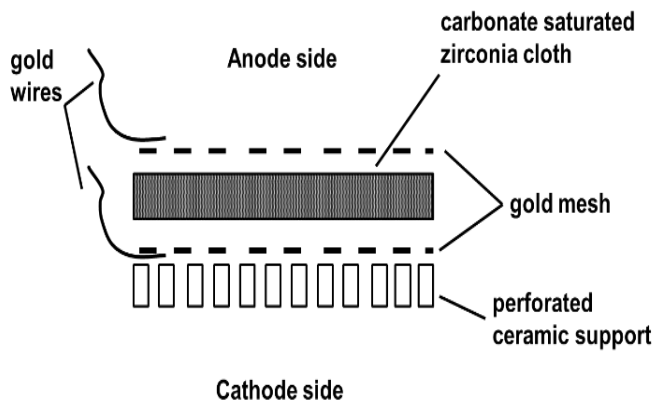

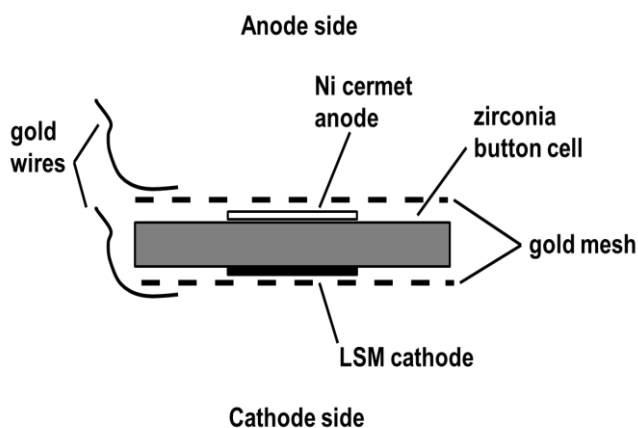Fig. 1, MCFC electrode assemblies.

Fig. 2, SOFC electrode assemblies.

As shown in Fig. 1 and 2, gold wires (0.4 mm diameter) lead the current from the cells. These wires had flattened ends and were held in contact with the gold mesh elements by the compressive force of the external springs.

The 15 wt.% of the carbon fuel in carbonate mixture was supplied to the anode side of the cell at a fixed mass of 3.0 g for all experiments. Nitrogen gas was connected to the inlet to the anode (to purge the system from CO_2 produced) while air/CO_2 and air was supplied to the cathode chamber of the MCFC and SOFC respectively. The material supply rates used throughout are shown in Table II.

TABLE II, MATERIAL SUPPLY RATES

Fuel cell	Fuel mass (g)	Anode N_2 flow rate (l/min)	Cathode flow rate (l/min)	
			Air	CO_2
MCFC	3.0	0.2	1.5	0.6
SOFC	3.0	0.2	1.5	-

V. RESULTS AND DISCUSSION

The cell performances were monitored over a range of temperatures and those demonstrated at a fixed temperature of 800°C are reported here. Performance is assessed in terms of voltage and power density achieved over a range of load currents, and the load currents are varied by varying the applied resistive load to the fuel cell system over the range from open circuit to 1.2 Ω. Currents are converted to current density by including the surface area of the cell anode area. Figs. 3 and 4 give the variation of cell voltage and power density with current density for the MCFC system using the three biomass chars, whilst Figs. 5 and 6 give the corresponding results for the SOFC geometry. Where mis = miscanthus, will = willow, and spr = spruce.

The voltage curves for both systems show behaviour which is consistent with that of most fuel cells, i.e. a voltage close to the predicted open circuit value at zero current, falling approximately linearly with increase in current due to Ohmic effects and followed by a more rapid fall at high currents due to mass transfer polarisation at the electrodes.
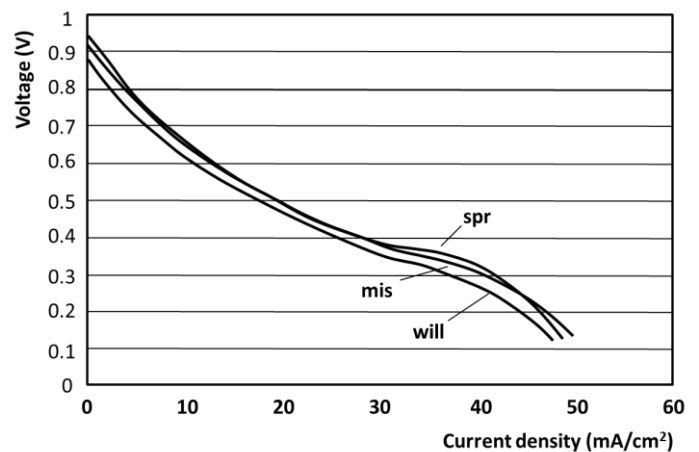

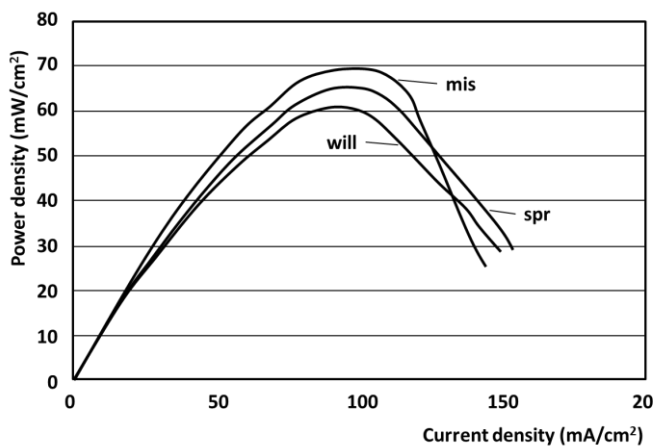Fig. 3, Voltage vs current density for MCFC

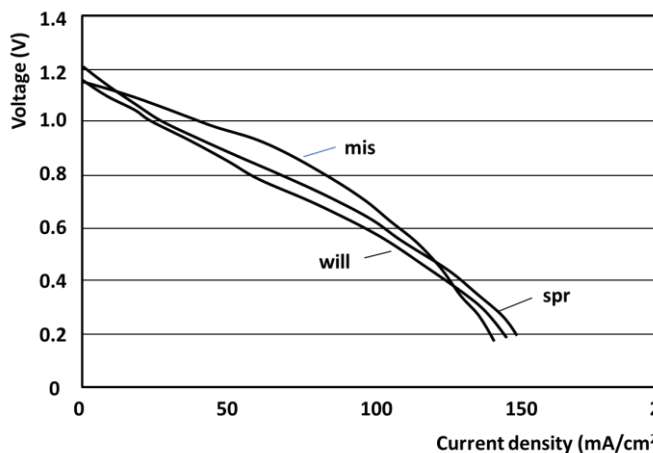Fig. 4, Power density vs current density for MCFC
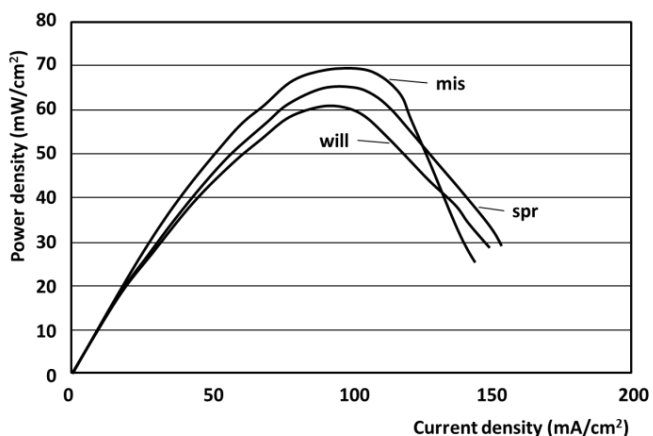

Fig. 5, Voltage vs current density for SOFC

Fig. 6, Power density vs current density for SOFC

The open circuit voltage is influenced by gas species concentration and on the anode side the CO_2 concentration may be well below the O_2 value on the cathode side, particularly when gas purging is applied as in our experiments. This is predicted to raise the OCV (open circuit voltage) at zero current above the E^o (cell EMF under standard conditions) value. The measured OCV for the SOFC system was in the range of 1.15 - 1.2 V, which is consistent with other recently reported values for carbons, e.g. 1.2 V with petcoke [10] and

coal [11] as carbonate fuel slurries. A lower value in the range 0.88 - 0.95 V was observed for the simpler MCFC geometry reported here. A reduction in OCV and its initial rapid fall at low currents is normally attributed to activation energy effects, and the lower value for the MCFC is attributed to the absence of any specifically chosen catalytic materials at the electrode surfaces. The more highly engineered SOFC system employs catalytic materials for both anode (Ni/cermet) and cathode (LSM), similarly to the authors reported who apply Ni and NiO [10] to the anode and cathodes respectively or who include mixed metal oxides incorporated in the fuel particles [11].

The linear sections of the the graphs in each case show closely similar gradients among the different source carbon materials indicating that their contributions to cell resistance is similar. The calculated overall values of area specific resistance ($\Delta V/\Delta I$) are 15.0 Ωcm^2 for the molten carbonate cell and 6.0 Ωcm^2 for the SOFC cell. These values reflect the effectiveness of the overall cell geometry and can be compared with recently reported values for molten hydroxide cells using coal derived fuel rods which are in the range 4.2 - 8.1 Ωcm^2 and based on areas of around 65 cm^2 [12].

The power density curves (Figs. 3-6) show a similar contrast in behaviour. These are derived as cell voltage x current density and of particular interest is the peak power density value as well as the useful range of current density, since the latter is a reflection of the overall scale of devices required to achieve an overall power level. Since the chosen operating current density will determine at which voltage level the device will be operated, the rate of voltage drop with current density will also influence the thermodynamic efficiency which can be represented by the ratio of the measured cell voltage and the theoretical OCV. It is therefore desirable that the voltage remains high as the current density rises and that the current density short circuit limit is as high as possible.

It can be seen that for the simpler MCFC, the current limit is around 50 mA/cm^2 with the peak power of 12 mW/cm^2 occurring at 30 mA/cm^2. This would be seen a being at the lower end of performance for carbon fuel cells. At the peak power level, the corresponding voltage is 0.4 V, corresponding to around 40% efficiency. Alternatively, to operate at 80% efficiency at a voltage around 0.8 V, would provide only 5 mA/cm^2. By contrast the more highly engineering SOFC system shows a current limit closer to 160 mA/cm^2, with a peak power of 70 mW/cm^2 at a current density of 100 mA/cm^2. These values arise from the better area specific ratio and higher OCV. The 80% efficiency operating level would then correspond to 75 mA/cm^2 current density.

These results using biomass chars in the SOFC geometry are generally comparable or in some cases better than the corresponding results reported for fossil fuel carbons [10–12] using a range of geometries and electrolytes and emphasises the value in considering fuel cell technology for certain components of biomass fuels in a similar way to their fossil fuel equivalents. It is clear however, that, as for fossil fuels, consideration must be given to the minimisation of cell resistance through careful choice and design of the ion transport system and catalytic enhancement of the active

surfaces. The difference in results for the simple MCFC compared with the SOFC system demonstrate these points. The results have a relevance to the wider objective of identifying strategies which can be used to reduce CO_2 emissions, by exploring routes to improved electricity generation efficiency.

Biomass is widely available, and the conventional processing route to electricity has been direct burning followed by a conventional steam cycle with energy efficiencies around 35%. Gasification processes are of increasing interest for the processing of solid fuels due to the benefits of using gas turbine technology (GT) combined with steam cycles, the so-called combined cycle routes. Such combined cycle processes are capable of achieving 50%+ in energy efficiencies and the gasification process is generally favoured since the gaseous product can be fully utilised in the GT system. The conversion process to gases however, carries an energy penalty of around 30% [13], which is very much reduced if a pyrolysis process is used. However, the char fraction of such pyrolysis processes cannot be used in GT systems and its use in fuel cell systems has not yet been widely considered. The increasing interest in the use of carbons directly in fuel cells, and the repeated demonstration of high conversion efficiencies, shows that alternative combined cycles including carbon fuel cells offer the prospect of efficiency gains for biomass similar to those which have been achieved for simple fossil fuel gases via combined cycles. Data on the distribution of the primary chemical energy among the three main pyrolysis products, gas, liquid and char, are widely published [14] and pyrolysis typically yields 25 - 30wt.% solids, 10 - 20wt.% liquids with the balance as combustible gas. By exploiting the higher efficiencies available from carbon fuel cells, it therefore becomes possible to consider electricity generation via independent routes for both the solid and gas/liquid streams, the latter following a gas turbine utilisation path.

The simple comparison in Fig 7 captures the main features of such a strategy for pyrolysis routes and and a conventional biomass burning steam cycle, and combines the energy content of the processed fractions with the generation efficiency of the technology which can make use of these fractions.
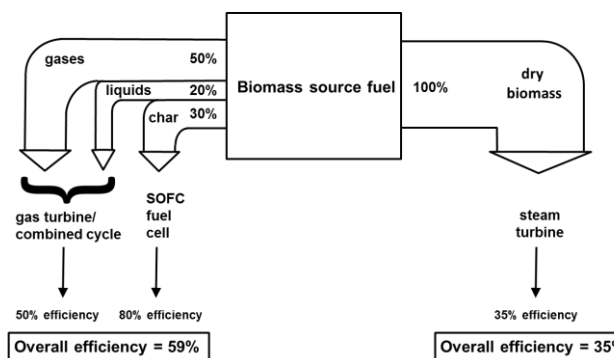

Fig. 7, Comparison of potential overall efficiencies.

As can be seen, the high efficiency of the fuel cell route for char significantly increases the overall conversion efficiency of electricity to 59% for the values chosen. The assumption here is that pyrolysis will produce around 30% char, which is a conservative figure since some reported processes achieve almost 60% char yields [9], which would further improve the overall efficiency through the fuel cell contribution.

VI. CONCLUSION

Two fuel cell designs and electrochemical performances have been reported using carbon fuel arising from the pyrolysis of commonly found biomasses. Results presented for the power density and cell voltage versus current density at 800°C showed that peak powers of 70 mW/cm^2 at current densities of 100 mA/cm^2 were obtained using the SOFC design which was better than the MCFC design. This show that power generation from biomass using more advanced electrochemical technologies, with higher thermal efficiencies, can make a useful contribution to the overall effort to reduce CO_2 emissions. High efficiency of the fuel cell route from char significantly increases the overall conversion efficiency of electricity to 59% when compared to the conventional route of 35%.

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