Chemical Society Reviews

Challenges in developing direct carbon fuel cells

Journal:	*Chemical Society Reviews*
Manuscript ID	CS-REV-10-2016-000784.R1
Article Type:	Review Article
Date Submitted by the Author:	26-Feb-2017

Complete List of Authors:	Jiang, Cairong; St Andrews Univwersity, Ma, Jianjun; St Andrews University, Corre, Gael; University of St Andrews Jain, Sneh; University of St Andrews, School of Chemistry Irvine, John; University of St Andrews, School of Chemistry

Chem Soc Rev

Review Article

Challenges in developing direct carbon fuel cells

Cairong Jiang, Jianjun Ma, Gael Corre and Sneh L. Jain and John T. S. Irvine†

powerReceived 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

A direct carbon fuel cell (DCFC) can produce electricity with both superior electrical efficiency and fuel utilisation compared to all other types of fuel cells. Although the first DCFC prototype was proposed in 1896, there was, until the 1970s, little sustained effort to investigate further, because of technology development issues. Interest in DCFCs has recently been reinvigorated as a possible method of replacing conventional coal-fired power plants to meet the demands for lower CO_2 emissions, and indeed for efficient utilisation of waste derived chars. In this article, recent developments in direct carbon conversion are reviewed, with the principal emphasis on the materials involved. The development of electrolytes, anodes and cathodes as well as fuel sources, are examined. The activity and chemical stability of the anode materials are a critical concern addressed in the development of new materials. Redox media of molten carbonate or molten metal facilitating the tranportation of ions offer promising possibilities for carbon oxidation. The suitability of different carbon fuels in various DCFC systems, in terms of crystal structure, surface properties, impurities and particle size, are also discussed. We explore the influence of a variety of parameters on the electrochemical performance of DCFCs, with regard to their open circuit voltage, power output and life time. The challenges faced in developing DCFCs are summarised, and potential prospects of the system are outlined.

1. Introduction

The demand for energy has increased rapidly over the last 20 years due to the rapid development of the global economy. The emission of greenhouse gases is, however, a major issue associated with the demand for energy, as most of the CO_2 comes from the process of energy conversion from fossil fuels. To decrease CO_2 emissions research has, typically, been focused on exploring the technology of increasing renewable energy.

As a newly developed technology, a Direct Carbon Fuel Cell (DCFC) is a very promising means of converting carbon sources to electricity, as it offers a much higher efficiency than other fuel cell systems. The overall reaction of this system is shown in equation (1).

$$C_{(s)}+O_{2(g)}\rightarrow CO_{2(g)} \tag{1}$$

ΔG for this reaction is -395 kJ mol^{-1} and the ratio $\Delta G/\Delta H$ = 1.003, meaning that this process theoretically offers 100% efficiency of converting chemical energy to electricity, more than twice that typically obtained from thermal conversion. Practical efficiency should be as high as 80%, which is a major improvement on the current inefficient traditional coal-fired power plants (< 40%), and on molten carbonate fuel cells or solid oxide fuel cells running on hydrogen or natural gas (where the efficiency is 40-60%).[1] Moreover, DCFC systems are scalable, and therefore suitable for decentralised electricity production. Opportunities for DCFC applications are further strengthened by the abundance of available fuels, which include both fossil fuels, such as petroleum coke or coal (the most abundant fossil fuel on earth), and renewable fuels, such as biomass and its chars (e.g., wood, nut shells, switchgrass, corn stover, palm, rice and algae) or even other sources of fuel (food waste, wood waste). This technology enhances the biomass conversion, which is an important long-term consideration in producing electricity from renewable biomass sources. The dominant potential application is in the conversion of coal, especially in China, where there is significant new commercial opportunities.

The topic of DCFC is attracting an ever increasing interest, evident in the exponentially growing number of review articles. In 2007, Cao et al. summarised the fundamental development of DCFC technology.[1] In 2009, a review article by Cooper and Selman explained the possible reaction mechanisms of carbon oxidation in molten carbonate fuel cells.[2] In 2012, Giddey summarised the recent progress and technical challenges of the DCFC technology, and discussed the future of this technology.[3] After this paper, Rady *et al.* introduced different types of DCFC systems along with discussions of the reaction mechanism. They focused on the properties and analytical techniques of coal fuels for DCFC application.[4] Gür provided a mechanistic overview of different modes and vehicles in a variety of DCFC systems.[5] He also demonstrated the carbon conversion mechanism of a variety of DCFC systems on the fundamental basis.[6] Recently, Zhou *et al.* [7] summarised anode material for DCFCs. Cao *et al.* gave a good review on the development of DCFC in recent years. [8]

EaStCHEM, School of Chemistry, University of St Andrews, KY16 9ST, United Kingdom
† Corresponding author jtsi@st-andrews.ac.uk (J. T. S. Irvine).

Despite all this considerable attention, the developmental progress of this technology has been relatively slow, as DCFCs face a number of challenges. Not least of these must be the difficulty of implementing practical systems of this nature and also the choice of materials. It should be noted, that the high resistance of the cell and the products formed during the reaction process with their structural and morphological changes are formidable challenges, resulting in unstable electrochemical power output. Moreover, when the cell contains aggressive components such as carbonate or hydroxide, the aggressive character can cause structural changes in the cell components, which tends to passivate both the electrodes, leading to a significant increase in cell resistance. These issues will result in poor utilisation of the carbon fuels, and in an inferior long-term durability and efficiency of the whole system.

Before this technology can be applied extensively, some important issues should be addressed. These issues include the optimisation of the operational system, the development of new electrode and electrolyte materials, and the processing of solid carbon fuels. In this review, we discuss some of the issues raised by DCFCs and the challenge faced in the development of such cells. Particular attention is given to the materials involved in DCFCs, electrolytes, anodes, cathodes and various fuels. Discussion focuses on the anode catalysts for carbon oxidation, and carbon fuels regarding a variety of the physical and chemical properties of carbon. The cell performance, including open circuit voltage, power output and life time, are also discussed. The overall challenge of the whole development of DCFCs is explored.

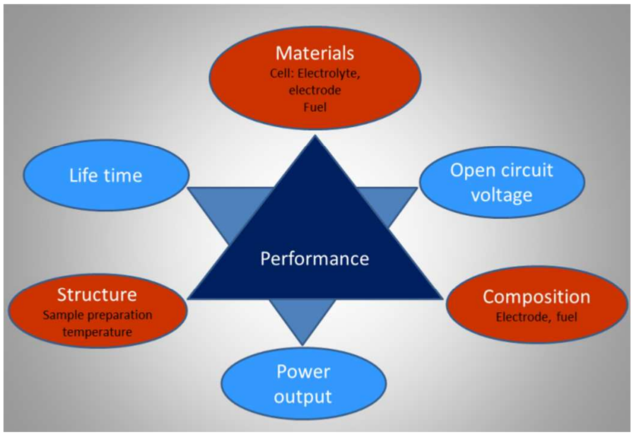


Figure 1 The relationship between the cell performance and materials, composition and structure being used in direct carbon fuel cell

Figure 1 shows the relationship between materials, composition and structure, and open circuit voltage, power output and life time. The broad cell performance includes cell life time, power output, and open circuit voltage, which is determined by the materials, composition and structure of the cell. In a DCFC, the materials used include an electrolyte, a cathode, an anode and a fuel. It should be noted, that the materials chosen determine the operating temperature of the cell, as the conductivity of the electrolyte is temperature dependent. The catalytic property of the materials determines the polarisation resistance; this in turn, results in different electrochemical performances. For the electrolyte, the most important property is its conductivity, and for the electrode, the catalytic property is critical. The type of the fuel is another important characteristic, as carbon has different structures (e.g. amorphous or graphitic). The composition of the cell components has a significant effect on the electrochemical performance as well. For example, the electrode of the cell is usually a composite component, therefore the ratio of the electrode material to the electrolyte material matters, especially when the composite electrode is composed of an electronic metal and an ion conductor or a mixed ionic and electronic conductor. Here for electrode, electrode materials provide electronic conductivity, while electrolyte materials provide ionic conductivity. For instance, in the NiO-GDC electrode, NiO yields metallic Ni for conduction, whilst GDC is a mixed ionic and electronic conductor. An optimal ratio of NiO-GDC will give the smallest cell resistance (NiO65:GDC35 is generally accepted as a good ratio). And there is often an optimal amount of catalyst for the electrochemical oxidation of ‘carbon’. We have to bear in mind that the ‘carbon’ here means hydrocarbon with a composition of $CH_x(x<1)$ as hydrogen exists in all sorts of carbon sources (coal, char, biomass). The microstructure of the cell (e.g. the porosity of the electrode, the thickness of the catalyst layer, the density of the electrolyte) is deemed a vital factor, determining the final power output of the cell. The sample fabrication process, the sintering temperature of the electrode etc. therefore have to be considered in the whole process of the cell preparation.

2. Electrolyte

DCFCs are classified into three types by the electrolyte used: molten hydroxide DCFCs, molten carbonate DCFCs and solid oxide DCFCs. Accordingly, the electrolyte of DCFCs is hydroxide, carbonate and solid oxide, respectively. Reactions in each cell are different depending on the electrolyte used. Figure 2 displays these three types of cells with a variety of reactions at the anode side and the cathode side. The anode reactions are strongly dependent on system design and the mechanism of carbon oxidation is discussed across differing configurations of DCFC through this review article. In previous review articles the technology development of hydroxide-DCFCs and carbonate-DFCs has been described in detail.[3, 6] The presentation of this work gives a brief introduction of these two types of DCFCs in 2.1 and 2.2. Focus is given to DCFCs with solid oxide as the electrolyte.

2.1. Hydroxide

The first hydroxide-DCFCs dates back to 1896, which is the earliest prototype carbon fuel cell.[9] The hydroxide-DCFCs offers some advantages over other types of DCFCs. Hydroxides have low melting points and high ionic conductivity properties, so they allow the cell to use less expensive materials and of course to operate at relatively low temperatures. Figure 2a

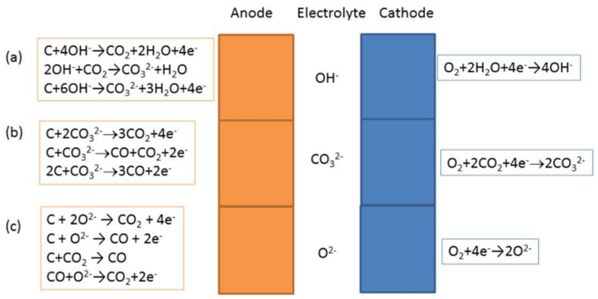


Figure 2 Schematic diagram of a DCFC with different electrolytes. (a) Hydroxide-DCFC; (b) carbonate-DCFC; (c) solid oxide-DCFC.

shows main reactions at the anode and the cathode in hydroxide-DCFCs.

The carbon is oxidised at the anode:

$$C+4OH^{-}\rightarrow CO_2+H_2O+4e^{-} \qquad (2)$$

Hydroxide is produced at the cathode:

$$O_2+2H_2O+4e^{-}\rightarrow 4OH^{-} \qquad (3)$$

As one of the earliest developed DCFCs, hydroxides have received little attention in the last few decades because the deterioration of the hydroxide electrolyte into a carbonate becomes a major technical problem. The carbonate can be produced either by a chemical or electrochemical reaction:

$$2OH^{-}+CO_2\rightarrow CO_3^{2-}+H_2O \qquad (4)$$

$$C+6OH^{-}\rightarrow CO_3^{2-}+3H_2O+4e^{-} \qquad (5)$$

A successful example of hydroxide-DCFC has been demonstrated by Scientific Applications and Research Associates Inc (SARA) using a humid atmosphere.[10] The high concentration of water is believed to shift the chemical equilibrium in equations (4) and (5) towards the left. Despite a renewal of the research into hydroxide-based DCFCs,[11, 12] it is still necessary to improve the stability of the hydroxide for the practical application.

2.2. Carbonate

Molten carbonates, which are commonly used in conventional Molten Carbonate Fuel Cells (MCFCs), have received attention in DCFCs. Compared to hydroxides, molten carbonates offer higher conductivity, a suitable melting temperature range (the working temperature range) and a good degree of stability in atmospheres containing CO_2. The composition of the carbonate electrolyte is an important factor because it determines the melting temperatures. Among all carbonates, binary or ternary carbonate mixtures allow a lower operating temperature than single carbonate compositions. Of the binary mixtures, Li_2CO_3-K_2CO_3 is commonly used as the electrolyte for DCFCs, because its melting temperature is below 550 °C. For example, Peelen *et al.*[13] and Cherepy *et al.*[14] used a 62/38 mol% lithium/potassium or a 32/68 mol% lithium/potassium binary carbonate eutectic mixture in their studies. A variety of carbon derived from oil, methane, coal, biochar, and petroleum coke were tested, and these DCFCs generated 50-125 mA cm^{-2} current density at a cell voltage of 0.8 V at 800 °C.[14] A high power density of 187 mW cm^{-2} was reported from coke fuel by Chen *et al*. using a ternary eutectic mixture of Li_2CO_3-K_2CO_3-Al_2O_3 (1.05:1.2:1 mass ratio).[15] Researchers have made efforts to reduce the operational temperature of the DCFCs. Kouchachvili developed a ternary eutectic carbonate with a composition of 43.4 mol% Li_2CO_3 and 31.2 mol% Na_2CO_3 and 25.4 mol% K_2CO_3 added by 20 wt% Cs_2CO_3 and this performed well at an operating temperature of 700 °C.[16] Vutetakis employed a ternary carbonate of $32.1Li_2CO_3/34.5K_2CO_3/33.4Na_2CO_3$ in coal fuelled DCFC[17] and was able to operate the cell as low as 500 °C.

Figure 2b presents the possible reactions in carbonate-DCFC, the reaction of the anode half-cell is as follows:

$$C+2CO_3^{2-}\rightarrow 3CO_2+4e^{-} \qquad (6)$$

CO can also be produced by the following reactions:

$$C+CO_3^{2-}\rightarrow CO+CO_2+2e^{-} \qquad (7)$$

$$2C+CO_3^{2-}\rightarrow 3CO+2e^{-} \qquad (8)$$

Carbonate is generated at the cathode by the combination of CO_2 with oxygen:

$$O_2+2CO_2+4e^{-}\rightarrow 2CO_3^{2-} \qquad (9)$$

The overall cell reaction is shown in equation (1).

Cooper *et al.* proposed that the carbon oxidation at the anode is complex and it constitutes a set of independent elementary reactions.[2] However, this proposal needs to be verified by experiments.

2.3. Solid oxide

A fast diffusion rate can be obtained at intermediate and high operating temperatures, and this is desirable for DCFCs. Hence, solid oxygen ion conductors, commonly used in SOFCs, have been proposed as the electrolytes in DCFCs with a view to achieving enhanced reaction rates with a higher operating temperature. The requirements for a solid electrolyte are mechanical and chemical stability, high ionic conductivity and low electronic conductivity at operating temperatures in both reducing and oxidising atmospheres, and low ohmic resistance. The first attempt to directly convert solid carbon into electricity at a high temperature using a solid electrolyte was reported by Baur.[18] Other researchers include Nakagva and Ishida, 1988, [19] Gür and Huggins, 1992, [20] Horita et al., 1995[21]. A 8 mol% yttrium stabilised zirconia (YSZ) is a conventional electrolyte for solid oxide fuel cells, and has been adopted for DCFCs. This material is one of the main electrolytes for DCFCs due to its good ion conductivity, stable structure and compatibility with cathode and anode materials. It is suitable for intermediate and high temperature operational conditions, generally in the range of 700-1000 °C.[22] Sr and Mg doped $LaGaO_3$ ($La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$)[23, 24] and ScSZ ($(Sc_2O_3)_{0.1}(ZrO_2)_{0.9}$)[25] have been considered used as the electrolyte in DCFCs as they offers better conductivity than the YSZ electrolyte. It is expected to have less contribution from ohmic loss from these two kinds of electrolytes, and therefore slightly higher cell performance could be obtained.[26, 27] More attention has to be paid on the selection of suitable electrode materials and thin film electrolyte manufacture.

Doped ceria (GDC) is another electrolyte often used in low and intermediate temperature ranges and has been used as an electrolyte in DCFCs[28, 29]. In comparison with YSZ, doped ceria has higher conductivity, especially at low temperatures.[30] By tailoring the electrode components with a special structure and/or morphology, excellent electrochemical performances has been achieved on the cell with GDC electrolyte using hydrogen fuel at low temperatures.[31] More efforts have to be made for carbon to be efficiently oxidised at low temperatures. Carbon oxidation is assumed to be the main reaction at the anode in a solid oxide-DCFC the anode, as shown in Figure 2c. Some other reactions become more dominant when catalysts are added. More details about the anode materials and reactions will be introduced in section 3 and 4.

3. Anode and catalyst

In a DCFC with a solid oxide electrolyte, SOFC technology is adopted for converting the chemical energy of carbon into electricity in a fuel cell in which carbon is oxidised by oxygen ions from the cathode at a relatively high temperature. The total reaction is as shown in equation (1) and the reactions in the anode and cathode as shown in equation (10) and (11).

$$O_2+4e^-\rightarrow 2O^{2-} \qquad \text{Cathode} \qquad (10)$$

$$C+2O^{2-}\rightarrow CO_2+4e^- \qquad \text{Anode} \qquad (11)$$

The basic requirements for the anode materials of DCFCs is similar to that for solid oxide fuel cells, which include high electronic and ionic conductivity, excellent catalytic activity towards electro-oxidation of fuel which is a solid carbon, suitable porosity to allow mass transport, chemical stability and thermal compatibility with other cell components during cell fabrication and operation, robust mechanical and thermal stability, easy fabrication, and low cost.[32] Among these characteristics, the most critical one is good ionic conductivity to allow the active sites to extend beyond the anode-electrolyte interfaces, since there is little reaction between the solid carbon and the solid oxide.

Due to the requirements of operating in a reducing environment and one of high electronic conductivity, pure porous metallic materials can, in principle, be used as anodes. Nickel and platinum are the common anodes for DCFCs. Carbides have also been investigated. Vanadium carbide was found to be a good catalyst, showing more stability in carbon than other carbides, such as ZrC, WC, TiC.[21] Many efforts were devoted to reducing sluggish reaction kinetics, and to improving any chance direct contact between the electrode and the solid fuel. Some approaches focused on the design of novel cell configurations with trapping interlayers, and efficient anode catalysts. Two kinds of anode configurations are presented in Figure 3, one is a solid oxide cell and the other is a combination of catalyst particles in the carbon and a solid oxide cell. The former is discussed in section 3.1-3.2 and the latter is discussed in section 3.3-3.5. Other representative configurations with a redox mediator, e. g. molten carbonate or molten metal is discussed in section 4 separately as the redox mediator is unique and plays an important role in DCFCs.

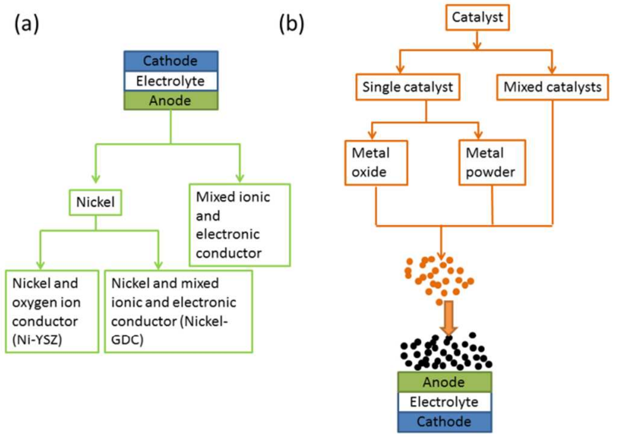


Figure 3 Configurations of anode materials and catalysts for DCFCS

3.1. Nickel/nickel oxide anode

When dealing with a variety of fuels including hydrogen and hydrocarbon, nickel is one of the extensively studied anodes for DCFCs because of its excellent catalytic activities over a wide range of temperatures. Here nickel refers to nickel oxide or nickel metal as most of the raw materials are nickel oxide for the convenience of fabrication procedure. Sometimes nickel oxide is pre-reduced in hydrogen and then used in DCFCs. In other cases, nickel oxide can be in-situ reduced by hydrogen or carbon monoxide released from the pyrolysis of carbon. The electronic conductivity of nickel is very high, but the ionic conductivity is low. The electronic conductivity of nickel is 2×10^4 S cm^{-1} at 1000 °C. The thermal expansion coefficient of nickel is 13.3×10^{-6} cm cm^{-1} K^{-1}, which is higher than that of a YSZ electrolyte (10.5×10^{-6} cm cm^{-1} K^{-1}). Taking into account of the thermal expansion and compatibility of the nickel anode with the electrolyte, an ionic conductor or a mixed ionic and electronic conductor is generally added to nickel oxide to form a composite electrode[33]. The DCFC with an anode of nickel metal or nickel oxide gives an excellent performance. A wide range of maximum power densities from 100 mW cm^{-2} up to 900 mW cm^{-2} at 700-900 °C have been obtained. Some representative examples have been given in the literature.[7] These hugely different power densities are caused by many parameters and it will be introduced in the following sections. It is worth mentioning that the addition of catalyst into the carbon/coal fuel and a redox mediator significantly improve the electrochemical performance of DCFCs. Details will be given in section 8.2

3.1.1. Nickel/nickel oxide and oxygen ion conductor (OIC).

Porous Ni/NiO-YSZ or Ni/NiO-ScSZ is the commonly used anode for DCFCs. It exhibits good compatibility with the electrolyte (YSZ or ScSZ) and good catalytic activity in carbon oxidation. It is chemically stable in a reducing atmosphere and is compatible with the electrolyte during the operation and fabrication processes. The intrinsic charge transfer resistance associated with the electrocatalytic activity at the boundary of Ni/OIC is low, since nickel serves as an excellent electrocatalyst for the electrochemical oxidation of a wide variety of carbon fuels. The OIC forms a framework for the dispersion of nickel particles and acts as an inhibitor for the coarsening of the nickel during both the consolidation and operation processes. The oxygen ion conductor plays a most significant part in the ionic conductivity, and the nickel provides the major electronic conductivity for the anode. A few parameters have been optimised in order to get a good electrode, such as the porosity of the anode being around 20-30 vol% to facilitate the transport of reactant and product gases. The nickel concentration falls into the range of 40-45 vol% in order to achieve the minimum overpotential over a wide range of current density. A significant number of references are available on this topic.[34-36] In this particular research area, extensive investigation was carried out on this type of electrodes for use with DCFCs.[37]

3.1.2. Nickel/nickel oxide and mixed ionic and electronic conductor (MIEC)

Efforts have been made to operate DCFCs at intermediate or low temperatures, as high temperatures cause an increase in cost. As described in the electrolyte section, a GDC/SDC electrolyte is a good choice, and therefore a Ni-GDC/SDC was developed for the anode on a ceria electrolyte-based DCFC. It became clear, that a cell with such an electrolyte operating at 650 °C generated reasonable power output. NiO-GDC was also selected as the anode material for DCFCs using a YSZ electrolyte.[38] In order to increase the compatibility with the YSZ electrolyte, 15 wt% YSZ was added to the mixture of 60 wt% NiO and 40 wt% of $Gd_{0.1}Ce_{0.9}O_{1.95}$. Although some efforts have been made to develop a DCFC that can operate at low temperatures, no ideal cell performance are achieved. A range of 40-250 mW cm^{-2} maximum power output has been generated. It seems that the performance with this type of electrode is not as good as that with Ni/YSZ operating at high temperatures. It can be seen from the literature that a redox mediator has to be taken into account for the DCFC operating at low temperature to achieve this reasonable performance.[28, 39] It is well known that the electrochemical reaction rate is low at low tempeartures, which is more severe for carbon oxidation. The microstructure of the anode and the configurations of the DCFC system have effect on the cell performance and need to be further investigated.

3.2. Mixed ionic and electronic conductor(MIEC)

The aim of using mixed ionic and electronic conductors (MIECs) is to extend the reaction zone in carbon oxidation from the anode/electrolyte interface to that of the anode/solid fuel. Some MIECs are excellent sulfur tolerant materials, which offer great promise for coal oxidation as sulfur often exists in coal.[40] A preliminary evaluation of such a catalyst indicated promising performance in DCFCs. Although extensive work has been done on MIECs, little has been reported on fuel cell performance using such catalysts in DCFCs.

Carbon oxidation using $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ as the anode was considered in DCFCs. The idea came from the good catalytic performance of this material in gaseous hydrocarbon fuel cells.[41, 42] The phase and microstructure stability and conductivity of this material in the operating conditions of DCFCs were investigated.[43] One drawback of using a LSCF MIEC anode is its low electronic conductivity in reducing atmosphere. Another issue involved is the erratic stability of the phase structure in reducing condition. Even though the rhombohedral LSCF phase remains the most dominant phase after heat treatment in a CO atmosphere at 800 °C for 50 hours, the major perovskite phase completely decomposes in hydrogen over this period of time and at this temperature.[43] In a practical DCFC system, the anode atmosphere is, in fact, a mixture of a variety of gases, such as hydrogen, carbon monoxide, carbon dioxide, methane and other gases. It is inevitable that hydrogen exist in the anode chamber, therefore the unstable phase structure of the LSCF is likely to be a major concern for long-term operation.

GDC has been widely used as the anode for solid oxide fuel cells because its excellent catalytic activity toward the oxidation of different fuels including hydrogen and hydrocarbon fuels.[35] GDC and also yttria-doped ceria (YDC) were investigated as the anode materials for DCFCs. In reducing atmosphere (typical anode environment), both these two candidate materials exhibit the characteristics of mixed ionic and electronic conductivity.[44] Since YDC shows greater electronic conductivity than GDC, and comparable ionic conductivity with YSZ, the anode reaction can be appreciably enhanced. It is, therefore, concluded that high electronic conductivity in the MIEC anode is beneficial in reducing anodic polarization, especially in reducing activation polarization. YDC does not always work well alone as the anode for DCFCs and in most cases a metal phase is needed to impregnate into the electrode. 20 mol% YDC infiltrated with a 2 wt% Ni anode, sprayed on a 0.45 mm thick YSZ electrolyte, was tested, using pure activated coconut charcoal carbon as a fuel and 33 mW cm^{-2} maximum power density was obtained at 800 °C.[45]

Titanates demonstrate excellent stability in reducing environments and present good resistance to sulphur and coking. They also have good compatibility with YSZ electrolytes,[46] and so, they were chosen as the anodes for the DCFCs. One of the examples is that $La_{0.3}Sr_{0.7}TiO_3$ (LST) and $La_{0.3}Sr_{0.7}Ti_{0.93}Co_{0.07}O_3$ (LSCT) investigated for the carbon oxidation.[47] Ionic conductivity is an important characteristic of the electrolyte of the cell as far as performance is concerned. The cell generated a low maximum power density of 6 mW cm^{-2} and 25 mW cm^{-2} when using LST and LSCT, respectively. This might be attributed to the lower ionic conductivity of LST as compared to LSCT as the testing condition is the same. The power output with this type of electrode is not comparable with nickel/nickel oxide based anode, not to mention that above power is produced with an addition of 2 wt% Ru into the titanate electrode.

3.3. Metal oxides

It seems that only limited cell performance can be obtained with a single solid oxide anode because the active sites for electrochemical reactions are not enough to contact solid carbon and solid oxide. Additives (catalysts), as shown in Figure 3b, are often added into the solid carbon fuel in order to extend the electrochemical reactions from three-phase boundary at the interface of solid electrode/electrolyte to the whole zone of carbon fuel. Among oxide catalyst (additives), metal oxides have received considerable attention in the application of DCFCs because of their high electrical conductivity. This criterion is essential for simultaneously accommodating the active material and enhancing the anode conductivity. Catalysts tend to increase both power density and open circuit voltage values. The addition of CeO_2 and 8YSZ to a commercial carbon black was also found to enhance the electrochemical performance. The degree of improvement of the current densities also depends on the conductivity of the oxide materials. These oxygen ionic conductors provide additional sites for oxygen ions, thereby creating more opportunity for the oxidation of carbon or carbon monoxide. A diagram of this system is shown in Figure 4.[26] Different amounts of these oxygen ion conductors were investigated. 10 wt% of oxide content in the fuel was found to be an optimal amount to obtain the highest power density.[26] The addition of GDC into the carbon fuel allows for a higher maximum power density than does the addition of 8YSZ. This is possibly because, with its good oxide ionic mobility as well as some redox activity, GDC not only reduces the cell resistance, but also plays a critical role as a catalyst for the CO oxidation or even the electrochemical oxidation of the carbon directly.

Fe_2O_3 is well known as excellent gasification catalyst and is similarly an efficient catalyst for carbon oxidation in DCFC systems. The catalyst loading method was investigated in two ways: one impregnating Fe_2O_3 into the carbon fuel, and the other impregnating Fe_2O_3 into the electrode. When Fe_2O_3 is impregnated into the anode, 17-times less amount of catalyst is consumed than with an impregnation into the carbon fuel for similar cell performance is to be obtained. It is believed that the introduction of Fe_2O_3 into the anode improves the electrochemical CO oxidation process by increasing the availability of electrochemical reaction sites and also by increasing the oxidation rate of the CO. This could be achieved in the real system by an optimisation of the anode chamber geometry or by an optimised amount of catalyst.[48] Direct oxidation of solid carbon should be enhanced, but more detailed experimental data are required before we can draw a conclusion. A representative example is that a maximum power density of 424 mW cm^{-2} at 850 °C was obtained on a cone design cell with a NiO(50wt%)-YSZ(50wt%) anode, a $La_{0.8}Sr_{0.2}MnO_3$ cathode, and a thin film YSZ electrolyte using activated carbon fuel loaded with 5% Fe_2O_3.[49]

CaO and MgO were reported to have a catalytic effect on the electrochemical oxidation of carbon, which might be related to the promoting effect of carbon gasification in the presence of CO_2.[50]

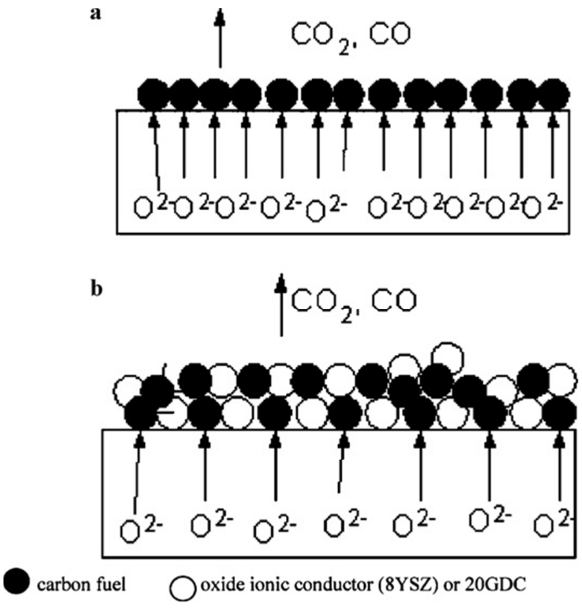


Figure 4 Demonstration of the interface of the electrode and solid carbon. (a) in the absence of oxygen ionic conductor in the solid fuel (b) in the presence of oxygen ionic conductor. Reproduced from reference [26] with permission from [Elsevier], copyright [2011].

3.4. Metal powder

Metal Fe powder enhanced the electrochemical performance when a hypercoal was used as a fuel for DCFCs. The maximum power density increased from 55 to 80 mW cm^{-2} at 700 °C.[37] Metal Ni and Ag were also investigated as catalysts added to the carbon fuel.[26] Ag gave a much better performance than did the Ni additive, which was possibly due to the formation of Ni_3C as an undesirable product.[26]

3.5. Mixed catalysts

In DCFCs, there are several alternative reactions, direct carbon oxidation, CO oxidation, gasification and steam reforming, are all possible. When considering the catalysts for those reactions, a single catalyst has its limitations, therefore, a mixture of two catalysts can be considered. A typical example of the mixed metal oxide with metal is Gd-doped ceria (GDC) mixed with Ag. It was used to catalyse the electrochemical oxidation of CO; an iron-based catalyst was loaded with the carbon fuel to enhance the Boudouard reaction, which produced CO via a reaction of C with CO_2.[51] It is believed that CO oxidation is enhanced as well.

A mixture of transition metal oxide and alkali metal oxide has the great advantage of acting both as a catalyst and a redox mediator via its carbonate. Iron oxide together with M_xO, (M_xO was a mixture of Li_2O, K_2O) was used as a catalyst in DCFCs. The reaction rate accelerated dramatically in the presence of the catalyst. Oxidation of carbon and coal are enhanced by the addition of Fe_mO_n-alkali metal oxide catalysts.[27, 52] A maximum power density of 100 mW cm^{-2} at 850 °C was obtained with pure coal char, while a maximum

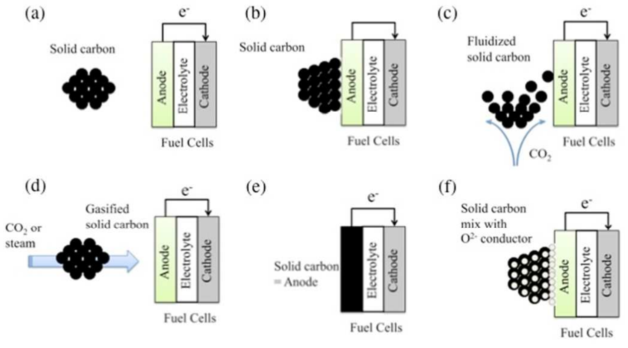


Figure 5 Different contact modes of solid carbon with the anode in direct carbon fuel cells using solid oxide electrolyte. Reproduced from reference [53] with permission from [Elsevier], copyright [2013].

power density of 204 mW cm^{-2} was obtained with Fe_mO_n-alkaline metal oxide catalyst impregnated coal char.[52] The gasification effect of these additives has been subsequently confirmed by the high intensity of CO products.

4. Redox media

Solid-oxide DCFCs can be categorised by the way solid carbon contacts with the surface of the anode, as shown in Figure 5.[53] Figure 5a shows the non-contact mode and it is shown here for completion, comparing to c, d as it is very difficult for carbon oxidation in this design. Some direct methods are used to increase the contact area by pressing the porous carbon pellets against the YSZ electrolyte, as shown in Figure 5b.[54] Some indirect methods are applied to increase the changes of carbon in contact with the solid electrode. Two physical approaches are applied, including a fluidised bed (Figure 5c)[55-58] and some in situ/external gasification (Figure 5d)[59, 60]. Solid carbon is used directly as the anode (shown in Figure 5e). Some other methods such as assistance by the redox mediator, are also investigated. The concept of mixing solid carbon and oxygen ion conductive oxides, shown in Figure 5f, is to extend the contact zone between the solid carbon and the oxygen ions, which could be additionally supplied from dispersed nanoparticles of the oxide electrolytes.

Because of the sluggish kinetics of the electrochemical oxidation of carbon, efforts have been made to improve the catalyst reaction rate by elevating the operational temperature or adding a redox mediator. The redox mediator is generally mixed with carbon feedstock, and sometimes is incorporated into the anode. A good mediator in DCFCs is an effective gasification catalyst as there is little reaction between solid and solid, making gasification one of the possible reactions in the anode chamber. It promotes the formation of CO when employed in the inert anode atmosphere in DCFCs. It delivers suitable ions to the carbon at the three phase boundary, where electrochemical reaction takes place. Some media have been investigated in various DCFC configurations. Molten carbonate, molten metal or composite components are being used in DCFCs.

4.1 Molten carbonate

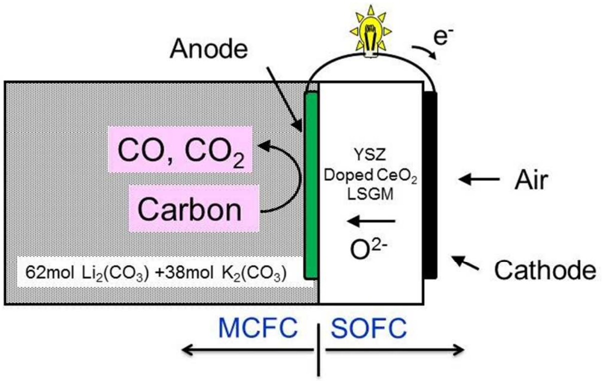


Figure 6 Demonstration of a hybrid direct carbon fuel cell with carbonate as a redox mediator. Reproduced from reference [61] with permission from [the Royal Society of Chemistry], copyright [2012].

4.1.1 Hybrid carbonate/ solid oxide

Hybrid carbonate and oxide has been developed with a configuration as shown in Figure 6.[61] This system is a combination of a molten carbonate fuel cell and a solid oxide fuel cell, and both reactions at the anode of a carbonate-DCFC and a solid oxide-DCFC take place, as shown in Figure 2b and Figure 2c.

At the cathode, oxygen is reduced to oxygen ions(equation (10). Oxygen ions are transported across the solid oxide electrolyte membrane to the anode compartment, where the carbon is oxidised to CO_2.[62, 63] At the anode, direct carbon oxidation is possible with either complete oxidation of the carbon to carbon dioxide, as shown in equation (11), or a partial oxidation of the carbon to carbon monoxide, as shown in equation (12).

$$C + O^{2-} \rightarrow CO + 2e^- \qquad (12)$$

Molten carbonate plays an important role in carbon oxidation.[64, 65] Although carbonate eutectic melts about 500 °C, the performance of HDCFC does not increase greatly until a temperature nearer 700 °C is reached, when, it is believed, the viscosity decreases and the wetting ability increases significantly.[61] Enhancement of the anode reaction with molten carbonate as an electrochemical mediator is also expected to occur, as recorded in equation (6), (7) and (8).[5, 14]

CO is oxidised into carbon dioxide by an oxygen ion or CO_3^{2-}. The chemical energy of the CO can still be converted to electric power via the electrochemical oxidation of CO at the anode of the DCFC.[66-68]

$$CO+O^{2-}\rightarrow CO_2+2e^- \qquad (13)$$

$$CO+ CO_3^{2--}\rightarrow 2CO_2+2e^- \qquad (14)$$

The reaction mechanism with carbonate medium is illustrated in Figure 7. Three different cells, both with and without physical contact with the anode, are prepared using a carbon fuel, both with and without molten carbonate; and the configuration is shown in Figure 7a. In cell I, as there is no molten carbonate and the carbon is physically in contact with

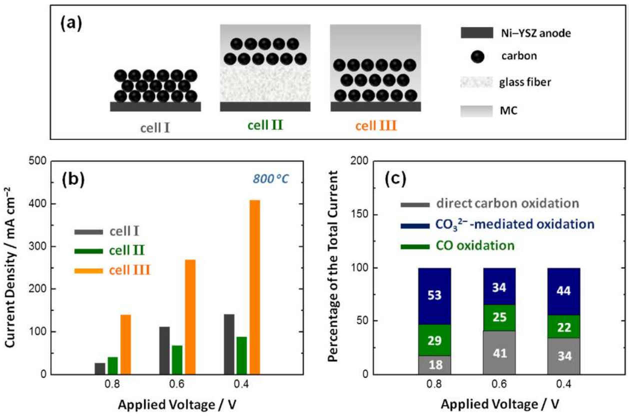


Figure 7 (a) Schematics of the fuel chamber configurations used, Cell I with only carbon as a fuel and carbon in contact with the anode; Cell II with a mixture of carbon and molten carbonate physically separated from the anode by a porous layer of glass fiber; Cell III with a mixture of carbon and molten carbonate contact with the anode (b) steady-state current densities of the cell measured at 800 °C with the application of various cell voltages, and (c) relative contributions of various oxidation modes to the total current density. The ratio of each reaction mode is calculated as i_I/i_{III}, i_{II}/i_{III}, $(i_{III} - i_I - i_{II})/i_{III}$ for the direct carbon oxidation mode, CO oxidation mode, and carbonate-mediated oxidation mode, respectively. Reproduced from reference [69] with permission from [Elsevier], copyright [2014].

the anode, the overall reaction is via the direct carbon oxidation mode. In cell II, carbon is mixed with the carbonate, but they are not physically in contact with the anode. The CO oxidation mode should make a major contribution to the overall reaction as seen in equation (13) and (14). In cell III, the reactions involve direct carbon oxidation, CO oxidation, and molten carbonate-mediated oxidation.

Due to the current of Cells I and II being mainly generated by direct carbon oxidation and CO oxidation, the current densities of these cells are lower than that of Cell III at a given voltage as shown in Figure 7b.[69] Direct carbon oxidation and CO oxidation has less effect than CO_3^{2-} mediated oxidation, as shown in Figure 7c. All these reactions should be followed by a regeneration of CO_3^{2-} ions so that the electric charge of the molten carbonate can be kept neutral.

$$CO_2 + O^{2-} \rightarrow CO_3^{2-} \tag{15}$$

The carbon can be converted via a non-electrochemical reaction known as the reverse "Boudouard reaction", which increases at higher temperatures[27]:

$$C + CO_2 \rightarrow 2CO \tag{16}$$

As we mentioned above, carbon has a composition of $CH_x(x<1)$. The species in the carbon fuels participate in the reactions in the process of cell operation. Hydrogen and CO released from the pyrolysis of carbon/coal can be oxidised.

$$H_2 + O^{2-} \rightarrow H_2O+2e^- \tag{17}$$

The electrochemical oxidation of H_2 can also be promoted by the carbonate.[70]

$$H_2 + CO_3^{2-} \rightarrow H_2O+CO_2+2e^- \tag{18}$$

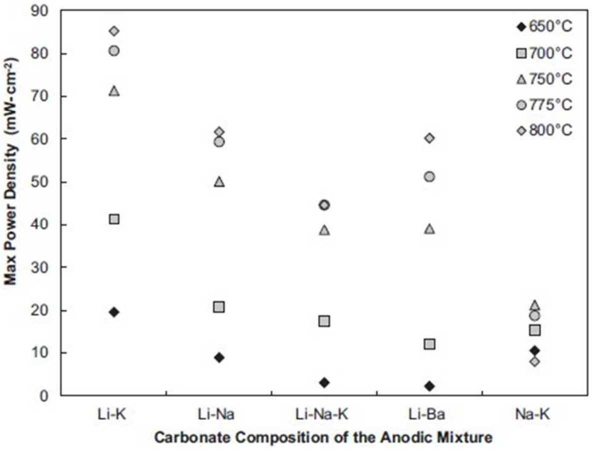


Figure 8 Maximum power density of the cells using the different carbonate compositions (Li-K, L-Na, Li-Na-K, Li-Ba, Na-K). These cells were tested using dense/porous GDC layers as the anode structure and a carbonate composition of 6 vol% in the anode mixture. Reproduced from reference [71] with permission from [Elsevier], copyright [2013].

There are some advantages that DCFCs can rely on carbonate, when a molten carbonate is added into the carbon, most importantly, a low melting temperature between 400 °C and 720 °C. The melting temperature for four eutectic carbonates of Li, Na, K and Ba is 498, 398, 609, and 709 °C.[71] In the presence of the carbonate with the required melting temperature, the viscosity of the solution can be reduced, leading to the enhancement of solid diffusion throughout the medium. Even though the liquid phase is not huge, the presence of this discontinuous liquid phase is beneficial to the improvement of the diffusion. Li-K exhibits the best catalytic activity for solid oxidation among all the eutectic carbonates (Figure 8). Na is not deemed to have a positive enough effect for carbon oxidation, and therefore the cell performance of DCFCs with Li-Na or Li-Na-K is not as good as that of one with Li-K. Li-Ba is similar to Li-Na. The weakest catalytic effect is found with Na-K carbonate, which might be due to its higher melting temperature. The enhanced power density is attributed to the acceleration of carbon gasification by the catalytic effect of potassium salt, which results in a significant reduction in the operational temperature of the gasification. The conversion rate at 725 °C with a K_2CO_3 catalyst is much higher than that at 900 °C without a catalyst.[72] Ternary carbonate (Li_2CO_3-Na_2CO_3-K_2CO_3) eutectics have a lower melting temperature than binary carbonate (Li_2CO_3/K_2CO_3 or Li_2CO_3/Na_2CO_3), and the melting temperature can be further decreased by adding the right amount of other carbonates or some oxides.[16]

An optimal carbonate concentration should be used in DCFCs system to achieve the best cell performance. 20-30 wt% of carbonate seemed to be a suitable amount. Adding 25 wt% carbonate into the carbon, markedly improved performance, thus verifying the need for a carbonate.[73] Since a high concentration of carbonate cause extra diffusion difficulty from the solid carbon fuel to the electrode, the electrochemical oxidation of the carbon must be limited. This is confirmed by a significant increase in the polarisation resistance of the DCFCs when the carbonate content in the mixture of carbon and carbonate is increased from 50 mol% to 80 mol%.[73] Except for binary carbonate, ternary carbonate has been investigated in hybrid carbonate and oxide based DCFC system. It displays low operational temperature compared to binary carbonate hybrid DCFCs.[74]

It is also found that mixing carbonate with carbon extended the active reaction zone from a two-dimensional Ni-YSZ anode to a three-dimensional zone, brought about by the mixed electronic and ionic conductivity in the carbon/carbonate slurry.[75] The mixing method has an influence on the catalytic behaviour of the carbonate. Jain *et al*. [76] investigated different methods of introducing a carbonate into pyrolysed medium density fiberboard (PMDF), using stick shaped originals: (I) sticks of PMDF were immersed in a molten carbonate mixture; (II) sticks of PMDF were immersed in molten carbonate and then put under pressure to degas pores; (III) carbonate powder was mixed with milled PMDF powder. The experimental results showed that powdered PMDF mixed with carbonate gave the lowest cell resistance at testing temperatures of 650 °C to 800 °C, which is due to well-mixed PMDF with carbonate.

Excellent cell performance is obtained in this designed system.[69, 77] An representative example is the remarkable power density of 878 mW cm^{-2} obtained at 750 °C on a DCFC with a composite NiO-YSZ anode and a mixture of Li_2CO_3 and K_2CO_3 using pyrolysed medium density fibreboard (PMDF) as the fuel. This is the highest power output as yet reported in DCFC systems.[61]

4.1.2 Hybrid carbonate/solid oxide with additives

A significant improvement with additives into the solid carbon has been discussed in Section 3.3-3.5. Some researchers have investigated a cell with a combination of carbonate and additives. Ag_2O was added into a mixture of carbonate and carbon. The satisfactory electrochemical performance of the DCFC was attributed to the enhanced activity and stability of nickel in the presence of Ag_2O.[78] By adding a variety of catalysts to the carbon fuel, Deleebeeck found a direct correlation between the enhancement of the power density and the high OCV values when the cells were operating at 755 °C in a mixture of nitrogen and carbon dioxide.[79] Some metal oxides have multiple oxidation states and can both store and release oxygen. It is believed that the formation of metal oxides at a lower potential can transform CO, or other carbonaceous species on the surface of metal to CO_2, thereby releasing active sites on an electrode for further reaction. Manganese oxide, Mn_3O_4, Mn_2O_3, MnO_2, MnO, showed different catalytic activity in the process of carbon oxidation. The cell with a Mn_2O_3 additive produced the best maximum power density, which might be due to the different oxidation state of manganese.[79]

4.2 Molten metal

Molten metals were first used to promote carbon gasification, rather than carbon direct oxidation. The first theoretical investigation using molten metal electrodes for coal gasification was done by Yentekakis *et al*.[80] The molten metal has to be a good electronic conductor, stable in oxygen environments; if oxidised, the resulting metal oxide must be a good ion conductor for oxide ion transportation from the electrolyte to the molten anode layer (Figure 5f). Another important parameter is the melting point. It is desired to use metals with low melting points. Molten In, Pb, Sb, Bi and Sn are common anodes for DCFCs. Bismuth exhibits low melting point and its oxides (Bi_2O_3) have good ionic conductivity (3 S/cm at 825 °C).[81] It allows the Bi_2O_3 to transfer from the electrolyte to the bismuth metal, even if a bismuth oxide is formed during the electrochemical reaction process. The oxygen diffusion coefficient is also important when a molten metal is chosen for DCFCs. Metals such as bismuth, silver and lead which have good oxygen diffusion coefficients: 5.3×10^{-5} cm^2/s, 1.5×10^{-5} cm^2/s and 1.29×10^{-5} cm^2/s, respectively.[82, 83]

It is reported that the open-circuit voltages (OCVs) of cells are close to the expected potential, based on the equilibrium between metals and their oxides, as shown in Equations (19) and (20).[84]

$$M+nO^{2-}\rightarrow MO_n+2ne^- \quad (19)$$

$$(n/2)C(M)+ MO_n \rightarrow(n/2)CO_2+M \quad (20)$$

For example, the electromotive force of a molten tin anode is generated as a result of its oxidation to tin oxide. The tin oxide can be reduced back to metal with carbonaceous fuel. This system produces a low open circuit voltage (0.7 V at 600 °C). Recently, a molten Sb anode was tested as the anode for the direct utilisation of carbon fuels at 700 °C. [85] The open circuit voltage of the cell is 0.75 V, which is the value of the equilibrium between Sb and Sb_2O_3 (equation (19)). The

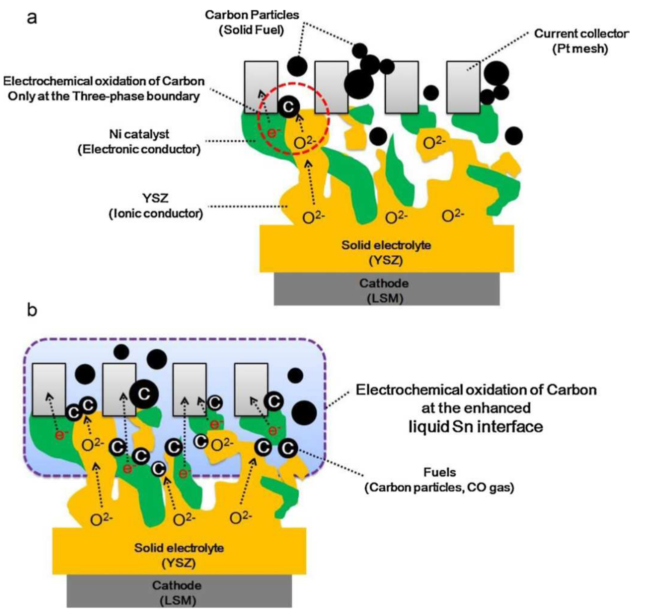


Figure 9 Schematic representation showing Ni-YSZ anode in DCFCs. Electrochemical oxidation of solid fuels can occur at the TPB with oxygen ions emerging from the solid electrolyte and to produce CO_2 and CO. (a) typical Ni-YSZ anode; (b) enhanced liquid Sn anode interface. Reproduced from reference [87] with permission from [Elsevier], copyright [2012].

electrochemical potential of the metal oxidation and the ability of the metal to be oxidised into metal oxides have major impacts on cell performance through their contribution to polarisation resistance.[84] The robustness of the molten tin oxide was proven by the use of a high sulphur concentration fuel (1350 ppm sulphur). No significant cell performance degradation was observed after 200 hours operation of testing; the sulphur was oxidised into SO_2 and escaped as a waste gas.[86]

Ju *et al*. developed a Ni-YSZ anode supported cell with a YSZ electrolyte and a LSM cathode. The loading of Sn into the carbon fuel plays a critical role both in building a favourable bridge between the solid fuel and the solid anode and in facilitating the electrochemical oxidation of carbon to CO, a maximum power density of 105 mW cm^{-2} at 900 °C was achieved.[87] In the DCFC based on a YSZ electrolyte (Figure 9), it is generally accepted that solid carbon fuels at the TPB react electrochemically with the oxygen ions emerging from the solid electrolyte (YSZ) and produce CO_2 and CO via simultaneously both 4- and 2- electron transfer reactions, as shown in equation (11) and (12). When CO is produced by reaction (12), it can be further electrochemically oxidised to CO_2, as a gaseous fuel in the DCFC, as seen in equation (13) and (14).

A maximum power density of 350 mW cm^{-2} at 700 °C was obtained on the DCFC with a molten metal Sb anode/ScSZ(100 µm)/LSF-ScSZ, as shown in Figure 10a.[85] In their study, a Sc-stabilised zirconia electrolyte-supported cell was used, which was considered to be the major factor contributing to the ohmic loss of 0.25 Ω cm^2 (Figure 10b). The function of carbon was confirmed by the study in Figure 10c with possible reaction as shown in equation (19). The cell with sugar char remained stable at 0.6 A cm^{-2} for 12 hours and the performance dropped down after that until all of the fuel had been consumed (Figure 10c). However, the cell without carbon fuel only lasted for 1 hour and the cell performance deteriorated after that. This was due to the accumulation of the insulating Sb_2O_3 in the anode.

4.3 Composite

A composite component with solid oxide and carbonate is used in DCFC systems. The solid oxide is generally a mixed ionic and electronic oxide of doped ceria. A composite electrolyte with solid oxide and carbonate has the advantages of both. Among the composite electrolyte of doped ceria and carbonate, SDC or GDC mixed with carbonate exhibits good conductivity.[88] The conductivity of SDC-$(Li/K)_2CO_3$ is dependent on the carbonate content; a significant increase in the conductivity of SDC-$(Li/K)_2CO_3$ was observed with about 30 vol% of carbonate.[89]

The overall conductivity of a composite electrolyte composed of an O^{2-} conductive porous phase and a CO_3^{2-} conductive molten carbonate phase is much higher than either when operating individually. In the anode chamber, the carbon contacting the solid oxide electrolyte reacts with oxygen ions to produce CO_2 and releases electrons; the reaction is shown in equation (11).

Meanwhile, the carbon particles dispersing in the molten carbonate phase directly react with the CO_3^{2-} ion, producing

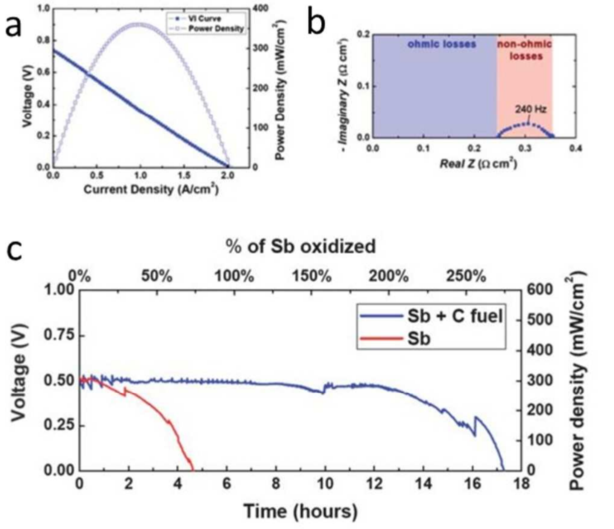


Figure 10 Voltage vs current density (V-I) polarisation and power density curves for the fuel cell with a 100 µm thick Sc-Stabilised zirconia electrolyte, a Sb anode and a $La_{0.8}Sr_{0.2}FeO_3$-ScSZ cathode, tested at 700 °C. The power density is calculated from the V-I curve. (b) Nyquist Plot of the impedance spectrum for the fuel cell at 700 °C. (c) long term performance plots for the cases of Sb anode with without sugar char Fuel at a constant current of 0.6 A cm^{-2}. Reproduced from reference [85] with permission from [the Royal Society of Chemistry], copyright [2011].

CO_2 and electrons simultaneously; this is the same as in carbonate-based DCFCs; the reaction is shown in equation (6). Some other reactions, like equation (7) and equation (8), are possible as well.

In the cathode chamber, the oxygen atoms can be directly reduced into oxygen ions, and also react with CO_2 to generate carbonate ions, as shown in equation (9). [64] This reaction at the interface close to the cathode is said to be presumably responsible for the enhancement of the oxygen conduction and CO_3^{2-} conduction in the composite electrolyte, as CO_2/O_2 is supplied in the cathode.[90]

One typical example of this system is that of Jia *et al.* who employed a composite electrolyte containing a Li/Na carbonate eutectic and a doped ceria oxide. The cell made with a silver powder/Lithiated NiO-electrolyte/electrolyte/silver powder generated a power output of 100 mW cm^{-2} at 700 °C.[91]

5. Fuel

Different types of carbon have been successfully used in DCFCs, such as graphite, carbon black, PMDF, biomass, coal, and coke.[9, 14, 17, 25, 50, 55, 75, 92-97] Graphite is desirable in molten carbonate-DCFCs due to its high conductivity, but is not suitable for solid oxide-DCFCs as it is relatively unreactive.[5] Knowledge of the chemical and physical properties of carbon, such as surface area, particle size, the concentration of the surface functional groups, crystal structure and impurities, are essential for understanding important factors that determines the electrochemical performance. Sometimes the cell performance is dependent on several properties of carbon and sometimes only one parameter dominates the electrochemistry.[14] For example, Cooper found that less crystalline carbons, such as chars, were reactive in carbonate-DCFCs due to a high concentration of edge atoms, but their electrical conductivity was low.[14] On the other hand, graphite is a useful fuel if the carbon is also used for current collection. It was observed that volatile matter, porosity and structure disorder correlate perfectly with the achieved power output. In contrast, high ash content and sulphur content notably inhibit the electrochemical performance. The latest research showed that the DCFCs with different coal samples as the fuel exhibited significant different electrochemical performance. Among the properties, crystal structure, volatile matter, carbon content and sulfur content have an influence on the power output and durability.[77, 98] In sections 5.1-5.4, the influences of crystal structure, surface properties, impurities and particle size on the DCFC performance are discussed.

5.1. Crystal structure

Carbon exists in many structural forms, including diamond, graphite, carbon black, coke, activated carbon, fibers, and nanotubes. In DCFCs, graphite and carbon black are often used as model fuels, but other carbons such as biomass derived chars, coal and coke are also being investigated. Researchers have found that the crystal structure of the carbon might be important in some DCFC systems. Nurnberger[54] and Kulkarni[29] reported that amorphous carbon black was more reactive than graphitic carbon in DCFCs using a solid oxide electrolyte, due to many types of reaction sites (edge, step, or other surface imperfection). A better cell performance was obtained with Vulcan XC72R than with graphite.[54] A similar phenomenon was found in Dudek's research by using a Ni-YSZ electrode and carbon black with disordered structures, a better electrochemical performance was obtained at 700-800 °C with carbon black than with graphite because of the disordered structure of the carbon black.[99] The higher activity of amorphous carbon has also been reported in molten carbonate-DCFCs.[14] Cherepy reported that in molten carbonate-DCFCs, the properties of carbon fuels, crystal structure and electrical conductivity, control their rate of discharge in the molten electrolyte.[14] A low crystallisation index is more reactive both chemically and electrochemically.[77] High electrical conductivity is desirable as the conductive particulate carbons themselves are the current collectors and provide adequate reactive surface sites for mass transportation, which has been proved in carbonate-DCFCs.[14]

5.2. Surface properties

Carbon oxidation is promoted when the carbon is washed by acid, leading to a change in the surface properties of the carbon. Up till now, HF, HCl, HNO_3 and NaOH have served as the catalyst additives in carbon fuel. The surface modification of carbon was found to have a positive effect on the electrochemical oxidation in the order of HNO_3>air plasma≈HCl in a carbonate-DCFC.[93]

Acid or base treatment of the carbon increases the amount of chemically-bonded oxygen on its surface, which enhances the carbonate-DCFC performance.[92, 100] The content of hydroxyl groups is increased by NaOH pre-treatment due to the changes from carbonyl or carboxyl groups to phenol or lactone groups.[101]

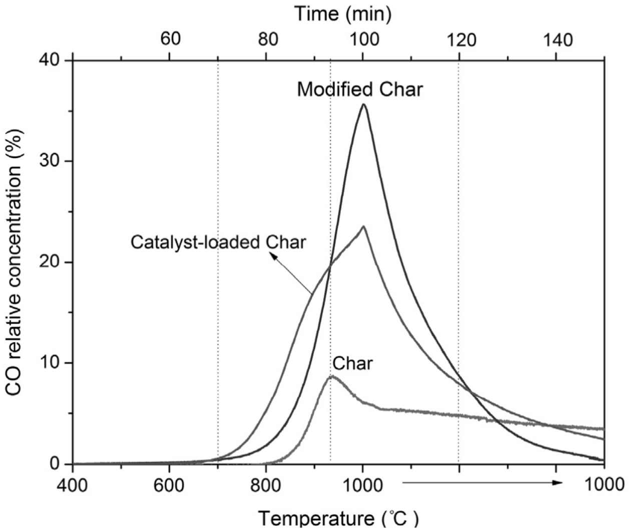


Figure 11 CO_2-temperature-programmed oxidation profiles of char, modified char and catalyst-loaded char. Reproduced from reference [102] with permission from [Elsevier], copyright [2015].

Cao *et al.*[100] pre-treated activated carbon with NaOH, HNO_3 or HF and found that the open circuit voltage of a carbonate-DCFC increased after acid and base treatments, indicating that the initial formation of the solid carbon/liquid molten carbonate reaction interface might be affected by changes in the surface chemistry. The different adsorption and desorption of these surface species might result in the different open circuit voltages. NaOH increased the number of hydroxyl groups. Oxidising acids such as HNO_3, increased the number of surface carbonyl, carboxyl and nitrate groups, while the non-oxidising acid, HF, produced phenols, ethers and lactones. They found that surface area and micropore volume increased after acid and base treatments, and this might be responsible for the enhancement of the electrochemical oxidation performance.[100] It was also observed that modified char using KOH and HCl along with heat treatment could change the volumes of carbon microcrystals, micropore surface areas and oxygen-containing functional groups. A modified char fuelled cell with a NiO-YSZ anode generated 220 mW cm^{-2} at 850 °C, compared with the otherwise expected 62 mW cm^{-2} at the same temperature. The structural changes and physicochemical properties were considered responsible for the improvement in the Boudouard reactivity of the modified char and these both led to an enhanced electrochemical performance (Figure 11).[102]

5.3. Impurities

Electrochemical coal oxidation has attracted significant attention to replacing the traditional coal-fired power plant. If this technology is to develop on a large scale, a low-ash coal or cleaned coal will be necessary to guarantee a reasonable cell lifetime.

The electrochemical reaction was enhanced by adding CaO, MgO and Fe_2O_3, whereas Al_2O_3 and SiO_2 reduced performance.[50] The addition of coal ash into the DCFC also verified this. The cell performance with the addition of ash from Blackwater coal is better than two other two ash additions from Germancreek and Newland, the fact that main inorganic contents in Blackwater coal are Fe_2O_3, Na_2O, K_2O, MgO and CaO, which could be catalysts for DCFC reactions, could account for these results. Some details have been shown in Section 3.3 and 3.5.

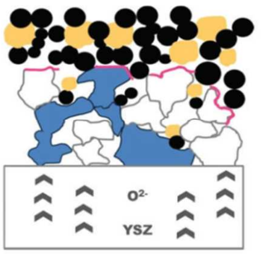
In addition to the ash impurities in coal, non-carbon species, such as sulphur, hydrogen, nitrogen and oxygen elements, or tars can also be present.[103] These species might improve, or degrade, the cell performance and activation. Sulphur is undesirable in DCFCs. DCFCs using cokes containing 2.5-6 wt% sulphur displayed a deterioration in performance over time, and the overall cell resistance increased from 6.1 to 9.3 Ω cm^2 over a two-day testing.[14] Sulphur in coal would limit the cell power output when nickel is used as the catalyst because nickel is sensitive to the presence of sulphur.[104, 105] Other chemical elements present in coal, such as hydrogen or oxygen, may also be involved in the electrochemical process. Hydrogen and methane could form during the high-temperature pyrolysis in impure carbon. These gases can be oxidised, generating electricity. A limited amount of oxygen might be beneficial to the high-temperature oxidation, but too much oxygen can cause carbon loss, lowering the fuel utilisation.

Raw coal generates roughly double the power output of ash-free coal.[106] The volatile organic compounds in raw coal seem to be accelerators for the electrochemical performance. This has been attributed to the additional release of gaseous fuel from the raw coal in the form of pyrolysis gases.

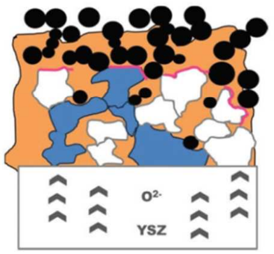
The removal of impurities by nitric acid wash was applied to remove impurities in coal samples. The ash content decreased from 3 wt% to 0.4 wt % by the purification process using nitric acid. A better performance was achieved on the coal samples after purification with nitric acid than on the raw coal samples.[107]

Thermal treatment process can significantly change the properties of coal, which definitely have an effect on the cell performance when coal is used as the fuel for DCFCs. Coal is classified as lignite, bituminous and anthracite by the rank. The carbon content and conductivity and crystal structure are different for lignite, bituminous and anthracite. Recent research on the coal-fuelled hybrid-DCFCs indicated the electrochemical reaction zone varied with the temperature highly depending on the type of coal for the fuel. Bituminous undergoes a plastic stage in the anode chamber when the cell is heated, while anthracite has not been the same (Figure 12).[70] The fluidity of the bituminous coal is a beneficial property for DCFCs operating in a batch mode as it creates more chance for the contact of coal with electrode. Extra caution should be given when using bituminous coal as a fuel in hybrid-DCFC. From another point of view, volatile matter decreases during the process of thermal treatment, which is deemed a beneficial for the increase of electrochemical performance.[108]

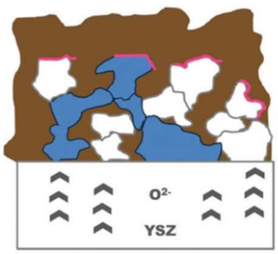
(a) HDCFC at room temperature



(b) HDCFC at working temperature (750 °C) with raw anthracite (or lignite) and carbonised coals



(c) HDCFC at intermediate temperatures with the raw bituminous coal. Melting point of CO_3^{2-} and plastic stage bituminous coal



(d) HDCFC at working temperature (750 °C) once the raw bituminous coal is re-solidified

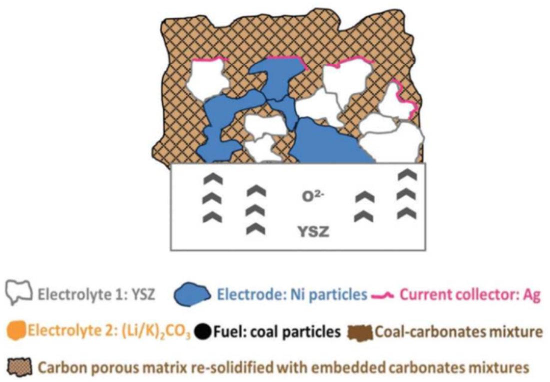


Figure 12 Schematic illustration of anode chamber depicting the possible active reaction zone of the Hybrid-DCFC(HDCFC) operated with coals in function of the temperature and type of coal: (a) initial situation in HDCFC at room temperature for all type of coals, (b) situation of HDCFC with raw anthracite (or lignite) and carbonised coal samples at working temperature (750 °C), (c) situation at intermediate temperature when the bituminous coal and the carbonates mixture reach the fluid point and (d) situation at 750 °C with the raw bituminous coal. The oxidised bituminous coal could be in an intermediate situation between raw and carbonised bituminous coals depending on how much its plasticity is reduced during the oxidation pre-treatment. Reproduced from reference [70] with permission from [the Royal Society of Chemistry], copyright [2016].

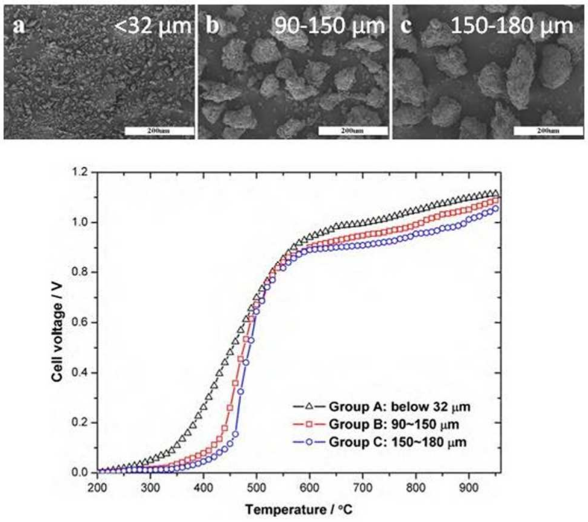


Figure 13 Influence of graphite particle size on the open circuit voltage of tubular DCFC with a YSZ electrolyte tube and Pt as both the anode and the cathode. Reproduced from reference [96] with permission from [Elsevier], copyright [2010].

5.4. Particle size

In Vutetakis's initial experiment, the dependence of the current density on the particle size was found to be based on the molten carbonate-DCFC system. Three types of carbon samples with 200-325 mesh, 50-100 mesh and 20-40 mesh were tested in 100% CO2 at 700 °C.[17] The current density of the cell increased as the particle size of carbon decreased when loading 1-5% carbon in carbonate. Kim et al. also found a similar trend in the SOFC mode for direct carbon oxidation.[96] Figure 13 displays the influence of the graphite particle size on the open circuit voltage of tubular cells. It was observed that the DCFC with a finer particle size (32 µm) of coal shows the highest open circuit voltage (OCV) in the temperature range of 200 °C to 1000 °C. The higher OCV could be explained by the increased number of available active sites implying a higher chemical activity of the fuel**.**

5.5 Other properties

To further develop the DCFC concept, researchers have been trying to lower the cost, while raising the performance and endurance using other carbon forms, such as nanofibres, nanotubes, and graphene.[109,110] The electrochemical performance of the DCFC relates to the carbon properties, and these depend on the operational system. In some systems, the surface area dominates the cell performance, whereas in other systems conductivity plays an important role. For example, in molten carbonate-DCFC, the wetting behaviour of the carbon may be critical to achieving enough reaction sites. One advantage for direct carbon fuel cells is that carbon can be used as both fuel and the anode. The anode shapes in common use are rods (cylindrical), plates or particulates. The preferred carbon is a high-density solid which can provide appropriate reactivity, and function as both the anode and the current collector. If the carbon anode is in the form of a particulate or powder, a current collector is necessary, which could be meshes, grids, felts, leads or another similar electronically conductive matrix that allows effective contact with the carbon fuel and transport electrons. The common carbon fuels so far reported on are rods.[10] In Cooper's research, nickel felt, gold or platinum mesh or a metalloid foam or sponge are used as an anode current collector.[14] A great benefit of using carbon rods is that it is not required extra current collector as carbon rod is the current collector. For carbon particulates, however, an additional current collector is needed. It has, for example, been reported that a current collector of copper in the form of a cage or basket, not only eliminates the effect of carbon fuel consumption but also increases the current density.

6. Cathode

The common cathode materials for DCFCs are the same as the Solid Oxide Fuel Cells. Silver[111] and platinum[112] were used in DCFCs. Lanthanum doped strontium manganite (LSM) was often selected as the cathode as it has good compatibility with YSZ electrolyte and good catalytic activity at intermediate and high temperatures. In order to operate DCFCs at relatively low temperatures, some perovskite materials, such as $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-d}$ and lanthanum doped strontium cobalt, showed better performance than LSM cathode.[113] It was found that cobalt (LSC, $La_{0.6}Sr_{0.4}CoO_{3-\delta}$) is a good choice for replacement purposes. The total resistance of a cell was reduced to ca. 0.44 Ω cm^2 and the maximum power density increased from 390 mW cm^{-2} to 680 mW cm^{-2} by replacing a LSM cathode with a LSC cathode.[61] By increasing the air flow within the cathode to provide sufficient gas for exchanging and diffusion, the cell performance can be further enhanced. The highest reported cell performance is currently 878 mW cm^{-2}, when the cell is operating at 750 °C with PMDF as a fuel and is supplied with 200 ml/min air at the cathode and nitrogen gas at the anode. [61]

7. Configurations

A DCFC can be assembled with different configurations, which include the different geometries of planar and tubular solid-oxide cells and also the different combination of materials in the same system. Different configurations with a planar or a tubular solid-oxide cell are shown in Figure 14. Planar cells (Figure 14a) are easy to manufacture and therefore are used in DCFCs. Tubular cells have some advantages, for examples, easy for scale-up and thermal cycling and cell sealing.[114] There are two types of tubular DCFC systems, one with the anode tube insert into a container with carbon fuel (Figure 14b), the other with the anode as the inner tube with carbon fuel (Figure 14c). Figure 14d displays a tubular cell with a configuration shown in Figure 14c. Oxygen ions from the cathode transport from the electrolyte to the anode and reacts with carbon and carbon in the anode chamber reacts with carbonate to produce carbon monoxide and carbon dioxide. Tubular cells are used in

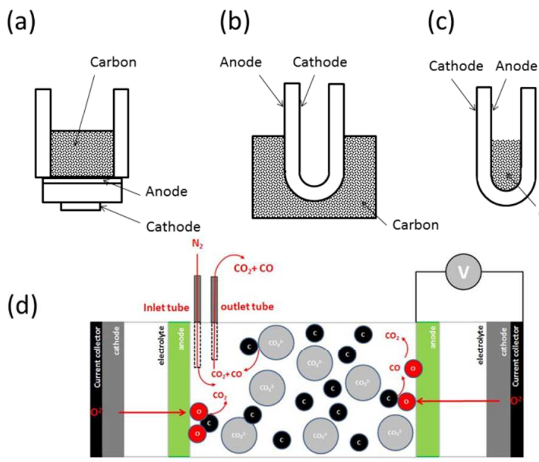


Figure 14 Schematic diagrams of different configurations of a DCFC system. (a) Planar solid-oxide cell with an alumina tube as the anode wall; (b) tubular solid-oxide cell with alumina container as the anode chamber; (c) tubular solid-oxide cell is assembled as the anode chamber with anode tube. (d) an example of a tubular DCFC with a configuration as shown in Figure 14 (c). Reproduced from reference [115] with permission from [Elsevier], copyright [2012].

DCFCs when carbonate is used to mix with carbon.[115] Some issues associated with the tubular cell is also reported (e. g. sealing).[116] This led to a low open circuit voltage (e.g. 1.00 V). Relatively low power density was obtained, such as 16.8 mW cm^{-2} because of high ohmic resistance from 1.5 mm thick YSZ electrolyte even though the cell was testing at a high temperature of 950 °C.[96]

8. Cell performance

8.1. Open circuit voltage

In DCFCs, the total reaction is carbon oxidation to produce carbon dioxide, as shown in equation (1). The overpotential of the cell is defined as follows:

$$E=-\Delta G/nF \tag{21}$$

where ΔG is Gibbs free energy of the reaction, n is the number of electrons involved in the reaction, and F is Faraday's constant. E is the equilibrium cell potential, that is, the open circuit voltage (OCV) of the cell. Theoretically, the OCV of the DCFC is a constant value, 1.02 V, as Gibbs free energy of equation (1) has little change with temperature. However, in practice, the OCVs of DCFCs are not always the same.[16] Although full oxidation of carbon in equation (1) is the desired reaction, practical reactions are more complex regardless of the system design. Except for full carbon oxidation, carbon is likely to be partially oxidised into carbon monoxide (equation (12)). At the start of this article, we mention that carbon is here referred to $CH_x(x<1)$ since hydrogen is present in all sorts of carbon sources. Therefore, the electrochemical oxidation of hydrogen is one of the possible reactions in most cases. As is well known, the overpotential of hydrogen oxidation (equation (22)) decreases with temperature.

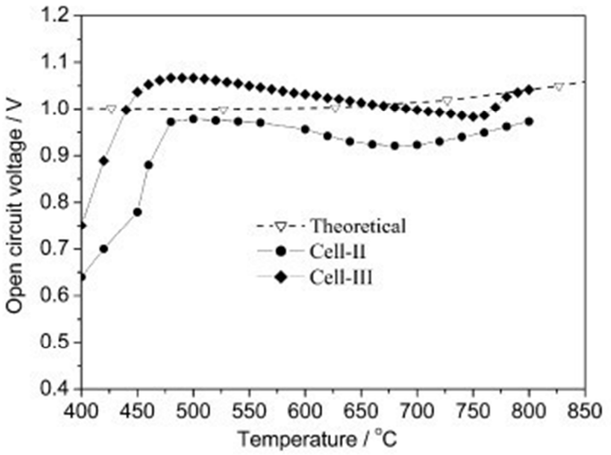


Figure 15 Open circuit voltage of the DCFCs with different configurations. Cell II has a configuration of activated carbon/Ag-GDC anode/GDC electrolyte/Ag cathode; Cell III has a configuration of Fe-loaded activated carbon/Ag-GDC anode/GDC electrolyte/Ag Cathode. Theoretical OCV values are plotted for comparison. Reproduced from reference [51] with permission from [Elsevier], copyright [2010].

$$H_2+O^{2-}\rightarrow H_2O \tag{22}$$

In practice, the OCVs of the DCFCs also change with temperature, so the functionality of hydrogen must not be ignored. With respect to the different system arrangements, the OCVs of the DCFCs are related to electrochemical reactions in the presence of other components (e.g. CO_3^{2-} or molten metal). For examples, the OCVs of the DCFCs are close to the equilibrium potential of the reaction in equations (19). Figure 15 demonstrates the OCVs of the DCFCs with activated carbon loaded with or without Fe. The cell with Fe-loaded carbon (Cell-III) presents higher OCV values that the cell without Fe (Cell-II).[51]

In DCFCs, it is possible to have some leaks and this often causes OCV lower than theoretical values. Some other systems are due to materials used. For example, there is the electronic leak when doped ceria is used as the electrolyte.[115] It is also found that the purge gas argon or nitrogen enhances open circuit voltage by 0.1-0.3V due to the reduced partial pressure of CO_2.[73] A very high open circuit voltage was obtained in Nabae's research. The experimental result was 1.5 V at 700 °C with Ni-XC-72R as the fuel in a Ni-YSZ/carbonate hybrid DCFC system.[94] This was significantly higher than the theoretical potential of carbon oxidation. It was interpreted by the thermodynamic calculations. The non-electrochemical endothermic reactions increased the Nernst potential of the electrochemical reactions. The potential of hydrogen oxidation at 700 °C is 1.01 V (Figure 16a), while that of carbon oxidation at 700 °C is 1.03 V (Figure 16b). Due to the presence of CO_3^{2-} $/O^{2-}$, CO_3^{2-} decomposes to CO_2 and O^{2-}, while CO_2 is produced electrochemically and CO_3^{2-} forms again by combing CO_2 and O^{2-}. The reaction in equation (23) shows the potential is 1.22 V (Figure 16c).

$$C+O_2+Li_2O\rightarrow LiCO_3 \tag{23}$$

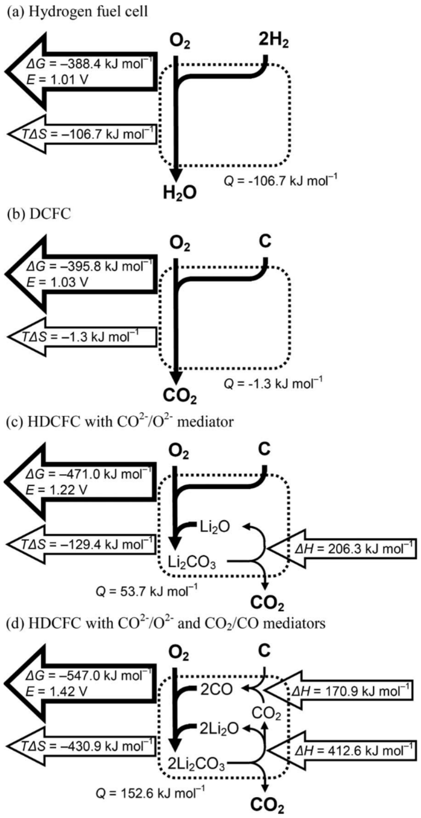


Figure 16 Schematic diagram of the thermodynamics for the fuel cells under various conditions. Bold arrows: electrochemical processes, normal arrows: nonelectrochemical processes. Reproduced from reference [94] with permission from [the Electrochemical Society], copyright [2009].

Another possible mediator is the CO_2/CO mediator. CO is produced by Boudouard reaction. Therefore equation (24) cannot be disregarded.

$$2CO+O^{2-}+2Li_2O\rightarrow 2\ LiCO_3 \qquad (24)$$

The potential of equation (24) is 1.42 V (Figure 16d), which is close to the experimental results.

As discussed in section 4.1, the reactions in the anode chamber are complicated. Different gas species, like H_2 and CO, contribute to the increase of the OCVs by electrochemical reactions.[70] So many reactions could take place in the anode chamber, and therefore we often find that the experimental OCV values are different with the theoretical value of carbon oxidation.

8.2. Power density

The electrochemical performance depends on many different parameters because of the complexities of a DCFC system: the fuel type with its physicochemical characteristics, the electrode components and structure, and the operating temperatures. Fuel pre-treatment methods, catalyst additives either to the fuel or the anode can have a significant effect on the final electrochemical performance. The anode gas also has to be considered, as the anode atmosphere plays a critical role in the carbon gasification rate.

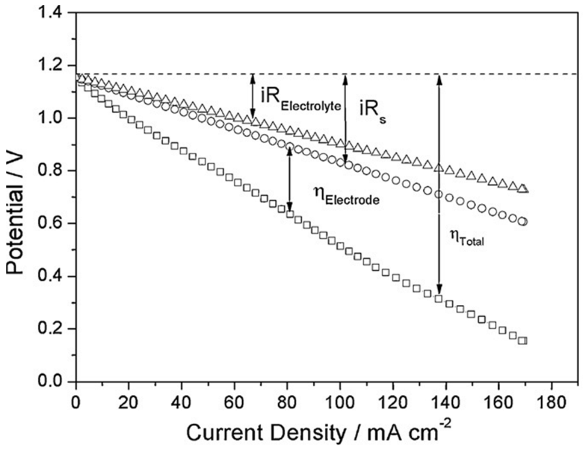


Figure 17 Potential of a HDCFC at 800 °C with a 1 mm thick YSZ electrolyte, a Ni-YSZ anode and a LSM-YSZ cathode using 20 mol% carbonate in the carbon fuel, $iR_{Electrolyte}$ in the graph shows the contribution from YSZ electrolyte. Reproduced from reference [73] with permission from [Elsevier], copyright [2011].

A few other parameters are often investigated: the anode catalyst, the fuel, the cathode materials and atmosphere. The anode catalyst has been discussed in Section 3 and a redox mediator is shown in Section 4. Table 1 lists the cell system and the maximum power density of the cell operating in various conditions. A thin electrolyte film, a high catalytic cathode and anode, and high operational temperatures are desirable.

In most cases, a big ohmic resistance of the cell from the electrolyte is a major loss to the whole cell and this limits the cell performance (Figure 17).[73] Decreasing the electrolyte thickness is essential. Jiang et al. demonstrated that the ohmic resistance of the cell (Rs, series resistance) responsible almost half of the total polarisation loss. It was also pointed out that 80% of the ohmic resistance came from the electrolyte if a thick YSZ electrolyte (e.g. 1 mm) was used in the system. From Table 1 it can be seen that the maximum power density is dependent on the thickness of the electrolyte, and a good cell performance can only be obtained with thin film electrolyte-based DCFCs. A remarkable improvement was found by changing the cell geometry from electrolyte-supported to anode-supported and with the ohmic resistances between 0.1-0.2 Ω cm^2, much smaller than the 2.89 Ω cm^2 recorded with a 1 mm thick YSZ electrolyte. The total cell resistances were reduced to below 1 Ω cm^2. The decrease in cell resistance on the anode-supported SOFC compared to the electrolyte-supported SOFC led to an improvement in the overall cell performance from 70 mW cm^{-2} to 390 mW cm^{-2}, when the HDCFC was operating at 750 °C with PMDF as the fuel.[61] A well designed hybrid carbonate-DCFC generate the maximum power density of 878 mW cm^{-2}, as shown in Figure 18. The enhanced performance was due to the higher amount of CO formation and its electrochemical oxidation at the TPB, The increased cell performance of the Ni-YSZ anode-supported SOFC with coke fuel and CO_2 as the carrier gas was attributed to the increased electrochemical oxidation of the CO. Recent research has shown that the maximum power density is related to the CO formation in open circuit conditions.[117]

Table 1 Summary of DCFC systems with a variety of components and cell performance

Electrolyte	Anode	Cathode	Fuel	Temperature	System	Maximum power density (mW cm^{-2})	Ref.
8YSZ, 9ScSZ or 20GDC(2mm)	Carbon black	Pt	Carbon black-Ag,Ni	600-880	Argon	Up to 10	[26]
YSZ 1.5 mm	Pt	Pt	Graphite	950	Argon Solid oxide-DCFC	16.8	[96]
YSZ(tube, 0.425 mm)	LSCF	LSCF	XC-72R	820	He MIEC anode	25	[43]
YSZ(disk) 0.2-0.3 mm	Ni-YSZ 50-100 µm	LSM 50-100 µm	Coal	900	Helium fluidised	43	[55]
YSZ 0.3 mm	Ag-GDC	Ag	Fe-loaded carbon	800	CO_2	45	[51]
YSZ 200 µm	Liquid tin 500 µm	LSM (Tube) 1 mm	JP-8 (petroleum-based diesels)	1000	Molten metal	117	[118]
3YSZ 100 µm	XC-72R	LSM-YSZ 45 µm	XC-72R	1000	Direct contact	40(0.4V)	[54]
3YSZ 100 µm	XC-72R	LSM-8YSZ 45 um	XC-72R	900	Direct contact	20	[119]
YSZ 30 µm	Ni-YSZ 850 µm	LSM 35 µm	6wt%Ni-(Sn-Carbon black)	900	N_2 Molten metal	60.5-105	[87]
YSZ 20 µm	Ni-YSZ 0.4mm	LSM-YSZ	Fe-activated carbon	850	No carrier gas	424 465 (3-cells stack)	[49]
YSZ(tube) 10 µm	Ni-YSZ 800 µm	(LaSr)MnO 100 µm	Biomass-derived activate carbon	905	Internal Gasification-DCFC	220	[62]
YSZ 5-10 µm	NiO-YSZ 1 mm	LSM-YSZ or LSC	PMDF	750	N_2 or CO_2 62Li_2CO_3.38K_2CO_3	390-878	[61]
ScSZ(tube)	Ni-YSZ/Ni-ScSz 0.5-0.6 mm	LSM-ScSZ	Carbon black	750	Nitrogen	47	[25]
				800		75	
				850		104	
ScSZ 100 µm	Sb	LSF-ScSZ 50 µm	Sugar char	700	Molten metal	360	[85]
ScSZ 20 µm	Ni-YSZ(680 µm)/Ni-ScSz (15 µm)	LSM-ScSZ 15 µm	Carbon black	900	External Gasification - DCFC	97.6	[59]
				950		147.3	
CeO_2-carbonate 0.65 mm	Ag current collector	Lithiated NiO 0.35 mm	Activated carbon	700	Nitrogen Composite carbonate-oxide	100	[91]
GDC 0.75 mm	LSCF	LSCF-Ag	XC-72R	600-800	He or CO_2	12-50	[29]
SDC	NiO-SDC 0.8mm	LSCF	Carbon black	650	Nitrogen 38K_2CO_3-62Li_2CO_3	68	[39]
			Bamboo			156	
			Waste paper			225	

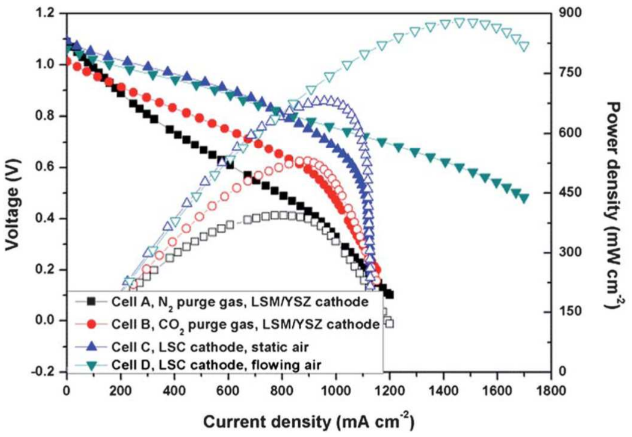


Figure 18 Cell performance of the hybrid direct carbon fuel cell at 750 °C with Ni-YSZ anode using 2 g mixture of pyrolysed medium density fibreboard (PMDF) and 62Li_2CO_3-38K_2CO_3. Cell A and Cell B exhibit the influence of purge gas at the anode and have same cathode LSM/YSZ; Cell C and Cell D demonstrate the influence of cathode atmosphere. Cell A and Cell C show the influence of the cathode materials. Reproduced from reference [61] with permission from [the Royal Society of Chemistry], copyright [2012].

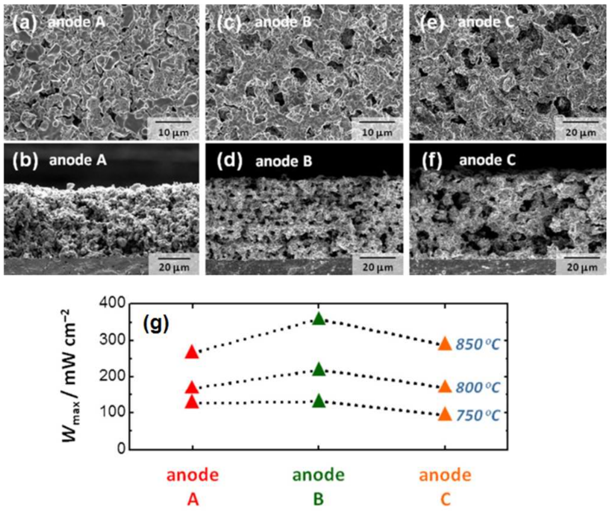


Figure 19 Maximum power densities of the cells with anode A, B or C with different cell microstructure, Anode A has no pore former, Anode B was made using the PMMA pore former with d_{PMMA}=5 µm, and Anode C was made using the PMMA pore former with d_{PMMA}=10 µm. Reproduced from reference [69] with permission from [Elsevier], copyright [2014].

In DCFCs, an inert gas or CO_2 is often used to purge the reaction gas away from the triple phase boundary. The two significant influences of the anode atmosphere are the open circuit voltage and the cell performance. In a physical contact-DCFC, a decrease in the flow rate from 1000 ml/min of helium to 50 ml/min of helium led to an increase of OCV from 0.71 V to 0.87 V, and accordingly, the current densities subsequently increased from 0.12 A cm^{-2} to 0.34 A cm^{-2}.[120] It has been suggested that this increase in the current density results from a longer residence time of the carbon monoxide and carbon dioxide at the electrode/electrolyte interface. It was also confirmed in Jiang's research that the cell benefited to some extent when the flow rate of argon decreased from 100 ml/min to 20 ml/min, even to 7 ml/min.[61, 73, 75] The presence of CO_2 is considered to enhance the Boudouard reaction at high temperatures, and therefore is responsible for the improvement of the cell performance, especially the maximum power density. Furthermore, the employment of pure CO_2 as a gasification agent at a minimum flow rate of 10 ml/min results in the best DCFC performance, in terms of maximum power, the ohmic resistance and the polarisation resistance of the electrode. More importantly, the addition of carbonates to carbon feedstock results in an increase in the maximum cell power density of up to 32% at 800 °C. These findings are ascribed to the in situ formed CO, plentiful in high CO_2 concentrations, and in the presence of both carrier gases and carbonates. The in situ formed CO seems to have a positive effect both on the ohmic resistance by modifying the redox state of the electrode and on the electrode resistance with its faster diffusion and electro-oxidation kinetics. These alterations are reflected in the cell characteristics leading to an enhanced DCFC performance.[121]

Some attention has been paid to the feasibility of employing lignite as fuel in DCFCs. Investigations have been made into the impact of several parameters on DCFC performance: anodic electrode composition, operation temperature, carrier gas composition, flow rate, and the co-addition of catalyst and carbonate to lignite feedstock. The results clearly indicated that the best performance was achieved by employing 20 wt%Co-CeO_2 in an anode electrode and using CO_2 instead of He as a purging gas.[121]

The physicochemical, electrical and structural characteristics of the electrode notably affect their electrochemical reactivity, and, as a consequence, the performance and lifetime of the DCFCs.

The microstructure of the anode plays an important role in the final cell performance. The effect of the anode microstructure on a hybrid DCFC performance was, therefore, investigated. The pore volume and surface area of the Ni-YSZ anode were appropriately tailored using PMMA pore-formers (Figure 19).[69] Microstructural and electrochemical experiments demonstrated that (i) the modification of the anode microstructure with the incorporation of PMMA-derived pores

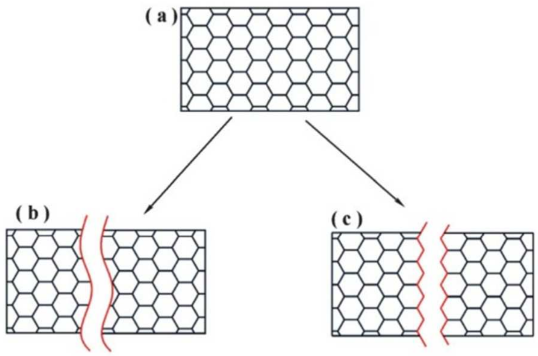


Figure 20 Surface of (a) fresh SDC before breaking; (b) fresh SDC after breaking; (c) treated SDC after breaking. Note: SDC pellets were immersed in eutectic carbonate mixture of 62 mol% Li_2CO_3 and 38 mol% K_2CO_3 and was kept at 700 °C for ten days, and then was washed by acid. Reproduced from reference [124] with permission from [the Royal Society of Chemistry], copyright [2014].

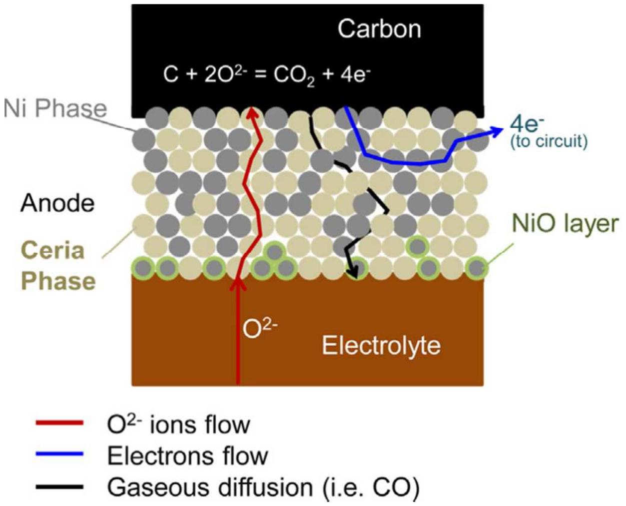


Figure 21 A schematic depicting the half-cell reaction (anode side) in a DCFC based on solid oxide electrolyte with Ni-doped ceria anode. Reproduced from reference [125] with permission from [Elsevier], copyright [2015].

leads to an increased power density; (ii) the anode surface area plays a dominant role in improving cell performance; and (iii) the reaction mechanism involves the CO oxidation mode as well as the direct carbon oxidation and the carbonate-mediated oxidation modes. The improved power capability of the hybrid DCFC can be understood in terms of the increased number of reaction sites for CO oxidation due to the presence of PMMA-derived pores. The incorporation of PMMA-derived pores into the anode leads to improved power capability at typical operating temperatures, which is the result of an enlarged active zone for electrochemical CO oxidation.

8.3. Life time

In any investigation into DCFCs, life time is of great concern. The performance degradation in the DCFC is attributed to carbon consumption, but other issues are also involved. The loss in cell performance is mostly due to the loss of carbon/anode contacts and to a reduction in the electron-conducting pathways as the fuel is consumed, leading to an overall increase in ohmic resistance.[122]

The stability of the current collectors and the electrolyte materials are considered to be an important issue in the presence of carbonate. Silver shows no significant solubility in molten carbonate systems, perhaps due to the formation of a surface layer of oxide.[123] A YSZ electrolyte is more stable in a reducing atmosphere than in an oxidising one,[61] but the atmosphere itself has no effect on the corrosion of the SDC by the eutectic molten carbonate. Besides, SDC is more corrosion resistant than YSZ in eutectic molten carbonates because corrosion develops along grain boundaries (Figure 20).[124] In the first 70 hours, the ohmic resistance of the SDC pellet decreased, whereas that of the YSZ electrolyte displayed a significant increase in the first 2 hours.[124] CeO_2 was proven to be more stable than YSZ in a mixture of lithium and potassium carbonate at 700C.[123] In the DCFC with a carbonate catalyst, an increase in the ohmic resistance was believed to be associated with a loss of contact between the carbon, the current collector and the anode. It is believed that the consumption of solid carbon causes a loss of conducting pathways, which cannot be replaced by the rest of the carbon bed because of the poorer fluidity of the solid phase in the anode.[122] The increase in the ohmic resistance is not particularly relevant to the anode structure, as supervision of the main phase of the LSCF anode was maintained throughout the testing time, and only small quality changes were found in other phases. [122]

A decrease in the open circuit voltage can be another factor that causing performance deterioration. The drop in the open circuit voltage was attributed to fuel consumption[91], but it might also have been due to a loss of contact, a delamination of the electrode from the electrolyte since the solid-solid contact is paramount.

The effect of impurities is obvious. Although the maximum power density of the cell from raw coal was double that of the cell with ash-free coal, a more durable power performance was obtained using the latter. [106]

9. Challenge

DCFCs have a promising future, because of their attractive potential features. They offer a method of generating clean energy, with reduced CO_2 emissions per unit of energy produced, high electrochemical conversion efficiency, and the possibility of using a wide range of fuels. There are many challenges to be addressed and many options to explore, requiring a strong interdisciplinary programme. A performance above 800 mW cm^{-2} was attained, so the first hurdle has already been overcome. Before DCFCs can be developed on an industrial scale and contribute to the global energy economy, some other issues need to be solved. One of these is the matter of long term durability.

The first issue that is related to the long-term durability is the increase in the ohmic resistance. In one example the ohmic resistance increased significantly with an increased current load. This was caused by the electrochemical oxidation of Ni into NiO at the electrolyte/anode interface, resulting in an increase in the ohmic resistance and in the charge transfer resistance (Figure 21).[125] This could eventually be used to clarify the major performance loss in DCFCs.

The second issue is the deactivation of electrode in DCFC operation conditions. This might be due to the utilisation of molten carbonate or molten metal. Examples can be found in references 66 and 134 (see Table 2). Two issues are involved in any molten metal-based DCFC system. One is the formation of metal oxides during operation, leading to an increase in the cell impedance. Sb electrodes are efficient at 700 ^{o}C, as the melting temperature of Sb_2O_3 is lower than the operating temperature of 700 °C; however for Pb, the impedance of the cell at 700 °C and 800 °C, is much higher than at 900 °C, as PbO melts at this temperature.[84] For tin the ohmic loss due to the transportation of oxygen through the tin layer is significant and impacts cell performance is assessed since a thick tin electrode is often used.[126] The other issue to be considered is the electrode, for the whole system suffers from the corrosion of the molten metal because of its aggressive nature. Not only the increase in the ohmic resistance but also the decrease in the open circuit voltage of the cells is deemed to be the result of nickel oxidation.[53]

Another matter is the consumption of solid carbon. At present, the prolonged running process under the current load is limited by the discontinuous supply of fuel. 8 grams of carbon were used in a DCFC system, the cell only ran for 25 hours under 50 mA cm^{-2} current density.[127] With 2 g of PMDF was used in a DCFC system, the cell ran at 0.7 V voltage for 13 hours.[61] Although the short-term performance of the DCFC is promising, a system with a continuous fuel supply is necessary to generate electricity with an adequate life time. Ash and clinker are also issues that may limit continuous feed. Scale-up has been achieved, for example, a single cell with an area of 100 cm^2 was reported using molten carbonate-based DCFCs.[128] So far the ultimate limits of a durable performance of fuel have been measured in batch modes, which can be resolved in continuous fuel supply concepts. Two or three-cell stacks (with an active area of 5.2 cm^2) have been successfully fabricated and operated to generated 2.4 W in total.[49] Even though success has been achieved in the laboratory, methods for manufacturing cell still pose technological obstacles that have to be addressed in a feasibility assessment of scale up to a commercial scale. The next task is to increase the durability of the cell and to enlarge the scale of the cell for potential use as a marketable commodity.

The development of new materials and suitable electrolyte film deposition techniques are still challenging to be addressed for achieving good cell performance. CGO is presumed to be stable under molten carbonate conditions, but the possibility of an electronic leakage presents a practical difficulty in its use as a viable DCFC electrolyte. Relatively low open circuit voltage is obtained with doped ceria as the electrolyte. The open circuit voltage is also dependent on the designed system. OCV of the cell with molten metal, molten hydroxide electrolyte or composite electrolyte is lower than the cell with solid oxide electrolyte (Table 2).

Electrodes represent the main challenge for the development of competitive SOFCs. To improve cell efficiency, effective catalysts must be found for high temperature-DCFCs. For example palladium, iron or even a ceramic catalyst could be worthy of study, to establish which one might be especially useful for the conversion of high-sulphur coal. Mixed ionic and electronic conductors were developed to be used in DCFCs for this purpose. The electrochemical catalytic activity using anodes such as LSCF, LSCT, is not good enough.[45, 47] The process usually requires metal catalyst additives, (e.g. nickel). A LSCT anode based cell generates a maximum power density of 6 mW cm^{-2} at 800 °C, whereas, with the aid of 2% Ru it can reach 25 mW cm^{-2} using XC-72R as fuel.[47] The infiltration of nickel (2 wt% into the YDC) into mixed ionic and electronic conductors is to improve the catalytic activity.[45] The less utilisation of metal the better, but the electrochemical performance needs to be further improved for the process of commercialisation.

10. Conclusions and outlook

In summary, we provide a comprehensive review of the development of direct carbon fuel cells, including electrolyte materials, anode materials, cathode materials, and fuels. Major advances in DCFC development have, however, been achieved in recent years. We have summarised the selection of materials for the application of DCFCs. Research on the DCFC is focused on developing efficient catalysts with a good electrochemical catalytic performance over carbon oxidation, on establishing cell configurations, and on understanding issues of deterioration and limitation with reference to long-term durability.

The utilisation of a nickel anode, facilitating fast electronic transport alongside good catalytic activity, is being intensively pursued as the anode for DCFCs. Composite nickel anodes, combined with an oxygen ionic conductor or a mixed ionic and electronic conductor, are the dominant anodes in the field of DCFCs, giving an excellent performance with high power output and long term durability at intermediate and high temperatures. New anodes offer more opportunities for improved redox tolerance and better resistance stability in carbon fuels. Mixed ionic and electronic conductors have the advantage of extending the reaction zone and sulfur tolerance. LSCF, YDC, LST and LSCT were investigated and gave a promising performance at intermediate and low temperatures. Redox media, molten carbonate, molten metal and composite materials, offer advantages of facilitating transportation of ions, therefore, efficient oxidation of carbon. Good cell performance can be obtained in a system with carbonate mediator, but there are some issues that should be further studied, such as the oxidation mechanism in this complex system, the dominant process for carbon oxidation, the choice of electrode and electrolyte materials to reduce carbonate induced corrosion and allow long term operation. Some strategies have been identified, based on catalysts such as metal oxide and mixed metal oxides. No single material fulfils all the current requirements, and therefore new composites are needed to act both as an active electrolyte layer and a current collector. Further research is required to optimise these materials, both in the field of composition and microstructure. It is particularly important to maximise the electronic conductivity without sacrificing the essential chemical stability under reducing conditions. Detailed studies are required on the most promising materials to establish and understand the dimensional stability of long-term operation, and how this can be improved without compromising electrical conductivity. Studies of oxygen diffusion, ionic conductivity and surface exchange in reducing environments are required on the most promising materials to improve our understanding of their electrocatalytic properties.

The efforts work on cathode materials has been concentrating on their application at these temperatures. The development of LSC and LSCF has advantages from this point of view.

Many types of carbon are tested in DCFC systems, such as carbon black, graphite, carbon waste, biomass, and coal. For pure carbons, parameters such as crystal structure, surface properties or particle size can have a significant influence on the DCFC performance while for impure carbons such as coal, additional components can make the research more complicated. Nickel is very sensitive to the presence of sulphur, which is one of the impurities in coal. Despite the considerable improvements achieved over the last decades, we are still facing a lot of challenges before DCFCs can be commercialised. Particular care is necessary to allow the reproducibility of results between laboratories, and especially to ensure that meaningful experiments are performed before their results are presented. The long term durability of current DCFCs are far below the minimum requirements at low temperatures and more research is required. There is still considerable work to be done before DCFCs can be applied on an industrial scale.

Acknowledgements

The authors would like to acknowledge the funding support from the Research Fund for Coal & Steel of the European commission with a reference number of RFCR-CT-2011-00004 and from DSTL with a reference number of DSTLX-1000101144 . JI acknowledges the Royal Society for a Wolfson merit award. CJ acknowledges the Royal Society of Edinburgh for a RSE/BP Hutton Prize in Energy Innovation 2015.

Table 2 Illustrative Examples of DCFC Development

Countries	Institute	System	Development	Challenge	Ref.
United States	University of Hawaii at Manoa	Molten hydroxide electrolyte	Aqueous-alkaline/carbonate carbon fuel cell	Low OCV（0.574 V at 240 °C）	2007, 2008 [129, 130]
	West Virginia University	Molten hydroxide electrolyte	Evaluation of carbon materials for use in a direct carbon fuel cell	High area specific resistance(ASR) for coal-derived rods	2007[97]
	Lawrence Livermore National Laboratory Livermore	Molten carbonate electrolyte	Direct Conversion of Carbon Fuels in a Molten Carbonate fuel cell	Increase of cell resistance with time	2005[14]
	Stanford University	Solid electrolyte membrane (YSZ)	Fluidised bed fuel cell, Gasification-integrated DCFC	Big cell resistance (0.2mm YSZ), Low diffusion rate	2008[56] 2009[62, 63]
	Materials and Systems Research Inc.	Solid electrolyte membrane (YSZ)	Dry gasified coal SOFCS	Gasifier is needed	[66]
China	Tsinghua University	Solid electrolyte membrane (ScSZ)	Catalytic gasification process, Pyrolysis of hydrocarbons as carbon fuels	Gasifier is needed, Low OCV (0.8-0.9V)	2010[59] 2008[68] 2011[131]
	Tianjin University	Composite electrolyte	Dry pressing four-layer cell, Utilisation of corn cob biochar, SnO_2-SDC anode	OCV decreases with time	2010[91] 2014[132] 2016[133]
	Tsinghua University	Samarium doped ceria-(Li, Na, K) carbonate composite, YSZ electrolyte	Operation of DCFC at low temperatures (450-600 °C), Sb anode for DCFC	Deactivation of electrodes Formation of Sb_2O_3	2006[66] 2016[134]
	University of Sfax Tianjin University	Composite electrolyte	Effect of biochar on the cell performance New design on cell components	Big anode polarisation resistance and low OCVs	[135, 136]
	Nanjing University of Technology	Solid electrolyte membrane (ScSZ)	Carbon fuel cell integrated with in situ catalytic reverse Boudouard reaction, In situ catalysed Coal char for DCFCs	High temperature is required	2009[27] 2015[52]
	Shanghai Inorganic Energy Materials and Power Source Engineering Center	Solid electrolyte membrane (ScSZ)	Direct carbon fuel cell with tubular SOFCs	Low OCV	2010 [25]
Europe	University of St. Andrews, UK	Composite electrolyte (solid electrolyte +	Hybrid electrolyte carbon fuel cells	Continuous feed	2008-2016[61, 73, 75, 94, 108, 116, 137-140]

		molten carbonate)	Carbon fuels from pyrolysed biomass Optmisation of electrodes Scaling up		
	ZAE Bayern, Garching, Germany	Solid electrolyte membrane (YSZ)	Direct carbon conversion in a SOFC-system with a non-porous anode, Direct oxidation of carbon	Low diffusion rate due to the contact of solid with solid, Decrease in power density with time(12h)	2010[54] 2011[119]
	DTU, Denmark	Composite electrolyte (solid electrolyte + molten carbonate)	DCFC characterisation with Three-electrode set up Catalytic enhancement of carbon-fuelled HDCFC	Electrode is required to be optimised	2014, 2015[78, 79, 141-143]
Australia	University of Queensland	Molten carbonate electrolyte, Hybrid DCFC	Carbon fuel evaluation, Direct carbon fuel cells, Stability of YSZ and SDC in carbonate for HDCFC	Fabrication of thin film cell	[50, 95] 2014[124]
	CSIRO Monash University	High temperature SOFC	Electrode materials for coal oxidation, Brown coal or demineralised brown coal for DCFCs, Gasification in a DCFC	Low OCV, Degradation of the cell performance, Scaling up	2012[43, 45, 47] 2014[144] 2016[145]
Korea	Korea institute of Science and Technology	DC-carbonate fuel cell	100 cm^2 cell area	Continuous fuel supply	2016[128]

References

1. D. X. Cao, Y. Sun and G. L. Wang, *J Power Sources*, 2007, **167**, 250-257.
2. J. F. Cooper and R. Selman, *Ecs Transactions*, 2009, **19**, 15-25.
3. S. Giddey, S. P. S. Badwal, A. Kulkarni and C. Munnings, *Progress in Energy and Combustion Science*, 2012, **38**, 360-399.
4. A. C. Rady, S. Giddey, S. P. S. Badwal, B. P. Ladewig and S. Bhattacharya, *Energ Fuel*, 2012, **26**, 1471-1488.
5. T. M. Gur, *J Electrochem Soc*, 2010, **157**, B751-B759.
6. T. M. Gur, *Chem Rev*, 2013, **113**, 6179-6206.
7. W. Zhou, Y. Jiao, S. D. Li and Z. P. Shao, *Chemelectrochem*, 2016, **3**, 193-203.
8. T. Cao, K. Huang, Y. Shi and N. Cai, *Energy & Environmental Science*, 2017, DOI: 10.1039/C6EE03462D.
9. W. W. Jacques, *Harper's New Monthly Magazine*, 1896-1897, **94**, 144-150.
10. S. Zecevic, E. M. Patton and P. Parharni, *Carbon*, 2004, **42**, 1983-1993.
11. L. Guo, J. M. Calo, E. DiCocco and E. J. Bain, *Energ Fuel*, 2013, **27**, 1712-1719.
12. L. Guo, J. M. Calo, C. Kearney and P. Grimshaw, *Appl Energ*, 2014, **129**, 32-38.
13. W. H. A. Peelen, M. Olivry, S. F. Au, J. D. Fehribach and K. Hemmes, *J Appl Electrochem*, 2000, **30**, 1389-1395.
14. N. J. Cherepy, R. Krueger, K. J. Fiet, A. F. Jankowski and J. F. Cooper, *J Electrochem Soc*, 2005, **152**, A80-A87.
15. C. Jin, C. H. Yang and F. L. Chen, *J Membrane Sci*, 2010, **363**, 250-255.
16. L. Kouchachvili and M. Ikura, *Int J Hydrogen Energ*, 2011, **36**, 10263-10268.
17. D. G. Vutetakis, D. R. Skidmore and H. J. Byker, *J Electrochem Soc*, 1987, **134**, 3027-3035.
18. E. Baur and H. Preis, *Z. Elektrochem.* , 1937, **43**, 727.
19. N. Nakagawa and M. Ishida, *Ind Eng Chem Res*, 1988, **27**, 1181-1185.
20. T. M. Gür and R. A. Huggins, *J Electrochem Soc*, 1992, **139**, L95-L97.
21. T. Horita, N. Sakai, T. Kawada, H. Yokokawa and M. Dokiya, *J Electrochem Soc*, 1995, **142**, 2621-2624.
22. J. Ma, C. Jiang, P. A. Connor, M. Cassidy and J. T. S. Irvine, *J Mater Chem A*, 2015, **3**, 19068-19076.
23. T. Ishihara, J. Tabuchi, S. Ishikawa, J. Yan, M. Enoki and H. Matsumoto, *Solid State Ionics*, 2006, **177**, 1949-1953.
24. L. Zhang, J. Xiao, Y. Xie, Y. Tang, J. Liu and M. Liu, *J Alloy Compd*, 2014, **608**, 272-277.
25. R. Z. Liu, C. H. Zhao, J. L. Li, F. R. Zeng, S. R. Wang, T. L. Wen and Z. Y. Wen, *J Power Sources*, 2010, **195**, 480-482.
26. M. Dudek and P. Tomczyk, *Catal Today*, 2011, **176**, 388-392.

27. Y. Z. Wu, C. Su, C. M. Zhang, R. Ran and Z. P. Shao, *Electrochem Commun*, 2009, **11**, 1265-1268.
28. X. Y. Xu, W. Zhou, F. L. Liang and Z. H. Zhu, *Appl Energ*, 2013, **108**, 402-409.
29. A. Kulkarni, S. Giddey and S. P. S. Badwal, *Solid State Ionics*, 2011, **194**, 46-52.
30. B. C. H. Steele, *Solid State Ionics*, 2000, **129**, 95-110.
31. J. G. Lee, J. H. Park and Y. G. Shul, *Nat Commun*, 2014, **5**.
32. P. I. Cowin, C. T. G. Petit, R. Lan, J. T. S. Irvine and S. W. Tao, *Adv Energy Mater*, 2011, **1**, 314-332.
33. M. Mori, T. Yamamoto, H. Itoh, H. Inaba and H. Tagawa, *J Electrochem Soc*, 1998, **145**, 1374-1381.
34. S. P. Jiang and S. H. Chan, *J Mater Sci*, 2004, **39**, 4405-4439.
35. S. Park, J. M. Vohs and R. J. Gorte, *Nature*, 2000, **404**, 265-267.
36. A. Atkinson, S. Barnett, R. J. Gorte, J. T. S. Irvine, A. J. Mcevoy, M. Mogensen, S. C. Singhal and J. Vohs, *Nat Mater*, 2004, **3**, 17-27.
37. M. Dudek, P. Tomczyk, R. Socha and M. Hamaguchi, *Int J Hydrogen Energ*, 2014, **39**, 12386-12394.
38. M. Dudek and R. Socha, *Int J Electrochem Sc*, 2014, **9**, 7414-7430.
39. W. Hao, X. He and Y. Mi, *Appl Energ*, 2014, **135**, 174-181.
40. Z. Cheng, J. H. Wang, Y. M. Choi, L. Yang, M. C. Lin and M. L. Liu, *Energy Environ Sci*, 2011, **4**, 4380-4409.
41. A. Hartley, M. Sahibzada, M. Weston, I. S. Metcalfe and D. Mantzavinos, *Catal Today*, 2000, **55**, 197-204.
42. J. C. Fisher and S. S. C. Chuang, *Catal Commun*, 2009, **10**, 772-776.
43. A. Kulkarni, F. T. Ciacchi, S. Giddey, C. Munnings, S. P. S. Badwal, J. A. Kimpton and D. Fini, *Int J Hydrogen Energ*, 2012, **37**, 19092-19102.
44. Y. Xiong, K. Yamaji, T. Horita, N. Sakai and H. Yokokawa, *J Electrochem Soc*, 2002, **149**, E450-E454.
45. A. Kulkarni, S. Giddey and S. P. S. Badwal, *J Solid State Electr*, 2015, **19**, 325-335.
46. S. Q. Hui and A. Petric, *J Eur Ceram Soc*, 2002, **22**, 1673-1681.
47. A. Kulkarni, S. Giddey, S. P. S. Badwal and G. Paul, *Electrochim Acta*, 2014, **121**, 34-43.
48. M. Skrzypkiewicz, I. Lubarska-Radziejewska and J. Jewulski, *Int J Hydrogen Energ*, 2015, **40**, 13090-13098.
49. Y. Bai, Y. Liu, Y. Tang, Y. Xie and J. Liu, *Int J Hydrogen Energ*, 2011, **36**, 9189-9194.
50. X. Li, Z. H. Zhu, R. De Marco, J. Bradley and A. Dicks, *J Power Sources*, 2010, **195**, 4051-4058.
51. Y. B. Tang and J. Liu, *Int J Hydrogen Energ*, 2010, **35**, 11188-11193.
52. Y. Jiao, W. Tian, H. Chen, H. Shi, B. Yang, C. Li, Z. Shao, Z. Zhu and S.-D. Li, *Appl Energ*, 2015, **141**, 200-208.
53. A. C. Chien and J. T. Irvine, in *Molten Salts Chemistry: From Lab to Applications*, eds. F. Lantelme and H. Groult, Elsevier, 2013, ch. 19, pp. 403-414.
54. S. Nurnberger, R. Bussar, P. Desclaux, B. Franke, M. Rzepka and U. Stimming, *Energy Environ Sci*, 2010, **3**, 150-153.
55. A. C. Lee, S. Li, R. E. Mitchell and T. M. Gür, *Electrochem Solid St*, 2008, **11**, B20-B23.
56. S. Li, A. C. Lee, R. E. Mitchell and T. M. Gür, *Solid State Ionics*, 2008, **179**, 1549-1552.
57. J. B. Zhang, Z. P. Zhong, D. K. Shen, J. M. Xiao, Z. M. Fu, H. Y. Zhang, J. X. Zhao, W. L. Li and M. Yang, *J Power Sources*, 2011, **196**, 3054-3059.
58. J. B. Zhang, X. X. Jiang, G. L. Piao, H. M. Yang and Z. P. Zhong, *Int J Hydrogen Energ*, 2015, **40**, 3321-3331.
59. C. Li, Y. X. Shi and N. S. Cai, *J Power Sources*, 2010, **195**, 4660-4666.
60. K. F. Chen, L. Zhang, N. Ai, S. Zhang, Y. Song, Y. C. Song, Q. Yi, C. Z. Li and S. P. Jiang, *Energ Fuel*, 2016, **30**, 1849-1857.
61. C. R. Jiang, J. J. Ma, A. D. Bonaccorso and J. T. S. Irvine, *Energy Environ Sci*, 2012, **5**, 6973-6980.
62. A. C. Lee, R. E. Mitchell and T. M. Gür, *J Power Sources*, 2009, **194**, 774-785.
63. A. C. Lee, R. E. Mitchell and T. M. Gür, *Aiche J*, 2009, **55**, 983-992.
64. C. Xia, L. Li, Y. Tian, Q. H. Liu, Y. C. Zhao, L. J. Jia and Y. D. Li, *J Power Sources*, 2009, **188**, 156-162.
65. J. B. Huang, L. Z. Yang, R. F. Gao, Z. Q. Mao and C. Wang, *Electrochem Commun*, 2006, **8**, 785-789.
66. T. M. Gür, M. Homel and A. V. Virkar, *J Power Sources*, 2010, **195**, 1085-1090.
67. M. Homel, T. M. Gür, J. H. Koh and A. V. Virkar, *J Power Sources*, 2010, **195**, 6367-6372.
68. X. Y. Zhao, Q. Yao, S. Q. Li and N. S. Cai, *J Power Sources*, 2008, **185**, 104-111.
69. J.-Y. Lee, R.-H. Song, S.-B. Lee, T.-H. Lim, S.-J. Park, Y. G. Shul and J.-W. Lee, *Int J Hydrogen Energy*, 2014, **39**, 11749-11755.
70. A. Fuente-Cuesta, C. Jiang, A. Arenillas and J. T. S. Irvine, *Energy Environ Sci*, 2016, **9**, 2868-2880.
71. B. Cantero-Tubilla, C. C. Xu, J. W. Zondlo, K. Sabolsky and E. M. Sabolsky, *J Power Sources*, 2013, **238**, 227-235.
72. X. K. Yu, Y. X. Shi, H. J. Wang, N. S. Cai, C. Li and A. F. Ghoniem, *J Power Sources*, 2014, **252**, 130-137.
73. C. R. Jiang and J. T. S. Irvine, *J Power Sources*, 2011, **196**, 7318-7322.
74. C. Jiang, J. Ma, A. Arenillas and J. T. S. Irvine, *Ecs Transactions*, 2014, **59**, 281-288.
75. Y. Nabae, K. D. Pointon and J. T. S. Irvine, *Energy Environ Sci*, 2008, **1**, 148-155.
76. S. L. Jain, J. B. Lakeman, K. D. Pointon, R. Marshall and J. T. S. Irvine, *Energy & Environmental Science*, 2009, **2**, 687-693.
77. A. C. Chien, A. Arenillas, C. R. Jiang and J. T. S. Irvine, *J Electrochem Soc*, 2014, **161**, F588-F593.
78. L. Deleebeeck, D. Ippolito and K. K. Hansen, *Electrochimica Acta*, 2015, **152**, 222-239.
79. L. Deleebeeck, D. Ippolito and K. K. Hansen, *J Electrochem Soc*, 2015, **162**, F327-F339.
80. I. V. Yentekakis, P. G. Debenedetti and B. Costa, *Industrial & Engineering Chemistry Research*, 1989, **28**, 1414-1424.
81. V. R. Yarlagadda and T. V. Nguyen, *Ecs Transactions*, 2011, **33**, 119-125.
82. S. Sunde, K. Nisancioglu and T. M. Gür, *J Electrochem Soc*, 1996, **143**, 3497-3504.
83. G. Bandyopadhyay and H. Ray, *Metall Mater Trans B*, 1971, **2**, 3055-3061.
84. A. Jayakumar, J. M. Vohs and R. J. Gorte, *Ind Eng Chem Res*, 2010, **49**, 10237-10241.
85. A. Jayakumar, R. K. Ungas, S. Roy, A. Javadekar, D. J. Buttrey, J. M. Vohs and R. J. Gorte, *Energy Environ Sci*, 2011, **4**, 4133-4137.

86. T. Tao, L. Bateman, J. Bentley and M. Slaney, *Ecs Transactions*, 2007, **5**, 463-472.
87. H. Ju, S. Uhm, J. W. Kim, R. H. Song, H. Choi, S. H. Lee and J. Lee, *J Power Sources*, 2012, **198**, 36-41.
88. Y. Li, Z. Rui, C. Xia, M. Anderson and Y. S. Lin, *Catal Today*, 2009, **148**, 303-309.
89. W. Zhu, C. Xia, D. Ding, X. Shi and G. Meng, *Mater Res Bull*, 2006, **41**, 2057-2064.
90. Z. Rui, M. Anderson, Y. S. Lin and Y. Li, *J Membrane Sci*, 2009, **345**, 110-118.
91. L. J. Jia, Y. Tian, Q. H. Liu, C. Xia, J. S. Yu, Z. M. Wang, Y. C. Zhao and Y. D. Li, *J Power Sources*, 2010, **195**, 5581-5586.
92. X. Li, Z. H. Zhu, R. De Marco, J. Bradley and A. Dicks, *J Phys Chem A*, 2010, **114**, 3855-3862.
93. X. Li, Z. H. Zhu, J. L. Chen, R. De Marco, A. Dicks, J. Bradley and G. Q. Lu, *J Power Sources*, 2009, **186**, 1-9.
94. Y. Nabae, K. D. Pointon and J. T. S. Irvine, *J Electrochem Soc*, 2009, **156**, B716-B720.
95. X. Li, Z. H. Zhu, R. De Marco, A. Dicks, J. Bradley, S. M. Liu and G. Q. Lu, *Ind Eng Chem Res*, 2008, **47**, 9670-9677.
96. J.-P. Kim, H. Lim, C.-H. Jeon, Y.-J. Change, K.-N. Kohm, S.-M. Choi and J.-H. Song, *J Power Sources*, 2010, **195**, 7568-7573.
97. G. A. Hackett, J. W. Zondlo and R. Svensson, *J Power Sources*, 2007, **168**, 111-118.
98. C. Jiang, J. Ma, A. Arenillas and J. T. S. Irvine, *Ecs Transactions*, 2013, **57**, 3013-3021.
99. M. Dudek, M. Sitarz and P. Tomczyk, *J Solid State Electr*, 2014, **18**, 3023-3032.
100. D. X. Cao, G. L. Wang, C. Q. Wang, J. Wang and T. H. Lu, *Int J Hydrogen Energ*, 2010, **35**, 1778-1782.
101. J. P. Chen and S. N. Wu, *Langmuir*, 2004, **20**, 2233-2242.
102. Y. Jiao, J. H. Zhao, W. T. An, L. Q. Zhang, Y. J. Sha, G. M. Yang, Z. P. Shao, Z. P. Zhu and S. D. Li, *J Power Sources*, 2015, **288**, 106-114.
103. T. Kivisaari, P. Bjornbom, C. Sylwan, B. Jacquinot, D. Jansen and A. de Groot, *Chem Eng J*, 2004, **100**, 167-180.
104. A. Hagen, J. F. B. Rasmussen and K. Thyden, *J Power Sources*, 2011, **196**, 7271-7276.
105. J. P. Trembly, A. I. Marquez, T. R. Ohrn and D. J. Bayless, *J Power Sources*, 2006, **158**, 263-273.
106. H. Ju, J. Eom, J. K. Lee, H. Choi, T. H. Lim, R. H. Song and J. Lee, *Electrochimica Acta*, 2014, **115**, 511-517.
107. M. Dudek, *Solid State Ionics*, 2015, **271**, 121-127.
108. C. Jiang, J. Ma, A. Arenillas, A. D. Bonaccorso and J. T. S. Irvine, *Int J Hydrogen Energ*, 2016, **41**, 18797-18806.
109. X. Li, J. L. Chen, Z. H. Zhu, R. De Marco, J. Bradley and A. Dicks, *Energ Fuel*, 2009, **23**, 5290-5290.
110. H. J. Li, Q. H. Liu and Y. D. Li, *Electrochim Acta*, 2010, **55**, 1958-1965.
111. Y. M. Xie, Y. B. Tang and J. Liu, *J Solid State Electr*, 2013, **17**, 121-127.
112. H. J. Wang, Y. X. Shi, W. Yuan, T. Y. Cao, N. S. Cai and X. S. Liang, *Solid Oxide Fuel Cells 13 (Sofc-Xiii)*, 2013, **57**, 2913-2922.
113. S. Giddey, A. Kulkarni, C. Munnings and S. P. S. Badwal, *Energy*, 2014, **68**, 538-547.
114. N. Q. Duan, Y. Cao, B. Hua, B. Chi, J. Pu, J. L. Luo and L. Jian, *Energy*, 2016, **95**, 274-278.
115. A. D. Bonaccorso and J. T. S. Irvine, *Int J Hydrogen Energ*, 2012, **37**, 19337-19344.
116. A. Damiano Bonaccorso, C. Jiang, J. Ma and J. T. S. Irvine, *Int J Hydrogen Energ*, 2016, **41**, 18788-18796.
117. N. Kaklidis, V. Kyriakou, I. Garagounis, A. Arenillas, J. A. Menendez, G. E. Marnellos and M. Konsolakis, *Rsc Adv*, 2014, **4**, 18792-18800.
118. A. C. Chien and S. S. C. Chuang, *J Power Sources*, 2011, **196**, 4719-4723.
119. W. A. G. McPhee, M. Boucher, J. Stuart, R. S. Parnas, M. Koslowske, T. Tao and B. A. Wilhite, *Energ Fuel*, 2009, **23**, 5036-5041.
120. P. Desclaux, S. Nurnberger, M. Rzepka and U. Stimming, *Int J Hydrogen Energ*, 2011, **36**, 10278-10281.
121. N. Kaklidis, I. Garagounis, V. Kyriakou, V. Besikiotis, A. Arenillas, J. A. Menéndez, G. E. Marnellos and M. Konsolakis, *Int J Hydrogen Energ*, 2015, **40**, 14353-14363.
122. A. C. Rady, S. Giddey, A. Kulkarni, S. P. S. Badwal and S. Bhattacharya, *Electrochimica Acta*, 2014, **143**, 278-290.
123. K. Pointon, B. Lakeman, J. Irvine, J. Bradley and S. Jain, *J Power Sources*, 2006, **162**, 750-756.
124. X. Y. Xu, W. Zhou and Z. H. Zhu, *Rsc Adv*, 2014, **4**, 2398-2403.
125. A. C. Rady, S. Giddey, A. Kulkarni, S. P. S. Badwal and S. Bhattacharya, *Electrochim Acta*, 2015, **178**, 721-731.
126. H. Abernathy, R. Gemmen, K. Gerdes, M. Koslowske and T. Tao, *J Power Sources*, 2011, **196**, 4564-4572.
127. C. G. Lee, H. Hur and M. B. Song, *J Electrochem Soc*, 2011, **158**, B410-B415.
128. S. H. Choi, D. N. Park, C. W. Yoon, S. P. Yoon, S. W. Nam, S. A. Hong, Y. G. Shul, H. C. Ham and J. Han, *Int J Hydrogen Energ y*, 2015, **40**, 5144-5149.
129. T. Nunoura, K. Dowaki, C. Fushimi, S. Allen, E. Meszaros and M. J. Antal, *Ind Eng Chemi Res*, 2007, **46**, 734-744.
130. M. J. Antal and G. C. Nihous, *Ind Eng Chemi Res*, 2008, **47**, 2442-2448.
131. C. Li, Y. X. Shi and N. S. Cai, *J Power Sources*, 2011, **196**, 754-763.
132. J. Yu, Y. Zhao and Y. Li, *J Power Sources*, 2014, **270**, 312-317.
133. B. Yu, Y. Zhao and Y. Li, *J Power Sources*, 2016, **306**, 387-393.
134. T. Y. Cao, Y. X. Shi and N. S. Cai, *J Electrochem Soc*, 2016, **163**, F127-F131.
135. A. Elleuch, A. Boussetta, J. S. Yu, K. Halouani and Y. D. Li, *Int J Hydrogen Energ*, 2013, **38**, 16590-16604.
136. A. Elleuch, A. Boussetta, K. Halouani and Y. Li, *Int J Hydrogen Energ*, 2013, **38**, 16605-16614.
137. S. Jain, B. Lakeman, K. D. Pointon and J. T. Irvine, *Ecs Transactions*, 2007, **7**, 829-836.
138. S. L. Jain, B. Lakeman, K. D. Pointon and J. T. S. Irvine, *Ionics*, 2007, **13**, 413-416.
139. S. L. Jain, Y. Nabae, B. J. Lakeman, K. D. Pointon and J. T. S. Irvine, *Solid State Ionics*, 2008, **179**, 1417-1421.
140. S. L. Jain, J. Barry Lakeman, K. D. Pointon, R. Marshall and J. T. S. Irvine, *Energy Environ Sci*, 2009, **2**, 687-693.
141. L. Deleebeeck, A. Arenillas, J. A. Menendez and K. K. Hansen, *Int J Hydrogen Energ*, 2015, **40**, 1945-1958.
142. L. Deleebeeck and K. K. Hansen, *J Solid State Electr*, 2014, **18**, 861-882.
143. L. Deleebeeck and K. K. Hansen, *J. Fuel Cell Sci Tech*, 2015, **12**.

144. A. C. Rady, S. Giddey, A. Kulkarni, S. P. S. Badwal, S. Bhattacharya and B. P. Ladewig, *Appl Energ*, 2014, **120**, 56-64.
145. A. C. Rady, S. Giddey, A. Kulkarni, S. P. S. Badwal and S. Bhattacharya, *Fuel*, 2016, **180**, 270-277.