Direct carbon fuel cell: Fundamentals and recent developments

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Abstract

The direct carbon fuel cell is a special type of high temperature fuel cell that directly uses solid carbon as anode and fuel. As an electrical power generator for power plants, it has a higher achievable efficiency (80%) than the molten carbonate and solid oxide fuel cells, and has less emissions than conventional coal-burning power plants. More importantly, its solid carbon-rich fuels (e.g. coal, biomass, organic garbage) are readily available and abundant. In this review, some fundamental study results of electrochemical oxidation of carbon in molten salts are summarized. Recent developments in direct carbon fuel cell configurations and performance are also discussed.
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Keywords: Direct carbon fuel cell; Carbon electrooxidation; Clean coal to electricity technology

1. Introduction

The direct carbon fuel cell (DCFC) is an almost forgotten fuel cell technology that actually has a long history date to mid-19 century [1,2]. The configuration and theoretical principles of the DCFC resemble those of the high temperature fuel cells, such as the molten carbonate fuel cell (MCFC) and the solid oxide fuel cell (SOFC). A DCFC consists of three key components: the anode, the cathode and the electrolyte. Differing from the MCFC and SOFC, instead of operating on a gaseous fuel, e.g. hydrogen generated by reforming of natural gas, coal gas, alcohol, etc., DCFC uses solid carbon as fuel. Solid carbon is directly introduced into the anode compartment and electro-oxidized to CO_2 at high temperature generating electrical power (Fig. 1). The overall cell reaction is given by Eq. (1).

$$C + O_2 = CO_2, \quad E^\circ = 1.02\,V \tag{1}$$

DCFC, the only fuel cell type using solid fuel, has several unique attractive features. First, the DCFC offers great thermodynamic advantages over other fuel cell types, such as MCFC and SOFC [3–9]. Its theoretical electrochemical conversion efficiency based on Eq. (1) slightly exceeds 100%. This is because the entropy change for the cell reaction is positive

($\Delta S = 1.6\,J\,K^{-1}\,mol$ at $600\,^\circ C$), which results in a slightly larger standard Gibbs free energy change ($\Delta G = -395.4\,kJ\,mol^{-1}$ at $600\,^\circ C$) than the standard enthalpy change ($\Delta H = -394.0\,kJ\,mol^{-1}$ at $600\,^\circ C$). The reactant carbon and the product carbon dioxide exist as pure substance in separate phases, therefore their chemical potentials (activities) are fixed and independent of extent of conversion of the fuel or position within the cell. This may allow a full conversion of the carbon fuel in a single pass with the theoretical voltage of DCFC remaining nearly constant at ∼1.02 V during the operation (minimal Nernst loss). Consequently, the fuel utilization efficiency could reach 100%, giving a practical typical coal to electricity efficiency of around 80% (direct electrical generation alone without cogeneration). This value is higher than MCFC or SOFC running on hydrogen or natural gas (nominal efficiency of 45–60%, see Table 1) [10]. So DCFC is potentially one of the most efficient electrochemical power generation systems.

Second, DCFC releases lower emissions than coal-firing power plants. DCFC may cut carbon emissions from coal by 50% and reduce off-gas volume by 10 times compared to conventional coal-burning power plants [11,12]. This is because, in contrast to combustion in a boiler, the oxidation of carbon in a DCFC occurs electrochemically at the anode compartment without the direct mixing with air, and thus the CO_2 produced is not mixed with other gases. The majority of the ingredients in the off-gas are carbon dioxide, which can be sequestered or injected into an oilfield to enhance oil recovery and at the same time used

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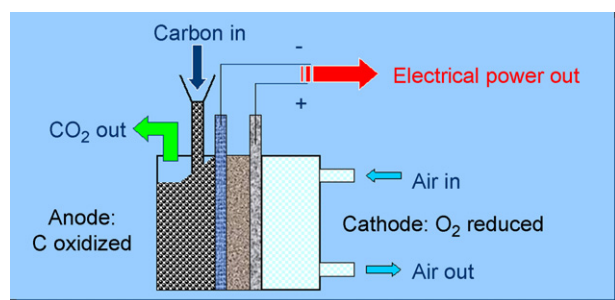*E-mail address:* caodianxue@hrbeu.edu.cn (D. Cao).

Fig. 1. Schematic of a direct carbon fuel cell configuration.

to store carbon dioxide permanently beneath the earth's surface. This can further reduce the release of CO_2 into air. The DCFC also releases no particulates (fly ash). These benefits to the environment brought about by using a DCFC to produce electricity are significant and important for those regions heavily relying on coal, for example, China, in which, around 80% of the electrical power is from burning coal, which releases 70% of its total CO_2 emission (ranked 2nd in the world), 90% of its SO_2 emission (ranked 1st in the world), 70% of its total particles, and 67% of its total NO_x [13,14]. Coal-fired plants produce 55% of electricity in the U.S., as well as a large amount of pollutants [15].

Thirdly, a solid carbon fuel can be easily produced from many different resources, including coal, petroleum coke, biomass (rice hulls, nut shells, corn husks, grass, woods) and even organic garbage. Coal is the earth's most abundant fossil resource, and accounts for 60% of the world's fossil fuel resources, and 80% of the coal belongs to the United States, Canada, the former Soviet Union and China. The vast energy reserves of coal remain underused. The pyrolysis production of tiny carbon particles which can be used in DCFC, consumes less energy and requires less capital than the production of hydrogen-rich fuels for MCFC or SOFC by steam-reforming processes. Billions of kilograms of carbon blacks were produced annually by pyrolysis in the United States [6]. Carbon releases a very high energy per unit volume on oxidation with oxygen ($20.0\,kWh\,L^{-1}$) exceeding, in this regard, many widely used fuel cell fuels, such as hydrogen ($2.4\,kWh\,L^{-1}$), methane ($4.0\,kWh\,L^{-1}$), gasoline ($9.0\,kWh\,L^{-1}$), and diesel ($9.8\,kWh\,L^{-1}$) [4,5].

Fourthly, DCFC system is mechanically simple because no reformers or heat engines required. It can be built on the site of a coal mine, thus eliminating coal transportation, consequently saving energy and reducing environmental pollution caused by coal shipping and handling. Therefore, the DCFC provides a possibility for the realization of the 150-year-old dream of

converting raw coal directly to electrical power without combustion, gasification (reforming) and the thermal efficiency limitations of heat engines.

The first literature-recorded DCFC may be traced back to the mid of 19 century. Bacquerelle in 1885 and Jablochkoff in 1877 built electrochemical devices using electrode-grade carbon as anode, Pt/Fe as cathode, and fused KNO_3 as electrolyte [16,17]. Such devices produced electrical power, but were unstable due to electrolyte degradation. In 1896, Dr. William Jacques demonstrated a large assembly of cells consisting of 100 single cells with rods of baked coal as anode, iron pots as cathode, and molten sodium hydroxide as electrolyte [2]. By blowing air to the iron pot containing the electrolyte and heating to 400–500 °C in a furnace, a current density of as high as $100\,mA\,cm^{-2}$ and an electrical power of 1.5 kW were achieved from the system. This could be considered the first DCFC, but there are many speculations over the actual performance and debates about the electrical power generation mechanism. For instance, the cell reaction was believed to be $C + 2NaOH + O_2 = Na_2CO_3$, $E^\circ_{298} = 1.42$ V [17], and since the electrolyte was consumed by an irreversible reaction equivalent to $CO_2 + 2NaOH = Na_2CO_3 + H_2O$, this device was regarded as not a fuel cell but rather a battery. The cell stack was even suspected to generate electricity not by electrochemical reaction, but by a thermoelectric effect. These doubts and the inability of reproducing Jacques's results by others, as well as the diminishment of incentive for seeking electrochemical conversion of coal caused by the improved efficiency of the steam-driven generator at the early of 20 century, put DCFC technology to rest for nearly more than two-third of a century until the 1970s, when a series of studies at SRI International (Menlo Park, CA, a National Energy Technology Laboratory (NTEL, Morgantown, WV) contractor) verified that it is practically possible to completely electro-oxidize carbon to generate electricity [18–20]. In recent years, with the significant development of fuel cell technology and the urgent needs than ever before for a clean and efficient coal to electricity technology imposed by the crude oil crisis and environmental deterioration, the fuel cell research community regained the interest of developing DCFC. Studies on the DCFC in the last few years have clarified the earlier misunderstanding of the DCFC, and have firmed the electrochemical foundation of the direct conversion of carbon to electricity, and have demonstrated the feasibility of a DCFC at least on a laboratory scale. Early research pertinent to the DCFC has been reviewed by Baur and Tobler [21], Howard [16], and Liebhafsky and Cairns [17]. The aim of this present review is to provide an overview on the recent progress in the development of DCFC and to point out the most important

Table 1
Efficiency of fuel cells

Fuel	Theoretical limit $= \Delta G^\circ(T)/\Delta H^\circ_{std}$	Utilization efficiency (μ)	$V(i)/V(i=0) = \varepsilon_V$	Actual efficiency $= (\Delta G/H^\circ_{std})(\mu)(\varepsilon_V)$
C	1.003	1.0	0.80	0.80
CH_4	0.895	0.80	0.80	0.57
H_2	0.70	0.80	0.80	0.45

Note: Efficiency of a fuel cell is defined as: (electrical energy out)/(heat of combustion (HHV) of fuels input) = [theoretical efficiency $\Delta G/\Delta H$][utilization fraction μ][voltage efficiency ε_V] = [$\Delta G(T)/\Delta H^\circ$][$\mu$][$V/V^\circ$] = [$\mu$][$nFV$]/$\Delta H^\circ$ (where $\Delta G(T) = -nFV^\circ = \Delta H - T\Delta S$).

technological challenges to be solved for DCFC becoming a viable power source.

2. Electrochemical oxidation of carbon

2.1. Basic findings

Electrochemical oxidation of carbon requires high temperature because of its sluggish kinetics and is therefore generally performed in molten salt electrolytes (e.g. cryolites, molten carbonates, and molten hydroxides) [3,12,22–25]. Some important experimental findings regarding anodic oxidation of carbon in molten carbonate electrolytes are summarized below:

(1) The predominant product is CO_2 at polarizations greater than around 0.1 V at temperatures above 700 °C. As early as to 1935, Tamaru et al. already found by analyzing the off-gas composition that CO_2 is dominant and concluded that the overall electrochemical oxidation of carbon was the same as its complete combustion [26]. Hauser later confirmed this result through the analysis of the gas evolved from graphite anode [27]. He found the current efficiency based on four electron process was more than 99% at applied current densities between 20 and 120 mA cm^{-2} over the temperature range of 650–800 °C. Weaver et al. measured the dependence of off-gas composition on current density and found that more than 90% of the anode gas was CO_2 at high current density [18,19]. Vutetakis et al. in a similar study reported that the anodic product was CO_2 and the CO/CO_2 ratio increases as current density decreases [23,28]. These results overturned the assumption that the anodic oxidation of carbon would produce CO as the dominant species at temperature above 750 °C according to the well-known Boudouard reaction equilibrium (Eq. (2)).
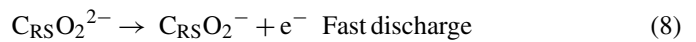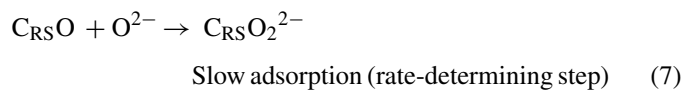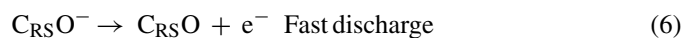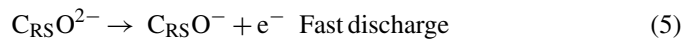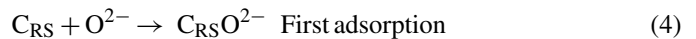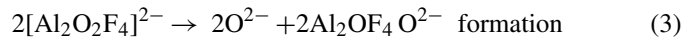
$$C + CO_2 = 2CO \qquad (2)$$

These observations proved that complete electrooxidation of carbon to CO_2 (a four-electron process) is feasible, and the formation of CO (a two-electron process) could be avoided at high current density (polarized condition), and therefore built the sound foundation for the DCFC.

(2) Carbon properties, such as, crystallization, electrical conductivity, surface area and particle size, affect, more or less, the reactivity of the carbon reaction. It seems that the poor crystallized, highly lattice disordered carbons are the more reactive probably due to the existence of more surface defects, such as, edges, steps, which act as active sites. Carbons with good electrical conductivity would lower the ohmic polarization and benefit the carbon electrochemical reaction [3]. Weaver et al. reported that devolatilized coal is more reactive than spectroscopic carbon and pyrolytic graphite [18]. They attributed the high reactivity to large surface area and poor crystallization. However, Cooper et al. found that surface area has no strong effects on carbon discharge rate.

2.2. Mechanism

The study of the mechanism is difficult due to the lack of techniques to detect the reaction intermediates in molten salts at high temperature (usually higher than 600 °C). Supported by some indirect evidence, a mechanism for the anodic oxidation of carbon in molten cryolite/alumina electrolyte (acidic melts) (Hall process) has been proposed and summarized by Haupin et al. as [3,29,30]

$$2[Al_2O_2F_4]^{2-} \rightarrow 2O^{2-} + 2Al_2OF_4 \, O^{2-} \quad \text{formation} \qquad (3)$$

$$C_{RS} + O^{2-} \rightarrow C_{RS}O^{2-} \quad \text{First adsorption} \qquad (4)$$

$$C_{RS}O^{2-} \rightarrow C_{RS}O^- + e^- \quad \text{Fast discharge} \qquad (5)$$

$$C_{RS}O^- \rightarrow C_{RS}O + e^- \quad \text{Fast discharge} \qquad (6)$$

$$C_{RS}O + O^{2-} \rightarrow C_{RS}O_2^{2-}$$
$$\text{Slow adsorption (rate-determining step)} \qquad (7)$$

$$C_{RS}O_2^{2-} \rightarrow C_{RS}O_2^- + e^- \quad \text{Fast discharge} \qquad (8)$$

$$C_{RS}O_2^{2-} \rightarrow CO_2(g) + e^- \quad \text{Fast discharge and evolution} \qquad (9)$$

The melt is the source of O^{2-}. The dissociation of a complex fluoaluminate ion generates a free oxide ion, which adsorbs on the reactive carbon surface sites (like edges or steps). The adsorbed oxygen ion undergoes discharge in two, single-electron steps to form a C–O–C ("C_2O") bridge between reactive carbon atoms on the exposed carbon surface (Fig. 2A). The second oxygen ion adsorbs right next to the C_2O site to extend the surface species to a C–O–C–O–C ("C_3O_2") bridge (Fig. 2B). This adsorption is kinetically hindered and requires considerable overpotential, and thereby constitutes the rate-determining step. The "C_3O_2" is discharged in two, one-electron steps to form an unstable group, and readily releases CO_2 by cutting of edge C–O bonds.

Cooper et al. suggested that the anodic oxidation of carbon in molten carbonates (basic melts) might follow a similar mechanism to the Hall process with the exception of the oxygen ion formation step [3,5]. Since molten carbonates readily dissociate into CO_2 and O^{2-} at the DCFC operation temperature, Cooper et al. proposed that carbonates decompose at a high temperature to form oxygen ions (Eq. (10)), which initiates the subsequent carbon oxidation reactions as shown in Eqs. (4)–(9).

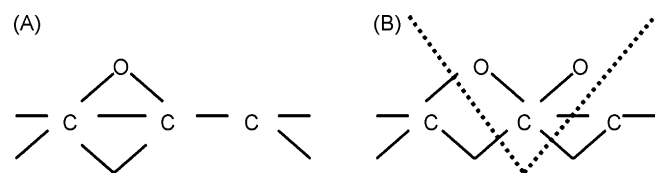$$2CO_3^{2-} \rightarrow 2CO_2 + 2O^{2-} \qquad (10)$$

Fig. 2. Pictorial description of the carbon electrochemical oxidation. (A) the first oxygen ion adsorption and (B) the second oxygen ion adsorption and CO_2 formation [3].

The mechanism for anodic oxidation of carbon in molten hydroxides is unknown at present. Whether the Cooper mechanism works or not for molten hydroxide electrolytes needs experimental verification. This is because in molten hydroxides other oxygen containing ions than O^{2-} exist, such as O_2^{2-}, O_2^{-} and OH^{-}, which may take part in the anode oxidation of carbon [4,5]. The electrooxidation of carbon contacting a solid electrolyte, like Y_2O_3–ZrO_2 (YSZ), might follow the similar process to molten carbonates due to presence of O^{2-}, however this is only this author's hypothesis.

3. DCFC with a molten carbonate electrolyte

Mixed molten carbonates (e.g. Li_2CO_3–K_2CO_3) have been widely used in the MCFC as electrolytes. They are also attractive for DCFC because of their high conductivity, good stability in the presence of CO_2 (the product of carbon electrooxidation), and suitable melting temperature [3,24]. In molten carbonate electrolytes, the anode and cathode reactions might be expressed by Eqs. (11) and (12), respectively. The cell voltage is given by Eq. (13). CO_2 is formed at the anode side and consumed at the cathode side, therefore, its partial pressure has an influence on the cell voltage.

$$C + 2CO_3^{2-} \rightarrow 3CO_2 + 4e^- \tag{11}$$

$$O_2 + 2CO_2 + 4e^- \rightarrow 2CO_3^{2-} \tag{12}$$
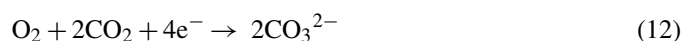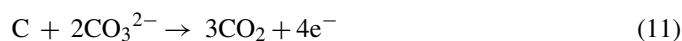
$$E_{cell} = E^\circ - (RT/4F)\ln[CO_2]^3_{anode}$$
$$+ (RT/4F)\ln([O_2][CO_2]^2_{cathode}) \tag{13}$$

Cooper et al. at Lawrence Livemore National Laboratory (LLNL, Livermore, CA) constructed a DCFC with a tilted orientation design (Fig. 3) [6,11,12,31,32]. A 32% Li_2CO_3–68% K_2CO_3 melt was used as the electrolyte. The anode is a paste of carbon particles (<100 μm) in the melt with open-foam nickel
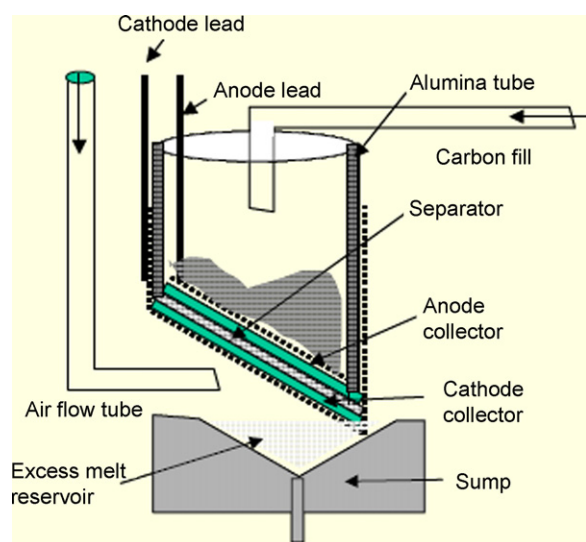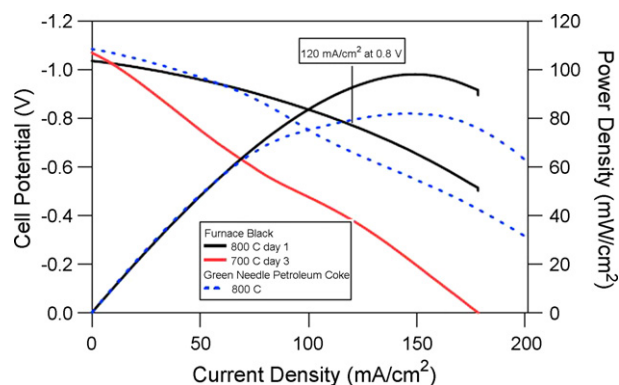
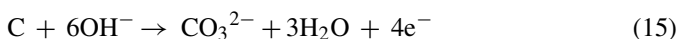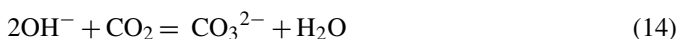Fig. 4. Performance of the LLNL tilted direct carbon fuel cell [11].

as the current collector. The cathode consists of a sintered frit of fine nickel particles (or a compressed foam nickel). Between the anode and the cathode is a separator made of several layers of zirconia felt. The cathode catalyst was activated by thermal treatments in air to form a compact layer of NiO, which was then lithiated by exposing to lithium salts to generate the catalytic active structure. The electrode assembly was positioned at an 5–45° angle from the horizontal. This configuration allowed the excess electrolyte to drain from the cell to avoid flooding of the cathode. Several carbon materials with different crystallinity, particle size, surface area and surface structure were tested at 800 °C. Current densities ranging from 58 to 124 mA cm^{-2} were achieved at a cell voltage of 0.8 V (80% of the standard potential) (Fig. 4) [12]. The tested carbons include coal-derived pitch, calcined petroleum pitch, biological char, furnace and thermal black, and graphite particles. It was concluded that the carbon properties affecting DCFC performance include crystallographic disorder, electrical conductivity and number of surface reactive sites. The influence of impurities in the carbon on DCFC performance was investigated [3]. The presence of sulfur was found to degrade the cell performance probably due to corrosion of the anode current collector Ni, leading to the formation of nickel sulfide and thus diminishing the current collection capability. The effects of ash (inorganic mineral containments) on anode polarization and electrolyte properties were not analyzed. LLNL also developed proprietary cathode catalyst and aerogel/carbon and xerogel/carbon composites anode for their DCFC [33–35]. Hemmes et al. at Delft University of Technology developed a DCFC model based on the LLNL cell design in order to provide a theoretical base for DCFC system [36]. The simulation results indicated the system having a net electrical efficiency of 78%.

4. DCFC with a molten hydroxide electrolyte

The first DCFC successfully demonstrated by William Jacques used molten sodium hydroxide as electrolyte. However, since then for a long time, molten hydroxides have been rejected as the DCFC electrolyte because they react with CO_2 produced by carbon oxidation to form carbonates. In recent years, researchers in Scientific Application & Research Associates

Fig. 3. Schematic of the LLNL tilted direct carbon fuel cell with carbon particle anode [11].

(SARS, Cypress, CA) revived the investigation of DCFC using molten hydroxide as electrolyte [37]. Comparing with molten carbonates, molten hydroxides have a number of advantages in acting as electrolytes, such as a higher ionic conductivity and a higher activity of the carbon electrochemical oxidation, which means a higher carbon oxidation rate and a lower overpotential [4]. So with molten hydroxides as the electrolyte DCFC can be operated at a lower temperature, typically around 600 °C. The low operation temperature allows the use of less expensive materials for DCFC fabrication and thus brings down the DCFC costs. Besides, the dominant product of carbon oxidation at low temperature (i.e. <700 °C) will be CO_2 according to the Boudouard equilibrium. Thus, CO formation can be avoided. The above-mentioned benefits can be achieved only after the carbonate formation issue is overcome. As pointed out by Goret and Tremillon [38,39], the formation of carbonates during carbon electrooxidation in molten hydroxides may undergo a chemical process (Eq. (14)) and an electrochemical process (Eq. (15)). The electrochemical process consists of two steps: a fast chemical step (Eq. (16)) and a slow electrochemical step (Eq. (17)), which is the rate-determining step.

$$2OH^- + CO_2 = CO_3^{2-} + H_2O \tag{14}$$

$$C + 6OH^- \rightarrow CO_3^{2-} + 3H_2O + 4e^- \tag{15}$$

$$6OH^- = 3O^{2-} + 3H_2O \tag{16}$$

$$C + 3O^{2-} \rightarrow CO_3^{2-} + 4e^- \tag{17}$$

The rate of carbonate formation depends on the concentration of O^{2-} and on water concentration. Consequently, increasing the water content in the hydroxide electrolyte will shift Eqs. (14 and 16) to the left and thus significantly reduce CO_3^{2-}. Taking advantage of Goret et al. results, Zecevic et al. in SARA developed DCFCs with a molten hydroxide electrolyte using humidified air as the oxidant [4,5]. The moisture brought into the electrolyte with the air not only reduces carbonate formation but also increases the ionic conductivity of the melt. SARA's DCFC takes a simple nontraditional fuel cell design that is much like a semi fuel cell [40]. As depicted in Fig. 5, a cylindrical pure graphite rod acts as the anode and fuel, which is immersed into molten sodium hydroxide contained in a cylindrical or prismatic container, serving at the same time as the cathode. Humidified air is fed into the cell from the bottom of the container via a gas distributor. The cell was operated between 400 and 650 °C. Several materials were tested as the cathode, among which, nickel foam lined steel and Fe2Ti steel show good catalytic activity. The cell performance depends on the cathode material, air flow rate, operating temperature and fuel cell scale. The open circuit voltage was between 0.75 and 0.85 V. The average power output achieved was 40 mW cm^{-2} at 140 mA cm^{-2} with over 450 h running time. The peak power output was 180 mW cm^{-2}. The maximum current density obtained was greater than 250 mA cm^{-2} (Fig. 6) [41]. The cell performance can be significantly improved by optimizing the cell design, the electrode material, and the operation condition. Since the cell has no separator to prohibit oxygen from direct contacting with carbon, a mixed potential resulting from oxygen reduction on
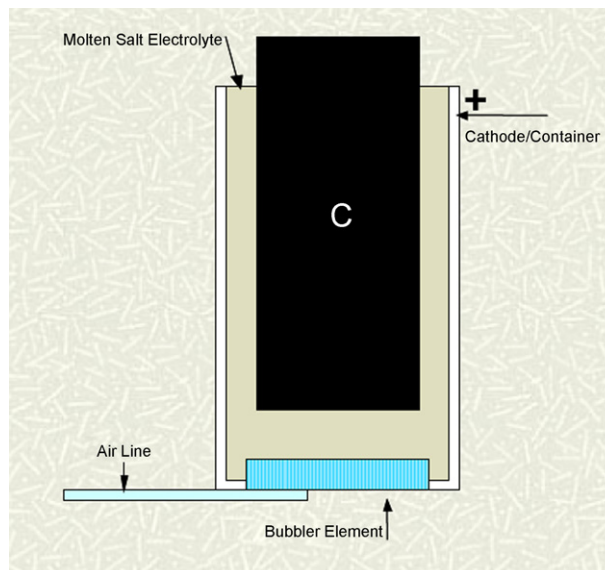

Fig. 5. Schematic of the SARA direct carbon fuel cell with a carbon rod anode [40].

carbon anode might reduce the cell performance. SARA recently proposed a separator containing cell design (patent pending) to address this problem. However, finding a suitable membrane that sustains the harsh molten hydroxide environment (basic, high temperature, corrosive) takes efforts. The stability of normal inorganic metal oxide film in molten hydroxide demands experimental tests. Development of new membranes may be required. In order to verify the effect of carbonate formed in molten NaOH electrolyte during cell operation, Zecevic et al. carried out two experiments, one with pure molten NaOH as electrolyte, the other with a mixture of 82 mol% NaOH and 12 mol% Na_2CO_3 melt as electrolyte [9]. The results indicated that the cell performance in carbonate containing electrolyte was lower, but the rate of cell performance decay was nearly the same as the one in initially pure NaOH. The reduced cell performance was mainly due to the reduced cathode performance. Therefore, it seems carbonate content does not significantly affect the cell deterioration rate within 35 mol% carbonates.
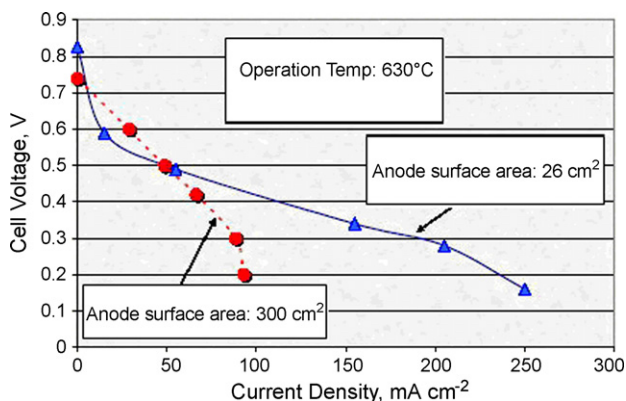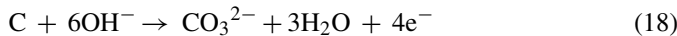

Fig. 6. Performance of the SARA direct carbon fuel cell with different anode area [40].

Saddawi et al. at West Virginia University developed a method to produce solid cylindrical carbon rods for SARA's DCFC [42]. The fuel rods were made with varying amounts of petroleum coke, coal tar binder pitch, and either one or two coal-derived fuels. The chemical composition, density, and electrical resistivity of the resulting carbon rods were analyzed. SARA test results indicated that coal-derived rods perform significantly better than their graphite counterparts due to increased electrochemical activity [9]. Notably, the mechanisms for the electrooxidation of carbon (anode reaction) and the electro-reduction of oxygen (cathode reaction) in molten sodium hydroxide are not well understood at present. The overall electrode reaction may be given by Eqs. (18) and (19) for anode and Eq. (20) for cathode [4].

$$C + 6OH^- \rightarrow CO_3^{2-} + 3H_2O + 4e^- \tag{18}$$

$$C + 2CO_3^{2-} \rightarrow 3CO_2 + 4e^- \tag{19}$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{20}$$

5. DCFC with YSZ-based solid electrolyte

Balachov et al. at SRI International patented an unique DCFC design which combined advances in SOFC and MCFC technology (Fig. 7A) [43,44]. The key component of their DCFC is a U-tube consisting of, from inner to outer of the tube, a
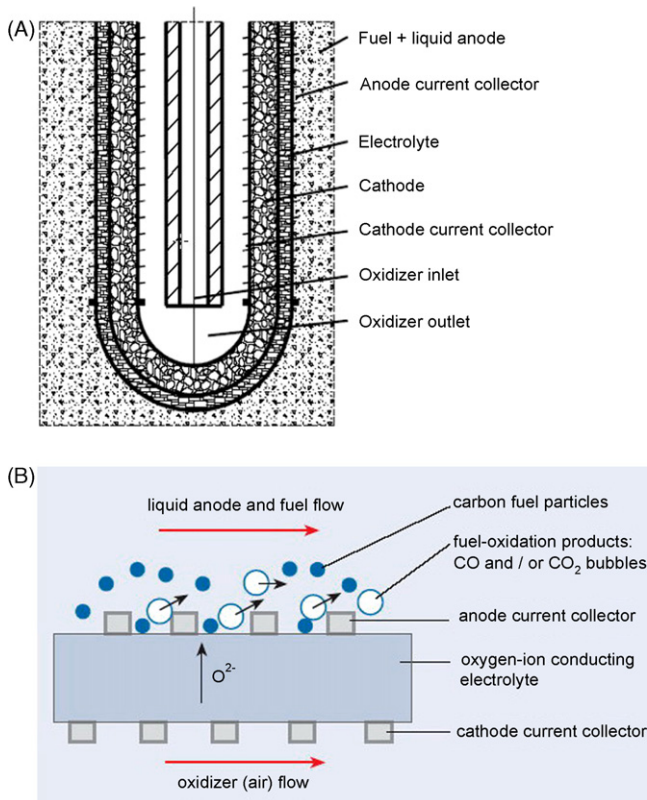

Fig. 7. Schematic of the SRI direct carbon fuel cell combining advances in the SOFC and MCFC technology. (A) cell configuration and (B) flowing liquid anode [43,44].
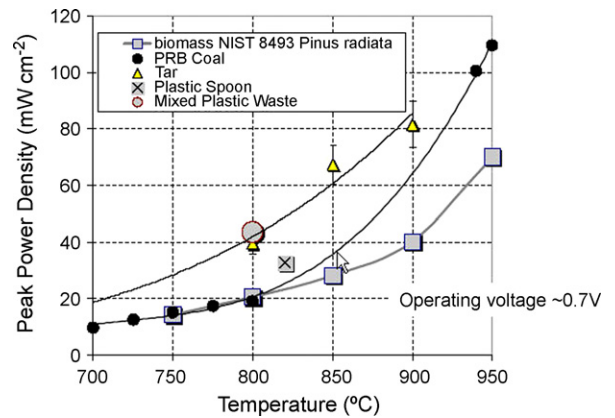

Fig. 8. Performance of the SRI direct carbon fuel cell liquid anode [43].

metal mesh cathode current collector, a cathode layer (e.g. Lanthanum Strontium Managanate, LSM), an electrolyte layer (e.g. YSZ), and a metal mesh anode current collector. The U-tube is immersed into a liquid anode comprising a mixture of molten $Li_2CO_3 + K_2CO_3 + Na_2CO_3$ and carbon particles. The DCFC is better operated in a flow mode (stirring) to facilitate the contact between carbon particles and anode current collector to enhance mass transport (Fig. 7B) [43]. A variety of fuels have been tested, including coal, tar, coke, acetylene black, plastic and mixed waste. Using conventional coal without pretreatment, SRI has achieved power densities greater than $100 \, mW \, cm^{-2}$ at $950°$ (Fig. 8) [43], which is comparable to the power densities achieved by commercial MCFC plants operating on natural gas. A similar study was recently reported by Pointon et al. The cell was used as a high energy density battery for military application [45].

Tao at CellTech Power LLC (Westborough, MA) tested direct oxidation of coal in a SOFC-like structure [46–48]. By using 0.6 mm thick $La_{0.84}Sr_{0.16}MnO_3$ as cathode, 0.12 mm thick $(ZrO_2)(HfO_2)_{0.02}(Y_2O_3)_{0.08}$ as electrolyte, carbon black as anode and Pt as anode current collector, a power output of $10 \, mW \, cm^{-2}$ at $0.248 \, V$ and $50 \, mW \, cm^{-2}$ at $0.507 \, V$ were obtained at 800 and 1002 °C, respectively. Chuang at University of Akron has recently started the investigation of SOFC with solid carbon as fuel [49]. The focus is on the anode catalyst. The preliminary results indicated that with coke as fuel, the open circuit voltage can reach to around 0.8 V at temperature around 700 °C, and a current density of $50 \, mA \, cm^{-2}$ at 0.8 V can be obtained at a cell temperature of 950 °C. The issues for DCFC using solid electrolyte include poor contact between the carbon anode and the electrolyte and the high operation temperature, which may lead to formation of CO due to Boudouard reaction [50]. Duskin and Gür at Clean Coal Energy (CCE, Stanford, CA) recently envisions a DCFC combining SOFC and fluidized-bed technologies (Fig. 9) [51,52], but they do not have an operating system at present. The configuration enables continuous carbon feeding and good contact between carbon fuel and solid electrolyte reducing mass transport limitation.
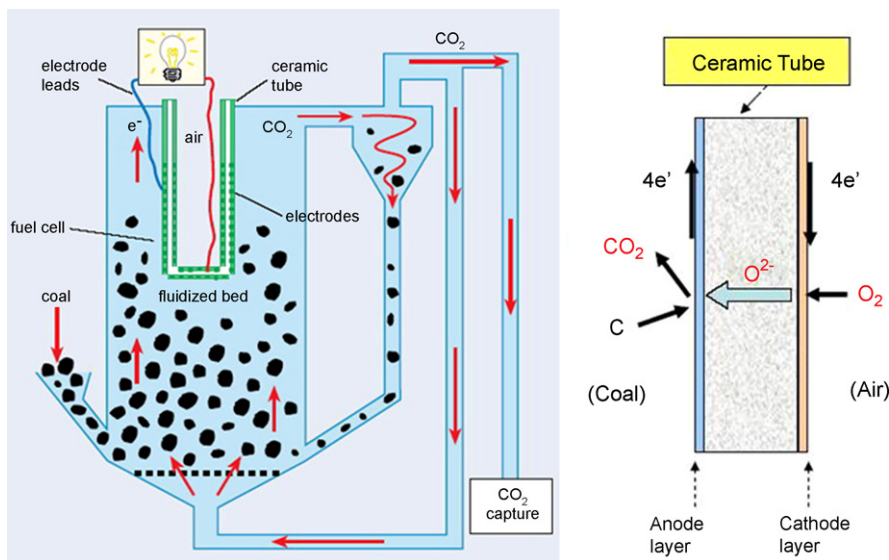
Fig. 9. Schematic of CCE envisioned direct carbon fuel cell combining SOFC and fluidized-bed technologies [52].

6. Conclusions and outlook

Studies in the last few years have demonstrated that direct conversion of solid carbon to electricity in a single, electrochemical step in a fuel cell is feasible. Several DCFCs with different configurations have been successfully tested on the laboratory scale. Efficiencies higher than 80% were shown to be achievable. The payoff for DCFC development is extraordinary considering that the DCFC might operate at about twice the efficiency of conventional steam power plant and more significantly might reduce the emissions of a coal-firing power plant to about one-tenth. Therefore, the DCFC provides a technical option for using coal and other solid carbon-rich fuels in a manner which is more efficient and cleaner.

Since DCFC technology is still at the beginning stage, substantial efforts need to be undertaken to address many serious challenges, both in the fundamental and the engineering aspects. The mechanism of electrochemical oxidation of carbon in various molten salt electrolytes and the dynamic behavior within the carbon-electrolyte double layer region should be further investigated in order to better understand the anodic process at the molecular level [22]. Understanding of the underlying science, e.g. the relationship between the carbon nanostructure and the electrochemical reactivity is required. Such studies will provide useful information for extraction of carbon from coal and for developing anode catalysts if needed. Many inexpensive and readily available carbon fuels, such as coal, coke, biomass and organic garbage (e.g. waste plastics) contain impurities, like sulfur, hydrogen, nitrogen and minerals. The influence of these impurities on the carbon electrooxidation rate, electrolyte, anode current collector and other fuel cell component materials should be examined. Such research is very important for the development of a practical DCFC, and the results will determine to what extent carbon fuels have to be pretreated. Ash accumulation could be a key factor determining the DCFC lifetime. The only literature on the ash effect was reported by Weaver et al. [20]. They claimed that addition of 10 wt% of coal fly ash to molten carbonate electrolyte did not measurably change the carbon polarization curve measured in a half cell system. The separation of ash from the electrolyte and recovery of electrolyte from exhausted melt also deserve research attention. A DCFC allowing continuous feeding of solid carbon without interrupting the cell operation and without explosive release of volatile components demands a smart cell design. Researchers at LLNL have recently proposed a self-feeding cell that can be refueled pneumatically with cleaned coal. Current DCFCs have adopted MCFC or SOFC components, such as, the cathode catalyst and/or electrolyte. The suitability of these components to the DCFC requires further confirmation. New electrocatalysts and molten salts systems might improve DCFC performance.

The scale-up of DCFC will face several real challenges. All the DCFCs tested so far are essentially mono-polar with a small electrode, and their scale-up will lead to a high IR drop and a large unit size. Fuel cells using gaseous fuel, e.g. MCFC and SOFC, adopt compact bipolar stack designs with large electrodes to scale-up for good economics. However, for a DCFC with a solid carbon feedstock, the bipolar configuration seems impossible. Raw coal might not be directly used as the DCFC fuel without cleaning because its impurities will decrease cell performance and shorten the cell life. So the DCFC requires cleaned and processed coal. Cleaning coal will increase the cost of electricity generated by DCFC power plants. Notably, the heat produced by a DCFC may not be enough to maintain the cell temperature. A possible solution to this problem might be the integration of a DCFC with a MCFC or a SOFC. Taking into account all these remaining issues, the DCFC system might be less feasible than other type of fuel cells, e.g. MCFC and SOFC.

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