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Experimental Investigation of a three-layer planar Direct Carbon Fuel Cell using almond shell biochar as fuel

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Résumé:

NiO-Samaria- Doped-Ceria (NiO-SDC) composite powders was synthesized by a traditional mechanical mixing process and tested as anode materials for Direct Carbon Fuel Cell (DCFC) using almond shell biochar as fuel and molten carbonate-doped ceria composite as electrolyte. A three-layer pellet cell, viz. cathode (Lithiated NiO-SDC), composite electrolyte and anode (NiO-SDC) is fabricated by a die-pressing, screen printing and sintering method. In this study, we report an improvement in the cell stability and performance by adding the (NiO-SDC) anode layer to the bi-layer pellet containing only cathode and electrolyte which is prepared and tested in previous work. The peak power density of the cell at 700 °C increases to reach 150 mW cm^{-2} and the stability period is doubled to be around 130 min when testing the bi-layer and the three-layer pellet, respectively. The experimental results indicated that this porous anode material is promising as anode for DCFCs.

Mots clés :
NiO-SDC anode, Direct Carbon Fuel Cell, stability, performance, almond shell biochar

1. Introduction

The integration of a fuel cell system and biomass thermo-chemical conversion process is a very attractive and eco-friendly technique of power generation (Figure 1). The Direct Carbon Fuel Cell (DCFC) is a recently developed technology which allows the conversion of the chemical energy in a solid carbon fuel into electricity directly without a need for a gasification process. So, the overall reaction of the DCFC is given by Eq. (1) in which CO_2 is the only gas released from the anode chamber.

$$C + O_2 \rightarrow CO_2 \qquad \Delta H = -393.5\ \text{KJ mol}^{-1} \text{ at } 298\ \text{K} \qquad (1)$$

A major advantage of a DCFC system is its very high theoretical and practical efficiency. This system has thermodynamic advantages in high temperature regions because the feedstock is solid and the products are gaseous. This means that the entropy change is near zero, and the theoretical efficiency of a DCFC system ($\Delta G/\Delta H$) approaches 100%.

Ordinary DCFC system operates at very high temperatures, in the range of 800-900 °C in order to generate high power output. It uses a variety of electrolytes such as molten carbonate [1, 2, 3], molten hydroxide [4], solid oxide (YSZ) [5, 6]. The most developed DCFC system is based on molten carbonate electrolyte [7]. Recently, a hybrid electrolyte based ceria-salt composite electrolyte type combining both molten carbonate and solid oxide features have been developed. The introduction of different inorganic salts could effectively suppress electronic conduction of the Somarium-Doped-Ceria (SDC) solid phase and ameliorate the material ionic conductivity and stability, thus leads to excellent performance at intermediate temperatures (400 °C-700 °C) [8, 9, 10].

The solid carbon can be derived from natural gas, petroleum, biomass and coal [1]. In a practical system, the gasification process (Boudouard reaction Eq. (2)) progresses along with the electrochemical reactions with direct carbon (Eq. (3) and Eq. (4)) and carbon monoxide (Eq. (5) and Eq. (6)) by simultaneously generating carbon dioxide, as described in the above reactions. The electrochemical reactions that take place at the three-phase boundary at the surface of the anode and the carbon particle are summarized as follows [11]:

Boudouard reaction: $C + CO_2 \rightarrow 2\,CO$ (2)

Anode half reaction: $C + 2\,O^{2-} \rightarrow CO_2 + 4\,e^-$ (3)

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

$CO + O^{2-} \rightarrow CO_2 + 2\,e^-$ (5)

$CO + CO_3^{2-} \rightarrow 2\,CO_2 + 2\,e^-$ (6)

Furthermore, the performance and specific reactions of the system are affected by various parameters such as fuel type, electrolyte components, and operating temperature. Many researchers have investigated the effects of these parameters in order to better investigate these complicated DCFC system processes.

In this work, almond shell biochar produced by a carbonization process is used as fuel in the DCFC based SDC-carbonate electrolyte (Figure 1) [12]. The biomass carbonization is a thermo-chemical conversion process that involves the conversion of biomass by heating in inert atmosphere to biochars, tars and to synthesis gas or syngas (essentially CO, H_2 and light hydrocarbons).

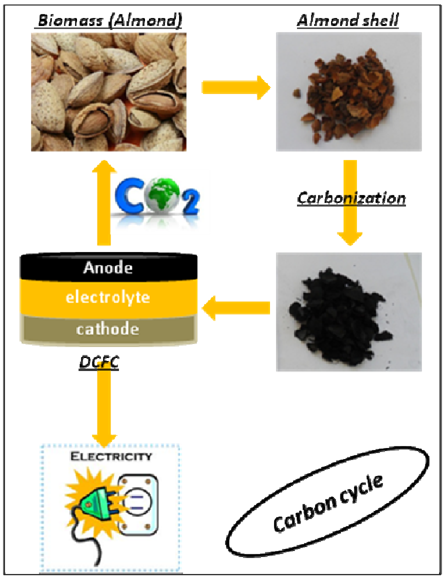

Figure 1: A clean and efficient integrated energy conversion system using almond shell biomass as fuel.

This work focuses on the electrochemical oxidation performance of the almond shell biochar in a three-layer planar DCFC system.

2. Experimental

2.1. Material preparation

SDC powder with a composition $Ce_{0.8}Sm_{0.2}O_{1.9}$ was prepared by an oxalate-co-precipitation method [10, 11, 12]. A binary carbonate eutectic powder of Li_2CO_3 and Na_2CO_3 with a mol ratio of 2:1was prepared by ball milling for 4 hours and heated at 700 °C in air for 1 hour.

SDC powder and the eutectic salt were mixed with a weight ratio of 7:3 and sintered at 700 °C in air for 1 hour to form a composite electrolyte. A mixture of LiOH and NiO with a mol ratio of 1:1 was sintered at 700 °C in air for 2 hours to prepare lithiated NiO.

The cathode material was prepared by using a mixture of lithiated NiO and the composite electrolyte with a weight ratio of 7:3 heated at 700 °C in air for 2 hours. A mixture of SDC and NiO with a weight ratio of 4:6 was sintered at 700 °C in air for 2 hours to prepare the anode material.

2.2. Three-layer pellet preparation

In this study, a three-layer single cell was prepared according to the electrolyte-supported cell structure. First, a bi-layer cell pellet was prepared same as what we use in our previous work [11]. It was manufactured by a co-pressing and sintering technique, which contained a composite electrolyte layer and a composite cathode layer (Figure 2(a)).

The anode material was prepared as slurry using a binder (10% ethyl cellulose + 90% terpineol). Then, the anode slurry was coated onto the composite electrolyte part of the bi-layer cell pellet followed by firing at 700 °C in air for 1 hour to form the three-layer cell pellet (Figure 2(b)). Silver paste was then coated on both sides of the pellet and used as the current collectors. The anode fuel was a mixture of almond shell biochar and the eutectic salt in 1:9 wt%, which was put in the anode side on the top side of the planar cell pellet during the *i-V* curve analysis.

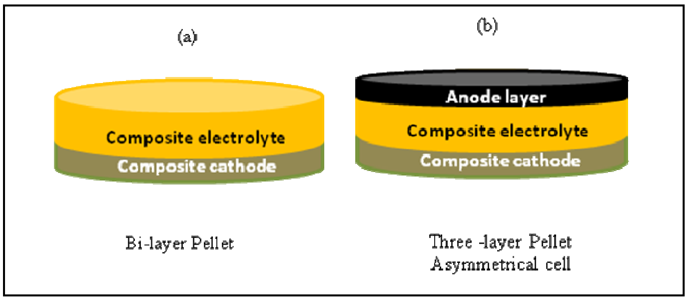

Figure 2: Schematic drawing of: (a) bi-layer cell; (b) three-layer cell configurations.

2.3. Fuel cell electrochemical analysis

Fuel cell performance tests were carried out using the same cell configuration as developed in [11]. Measurement of the fuel cell electrochemical parameters was carried out using a VersaSTAT 3 electrochemical System with Versa Studio software for automatic data collection. All electrochemical tests were started once a steady state OCV had been achieved at each temperature ranging from 600 °C to 750 °C.
Moreover, during all the heating process, the open circuit potential of the DCFC was recorded using a Potentiostat (Shanghai Electric) for a durability test analysis. A constant flow rate of inert gas (N_2, 100 ml min^{-1}) was purged into the anode compartment inlet and a constant mixture of O_2 (60 ml min^{-1}) and CO_2 (120 ml min^{-1}) was purged into the cathode compartment inlet.

3. Results and discussion

For comparative purpose with previous work of the electrochemical behavior of the DCFC system after the design modification by the additional NiO-SDC anode layer, the analysis of the effect of temperature on the three-layer planar DCFC system is investigated. High performance is achieved although some difference is depicted in the *i-V* curve's profiles (Figure 3).

The three-layer pellet performance indicates a noticeable difference in the electrochemical behavior not previously shown in the bi-layer DCFC system [12]. A very high OCV (1.12 and 1.15 V) is reached respectively at 650 and 700 °C. Some chemical reactions inside the surface functional groups of the biochar are catalyzed by nickel and are those responsible of this increase in the cell performance. Indeed, nickel is assumed to act as a catalyst in the Three Phase Boundary (TPB) of the DCFC anode region. It can enhance also the specific rate of the reverse Boudouard reaction (Eq. (2)) in the carbon/carbonate fuel slurry [13]. Carbon reaching the TPBs reacts with both oxide ions conducted in the SDC phase and carbonate ions conducted in the carbonate phase while released electrons conducted through the carbon and the nickel particles to the external circuit. So, a good electronic conductivity of the carbon is noticed ensuring a high power output of about 150 mW cm^{-2} at 700 °C.

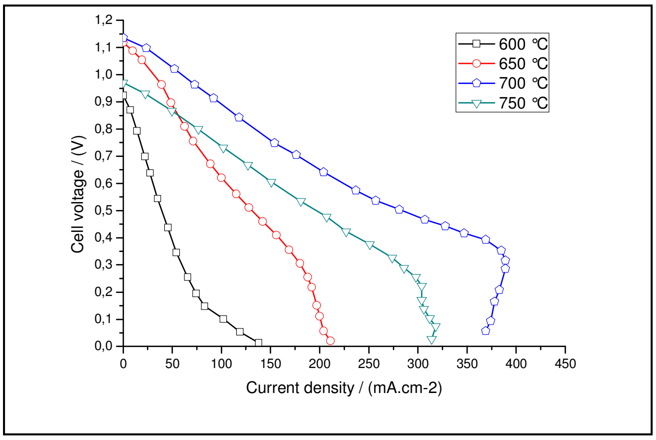

Figure 3: Temperature effect on the *i-V* curves of a three-layer pellet DCFC system.

A clear concentration polarization limitation is considered in the *i-V* curves which are caused by a concentration gradient appeared at high current density due to this additional NiO-SDC anode layer creating some mass transfer resistance. So at high current density, the fuel is may be consumed faster than it is supplied to the electrode reaction site by the catalysis effect of nickel on the carbon slurry, which is known as a transport limitation. This limitation may be also a result of the higher formation rate of the CO_2 bubbles (640 µm min^{-1} at 700 °C and OCV) that may causes a barrier for the carbon particles to reach the TPBs and to undergo the anodic electrochemical process. The formation rate of CO_2 is proportional to the power output delivered by the cell. So, the higher the electrochemical performance is the higher the CO_2 content in the anode side.

It is obvious that increasing the cell temperature lifts the OCV to higher values for the *i-V* curves recorded at 600 °C, 650 °C and 700 °C. This observation is sustained by the theoretical work of Hemmes et al. [14] who derived the anode potential versus standard cathode potential as a function of temperature. At 750 °C, a sharp decrease in the OCV (0.98 V) is noted. In addition, at 750 °C, the curve is bending back which leads to undefined cell voltage at a given current density especially at higher current density from 365 mA cm^{-2} to 390 mA cm^{-2}. This unexpected profile leads to undefined cell voltage at a given current density. This problem may be a result of a time limiting effect or an aging of the DCFC pellet where performance decreases during the *i-V* curve records. So, it is related to the instability of the three-layer pellet DCFC dependently of cell operation period.

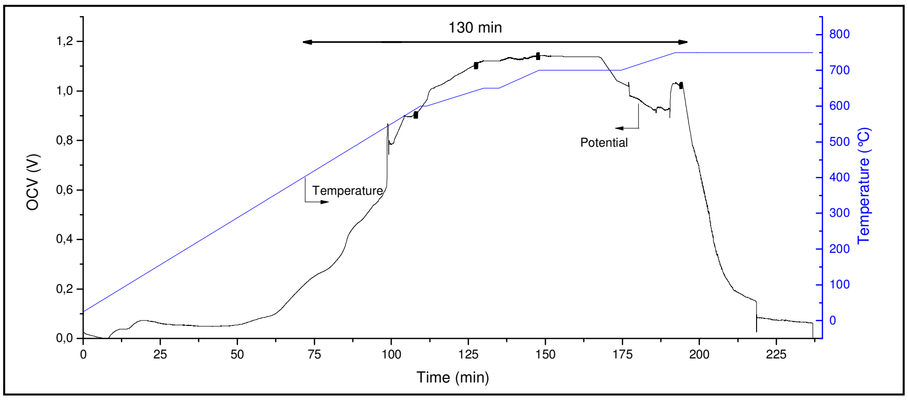

Figure 4: OCV vs. time of a three-layer DCFC lab-scale system.

According to the experimental tests, the durability of the three-layer DCFC system demonstrates an enhanced and stable performance of the fuel cell based on SDC-carbonate composite electrolyte with 60/40 wt% NiO-SDC anode layer. The stability test shows a stable duration life of around 130 min as shown in Figure 4. At 500 °C (melting temperature), the OCV starts to increase reaching almost 0.9 V at 600 °C. Despite the *i-V* curve analysis at 600 °C that starts at stable state of OCV for a period, the potential remains increasing with the rise in temperature. At 650 °C and 700 °C, the OCV is very high reaching about 1.15 V even compared to the theoretical value (1.02 V). This is may be due to the catalytic effect of the NiO-SDC anode layer on the fuel performance. The nickel particles in the anodic Three Phase Boundaries (TPBs) act as active sites for the carbon oxidation, while the SDC particles serve as mechanical support for nickel. So, the distribution between Ni and SDC particles are of great importance for improving the DCFC system.

At 750 °C, the potential shows a surge from 0.9 V to 1.01 V although we are expecting a decrease because of the over consumption of the fuel slurry. We suggest that this sudden potential rise may be a result of the high formation rate of the CO gas at this high temperature. Indeed, the CO gas is produced via electrochemical reactions of carbon oxidation in both carbonate and SDC phases as given by Eq. (7) and (8) that could possibly take place at the anode side of the DCFC [14, 11].

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

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

The CO may have also two chemical origins; firstly through the Boudouard reaction (Eq. (2)) that may take place between carbon and carbon dioxide at high temperature [15-19] and secondly through a possible chemical reaction that may occurs between carbon and carbonate when it melts (Eq. (9)) [20].

$$CO_3^{2-} + C \rightarrow 2\,CO + O^{2-} \qquad (9)$$

The increase in the produced CO partial pressure leads also to this increase in the OCV according to the theoretical expression of the C/CO DCFC potential evaluated by Hemmes et al. [14]:

$$E_{DCFC} = 0.575 + (4.30866\ 10^{-5}.\ \ln(1/(P_{CO}.P_{CO2})) + 4.638\ 10^{-4}).T \qquad (10)$$

After the three-layer DCFC system experiments, an enhancement in the three-layer pellet state is considered. All the DCFC parts are distinguished. The carbonate doesn't deteriorate the cathode. The additional NiO-SDC anode layer has demonstrated the ability of holding the molten carbonate from the carbon fuel slurry inside its porous structure due to change in its wetting ability. In fact, the three-layer cell seems to rely on a balance in capillary pressures in order to establish the electrolyte interfacial boundaries in the porous electrodes [21]. This capillary balance seems to be ensured by a properly coordination between pore diameters in the NiO-SDC anode and Lithiated NiO-SDC cathode with those of the composite electrolyte having the smallest pores. So, by using this additional anode layer the three-layer cell leads to a well established electrolyte distribution permitting the electrolyte to be completely filled with molten salts and the porous anode and cathode to be partially filled depending on their pore size distribution. Thus, we can notice that the transport of carbonate could be impeded and controlled by the changes in the wetting ability through the porous DCFC components.

The reaction distribution could explain also the rising in electrical performance observed during the three-layer pellet analysis as the anode electrochemical reaction occurs on the three phase boundary (TPB) containing both Ni and SDC. At the TPB, the anode oxidation reaction yields CO_2 gas which can impede the carbonate transport. Mizusaki et al. [22] demonstrated that the length of the TPB in the NiO-SDC anode is related to the Ni content, grain size and phase distribution of Ni and SDC. In fact, an optimized anode microstructure could be the cause of this enhancement in performance and lifetime. Yu et al. [23] analyzed the XRD patterns of the NiO-SDC anode prepared using the same technique adopted in the present study. The pattern consists of SDC and NiO two crystal phases without any other crystal phased. This indicates that the NiO-SDC composite powders have been successfully synthesized to ensure an optimized anode structure.

Another noticed contribution of the NiO-SDC anode layer is also explained by incorporating an electrolyte-filled barrier layer i.e., a bubble pressure barrier as an integral part of the anode structure [24-26]. This bubble pressure barrier prevents leakage of CO_2 produced gases from the anode into the composite cathode while allowing the flooding of the electrolyte with molten salt. Furthermore, the pore size of the bubble barrier seems to be sized significantly smaller than the pore of the anode and sized also to fill the electrolyte.

The added value of the NiO-SDC ande layer was explained by some physical properties including change in wetting ability, pore size, froming product gas barrier… In fact, experimental measurements of the above properties could brought forth to explain the lowered rate of carbonate transport through the three-layer DCFC pellet.

As a perspective, the effect of time on the OCV should be carried out at constant temperature in order to determine the effective stability of the DCFC. In addition, the effect of carbon loading to the durability test at fixed temperature may have an influence on the DCFC performance.

Conclusion

NiO-SDC layer has been demonstrated a compatible and stable anode for Direct Carbon Fuel Cell based on molten carbonate- doped ceria composite electrolyte. An improvement in the three-layer DCFC performance reaching almost 1.15 V at 700°C was observed. The power output was also increased to 150 mW cm^{-2} at a current density of 350 mA cm^{-2} and a temperature of 700 °C. Amelioration in the three-layer DCFC system stability was noted to be around 130 min when using 0.3 g slurry of biochar/ molten carbonate as fuel although further investigation is needed for longer term stability. Some physical properties including change in wetting ability, pore size, reaction distribution, gas product barrier could possibly explain the added value made by the NiO- SDC anode layer.

Nomenclature

Symbole	
T	Temperature, *K*
OCV	Open circuit voltage, *V*
i	Current density, mA cm^{-2}
V	Cell voltage, V

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