Investigation of the anode reactions in SO-DCFCs fueled by Sn–C mixture fuels

Kai Xu, Zehua Li, Mengya Shi, Haoxuan Xing, Huan Liu, Xian Li, Hongyun Hu, Guangqian Luo, Hong Yao*

State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan 430074, China

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Abstract

Direct carbon fuel cells based on solid oxide electrolyte (SO-DCFCs) suffer from the poor contact between the anode surface and the carbon particles. By mixing the carbon fuel with Sn, the contact can be enhanced due to the fluidity of liquid Sn at the high operation temperature. However, Sn is an active fuel and can be oxidized electrochemically. In this study, the effect of Sn on the performance of SO-DCFCs was investigated. Four carbon fuels, including a graphite (GC), an anthracite coal (PYQ), a lignite (PCF) and an activated carbon (PAC), were mixed with Sn powder respectively and used as anode fuels. The electrochemical performances, including the polarization performance and the long-term durability, were measured at 1023–1123 K in Sn-only, Sn–C mixture and C-only mode. The morphology and elemental composition of the anodes were analyzed by SEM–EDX after the durability tests. The results show that pure Sn fueled cell degraded rapidly due to the accumulation of SnO2 in the anode. Sn–GC, Sn–PYQ and Sn–PCF displayed similar open circuit voltages (OCVs) and maximum power densities (MPDs) with pure Sn. For Sn–PAC, the OCV was as high as 1.0 V and the MPD (150.8 mW/cm2) was much higher than the other Sn–C mixtures. The SEM–EDX results show that SnO2 accumulation on the anode surface was the key factor affecting the cell performance. For Sn–GC, Sn–PYQ and Sn–PCF fueled cells, SnO2 reduction rate was lower than the electro-oxidation rate of Sn, leading to SnO2 accumulation on the anode surface. The cell performance was mainly governed by electro-oxidation of Sn. While for Sn–PAC fueled cell, PAC reduced SnO2 much faster than the other fuels and no SnO2 was detected in the anode pores due to its high BET surface area. The main anode reactions were CO electro-oxidation and C-CO2 gasification.

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1. Introduction

Direct carbon fuel cells (DCFCs) based on solid oxide electrolyte (SO-DCFCs) are a promising technology which can utilize the solid carbon
fueled directly to generate power. At the operating temperature range (973–1273 K), solid carbon fuels can be oxidized directly through the electrochemical reactions in SO-DCFCs. There are two significant advantages of SO-DCFCs, namely the high theoretical efficiency and low pollutant emissions [1,2]. As a novel technology, SO-DCFCs are expected to utilize the solid carbon fuels in a more efficient and environmental friendly way. The ideal operation process of SO-DCFCs is that the electricity is all produced by the direct electro-oxidation of carbon (Reaction (1) ) and the exit stream is high pure CO₂ at the operation temperature range of 973–1273 K. However, during actual fuel cell operation, CO is inevitably situ formed via the Boudouard reaction (Reaction (2) ) and then electrochemically oxidized to CO₂ (Reaction (3) ) [3]. Many investigations have been conducted to reveal the anode reaction mechanism and clarify the contribution of C and CO to the cell performance [4–11]. It is widely acknowledged that the direct carbon electro-oxidation is limited by the poor contact between the carbon particles and the anode.  

\[ C + 2O^2– = CO_2 + 4e^- \]  

\[ CO_2 + C = 2CO \]  

\[ CO + O^2– = CO_2 + 2e^- \]  

Liquid tin anode SOFCs (LTA-SOFC) have been demonstrated feasibly with various fuels, including gas fuels, liquid and solid carbonaceous fuels [12–15]. At the cell operation temperature, the liquid Sn improves the mass transformation of carbon particles and may favor the direct electrochemical oxidation of carbon [16]. Also, Sn was reported to have a catalytic effect on the Boudouard reaction [17,18], contributing to higher CO concentration in the anode. However, the liquid Sn itself can be electro-oxidized to SnO₂ (Reaction (4) ). The produced SnO₂ is reduced to metallic Sn by carbon via the carbothermal reduction (Reaction (5) ). Some efforts have been focused on the liquid metal anode reaction mechanism in carbon fueled LTA-SOFCs. Wang et al. [19] compared the electrochemical performance of LTA-SOFC in battery mode and CO/H₂/C mode. It was found that the cell performance was governed mainly by Sn electro-oxidation in the carbon fuel mode. The produced SnO₂ layer was accumulated at the interface between anode and electrolyte. Ju et al. [20] investigated the role of Sn in a DCFC with Ni/YSZ anode and reported that liquid Sn facilitated the contact between carbon fuels and the anode and promoted the electrochemical oxidation of C and/or CO. Khurana et al. [21] conducted a similar study and pointed out that the OCV was governed by both Sn and C oxidation under Sn–C mode. The cell degradation was mainly caused by the formed SnO₂ layer. In the literatures reviewed above, the role of Sn in SO-DCFCs was controversial.  

\[ Sn + 2O^2– = SnO₂ + 4e^- \]  

\[ SnO₂ + C = Sn + CO₂ \]  

The effect of Sn on the anode reactions is important for the conversion of carbon in SO-DCFCs. Greater understanding of the electrochemical reactions, the effect of carbon fuel properties and the degradation cause in Sn–C fueled SOFCs is needed to improve the cell performance. In this study, we aim to investigate the roles of carbon and Sn respectively in Ni/YSZ anode supported SOFCs fueled by Sn–C fuels. The electrochemical performances of four types of carbon fuels were measured at 1023–1123 K and compared to determine the effect of fuel properties on the anode reactions. The polarization performance was tested to clarify the anode reactions and the long-term durability was tested to investigate the cell degradation.

2. Experimental  

2.1. Properties of carbon fuels  

Four thermal pretreated carbon fuels, including a 325-mesh graphite (GC), an anthracite coal (PYQ), a lignite (PCF) and an activated carbon (PAC) were used as carbon fuels in SO-DCFCs. The particle diameter range was 74–106 μm for PYQ and PCF and 200–300 μm for PAC. Proximate analysis of the coal fuels was performed. N₂ isothermal adsorption experiments were conducted to analyze the pore structure. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method.  

The temperature-programmed reduction experiments were carried out to investigate the carbothermal reduction of SnO₂ in a fixed bed reactor. The carbon particles (0.3 g) were mixed with SnO₂ powder (4.0 g) mechanically in a mortar. The mixture was loaded in a ceramic boat. The temperature was increased from 298 to 1123 K at a heating rate of 5 K/min and then maintained at 1123 K for 5 h. During the process, 150 mL/min Ar was used as the carrier gas and CO₂/CO concentration in the outlet gas was monitored continuously by a gas analyzer.

2.2. Apparatus for electrochemical measurements  

A schematic of experimental DCFC system is shown in Fig. 1. The Ni/YSZ anode-supported button SOFCs are composed of a 400 μm Ni/Yttria-stabilized zirconia (Ni/YSZ) anode layer, a YSZ electrolyte layer, a GDC diffusion barrier layer and a LSCF/GDC cathode layer. The diameter of the anode is 20 mm and the active reaction area corresponding to the cathode is 0.785 cm². The cell anode was mounted onto the end of a vertical ceramic
tube by silver paste. Silver wires were served as current collectors. The ceramic tube was placed in a vertical tube furnace. The electrochemical behaviors were tested by a electrochemical workstation.

2.3. Fuel cell testing and characterization

1.0 g carbon and 4.0 g Sn powder were pre-mixed mechanically in a mortar and loaded into the anode chamber. The SOFCs fueled by Sn–C mixtures were heated from 298 to 1023 K in 60 min and maintained at 1023 K for sufficient time. 150 mL/min H₂/Ar mixture (50.1% vol. H₂) was fed into the anode chamber during the heating process to reduce NiO to Ni, which served as the transporter of the electrons and contributed to high anode electronic conductivity. Once the OCV reached approximately 1.0 V, the anode was considered to be completely reduced. The anode gas was switched to 150 mL/min Ar and the polarization performance was measured at 1023, 1073 and 1123 K respectively. The long-term durability tests were conducted at a constant potential of 0.5 V at 1123 K while monitoring the current density as a function of time. For the benchmark purpose, the electrochemical performance of Sn-only was tested at 1023–1123 K. After the durability tests, the morphologies and the elemental qualitative analysis of the cell anode surface and cross section were carried out using the field emission scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX).

3. Results and discussion

3.1. Carbon fuel properties

The proximate analysis (Table 1) shows that the contents of the moisture and volatile matter were very low (<5%) for the carbon fuels. The carbon fuels mainly consisted of fixed carbon and ash. PCF and PYQ had considerable amount of ash, while GC and PAC had higher content of fixed carbon. The derived BET surface area and total pore volume of the four chars are also listed in Table 1. PAC possessed a high porous structure, with the BET surface area of 599.29 m²/g and total pore volume of 0.30 cm³/g. GC and PCF possessed moderate and similar BET surface areas. PYQ was nearly a nonporous carbon material.

The variation of CO₂/CO concentration is shown in Fig. 2. It can be seen that CO₂ began to be produced around 573–673 K. When the temperature reached 1123 K, CO₂ concentration increased sharply and a concentration peak was observed for the four carbon fuels. Obviously, the reaction rates of PCF and PAC were much higher than PYQ and GC. CO concentration in the outlet gas was lower than that of CO₂. For PYQ and GC, there was very little amount of CO detected at 1123 K. PAC had a much higher CO concentration peak than the other fuels. Two mechanisms have been proposed to describe the carbothermal reduction process of SnO₂: one was the direct reduction of SnO₂ by carbon, designated as solid–solid mechanism. The other mechanism was based on two steps: the reduction of SnO₂ by CO and the C–CO₂ gasification,
designated as solid–gas mechanism [17,18,22,23]. In the solid–gas mechanism, metallic Sn was reported to have a catalytic effect on the Boudouard reaction [17,18]. Levêque and Abanades [23] used two different amorphous carbon sources to investigate the reduction mechanism of SnO₂. The results showed that the activated carbon favored the solid–gas mechanism while the carbon black favored the solid–solid mechanism. In our study, the position and width of CO₂ concentration peak was in good accordance with that of CO for PAC. It can be deduced that PAC reduced SnO₂ through the solid gas mechanism, which was probably attributed to its high BET surface area [23].

3.2. Electrochemical performances of Sn-only fuel

Figure 3a shows the polarization characteristics of Sn-only in a SOFC at 1073 K. It can be seen that the open circuit voltage (OCV) of Sn-only was 0.86 V at 1073 K, very close to the expected theoretical potential for the oxidation of Sn (0.89 V). The maximum current density and maximum power density (MPD) were 237 mA/cm² and 79.67 mW/cm² respectively. It can be also observed at 135 mA/cm² that the polarization curve experienced a dramatic drop and a rapid decrease of the cell voltage then followed, which was mainly attributed to the SnO₂ formation. The durability in Sn-only mode is shown in Fig. 3b. It can be observed that the current density decreased from about 82 to 0 mA/cm² in less than 25 min.

After the long term run, the cell was cooled down to the room temperature under Ar flow. The cell anode morphology and elemental composition were analyzed by the SEM–EDX. Figure 4 shows the surface and cross sectional images of a blank SOFC and the SOFC with Sn-only as fuel. The high porosity structure can be observed both from the surface and cross section images of the blank cell. For the cell fueled with Sn, there was some aggregation accumulated on the anode surface, covering the anode pores. In the cross sectional image (Fig. 4d), the thickness of the whole cell cross section was approximately 600 μm, far exceeding the thickness of the blank cell (∼450 μm). Although the whole cell cross section (including the anode, electrolyte and cathode) was inside the field of view, it was difficult to point out where the anode, electrolyte and cathode layers were. The whole cell was powdered and no micropores were observed, indicating the anode porous structure was completely destroyed. The EDX analysis shows that considerable amount of elemental Sn penetrated into the porous structure. Zhou et al. [24] observed the similar etching phenomenon in YSZ-SOFCs with Sb anode and claimed that the etching was caused by the chemical reactions between SnO₂ and the zirconia. In Sn fueled Ni/YSZ supported SOFC, the anode failure was cause by the penetration of SnO₂, which probably reacted with zirconia in the anode.

3.3. Electrochemical performances of Sn–C fuels

The polarization performances of Sn–C mixtures were tested at the same procedure and shown in Fig. 5. The power density and OCV values at 1023–1123 K were summarized in Table 2. In Sn–C mode, the four carbon fuels displayed different
polarization characteristics. For Sn–GC, Sn–PYQ and Sn–PCF, the OCVs at 1023–1123 K varied in the range of 0.72–0.91 V, similar to that of Sn-only fueled cells. It was suggested that the anode performance was mainly governed by Sn electro-oxidation. For Sn–PAC, the cell power densities were greatly higher than that of Sn-only fueled cells. Moreover, the OCV of Sn–PAC was as high as about 1.0–1.03 V, corresponding to the expected potential of carbon/CO electro-oxidation. The polarization characteristics indicated that the anode performance was mainly controlled by the electro-oxidation of carbon or CO rather than Sn for Sn–PAC fueled SOFC.

The long-term durability of Sn–C fuels is shown in Fig. 6. For Sn–GC, Sn–PYQ and Sn–PCF fueled cells, the whole discharge performance was greatly improved compared with pure Sn in the view of the duration and the current density. The enhancement demonstrated that the SnO$_2$ insulation layer at the interface between the anode and Sn was partially reduced by the carbon (GC, PYQ and PCF). At the beginning of discharge the current densities were almost the same as that in Sn-only mode. However, the current density could not be maintained steady, suggesting that the chemical reduction of SnO$_2$ was
slower than the electrochemical oxidation of Sn. The cell degradation was still caused by the SnO2 accumulation on the anode surface. For Sn–PAC fueled SOFC, the durability performance was dramatically higher than that of the other Sn–C fuels. The current density fluctuated at a range of 200–215 mA/cm2 from 0 to 480 min and then decreased to 185 mA/cm2 from 480 to 600 min. After that, the current density dropped quickly to 0 mA/cm2. A visual observation of the anode fuel residue confirmed that there was no PAC remaining in the anode chamber after the discharge. The metallic Sn was agglomerated on the anode surface and formed a large cluster. It also indicated that the cell failure at the end of the experiment was due to the complete consumption of the carbon. The carbon fuel utilization \((U)\) was defined as the ratio of the carbon calculated assuming all the carbon was oxidized through the four electron reactions (Reaction \((1)\)) to the amount of carbon loaded into the anode. Based on the Faraday Law, \(U\) can be defined as

\[
U = \frac{\int I \, dt / 4F}{m_0 / M_c}
\]

where \(U\) is the fuel utilization of carbon fuel, \(I\) is the current during the discharge process, \(t\) is power generation time, \(F\) is the Faraday constant, \(m_0\) is the mass of carbon material loading into the anode initially, \(M_c\) is the atomic weight of carbon. For Sn–PAC fueled SOFC, the carbon fuel utilization was 26.2%. It can be deduced that carbon was consumed via C–CO2 gasification and CO electro-oxidation rather than the direct carbon electro-oxidation. The loss of the carbon fuels was attributed to CO removal by 150 mL/min Ar purging the anode. It is also worth noting that the electrochemical performances of Sn–PAC were much better than that of Sn–GC, although GC and PAC were both cleaner fuels. That’s due to the reactivity of PAC with SnO2, which was significantly faster than that of GC, saving the anode from the damage caused by SnO2. Besides, considerable CO was produced during the reduction of SnO2 with PAC, as shown in Fig. 2. CO can be directly electro-oxidized in the anode and activate the anode reaction shuttle cycles (Reactions (2) and (3)). Both of the two characteristics contributed to the much higher electrochemical performance of PAC than GC.

The polarization curves were also tested in C-only mode for PCF and PAC. In each cell, 1.0 g carbon fuel was loaded in the anode chamber and the measurement procedure was the same as that in the Sn–C mode. Table 2 also shows the comparison of the MPDs and OCVs at 1023–1123 K for PCF and PAC in Sn–C and C-only modes. It was found that PCF in C-only mode had higher MPDs and OCVs than that in Sn–C mode. But for PAC, the MPDs and OCVs were much higher in Sn–C mode than in C-only mode. The opposite regularity was in good agreement with the different reaction mechanisms of PCF and PAC in Sn–C mode. In Sn–PCF fueled SOFC, the anode reactions were mainly the electrochemical oxidation of Sn and the chemical reduction of SnO2 by carbon. While in Sn–PAC fueled SOFC, the anode reactions were mainly CO electro-oxidation and the Boudouard reaction. It has been demonstrated that the dominant reactions in anode supported SO-DCFCs were the CO electro-oxidation coupled with the C-CO2 gasification [4]. The electrochemical reactions were the same for PAC in Sn–C and C-only mode. The better polarization performance revealed that the Sn in Sn–PAC fueled SOFC acted as the catalyst for the Boudouard reaction and improved the CO concentration near the anode surface.

### 3.4. Anode SEM–EDX analysis of Sn–C fueled SOFCs

The anode surface and cross sectional morphologies of Sn–PYQ and Sn–PAC fueled SOFCs were analyzed and shown in Fig. 7. The EDX data of the red frame areas in Fig. 7 is shown in Table 3. For Sn–PYQ, the anode surface was covered with a dense layer, which contained mainly elemental Ni, Sn and C (spectra 1). In Fig. 7b, a 5–10 um dense insulation layer was observed on the anode surface (spectrum 2) of Sn–PYQ fueled SOFC. The EDX analysis (spectrum 3) also showed that considerable amount of Sn penetrated into the porous

### Table 3

EDX analysis of the designated areas in Fig. 7.

<table>
<thead>
<tr>
<th>Element (at%)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td>13.05</td>
<td>31.47</td>
<td>29.72</td>
<td>11.51</td>
<td>–</td>
</tr>
<tr>
<td>C</td>
<td>66.43</td>
<td>17.67</td>
<td>21.51</td>
<td>46.26</td>
<td>63.1</td>
</tr>
<tr>
<td>O</td>
<td>2.44</td>
<td>1.96</td>
<td>1.46</td>
<td>22.25</td>
<td>0.61</td>
</tr>
<tr>
<td>Ni</td>
<td>18.08</td>
<td>47.35</td>
<td>44.63</td>
<td>2.21</td>
<td>0.03</td>
</tr>
<tr>
<td>Zr</td>
<td>–</td>
<td>1.56</td>
<td>2.68</td>
<td>17.77</td>
<td>36.25</td>
</tr>
</tbody>
</table>
structure of the anode. For Sn–PAC, no dense covering layer was formed and the micropores can be clearly observed on the anode surface (Fig. 7c), although there were some Sn and C depositing on the anode surface (spectrum 4). Besides, no elemental Sn was detected in the porous anode (spectrum 5). SnO₂ accumulation on the anode surface was the key factor affecting the cell performance. In the discharge process of Sn–PAC, the main anode reactions were CO electro-oxidation and C-CO₂ gasification. CO/CO₂ atmosphere in the anode was more effective than the solid carbon particles to keep Sn from being oxidized. Even if there was some Sn electro-oxidized, the produced SnO₂ was reduced immediately and did not accumulate on the anode surface. Sn had a catalytic effect on the Boudouard reaction and favored the cell operated on the CO electro-oxidation. For Sn–GC, Sn–PYQ and Sn–PCF, although the SnO₂ can be directly reduced by carbon, the reduction rate of SnO₂ was slower than that of the Sn electro-oxidation, resulting in the accumulation on the anode surface. SnO₂ penetrated into the anode porous layer and caused rapid cell degradation. Some ash elements such as Fe, Ca, Mg, S, Al and Si were also analyzed along with Sn, C, Zr, O, Ni using EDX. The results show that these ash elements (Fe, Ca, Mg, S, Al, Si) were not detected on the anodes of Sn–coal mixture fueled SOFCs. Tao et al. [25] investigated the state of ash and impurities in a liquid Sn anode-SOFC using Illinois #6 coal as fuel. It was found that coal ash floated on the top of liquid Sn because of the lower densities of the ash species.

4. Conclusions

The electrochemical performances of Sn–C mixtures were measured to investigate the roles of Sn and C in SO–DCFCs. The results show that SOFCs fueled with pure Sn degraded rapidly due to the formation of SnO₂. SnO₂ can penetrate into the anode pores and destroy the anode porous structure. For Sn–C mixtures, the carbothermal reactivity of SnO₂ was the key factor determining the cell performances. For Sn–GC, Sn–PYQ and Sn–PCF, SnO₂ reduction rate was lower than the electro-oxidation rate of Sn, leading to SnO₂ accumulation on the anode surface and subsequent cell degradation. The OCVs and MPDs were similar with that of Sn-only fueled cell, indicating that the dominant anode reactions were the electro-chemical reaction of Sn and the chemical reduction of SnO₂ by C. While for Sn–PAC, the reactivity of PAC with SnO₂ was significantly faster than the other fuels probably due to its high surface area. SnO₂ once produced can be reduced immediately via the solid–gas mechanism. The OCV was approximately 1.0 V and the MPD was as high as (150.8 mW/cm²). The electrochemical behaviors of Sn–PAC suggested that the main anode reactions were the electro-oxidation of CO and C-CO₂.
gasification. Sn acted as the catalyst for the C-CO_2
gasification.

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