



# In situ catalyzed Boudouard reaction of coal char for solid oxide-based carbon fuel cells with improved performance



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## HIGHLIGHTS

- Industrial coal char was used as a fuel for solid oxide-based carbon fuel cells.
- The Boudouard reactivity of coal char is higher than that of a commercial activated carbon.
- The mineral matter in coal char has a catalytic effect on the Boudouard reaction.
- Added catalysts and the inherent catalysts synergistically improved cell output.

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## ABSTRACT

The use of industrial coal char as a fuel source for an anode-supported solid oxide-based carbon fuel cell (SO-CFC) with a yttrium-stabilized zirconia electrolyte and  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  cathode was investigated. Both the Boudouard reactivity and electrochemical performance of the coal char samples are higher than those of activated carbon samples under the same conditions. The inherent catalytic activity of the metal species ( $\text{Fe}_m\text{O}_n$ , CaO, etc.) in the coal char mineral matter leads to good cell performance, even in the absence of an external catalyst. For example, the peak power density of a cell fueled with pure coal char is  $100 \text{ mW cm}^{-2}$  at  $850^\circ\text{C}$ , and that of a cell fueled with coal char impregnated with an  $\text{Fe}_m\text{O}_n$ -alkaline metal oxide catalyst is  $204 \text{ mW cm}^{-2}$ . These results suggest that using coal char as the fuel in SO-CFCs might be an attractive way to utilize abundant coal resources cleanly and efficiently, providing an alternative for future power generation.

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## 1. Introduction

Coal is the most abundant and cheapest fossil fuel and presently accounts for approximately 30% of the world's primary energy consumption and over 40% of global electricity production [1,2]. Coal will remain a major energy resource in the world's energy portfolio in the foreseeable future [1–3]. However, conventional coal-fired electricity generation has a low conversion efficiency and releases large quantities of  $\text{CO}_2$  and other contaminants into the environment [2–4]. Therefore, new coal-based power

generation technologies with higher efficiencies and lower emissions must be developed.

Direct carbon fuel cells (DCFCs) are promising energy converters with high efficiencies and low environmental impact because they directly use carbon as the fuel for electricity generation [5,6]. The primary challenge for DCFCs is the solid-to-solid contact problem at the interface between the solid fuel and anode [4–6]. To avoid this problem, most DCFCs use molten carbonates or hydroxides as the electrolyte [5–8]. An alternative hybrid-type DCFC combines molten carbonate with a solid oxide electrolyte to obtain better performance [9,10]. The most serious problems associated with these cells are electrolyte degradation and the risk of liquid electrolyte leakage.

Because solid oxide fuel cells (SOFCs) are solid-state devices, they do not suffer from these problems inherent to molten

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## Nomenclature

AC	activated carbon	$M_xO$	mixture of $Li_2O$ , $K_2O$ and $CaO$
CC	coarse particle coal char	OCV	open-circuit voltage
$CO_2$ -TPO	carbon dioxide temperature-programmed oxidation	PPD	peak power density
$d_{002}$	inter-layer spacing (Å)	$R_E$	electrode polarization resistances
D bands	disorder carbon bands of Raman spectra	$R_{ohm}$	ohmic resistances
DCFCs	direct carbon fuel cells	SCD	shorted current density
DC-SOFC	direct carbon SOFC	SO-CFC	solid oxide-based carbon fuel cell
EIS	electrochemical impedance spectra	SOFCs	solid oxide fuel cells
FC	fine particle coal char	TPB	triple phase boundary
G bands	graphite carbon bands of Raman spectra	YSZ	yttrium-stabilized $ZrO_2$
$I$ - $P$	current–power density		
$I$ - $V$	current–voltage		
$K$	constant depending on reflection plane	<i>Greek symbols</i>	
$L_a$	average crystallite diameter (Å)	$\beta$	peak width at the half-maximum intensity (radian)
$L_c$	average crystallite height (Å)	$\lambda$	X-ray wavelength (Å)
LSM	$La_{0.8}Sr_{0.2}MnO_3$	$\theta$	diffraction angle ( $^\circ$ )
MC-CFCs	molten carbonate electrolyte CFCs	$\theta_{002}$	diffraction angle of the (002) peak ( $^\circ$ )

electrolyte DCFCs and have other significant advantages, such as high quality exhaust heat that can be used for combined heat and power generation, and concentrated  $CO_2$  product streams that can be directly collected for industrial use or sequestration [4–6,11]. An SOFC-based DCFC was proposed by Nakagawa et al. and Gür et al. [12,13] and was later named a direct carbon SOFC (DC-SOFC) or solid oxide-based carbon fuel cell (SO-CFC) [4,14]. A series of studies demonstrating the feasibility and superiority of SO-CFCs have been recently reported [12–19]. The SO-CFC anode reaction mechanism has been proposed [12,17] and basically proven [14,19–23] to involve a two-reaction cycle: the electrochemical oxidation of CO at the anode (1) and the Boudouard reaction of the carbon fuel (2):



Solid carbon fuels are readily transported to the triple phase boundary (TPB) by this “CO shuttle” mechanism [17]. Therefore, the reciprocal coupling reactions (1) and (2) are the key anode reactions dominating the SO-CFC performance. Cai et al. reported that it might be possible to reduce the SO-CFC operating temperature to the intermediate temperature range of solid oxide electrolytes (600–800 °C) while improving its performance using a catalytic Boudouard reaction [20]. Liu et al. improved the peak power density (PPD) of a tubular electrolyte-supported SO-CFC from 4  $mW\ cm^{-2}$  to 45  $mW\ cm^{-2}$  by catalyzing both reactions [14]. In our previous work, a PPD of 158  $mW\ cm^{-2}$  was achieved with an SO-CFC with a Ni-ScSZ anode operating at 800 °C when a catalyst was used to promote the Boudouard reaction [22].

Increasing evidence has indicated that the Boudouard reaction plays a crucial role in SO-CFC operation. In addition to the catalyst, the carbon fuel type and its properties are key factors affecting the reaction [6,24]. Commercial carbons, such as carbon black and activated carbon, have been widely used as demonstration fuels for DCFCs [25–28]. However, to the best of our knowledge, limited studies have utilized coal or coal-derived carbon as the fuel in SO-CFCs [18,29,30]. Coal char is a solid carbonaceous residue derived from coal pyrolysis, during which approximately 30% of the total sulfur and other impurities are removed as tars or other gaseous, condensable species [31]. Sulfur is a well-known catalyst poison of SO-CFC Ni-based anodes [32]. Coal char is a promising SO-CFC fuel; however, knowledge of its use in these fuel cells is very limited. Herein, this work focuses the feasibility of industrial

coal char as an SO-CFC fuel. Using activated carbon as the baseline reference, the Boudouard reactivity and electrochemical performance of coal char with and without a catalyst were investigated. The inherent catalytic activity of coal char is discussed in terms of its properties.

## 2. Experimental

### 2.1. Preparation of coal char samples

Coal char and raw coal samples were obtained from Shanxi Lasen Energy Corporation (Shanxi Province, China). Coal char was produced from a coal pyrolysis process, in which coal was heated at the temperatures normally greater than 900 °C in the absence of air, and volatile products (gaseous and liquid) were driven off, leaving a solid residue called char or coke. Coal char and raw coal samples were ground and sieved to 0.1–0.2 mm particle sizes. These particles were subjected to further pretreatments. A commercial low-ash activated carbon (less than 1.5 wt% ash, Sigma-Aldrich, USA) designated AC was used for comparison. The coarse char (CC) was further ground to <5  $\mu m$  by a Fritsch Pulverisette 6 planetary ball mill and designated FC (fine coal char). A catalyst was loaded on the CC, FC, and AC samples by an impregnation/calcination method.  $Fe_mO_n$ - $M_xO$ , where  $M_xO$  is a mixture of  $Li_2O$ ,  $K_2O$ , and  $CaO$ , was employed as the catalyst for the Boudouard reaction. The catalyst synthesis is described elsewhere [22].

### 2.2. Carbon dioxide temperature-programmed oxidation experiments

Carbon dioxide temperature-programmed oxidation ( $CO_2$ -TPO) was performed to analyze the Boudouard reaction efficiency of the carbon samples. Approximately 0.035 g of the catalyst-modified carbon material or 0.03 g of the pure sample 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 h to remove adsorbed water. After cooling the sample to room temperature, pure  $CO_2$  was flowed over it at a rate of 15  $mL\ min^{-1}$  (standard temperature and pressure, STP) for approximately 30 min. Then the temperature was increased to 930 °C at a heating rate of 10  $^\circ C\ min^{-1}$ , 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 in situ monitoring of the  $CO_2$  concentration. In some cases, the Boudouard reaction was not completed at

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