

Solid state electrochemistry of direct carbon/air fuel cells

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In direct carbon fuel cells (DCFCs), elemental carbon is electrochemically oxidized to generate electrical power. Carbon is readily available, easily transported and stored and, therefore, affordable to the global energy economy. Further operational advantages include the use of fully renewable solid biocarbon fuel sources and the opportunity for scale-up. Here we discuss a DCFC which utilizes a molten mixed alkali metal carbonate eutectic as a secondary electrolyte, contained within a solid oxide fuel cell. The operation of small cells working as semi-fuel cells has been successfully demonstrated over an extended temperature range (525–900°C) using a range of carbons derived from fossil, renewable and waste sources. Preliminary mechanistic studies demonstrate open-circuit voltages (OCVs) well in excess of 1 V, and indicate that direct oxidation and Boudouard conversion both contribute to the conversion process, with the dominant process changing with both temperature and extent of molten electrode/electrolyte component.

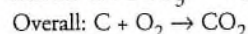
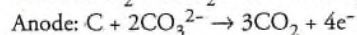
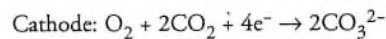
While the established economies are endeavouring to reduce carbon emissions, the energy demands of the emerging economies in countries such as India and China are soon going to outstrip those of the OECD countries.^[1] Coal is almost certainly going to be the dominant fuel in the coming decades due to its extensive reserves in such important energy economies as the US and China. The net effect is likely to be very significant increases in global CO₂ emissions, unless more efficient means of carbon conversion are achieved.

At present the dominant technology approach is clean coal technology with sequestration of CO₂. Sequestration is certainly going to be an important technology, but will be difficult to achieve universally as suitable geologies are likely to be fairly localized. There are also very significant efficiency and cost penalties with the sequestration process. Another major disadvantage is that waste heat cannot easily be utilized for heating, cooling or process technology on the gigawatt scale of generation likely to be necessary for sequestration systems. This mitigates strongly against the decentralized energy concepts that are so important for the energy future.

Direct carbon fuel cells are a potentially very important technology that could be utilized to complement large-scale sequestered clean coal systems. Carbon fuel cells offer

very high efficiency of conversion, due to favorable thermodynamics for processes such as direct oxidation to CO₂, and if implemented in decentralized, MW-scale systems, can yield 2–3 times the amount of energy for a given amount of coal. Carbonaceous materials have a high energy value and, in this era of diminishing fossil reserves, could provide clean fuels for use in appropriate technologies.

In direct carbon fuel cells (DCFCs), the reactions occurring in the cell are:^[2]



Although a prototype DCFC, based on molten sodium hydroxide, was invented in 1896,^[3] other fuel cells, such as hydrogen, have received wider attention. This is despite the fact that the energy released per unit volume on the oxidation of carbon with dioxygen (23.95 kWh/l) substantially exceeds that of many other fuels, for example, that of liquid methane (5.9 kWh/l), liquid hydrogen (2.6 kWh/l) or diesel (10.6 kWh/l).^[4] Further operational advantages of DCFCs include the possibility of a fully renewable solid fuel.

Elemental carbon exists in several allotropic forms. Carbon blacks are amorphous carbons produced in an inert atmosphere, and consist of agglomerates of small particles, giving a high surface area. Active carbons can be derived from, for example, waste tires,^[5] following suitable processing. A very attractive method of producing carbon that is CO₂-neutral is through pyrolysis of biofuels or carbonaceous wastes. The difference between fuel cells and batteries in this case is not very distinct; however, if one was considering portable applications the mode of operation would be akin to a battery, i.e. as a semi-fuel cell. For stationary applications carbon could be continuously fed to the fuel cell, which would then be a carbon fuel cell.

The first consideration for a DCFC was in 1896 by W.W. Jacques^[6] who used a molten hydroxide electrolyte in the temperature range of 400–500°C. The Anbar et al. patent of 1976 sought to use carbonate as the electrolyte,^[7] proposing to use the CO₂ by-product of the carbon oxidation to keep the electrolyte

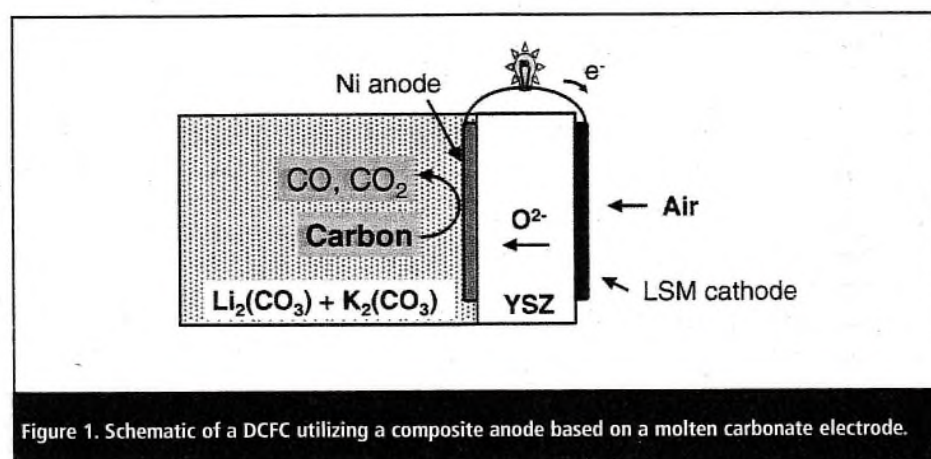


Figure 1. Schematic of a DCFC utilizing a composite anode based on a molten carbonate electrode.

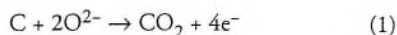
invariant. The cell consisted of a molten lead anode with the fuel-rich molten carbonate electrolyte (40% Li_2CO_3 /30% K_2CO_3 /30% Na_2CO_3) floating on top at an operating temperature of 650–750°C. More recently, the considerable advances in molten carbonate fuel cell (MCFC) technology^[8] for the electrochemical conversion of hydrogen have led to two new patents being issued to Cooper et al. for the direct conversion of carbon.^[9, 10]

The intrinsic difficulty in implementing carbon fuels is that most fuel cells are based on a solid membrane, and with a solid fuel there is very little interaction between the solid fuel and the solid electrode/electrolyte membrane. Therefore, most research to date has focused on high-temperature liquid electrolyte concepts.

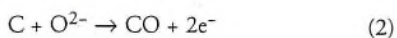
An alternative way to solve this problem uses a solid electrolyte with a fuel electrode/electrolyte based on a slurry of liquid electrolyte and solid electrode.^[11–13] This liquid interface removes solid/solid contact problems, and seems to provide a very attractive way forward. By employing a solid oxide electrolyte to separate the cathode and anode compartments, while utilizing a molten carbonate electrolyte on the anode side, it is possible to avoid the need for CO_2 circulation. A similar idea utilizing a liquid metal/oxide redox shuttle has recently been published in the US.^[14]

Our approach is to merge solid oxide fuel cell (SOFC) and MCFC technologies, using a solid oxide electrolyte to separate the cathode and anode compartments, while a molten carbonate electrolyte is utilized to extend the anode/electrolyte region (Figure 1). Oxygen is reduced to O^{2-} ions at the cathode and transported across the solid electrolyte membrane to the anode compartment, where carbon is oxidized to CO_2 .

Molten carbonate could enhance the carbon oxidation in two ways: as a fuel carrier, or as an electrochemical mediator. The ideal anode reaction is the direct electrochemical oxidation of carbon to CO_2 :



However, the actual anode reactions are more complicated. A partial oxidation of carbon to CO is also possible:



These two reactions require solid/solid interaction as O^{2-} ions are supplied from the solid electrolyte; however, the fluidity of the molten carbonate would enhance the transport of the carbon fuel to the anode. Enhancement

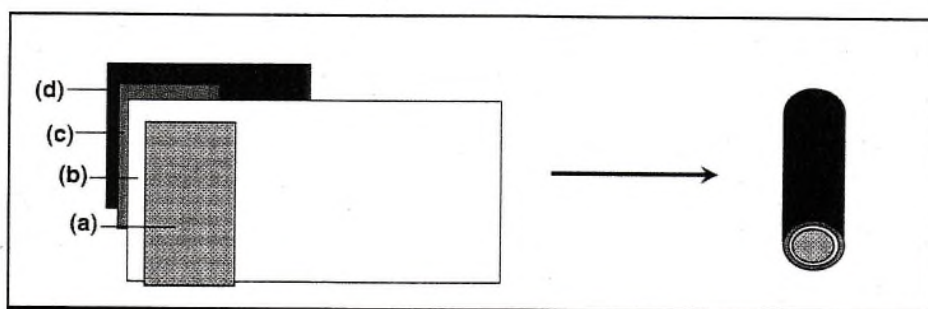


Figure 2. Cell components and construction of short tube semi-fuel cells: (a) NiO anode, (b) YSZ electrolyte, (c) LSM/YSZ composite cathode, and (d) LSM (current collector).

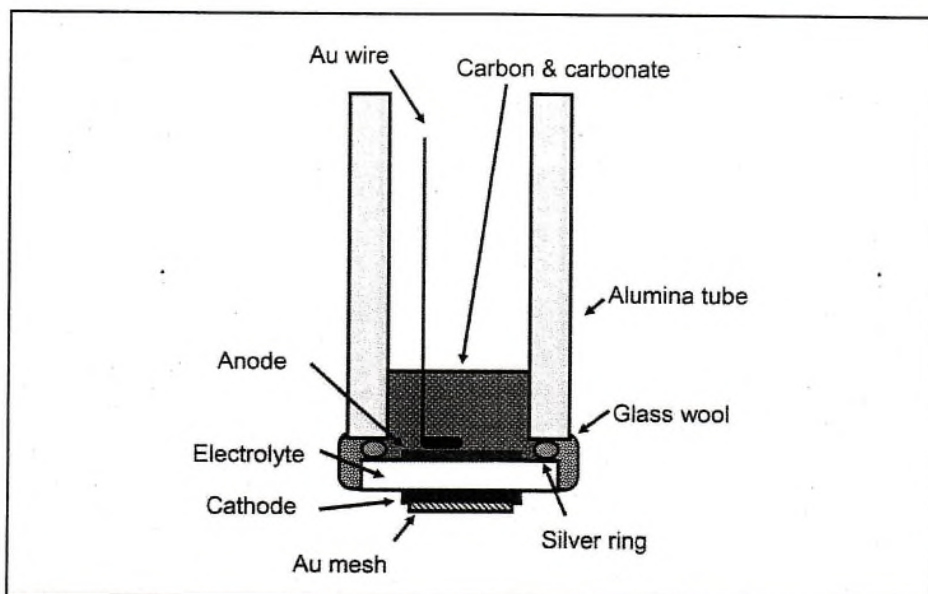
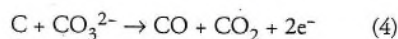
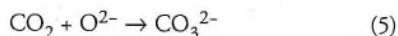


Figure 3. Schematic diagram of the test button cell utilizing the extended anode/electrolyte concept.

of the anode reaction by the molten carbonate as an electrochemical mediator is also expected:



These reactions should be followed by the regeneration of CO_3^{2-} ions:

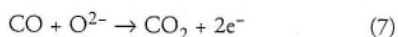


in order that the electric charge of the molten carbonate can be kept neutral.

The carbon can be converted via a non-electrochemical reaction known as the reverse 'Boudouard reaction':



Although considerable amounts of CO can be produced via reactions (2), (4) and (6), the chemical energy of CO can be converted to electric power via the electrochemical oxidation of CO at the anode in the DCFC:



The maximum energy density can be achieved by fully oxidizing carbon to CO_2 .

This new concept avoids the need for CO_2 circulation and the protection of the cathode from molten carbonate, and allows the use of materials already developed for SOFC applications.

We have demonstrated this concept using tubular DCFCs,^[12, 15] which are suitable for practical demonstrations, and we present some further results here. However, it is difficult to probe the detailed anode reaction with these tubular cells, because the available surface areas of the electrolyte and electrode are difficult to control and sealing is necessarily not complete, so we have developed a button cell test geometry which is also reported here.

Experimental

Solvents and reagents, yttria-stabilized zirconia (8-YSZ, Pi-Kem), lanthanum strontium manganate (LSM, Pi-Kem), NiO 325 mesh (Aldrich), super-S carbon (Timcal) were used as received. Omegabond 600 ceramic cement sealant (Omega Engineering) was prepared according to the manufacturer's specifications.

Lithium carbonate and potassium carbonate (Aldrich Chemical Co) were air-dried at 300°C prior to use.

Electrochemical measurements were recorded on a 1280B Electrochemical Workstation over the temperature range of 550–900°C, measuring at 50°C intervals with the cathode in static air. Scanning electron micrographs of the cell were recorded on a Jeol JSM-5600 for SEM (accelerating voltages up to 30 keV and magnification $\times 300\,000$).

Tubular semi-fuel cell design and preparation^[12]

Green tapes of NiO/YSZ (containing 55 wt% NiO) anode, YSZ, LSM/YSZ (containing 50 wt% LSM) cathode and LSM current collector were prepared using a standard tape-casting technique with the aid of organic solvent, binder and dispersants. The starting powders were ball-milled for 18 h in an appropriate solvent mixture, and the organic binder and plasticizer were added to the suspension and milled for a further 4 h. The resulting slurries were then tape-cast in a laboratory model tape-casting unit (TTC-1000, Mistler Inc).

The resultant tapes were subsequently dried and machined to the appropriate size, laminated, shaped appropriately (Figure 2) and fired to 1350°C for 5 h. Once sintered, the cells of appropriate geometry and dimensions, e.g. 5 mm inner diameter and 4 cm length, were sealed using the Omegabond commercial sealing cement.

Current collectors (gold wire on the anode side and silver wire on the cathode side) were attached to the anode and cathode using the appropriate metal pastes, and the pastes were sintered. A composition of 62 mol% Li_2CO_3 and 38 mol% K_2CO_3 (eutectic carbonate mixture) with carbon, e.g. Super-S (1:1), was prepared and used to fill the sintered tube, which was presealed at one end. The unit was sealed using Omegabond 600.

Planar button cell tests

A YSZ pellet of 2 mm thickness and 20 mm diameter was prepared from YSZ powder (8-YSZ, Pi-Kem) by sintering at 1500°C. A NiO/YSZ (NiO:YSZ = 8:2 weight) anode and an LSM/YSZ composite cathode were applied on opposite surfaces of the YSZ pellet by screen printing. The LSM/YSZ cathode consisted of three layers: the first and second layers contained 50% LSM ($(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{MnO}_3$, Praxair), and the third layer contained 100% LSM for current collection. The sintering temperatures of the anode and cathode were 1300 and 1250°C, respectively. The surface area of the sintered electrodes was 1.13 cm².

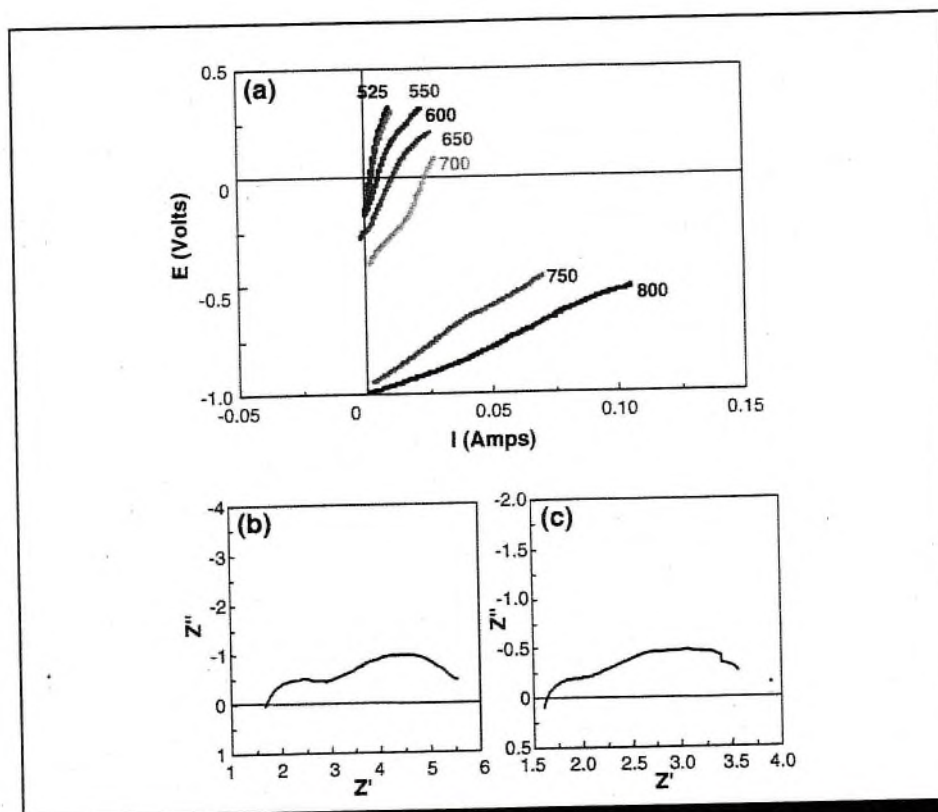


Figure 4. Electrochemical data obtained in a tubular semi-fuel cell for medium density fiber-board that had been pyrolyzed at 450°C, (a) current voltage data obtained at 10 mV/s for different temperatures from 525–800°C, impedance data obtained at (b) 750°C and (c) 800°C.

Figure 3 shows a schematic diagram of the test cell. For current collection, a gold mesh and a gold wire for the cathode and another gold wire for the anode were attached to the pellet using gold paste. The pellet was attached to an alumina tube with a silver ring. The cell was presealed at 900°C, and then glass wool was applied on the silver ring at room temperature, to give a secondary glass seal at high temperature.

A high-surface-area carbon black (Super-S, Timcal; 45 m²/g) was used as the fuel. A composition of 62 mol% Li_2CO_3 (Sigma-Aldrich) and 38 mol% K_2CO_3 (Fisher) with the carbon (carbonate:carbon = 1:1 mol) was put into the sealed cell. Argon gas was fed to the anode compartment to prevent combustion of the carbon fuel, and the cathode was exposed to air.

Carbon semi-fuel cell/battery

The co-sintered cell consists of a porous NiO anode (50 μm), a dense YSZ electrolyte component (60 or 120 μm), and a porous LSM cathode (120 μm) as confirmed by cross-sectional SEM. A wide variety of carbons have been investigated either as pyrolyzed products starting from starch, medium density fiber-board, polyamide fibers, old tires and woodchips, or as direct carbon sources such as graphite, glassy carbon, super-S carbon and activated charcoal.

The performance is very sensitive to the nature of the carbon and degree of processing. All carbons were found to yield good OCV (0.8–1 V) in the semi-fuel cell, depending on temperature and quality of sealing, which could not be complete as exhaust of CO_2 had to be allowed to avoid rupture. Electrochemical performance was found to be enhanced for high-surface-area carbons, and especially for incompletely pyrolyzed carbons. A typical example is for medium density fiber-board pyrolyzed at 350°C, shown in Figure 4.

Intermediate pyrolysis temperatures (300–500°C) were generally used, as both higher and lower pyrolysis temperatures for organic and waste-derived carbons had yielded inferior performance, indicating that some residual impurities assist in the activation of carbon. The current/voltage curve (Figure 4a) yields a current of 100 mA at 500 mV at 800°C. It is quite clear that heating to above 700°C greatly increases both OCV and current, and this is thought to relate to a decrease in molten carbonate viscosity as it is well above the eutectic melting point.

Impedance data are consistent with I/V data (Figures 4b and 4c). The impedance plots show three elements: the series resistance, high-frequency intercept R_s and two elements related to electrode phenomena that combine to give the polarization resistance R_p . The lowest frequency element often shows a strong diffusion limitation.

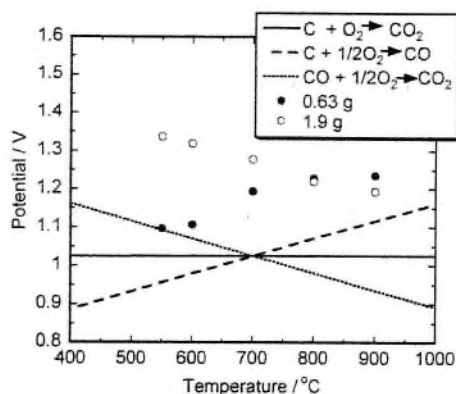


Figure 5. Theoretical standard potentials for possible anode reactions and OCVs measured with the button test cell with differing amounts of carbon/carbonate slurry.

An important point is that R_s has been found to scale with the zirconia electrolyte thickness between the investigated 60 and 120 μm thicknesses, showing that it is dominated by the ionic resistance of the zirconia.^[15] This allows us to estimate the effective area as the electrolyte specific resistance can be calculated. For the 120 μm thick YSZ electrolyte the expected specific resistance would be about $0.38 \Omega\text{cm}^2$ and $0.26 \Omega\text{cm}^2$ at 750°C and 850°C, respectively. The observed R_s values at these temperatures were 1.73 Ω and 1.60 Ω with an effective active area of 0.18 (± 0.02) cm^2 . The effective area-specific resistance (ASR) of the whole cell is therefore 0.68 (± 0.07) Ωcm^2 ; however, utilization of the geometrically available area is poor, on the order of 10–20%, due to poor current collection.

Carbon fuel cell mechanism

Figure 5 shows the OCV values measured with the button test cell with 0.63 g and 1.9 g of the 1:1 carbon and carbonate mixture in the temperature range of 550–900°C. The measurement was started at 900°C, and then the temperature was decreased. Theoretical standard potentials of possible reactions are also shown in Figure 5. The test cell showed high OCV values, which were higher than the standard potentials, suggesting that sealing was effective. The standard potentials are based on the activity values of 1 for all reactants, whereas the OCVs of real cells should reflect the actual activities. The high OCV values of the test cell compared with the theoretical values can be attributed to low activities of CO or CO_2 in the anode compartment.

For the smaller amount of electrode/electrolyte, the OCV at 900°C was 1.24 V, and decreased slightly with the decrease in temperature. This influence of temperature on the OCV suggests that the electrochemical oxidation of

carbon to CO (reaction 2) was the dominant anode reaction. For the larger amount of electrode/electrolyte mixture the OCV increased as temperature increased, indicating a change in the dominant mechanism to CO oxidation, and hence that the overall oxidation of carbon is a two-stage process via CO.

Conclusions

A direct carbon fuel cell that is a hybrid SOFC/MCFC carbon/air fuel cell system has been shown to effectively utilize a range of carbon fuels, including pyrolyzed waste. Electrochemical performance with effective area-specific resistances as low as $0.68 \Omega\text{cm}^2$ has been achieved along with operating potentials as high as 1.3 V; however, due to insufficient current collection, only a fraction of the available geometric cell area is utilized.

The overall oxidation process seems not to be a single-step oxidation of carbon to CO_2 , as it seems to involve a CO intermediate which may be produced electrochemically or via the Boudouard equilibrium. Direct carbon fuel cells are a very important new technology stream attracting considerable interest in the research community,^[16] and although the technology still requires significant development, there is significant promise of future success.

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