Research on the Discharge Properties of the Direct Carbon Fuel Cell with a Molten Metal Anode

Y B Zhao¹,², T L Xiao¹,² and D Ding¹,²

¹ Shanghai Institute of Measurement and Testing Technology, 1500 Zhangheng Road, Shanghai 201203, China
² Shanghai Key laboratory of Online Test and Control Technology, 1500 Zhangheng Road, Shanghai 201203, China

E-mail: zhaoyibo@163.com

Abstract. In order to research the discharge properties of the direct carbon fuel cell (DCFC) with a molten metal anode, the experimental system with a reactor is designed and constructed. The reaction mechanisms at both anode and cathode are analyzed. The molten Sn and Sb are used as the anodic material for comparison. The cell performance of DCFC is tested before and after discharging in the battery mode and the carbon fuel mode, respectively. In the battery mode, due to the different states of metallic oxides, the current density is not degraded after discharging with the molten Sb anode, but sharply decreases with the molten Sn anode. On the contrary, the cell performance with Sb is much worse than that with Sn after discharging in the carbon fuel mode, which is result from the volatility of Sb together with the reduction of its oxide. The above studies will help to thoroughly understand the underlying mechanism of DCFC with a molten metal anode.

1. Introduction

As one type of the fuel cell, the direct carbon fuel cell (DCFC) can convert the chemical energy in carbon fuels directly and continuously into electrical energy. Similar to other fuel cells, the DCFC is composed of an anode, a cathode, an electrolyte membrane and a current collector. The main difference is that the solid carbon is used as the fuel. Therefore, it has several remarkable advantages including the high efficiency, the light weight and the rich fuel sources [1]–[3].

In order to improve the cell performance, the molten metal is chosen as the anode material instead of the porous solid in the experiment. The most advantage is that the molten metal, as an energy storage medium, can be operated for a short period of time without fuels, which can be called the battery mode. Therefore, the effect of discontinuous solid fuel delivery on the stability of the cell performance can be minimized.

Several kinds of molten metal can be used as the anode materials, including Sn, Sb, Cu, In, Pb and so on. According to the study [4], the cell performance using molten In and Pb anodes suffered significant deterioration due to the solid metallic oxide film produced on the electrolyte surface when the reaction temperature was between 973 K and 1173 K. In addition, the direct electrochemical conversion of carbon fuel cannot be realized at the reaction temperature of 1373 K when the molten Cu was used as the anode material. As a result, molten Sn and Sb are selected as two suitable anode materials.

In this paper, an experimental system of the DCFC with molten Sn and Sb anodes is established, and the discharge properties, intuitively reflecting the cell performance, are tested and compared.
2. Reaction mechanisms

When the DCFC is working, both the fuels and oxidants should be continuously added into the cell, while the reaction products are discharged out of the instrument. Figure 1 shows the reaction mechanism of the DCFC with a molten metal anode, where M represents the molten metal.

The anodic reactions are very complex. Firstly, the conventional electrochemical chain reactions are given by [5]–[6]

\[
\begin{align*}
M(l) + O^{2-} &\rightarrow MO_x + e^- \\
C(s) + MO_x &\rightarrow M(l) + CO_2(g) \\
C(s) + CO_2(g) &\rightarrow 2CO(g) \\
CO(g) + MO_x &\rightarrow M(l) + CO_2(g)
\end{align*}
\]

Therefore, the overall reaction in the anode is given by

\[
C(s) + 2O^{2-} \rightarrow CO_2(g) + 4e^- \tag{5}
\]

Secondly, the carbon oxidation reaction may happen in the anode due to the relatively high oxygen solubility in molten Sn and Sb. Moreover, the molten metal can conduct O\(^{2-}\), and its oxygen ion conductivity is even better than YSZ solid electrolyte at the same temperature. A three-phase interface may be formed between the molten metal, the metallic oxide and the carbon fuel, and the reactive area may be extended. Therefore, the direct electrochemical oxidation of carbon and O\(^{2-}\) in the molten metal anode is entirely possible. All of three possible anodic reactions vie with each other.

The overall cathodic reaction is given by

\[
O_2(g) + 4e^- \rightarrow 2O^{2-} \tag{6}
\]

When the supply of carbon fuel is insufficient, the DCFC will change to a short-lived battery mode, in which the anode only undergoes the oxidation of molten metal:

\[
M(l) + O^{2-} \rightarrow MO_x + e^- \tag{7}
\]

At this time, it is possible to temporarily provide short-term electric energy, but the molten metal is always oxidized, and the battery performance is getting much worse. Therefore, the best way is to charge the fuel cell, that is, continue to pass reducing gases such as H\(_2\) and CO into the anode. At this point the anode will react as follows:

\[
\begin{align*}
H_2(l) + MO_x &\rightarrow M(l) + H_2O(g) \\
CO(g) + MO_x &\rightarrow M(l) + CO_2(g)
\end{align*} \tag{8, 9}
\]

As a result, the fuel cell performance can be recovered by using the reducing gases to reduce metal oxides.
3. Experimental setup

Figure 2 shows the experimental system of the DCFC with molten metal anode. After passing the cut-off valve, the pressure reducing valve, the mass flowmeter and the check valve, the anodic and cathodic gases are added into the reactor through two isolated pipes. The reactor is placed inside the heating furnace, which can adjust the reaction temperature from 100 °C to 1000 °C. The carbon fuels are also added through the anodic inlet. The YSZ single crystal cell is employed as the electrolyte. The current-collecting device in the reactor is connected to the electrochemical workstation, which can test the cell performance, including the electrochemical impedance spectra (EIS), the voltage-current curve (VI) and the constant voltage discharging curve.

![Figure 2. Experimental system of the DCFC](image)

Table 1 gives the detailed operating parameters in different cases in the experiment. The anodic and cathodic gases are 50 mL/min of Ar and 200 mL/min of air, respectively. In the battery mode, the reaction temperature is set at 800 °C, and no carbon fuel is added in the reactor. In the carbon fuel mode, the added carbon fuel is 0.2 g, and the temperature is increased to 900 °C. The EIS and IV curves of DCFC are tested before and after each discharging process.

**Table 1. The operating parameters in the experiment**

| Case number | Temperature (°C) | Metal (g) | Carbon (g) | Testing time | Reaction mode |
|-------------|------------------|-----------|------------|--------------|---------------|
| 1           | 800              | Sn/2.0    | 0          | Before discharging | Battery mode |
| 2           | 800              | Sn/2.0    | 0          | After discharging | Battery mode |
| 3           | 800              | Sb/2.0    | 0          | Before discharging | Battery mode |
| 4           | 800              | Sb/2.0    | 0          | After discharging | Battery mode |
| 5           | 900              | Sn/2.0    | 0.2        | Before discharging | Carbon fuel mode |
| 6           | 900              | Sn/2.0    | 0.2        | After discharging | Carbon fuel mode |
| 7           | 900              | Sb/2.0    | 0.2        | Before discharging | Carbon fuel mode |
| 8           | 900              | Sb/2.0    | 0.2        | After discharging | Carbon fuel mode |

4. Results and discussions

4.1. Battery mode
Cases 1–4 represent that the DCFC with a molten Sn or Sb anode operates in the battery mode, in which there is no carbon fuel in the reactor. Two discharges with 0.3 V of constant voltage are carried, and its interval time is 90 min.

Figure 3 shows the constant voltage discharging curve of the DCFC. It can be observed that, the cell performance is not degraded when the molten metal is antimony. Furthermore, the current density gradually rises during the second long-time discharges, which indicates that the volatilization of antimony is not serious at a reaction temperature of 800 °C, and the conduction and diffusion of oxygen ions will not be hindered due to the liquid antimony trioxide, thereby maintaining a sustained high level of performance. On the contrary, there is a significant attenuation in the current density when the molten Sn anode is employed. The main reason is that SnO₂ is a solid at 800 °C, which hinders the transport of O²⁻.

**Figure 3.** The constant voltage discharging curve of the DCFC in the battery mode

The EIS and IV curves can also prove the above analyses, as shown in figure 4. It is worth noting that a bending occurs after discharging in the IV curve when the molten metal is Sn. However, it does not occur in the experiment with a molten Sb anode. It can be supposed that the bending represents the accumulation of metallic oxide. As the discharge deepens, the solid SnO₂ gradually increases with the decrease of Sn, and thus raising the ohmic and anodic resistances.

**Figure 4.** The cell performance of the DCFC in the battery mode, (a) IV curve (b) EIS curve
4.2. Carbon fuel mode
Cases 5–8 represent the carbon fuel mode of the DCFC, in which 0.2 g of carbon fuel is added in the reactor. The DCFC discharges only once with a constant voltage of 0.3 V. Figure 5 shows the constant voltage discharging curve of DCFC in the carbon fuel mode. Surprisingly, the current density with the molten Sb anode is stable at only about 40 A/m², which is much worse than that with the molten Sn anode. The most reason is that 900 ℃ has not reached the suitable reaction temperature for reduction of Sb₂O₃ by carbon black.

Figure 6 shows the EIS and IV curves of the DCFC in the carbon fuel mode. As discussed above, the cell performance with the molten Sb anode is much worse than that with the molten Sn anode. However, there is almost no change in performance before and after discharging, and the impedance is basically the same, which indicates that the DCFC with the molten Sb anode can maintain a stable output in the carbon fuel mode. Because the volatility of Sb at 900 ℃ is very strong, it is very likely that the available Sb is too less after a period of time. At this time, the direct electrochemical reaction of carbon fuel may compensate for part of losses from the electrochemical chain reaction.

Figure 5. The constant voltage discharging curve of the DCFC in the carbon fuel mode

Figure 6. The cell performance of the DCFC in the carbon fuel mode, (a) IV curve (b) EIS curve

5. Conclusions
This paper investigates the discharge properties of the DCFC with a molten Sn or Sb anode. Both the anodic and cathodic reaction mechanisms are analyzed. The experimental system with a reactor is designed and constructed. The YSZ single crystal cell is used as the electrolyte. The DCFC operates in the battery mode and the carbon fuel mode, respectively.
The cell performance including the constant voltage discharging, EIS and IV curves is tested before and after discharging. In the battery mode, the cell performance is not degraded with the molten Sb anode, but there is a significant attenuation in the current density with the molten Sn anode. The most reason is that Sb₂O₃ and SnO₂ are liquid and solid at the reaction of 800 ℃, respectively. On the contrary, the cell performance with the molten Sb anode is much worse than that with the molten Sn anode in the carbon fuel mode. The possible reason is that 900 ℃ is not the suitable reaction temperature for Sb₂O₃ reduction, and the volatility of Sb at 900 ℃ is too strong. The corresponding optimization will be conducted in the future.

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