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# A steel slag-derived Boudouard reaction catalyst for improved performance of direct carbon solid oxide fuel cells

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#### **Summary**

Solid oxide fuel cells (SOFCs) can directly utilize solid carbon as fuel by integrating with the reverse Boudouard reaction in the anode chamber. Efficiency of the Boudouard gasification of solid carbon fuel is one of the crucial factors influencing the performance of direct carbon SOFCs (DC-SOFCs). In this paper, a novel Boudouard reaction catalyst derived from steel slag was first introduced into DC-SOFCs for improving the electrochemical performance. The catalytic activity of the steel slag was activated using the molten alkali method to decompose the inert mineral phases of the raw material. The steel slag-derived catalyst was loaded on the activated charcoal by a wet ball milling method. This kind of catalyst can match up to the readily available solid carbon fuels in cost. Promoted by this highly active Boudouard reaction catalyst, the initial Boudouard gasification temperature of the carbon fuel decreased by 99°C, and the producing rate of carbon monoxide doubled. Furthermore, the power outputs of the fuel cells increased from 91 to 159 mW cm<sup>-2</sup>, and the fuel utilization increased from 17.10% to 46.43% at 825°C. This study demonstrates that the steel slag-derived catalyst is a promising material for the performance improvement of DC-SOFCs and may make a valuable contribution to their commercial application.

#### **KEYWORDS**

Boudouard reaction, catalyst, direct carbon fuel, molten alkali method, performance improvement, steel slag, solid oxide fuel cell

# **1** | INTRODUCTION

Solid carbon fuel, including coal and biomass, is the most abundant and cheapest energy source on the earth.<sup>1-3</sup> Nowadays, it is typically utilized by combustion-based technologies, such as coal-fired power plants, in a lowenergy conversion efficiency and high-pollution emission mode.<sup>1</sup> Novel technologies to utilize solid carbon cleanly and efficiently are urgently demanded for a sustainable energy future. Direct carbon fuel cells (DCFCs) are power generation devices that directly convert the chemical energy of solid carbon to electricity via electrochemical routines.<sup>1-9</sup> Without the constriction of the Carnot cycle, DCFCs offer much high-energy conversion efficiency (slightly more than 100% in theory or approximately 80% in practice), which is more than twice that obtained from conventional coal-fired power plants.<sup>3-6</sup> Furthermore, since the gas-tight electrolyte of DCFCs just allows  $O_2$  in the air to transport to the anode in ionic forms, the highly concentrated  $CO_2$  product streams can be directly

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captured for industrial use or sequestration.<sup>1,2</sup> Therefore, DCFCs provide a promising alternative to meet our increasing energy demand and alleviate the concerns about global warming and climate change.

According to the electrolyte used, DCFCs are mainly classified into three types: molten hydroxide, molten carbonate, and solid oxide DCFCs.<sup>1-4</sup> The DCFCs with molten media as electrolyte have the advantage to ensure the intimate contact between the solid carbon fuel and the molten state electrolyte by an extended solid/liquid interface upon wetting.<sup>7,10-13</sup> In the presence of  $CO_2$ , the molten carbonate has higher stability than the molten hvdroxide.<sup>11</sup> In addition, the hybrid DCFCs combine molten carbonates with solid oxide electrolytes to obtain improved electrochemical performance, in which molten carbonates with dispersed solid carbon particulates are remained at the anode, and the cathode is isolated from carbonates by a solid oxide electrolyte.<sup>12,13</sup> The hybrid DCFCs totally eliminate the CO<sub>2</sub> recirculation and management needed in molten carbonate DCFCs.8,13 Solid oxide electrolyte DCFCs, also called direct carbon solid oxide fuel cells (DC-SOFCs), are the only type of DCFCs with all-solid-state structure.<sup>4-6</sup> As one of the most promising types of fuel cells, SOFCs have a variety of electrode materials and configurations to suit different types of fuel.14-21 Compared with the DCFCs with molten electrolytes. DC-SOFCs are free from the troubles of corrosion of cell components and leakage of molten matter.<sup>5</sup> However, the efficient mass transfer of solid carbon in the solid anode is the major challenge that DC-SOFCs must face.<sup>1,2</sup>

A series of investigations have essentially revealed that the anode processes of DC-SOFCs are the coupling of the reverse Boudouard reaction (R1, Figure 1) and the electrochemical oxidation of CO (R2, Figure 1).<sup>22-37</sup> In fact, the anode processes are kinetically controlled ones.<sup>5</sup> Even the operation of DC-SOFCs is in a steady state, still no thermodynamic equilibrium could arrive.<sup>25,32</sup> A detailed kinetic study on the anode processes has revealed that only when the reaction rates of R1 and R2, ie,  $r_1$  and  $r_2$ , satisfy the relationship  $\frac{1}{2}r_1 \le r_2 \le r_1$ can the fuel cell run steadily.<sup>33</sup> In the CO-CO<sub>2</sub> cyclic system shown in Figure 1, the reverse Boudouard reaction is



**FIGURE 1** Illustration of the CO-CO<sub>2</sub> cyclic system of direct carbon solid oxide fuel cells (DC-SOFCs)

usually the control process of this system.<sup>38</sup> The Boudouard gasification rates determine the mass transfer efficiency of solid carbon fuel and further the cell performance. The diffusion rates of CO and CO<sub>2</sub>, ie,  $r_{d1}$  and  $r_{d2}$ , respectively, have been proved to be much faster than the rates of R1 and R2; hence, the diffusion processes have almost no impeding effect on the cell performance.<sup>33,34</sup> The  $r_2$  can be controlled by tuning the current densities; however, the  $r_1$  normally decreases due to carbon consumption and other reasons.<sup>33-44</sup>

The reverse Boudouard reaction is an endothermic reaction with the free energy change expressed as  $\Delta G$  $(kJ mol^{-1}) = 170 - 0.1745T$ , where T is temperature in °K. The CO formation is strongly favored at temperatures above 974.2 K.<sup>6</sup> From the viewpoints of thermodynamics and kinetics, elevated temperatures are the key factor that determines the rate of Boudouard reaction to reach equilibrium and the partial press of CO in the system.<sup>6</sup> In fact, even at the reaction temperature as high as 800°C, a typical operating temperature for intermediatetemperature SOFCs, the Boudouard reaction rates of most carbon fuels are still not fast enough to supply sufficient CO to the anode.<sup>24-26</sup> There is a need to introduce catalysts into the Boudouard reaction to reach a faster reaction rate at the rational operating temperatures of SOFCs. Many types of metal compounds, such as the oxides of iron, nickel, calcium, and cerium, and the carbonates of lithium and potassium, have been adopted as Boudouard reaction catalysts in DC-SOFCs, which exhibit significant effects on accelerating the Boudouard reaction and improving the fuel cell performance.<sup>24-29</sup> However, almost all of these catalysts are made of commercially available reagents. Up to now, there still lacks cost-effective Boudouard reaction catalysts to match up to the relatively cheap carbon fuels. This gap may delay the practical application of DC-SOFCs. Therefore, it is of great significance to prepare cost-effective Boudouard reaction catalysts from available and cheap raw materials.

Steel slag is a by-product of steelmaking process. A huge volume of steel slag is produced every year worldwide, which puts a heavy burden on the environment. Just in China, approximately 100 million t of steel slag were produced in 2016.<sup>43</sup> Many great efforts have been made to properly treat and utilize this type of industrial solid waste. Today, steel slag has been used as raw materials to produce value-added materials, such as cement, fertilizers, soil conditioners, sewage treatment agents, and so on.<sup>44</sup> However, there is still large space to take full advantage of steel slag. Steel slag is a promising raw material to prepare Boudouard reaction catalysts due to being rich in metal oxides such as CaO and Fe<sub>m</sub>O<sub>n</sub>. To the best of our knowledge, our group should be the first one studying the steel slag–derived Boudouard catalysts for DC-SOFCs.<sup>45</sup> In our previous work, the steel slagderived catalyst was prepared by an acid-activated method, and its catalytic effects were studied preliminarily.<sup>45</sup> In this paper, the molten alkali method was used to activate the raw steel slag for high catalytic activity. The promotion effects of the steel slag-derived catalyst on the Boudouard reaction and further on the electrochemical performance of DC-SOFCs were systematically studied. The phase structure and the morphology of the catalysts were characterized by XRD and SEM methods, respectively. The catalytic Boudouard gasification process was monitored by an online gas mass spectrometer. The improved electrochemical performance, including the power output and the fuel utilization, was evaluated detailedly.

## 2 | EXPERIMENTAL

# 2.1 | Catalyst preparation and characterization

The raw steel slag sample was obtained from the Taiyuan Iron and Steel Group Co., Ltd. (TISCO), China. A modified molten alkali method was used to prepare the steel slag-derived catalysts.44 The processing procedures are as follows. The steel slag powder in 120 mesh was mixed evenly with solid potassium hydroxide in three weight ratios of slag to alkali, ie, 1:1, 1:2, and 1:3. The mixture set in a nickel crucible was heated to 650°C at a rate of 10°C min<sup>-1</sup> in a muffle furnace and then held at the final temperature for 2 hours. After the temperature of the calcined mixture dropping to 100°C, an appropriate amount of distilled water at 90°C to 100°C was added to the mixture. Hot filtration was performed after stirring the mixture for half an hour at 90°C to 100°C. The catalysts were obtained after repeating the washing and filtration procedures three times and drying the solid samples at 110°C for 12 hours. The catalysts with the slag to alkali weight ratios of 1:1, 1:2, and 1:3 are designated as K1, K2, and K3, respectively. The yields of the K1, K2, and K3 catalysts were approximately 84, 80, and 80 wt%, respectively.

A D8 Advance X-ray diffractometer (Bruker, Germany) was employed to record X-ray diffraction patterns of the samples. The sample was packed into the rectangle cavity of a vitreous sample holder and scanned in a step-scan mode (0.02° per step) over the 20 range from 10° to 90° under the condition of 40 kV, 200 mA, and Cu K $\alpha$  radiation. The morphologies of the samples were examined using a JEOL JSM-7001 scanning electron microscope (SEM) system. Sample degassing and adsorption experiments were performed using a Micromeritics

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ASAP-2020 M automated surface area and pore size distribution analyzer (Micromeritics, USA). Prior to the N<sub>2</sub> adsorption measurements, all samples were degassed at 200°C for 24 hours under vacuum to a final pressure of 0.33 Pa. N<sub>2</sub> adsorption isotherms were measured at 77 K over a relative pressure ( $P/P_0$ ) range from 0.01 to 0.99. The specific surface areas of the samples were calculated using the multiple-point Brunauer-Emmett-Teller (BET) method. Chemical composition analyses of the samples were performed by the Center for Analysis and Testing of TISCO, a professional and authorized institution attached to the State Key Laboratory of Advanced Stainless Steel Materials at TISCO.

#### 2.2 | Catalyst loading

The activated charcoal (Aladdin, Shanghai, China; A.R.) was used as solid carbon fuel, and the steel slag-derived catalyst was loaded on it by a wet ball milling method. The weight ratio of carbon fuel to catalyst was 7:1, the same as that in the literature.<sup>38</sup> The mixture of the catalyst with particle sizes within 200 mesh and the charcoal power was ground by a planetary ball mill (Fritsch Pulverisette 6, Germany) with distilled water as milling medium. The milling speed and milling time were fixed at 400 rpm and half an hour, respectively. Then, the catalyst-loaded charcoal was dried in an oven at 110°C for 12 hours. The composite catalyst  $Fe_m O_n - M_x O$  (M = K, Li, Ca) made of chemical reagents (designated as R) was prepared according to the literature and loaded on the charcoal by an impregnation and calcination method.<sup>24</sup> The charcoal loaded with the raw steel slag, K1, K2, K3, or R catalyst is designated as C/M, C/K1, C/K2, C/K3, or C/R, respectively. The charcoal without catalyst is designated as C.

# 2.3 | Carbon dioxide temperatureprogrammed oxidation experiment

Carbon dioxide temperature–programmed oxidation (CO<sub>2</sub>-TPO) experiments were carried out to analyze the Boudouard reaction efficiency of the carbon samples with various catalysts. The solid carbon sample (50 mg) without catalyst or with a certain amount of catalyst was loaded into a quartz tube reactor with an inner diameter of approximately 3 mm. The sample was then heated under a nitrogen atmosphere from room temperature to 200°C and held at that temperature for 1 hour to remove adsorbed water. After cooling the sample to room temperature, pure CO<sub>2</sub> was flowed over it at a rate of 20 mL min <sup>-1</sup> (standard temperature and pressure (STP)) for approximately 30 minutes. Then, the temperature was increased

to 1000°C at a heating rate of  $10^{\circ}$ C min<sup>-1</sup>, and the sample was gradually oxidized into CO. The effluent gas from the reactor was fed into a Hiden QIC-20 mass spectrometer (MS) for monitoring CO concentrations.

# 2.4 | Electrochemical performance evaluation of DC-SOFCs

According to the established procedure in the literature,46,47 the anode-supported SOFCs were fabricated and tested in this work. The anode was made of nickle oxide (NiO, 60 wt%; Chengdu Shudu Nanomaterials Technology Development Co. Ltd., China) and yttrium stabilized zirconia (YSZ, 40 wt%; Tosoh Corporation, Japan). The electrolyte and cathode layers were made of YSZ and La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub> (LSM; Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences, China), respectively. The NiO-YSZ anode and YSZ electrolyte layers were fabricated using a dual dry pressing method.<sup>47</sup> The cathode was fabricated using a spraying coating method.<sup>47</sup> The active area of the cathode was 0.48 cm<sup>2</sup>. The current collector on the cathode was the silver meshes painted using the silver paste (DAD-87, Shanghai Research Institute of Synthetic Resins, Shanghai, China). The Ni-YSZ anode layer also functioned as current collector. The thicknesses of the anode, cathode, and electrolyte layers were approximately 430, 35, and 30  $\mu$ m, respectively (Figure 2A). The electrolyte layer was dense and in intimate contact with the anode layer (Figure 2B). The porosities of the anode and cathode were approximately 30% and 45%, respectively, measured by the Archimedes method. The setup to test the fuel cell performance was the same as that in the literature.<sup>20</sup> To build the testing system, the button cell was sealed tightly onto quartz tubes by silver paste, with the cathode surface exposed to ambient air. The solid carbon fuel was set into the anode chamber very close to the anode surface using

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asbestos and quartz sand as a support. A thinner quartz tube was placed under the support layer to allow gases out the anode chamber.

A four-terminal configuration was used to collect polarization curves (current-voltage curves).<sup>38</sup> The charcoal of 50 mg was used during the polarization tests. The conditions for electrochemical impedance spectra (EIS) measurements were as follows: open-circuit, frequency range from 0.1 Hz to 100 kHz, and an alternate current signal amplitude of 10 mV. The fuel utilization tests for the solid carbon samples (40 mg) with or without catalyst were conducted at 825°C under the constant current density of 52.1 mA cm<sup>-2</sup>. All electrochemical data were collected using an Iviumstat electrochemical analyzer (Ivium Technologies B.V., Netherlands).

## **3** | **RESULTS AND DISCUSSION**

# 3.1 | Chemical composition and structures of the catalysts

Table 1 shows the normalized major chemical composition of the steel slag and the derived catalysts, K1, K2, and K3. The major chemical constituents of the steel slag are calcium oxide, iron oxide, silicon dioxide, magnesium oxide, aluminum oxide, and manganese oxide. The minor

**TABLE 1** Normalized major chemical composition of the samples

Chemical Composition, wt%	CaO	Fe <sub>m</sub> O <sub>n</sub>	SiO <sub>2</sub>	MgO	Al <sub>2</sub> O <sub>3</sub>	MnO
Steel slag	47.82	19.57	19.00	9.67	1.82	2.12
K1	47.35	20.75	18.84	9.77	1.50	1.79
K2	47.25	21.63	18.26	9.97	1.43	1.44
К3	47.41	21.43	18.75	9.73	1.22	1.46



**FIGURE 2** SEM images of the as-prepared solid oxide fuel cell (SOFC): A, cross section and B, interface between the electrolyte and anode [Colour figure can be viewed at wileyonlinelibrary.com]

constituents, including chromium oxide, titanium oxide, etc, are excluded from the consideration. Compared with the raw steel slag sample, the content of iron oxide in K1, K2, and K3 increases by 6%, 10.5%, and 9.5%, respectively; the content of calcium oxide in all of them, however, decreases slightly by approximately 1%. The increase of magnesium oxide content in the catalysts is about 3.1% or less, and the decrease of silicon dioxide content in them is about 3.9% or less. In addition, the contents of major constituents of these catalysts show slight or moderate differences among themselves, indicating that the weight ratio of steel slag to alkali hydroxide had a limited effect on the chemical composition of the catalysts under the processing conditions.

Figure 3A shows the XRD pattern of the raw steel slag sample. The major mineral phases of the steel slag are dicalcium silicate (2CaO-SiO<sub>2</sub>), the RO phase (solid solution of MgO with FeO and/or MnO), calcium aluminoferrite (Ca<sub>2</sub>(Fe,Al)O<sub>5</sub>), and dicalcium ferrite



**FIGURE 3** XRD patterns of the steel slag A, and the catalysts B, [Colour figure can be viewed at wileyonlinelibrary.com]

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Figure 3B shows the XRD patterns of the catalysts, K1, K2, and K3. The major phases of K1, K2, and K3 are simple oxides and hydroxides, such as CaO, MgO, and Ca  $(OH)_2$ , and the residues of some complex oxides, such as  $2CaO-SiO_2$ ,  $(MgO)_x$  (FeO)<sub>y</sub>, and  $2CaO-Fe_2O_3$ . By comparing Figure 3B with Figure 3A, it can be seen that most of the complex mineral phases of the steel slag were decomposed to the simple oxide phases by the molten alkali method.

Based on the major chemical constituents of the steel slag-derived catalysts and the position of the catalysts (always mixed with the carbon fuel) relative to the anode, the potential corrosion of the catalysts to the anode and electrolyte materials of DC-SOFCs should not occur due to no intimate contact of the catalysts with the anode surface. As seen in Figure 4, there is a certain distance between the carbon fuel and anode surface, ie,  $D_{carbon-anode}$  (approximately 1 mm normally). In addition, under the operating temperatures of DC-SOFCs from 750°C to 850°C, all the constituents of the catalysts are in solid state with negligible vapor pressures. Therefore, the incidence of reactions of the vapor from the catalysts with the solid anode and electrolyte materials could be neglected.

Figure 5 shows the SEM images of the steel slag and the catalysts. As seen in Figure 5A, the morphological features of the raw steel slag are dense, coarse, and glassy-granulated. In general, the molten steel slag is quenched rapidly using a large amount of water in the conventional processes and hence produces glassygranulated solid slag. In contrast with the raw steel slag, the morphologies of K1, K2, and K3 samples shown in Figure 5B, 5C, and 5D, respectively, are loose, fine, and porous. In addition, Figure 5 shows that the particle sizes of the catalysts seemed to become smaller with the



**FIGURE 4** Schematic of a direct carbon solid oxide fuel cell (DC-SOFC) focusing on the anode chamber [Colour figure can be viewed at wileyonlinelibrary.com]



FIGURE 5 SEM images of the steel slag A, K1 B, K2 C, and K3 D

increase of weight ratio of alkali to steel slag. In fact, the BET specific surface areas of K1, K2, and K3 were approximately 60, 85, and 90 cm<sup>2</sup> g<sup>-1</sup>, respectively, which may be a further proof for this inference.

# 3.2 | Catalytic effect of the steel slagderived materials on the Boudouard reaction

The reverse Boudouard reaction is a strongly endothermic reaction in thermodynamics. The temperatures should be at least greater than 700°C to facilitate the reaction going. In fact, the reaction rates of most of the solid carbon fuels in the temperature range from 700°C to 900°C are still not fast enough to supply sufficient CO to DC-SOFCs.<sup>4-6</sup> The introduction of proper catalysts can accelerate the reaction and reduce the reaction temperature.<sup>25-28</sup> The catalytic effects of the K1, K2, and K3 catalysts on the solid carbon sample were evaluated by the CO<sub>2</sub>-TPO method, which is a powerful tool to monitor the Boudouard gasification process in real time.<sup>36</sup> Meanwhile, the samples of C, C/M, and C/R were examined as contrasts.

Figure 6A shows the  $CO_2$ -TPO curves of the C/K1, C/K2, C/K3, and C samples, where the C sample was taken as the benchmark. The related information is listed in Table 2. As seen in Figure 6A, the CO<sub>2</sub>-TPO curves of the samples with catalyst are very similar and almost

overlap one another except their peak gasification temperatures  $(T_p)$  are different. The  $T_p$  values of C/K3, C/K2, and C/K1 are 889°C, 901°C, and 907°C, respectively. From Table 2, some points can be drawn as follows. (1) The initial gasification temperatures  $(T_i)$  for C/K2 and C/K3 are 654°C and 651°C, respectively, which are nearly equal and lower than that of C/K1 (659°C); (2) the CO peak intensities for C/K2 and C/K3 are almost the same, and both less than that for C/K1; and (3) the integral values of CO produced within the temperature range from 750°C to 850°C can be arranged in the increasing order of C/K1, C/K2, and C/K3. Overall, the K3 sample exhibited the best promotion effect on the Boudouard gasification among these three samples. Figure 6B shows the CO<sub>2</sub>-TPO curves of the C/K3, C/M, C/R, and C samples. It is clear that the  $T_p$  values for these samples increase in the order of C/R, C/K3, C/M, and C. Table 2 shows that the integral values of CO for these samples increase in a reverse order as that for  $T_p$ , that is, in the increasing order of C, C/M, C/K3, and C/R. The CO peak intensities for C/R, C/K3, and C/M samples are almost equal, and all are higher than that for the C sample.

Based on Figure 6 and Table 2, more conclusions can been drawn as follows. First, the catalytic activity of K3 is stronger than that of M, but weaker than that of R. In fact, as a composite catalyst, R possesses synergistically catalytic activity stemming from its multiple components, although all of them are pure chemical reagents with high cost. Second, the data for C/M reveals that the steel



**FIGURE 6** CO<sub>2</sub>-TPO curves of A, C, C/K1, C/K2, and C/K3 and B, C, C/M, C/K3, and C/R [Colour figure can be viewed at wileyonlinelibrary.com]

slag processed by high-energy ball milling also has certain catalytic activity. In general, steel slag is produced by an air/water-quenching process at high temperatures up to 1650°C, resulting in dense, glassy crystallization phases.<sup>43</sup> These stable mineral phases have very limited catalytic effects on the Boudouard gasification. Mechanical activation methods, such as high-energy ball milling, process samples by strong mechanical

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force to destruct dense phase structures and produce grain defects, and hence increase samples' activity. However, the activating effect of high-energy ball milling processing is weaker than that of the molten alkali method. The oxides of calcium and iron are the main active components of the K3 catalyst. The oxygen transfer mechanism for iron oxides has been widely accepted by the academic community<sup>24</sup>:

$$Fe_mO_n + CO_2 \rightarrow Fe_mO_{n+1} + CO$$
 (1)

$$Fe_mO_{n+1} + C \rightarrow Fe_mO_n + CO$$
 (2)

There is still no consensus on the catalytic mechanism of CaO. One of the viewpoints believes that calcium oxide may also have an oxygen transfer mechanism similar to iron oxides.<sup>45</sup>

## 3.3 | Effects of the steel slag-derived catalyst on the output performance of DC-SOFCs

Figure 7 shows the results of electrochemical performance tests of the fuel cells. The cell (1), cell (2), and cell (3) used the C, C/K3, and C/R fuel, respectively. The detailed information extracted from Figure 7 are shown in Table 3. According to Figure 7 and Table 3, the Boudouard reaction catalysts (K3 and R) exhibited significant effects on the electrochemical performance of the fuel cells. Detailed discussions are described as follows.

First, as seen in Figure 7, the peak power density (PPD) of cell (2) at 800°C was 117 mW cm<sup>-2</sup> (Figure 7 C), which is more than twice that of cell (1) (58 mW cm<sup>-2</sup>, Figure 7A) and slightly less than that of cell (3) (123 mW cm<sup>-2</sup>, Figure 7E) at the same temperature. The PPDs at 825°C and 850°C have the same trend as that at 800°C, that is, they can be arranged in the increasing order of cell (1), cell (2), and cell (3). These results suggest that K3 had the capability to significantly enhance the power

TABLE 2 CO<sub>2</sub>-TPO information of the carbon fuels with various catalysts

Fuel	T <sub>i</sub> , °C	$\Delta T_i$ , °C	<i>T<sub>p</sub></i> , °C	$\Delta T_p$ , °C	CO Intensity (×10 <sup>-7</sup> Torr)	Integral value <sup>a</sup> (×10 <sup>-5</sup> Torr h)
С	750	0	967	0	4.32	1.28
C/M	664	-86	938	-29	4.77	1.87
C/K1	659	-91	907	-60	5.23	2.37
C/K2	654	-96	901	-66	4.77	2.48
C/K3	651	-99	889	-78	4.78	2.56
C/R	657	-93	866	-101	4.63	3.23

Note:  $T_i$  = initial gasification temperature;  $T_p$  = peak gasification temperature.

<sup>a</sup>Integral value of the CO peak within a period of 10 hours corresponding to 750°C to 850°C.



**FIGURE 7** *I-V* and *I-P* curves (A, C, and E), and the impedance spectra (B, D, and F) of the fuel cells at various temperatures [Colour figure can be viewed at wileyonlinelibrary.com]

Fuel Cell	Operating Temperature, °C	Open Circuit Voltage (OCV), V	Peak Power Density, mW cm <sup>-2</sup>	Impedance at 9.31 Hz, $\Omega \text{ cm}^2$
Cell (1)	800 825	0.813	58	2.281
	825 850	0.879	128	1.490
Cell (2)	800	0.901	117	1.501
	825	0.923	159	1.254
	850	0.943	207	1.056
Cell (3)	800	0.884	123	1.239
	825	0.902	169	1.011
	850	0.935	236	0.925

**TABLE 3** Electrochemical performance of the fuel cells

output of the fuel cells and nearly matched up to R in catalytic activity.

Second, as shown in Table 3, the open circuit voltage (OCV) of cell (2) is 0.901 V at 800°C, which is 88 mV higher than that of cell (1) (0.813 V) at 800°C and even is 22 mV higher than that of cell (1) (0.879 V) at 850°C. According to the Nernst equation (Equation (3)) of DC-SOFCs, OCV values positively correlate with the ratio of  $(P_{CO}^a/P_{CO_2}^a)$ . The greater the ratio, the higher the corresponding OCV. Therefore, cell (2) must have higher  $P_{CO}^a/P_{CO_2}^a$  values than cell (1) at each corresponding temperature. These results demonstrate that K3 catalyzed the reverse Boudouard reaction in the anode chamber very efficiently. The Nernst equation is as follows:

$$E = E^{0} + \frac{RT}{4F} \ln \left[ P_{O_{2}}^{c} \cdot \left( \frac{P_{CO}^{a}}{P_{CO_{2}}^{a}} \right)^{2} \right]$$
(3)

where  $E^{\circ}$  denotes the standard electromotivated potential;  $P_{O_2}^c$  the partial pressures of  $O_2$  at the cathode;  $P_{CO}^a$ and  $P_{CO_2}^a$  the partial pressures of CO and CO<sub>2</sub> in the anode chamber, respectively; and R, F, and T the universal gas constant, the Faraday constant, and the operating temperature in Kelvin, respectively.

The OCV values in Table 3 are all smaller than the corresponding theoretical values to different extents.<sup>28-30</sup> The slight gas leakage across the silver paste sealing may be a reason leading to the negative deviations.<sup>25</sup> The other possible reason is that the ratio values of  $P_{CO}^a/P_{CO_2}^a$  at the electrochemical reaction sites of the anode may be lower than the values in thermodynamic equilibria.<sup>34</sup>

Third, the results of the impedance spectra of fuel cells are consistent well with the PPD and OCV data. The EIS spectra for anode-supported SOFCs normally exhibit four or five impedance responses with considerably varied magnitudes from cell to cell.<sup>49</sup> A response at approximately 10 Hz associated with concentration polarization was observed previously for anode-supported cells.<sup>49</sup> Barnett et al reported that the responses of EIS spectra at approximately 0.5 and 10 Hz just vary with fuel composition (Ar/H<sub>2</sub> ratio), suggesting that they are related to gas diffusion.<sup>49</sup> For DC-SOFCs, it has been shown that the impedance spectra in the low frequency range ( $\leq 10$  Hz) are mainly dependent on the partial press of CO in the anode chamber.<sup>37,47</sup> The higher the values of CO partial press, the lower the EIS values at the low frequency range.<sup>26,37</sup> Herein, we choose the EIS values at 9.31 Hz for comparison. As seen in Table 3, the EIS value of cell (2) at 9.31 Hz and 800°C is 1.501  $\Omega$ , which is approximately equal that of cell (1) at 9.31 Hz and 850°C (1.490 Ω). This suggests that cell (2) using C/K3 fuel at  $800^{\circ}$ C had a similar CO partial press in the anode chamber like -WILEY- ENERGY RESEARCH

that cell (1) using C fuel had at 850°C. This conclusion is very similar to that drawn from the OCV values of cell (2) at 800°C (0.901 V) and cell (1) at 850°C (0.879 V), because both the OCV value and the EIS value in the low frequency range ( $\leq 10$  Hz) are closely related to the partial press of CO at the anode. In addition, based on the EIS spectra in Figure 7 and the method presented in the literature,<sup>50</sup> the estimated values of anodic exchange current density ( $j_{0,an}$ ) of cell (2) using C/K3 fuel were obtained, that is, approximately 770 and 960 A m<sup>-2</sup> at 800°C and 850°C, respectively.

# 3.4 | Effects of the steel slag-derived catalyst on the stability/duration of DC-SOFCs

Figure 8 shows the results of stability tests of cell (1), cell (2), and cell (3) operating at 825°C. As seen in Figure 8, the stability curve of cell (1) differs from that of cell (2) or cell (3). The former can be divided into two segments and the latter four segments according to the change of slopes. The initial discharging voltage of cell (1) is just 0.57 V, reflecting the low Boudouard gasification reactivity of the pure carbon fuel. The fuel without catalyst had no capability to produce and supply sufficient CO to the anode. The power output of cell (1) declines continuously until the discharging voltage drops to 0.35 V at the end of the segment 1, which corresponds to the period lasting 55 minutes. Then in the segment 2, the cell is dominated by the concentration polarization and the power output declines quickly to zero within 20 minutes.

As shown in Figure 8, the initial discharging voltage of cell (2) using the C/K3 fuel reaches 0.84 V, and the power



**FIGURE 8** Stability tests of the fuel cells operating at 52.1 mA cm<sup>-2</sup> and 825°C [Colour figure can be viewed at wileyonlinelibrary.com]

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output maintains relatively stable in the segment 1 (approximately 90 min); then, the power output enters the continuous decline stage (the segments 2 and 3, approximately 90 min) corresponding to the discharging voltage dropping from 0.74 to 0.35 V. The segment 4 (approximately 20 min) of cell (2) is similar to the segment 2 of cell (1), a totally concentration polarizationcontrolled stage. It is clear that the introduction of K3 catalyst significantly improved the operating stability of cell (2). It is interesting to understand the appearance of segments 2 and 3 in the curve of cell (2) in Figure 8. The segments 2 and 3 should reflect the different decreasing rates of the reverse Boudouard reaction resulting mainly from the change of catalytic activity of K3. First, it is reasonable to assume that the catalyst in the segment 1 was in a well-dispersed state with a relatively stable catalytic activity. In the segment 2, a severer agglomeration state of the catalyst appeared due to the accumulation of catalyst agglomerating with the consumption of solid carbon. The catalytic activity of K3 thereupon decreased, leading to an accelerated decrease of the rate of the reverse Boudouard reaction and thus CO supply to the anode. These changes were expressed finally by the increase of concentration polarization overpotentials at the anode and the sharp decrease of discharging voltages of cell (2). In the segment 3, the catalyst agglomerated to certain extent had lower catalytic activity but slower agglomerating (or higher thermostability) than in the segment 2 and continuously catalyzed the Boudouard reaction until the solid carbon nearly being used up. During the segments 2 and 3, the reactive surface areas of solid carbon continuously decreased, which also contributed to the accelerated decreasing rates of the reverse Boudouard reaction. In brief, the faster decreasing rate of the catalytic activity of K3 in the segment 2 than that in the segment 3 may be the major reason leading to the different slopes of the segments 2 and 3.

The stability curve of cell (3) is very similar to that of cell (2) in shape except that the segment 1 of cell (3) is shorter approximately 30 minutes than that of cell (2). This suggests that K3 may have higher thermostability than R under the same test conditions. The reasons are as follows.

The components of K3 can be divided into two types: One type is catalytically active, including  $Fe_mO_n$ , CaO, MgO, and MnO; the other one is catalytically inert, including SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, which are usually used as catalyst supports due to their high thermostable.<sup>51,52</sup> Under the operating temperatures of DC-SOFCs in this study, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> are thermostable enough to act as agglomeration/sintering inhibitors for K3.51,52 A recent study has demonstrated that under the promotion of a Boudouard reaction catalyst with Al<sub>2</sub>O<sub>3</sub> as a

sintering inhibitor, the operation stability and the fuel utilization of the DC-SOFCs were significantly improved.<sup>51</sup> Herein, the contents of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in K3 may play a certain role in improving the resistance of agglomeration/sintering, ie, the thermostability, of K3 and thus delay the decrease of its catalytic activity. Therefore, the C/K3 mixture was capable of producing more CO than the C/R mixture resulting in the more power output and higher stability of cell (2) (Figure 8).

On the other hand, the contents of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> may have negative effects on the catalytic activity of K3.53 This may be one of the major reasons leading to K3 possessing lower catalytic activity than R. As seen in Figure 6B, the higher CO-producing rate of the C/R mixture than that of the C/K3 mixture indicates that R had higher catalytic activity than K3. Another evidence comes from the I-V curve tests (Figure 7). Because the C/R mixture had higher CO-producing rate than the C/K3 mixture, it was capable of better meeting the increasing need of CO at the anode with increasing polarization current densities and finally led to the lower concentration polarizations and higher peak power densities of cell (3) than those of cell (2) (Figure 7 and Table 3). Based on the reasons aforementioned, it can be understood why the peak power densities of cell (3) were higher than those of cell (2) (Table 3 and Figure 7), but the operating stabilities for them were opposite (Figure 8).

In order to distinguish the difference between K3 and R in a quicker mode, the amount of 40-mg carbon fuel was used. As seen in Figure 8, the stability tests of cell (3), cell (2), and cell (1) lasted 198.8 minutes (approximately 3.3 h), 174.6 minutes (approximately 2.9 h), and 73.2 minutes (approximately 1.2 h), respectively. In these limited durations, the promotion effect of K3 on the stability of cell (2) exhibited significantly, especially compared with cell (1) with no use of catalyst for the fuel. In addition, the stability of cell (2) was obviously higher than that of cell (3), which may result from the higher thermostability of K3. Combining the results in Figures 7 and 8, it can be concluded that the catalytic activity of R is higher than that of K3; however, as for the thermostability, the case is reverse.

The fuel utilization is a key parameter to evaluate the applicability of solid carbon. This parameter was calculated following the equation below:

$$\eta = \frac{C_{elec}}{C_{ld}} \times 100\% \tag{4}$$

where  $C_{\text{elec}}$  and  $C_{\text{ld}}$  are the masses of carbon converted electrochemically and carbon loaded in the anode chamber, respectively. As seen in Table 4, the  $\eta$  values for cell (1), cell (2), and cell (3) are 17.10%, 46.43%, and 40.78%,



#### TABLE 4 Results of the stability tests

Cell	Discharge Time, min	Electric Quantity, C	Carbon Converted, mg	Carbon Loaded, mg	Fuel Utilization, wt%
Cell (1)	73.2	109.84	6.84	40	17.10
Cell (2)	198.8	298.30	18.57	40	46.43
Cell (3)	174.6	261.98	16.31	40	40.78



**FIGURE 9** Digital photos of the anode chambers of cell (1) A, cell (2) B, and cell (3) C, after the stability tests [Colour figure can be viewed at wileyonlinelibrary.com]

respectively. The fuel utilization of the C/K3 fuel is 2.7 times that of the C fuel and is higher 5.65% than that of the C/R fuel. These results indicate that the K3 catalyst markedly improved the fuel utilization of the carbon fuel, and its effect even exceeded that of the R catalyst.

Figure 9 shows the side views of the anode chambers of these fuel cells after the stability tests. The residues of the carbon fuels with or without catalyst in the anode chambers can be seen clearly through the quartz tubes. As seen in Figure 9A, there are quite a lot of black residues in the anode chamber of cell (1), which is consistent well with the lowest fuel utilization of 17.10% for cell (1), and indicates that the majority of carbon fuel in cell (1) was unable to be gasified under the operating temperatures without the promotion of catalysts. In contrast, there are almost no black carbon remained, and only a small amount of brown residues in the anode chamber of cell (2) (Figure 9B). This result agrees with the highest fuel utilization of 46.43% for cell (2) and reveals that almost all of the carbon fuel was gasified under the catalysis of K3. In addition, the dark brown residues in the anode chamber of cell (3) indicate that some carbon fuel residues mixed with the R catalyst were left (Figure 9C), which matches up with the lower fuel utilization (40.78%) for cell (3) than that for cell (2). The difference between the residues of cell (2) and cell (3) may result from the contents of silicon and aluminum oxides in the K3 catalyst, which can function as sintering inhibitors to prevent the catalyst from agglomeration or sintering.<sup>51,54,55</sup> It has been reported that the introduction of Al<sub>2</sub>O<sub>3</sub> can significantly inhibit the sintering of the

 $Fe_mO_n$ -K<sub>2</sub>O catalyst mixed with solid carbon in an SOFC-based carbon-air battery.<sup>51</sup> In a word, the residues in the anode chambers provide direct clues for better understanding the data of fuel utilization in Table 4.

#### 4 | CONCLUSIONS

In this paper, the catalytic effect of the steel slag-derived materials on the reverse Boudouard reaction and the promotion effect on the electrochemical performance of DC-SOFCs were studied. The catalytic activity of the steel slag was activated using the molten alkali method to decompose the mineral phases of the raw steel slag, such as 2CaO·SiO<sub>2</sub>, RO phase, and Ca<sub>2</sub>(Fe,Al)O<sub>5</sub>, into CaO, MgO, Ca (OH)<sub>2</sub>, and calcium iron oxide. The initial Boudouard gasification temperature was decreased by 99°C, and the CO production was doubled when introducing the K3 catalyst into the solid carbon fuel. Furthermore, the peak power densities of the fuel cells increased from 58 to 117 mW cm<sup>-2</sup> at 800°C, and the fuel utilization increased from 17.10% to 46.43% at 825°C. These results demonstrate that the steel slagderived Boudouard reaction catalyst is a promising material to improve the power output and operation stability of DC-SOFCs.

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