



## Short communication

## Carbon deposition on nickel cermet anodes of solid oxide fuel cells operating on carbon monoxide fuel

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## H I G H L I G H T S

- ▶ Carbon deposition degree variation with discharging time, temperature and CO mole fraction.
- ▶ Distinguished differences between the CO and CH<sub>4</sub> deposited carbon characteristics.
- ▶ Carbon mainly deposited on the Ni surface for CO with mainly regular crystal graphitic carbon structure.

## A R T I C L E I N F O

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## A B S T R A C T

Carbon deposition characteristics of CO/CO<sub>2</sub> fuel on an anode support button cell are investigated. The anodic carbon deposition degree increases with the discharging time, the operation temperature and the CO mole fraction in anode gas. The deposited carbon on the anode cross-sections is characterized by an X-ray photoelectron spectroscopy and a Raman spectrometer to analyze the differences and similarities of CO and CH<sub>4</sub> deposited carbon microstructure. The carbon is mainly deposited on the Ni surface for CO while the deposited carbon consists of carbon on the Ni surface and carbonyl group C=O for CH<sub>4</sub>. Not similar to CH<sub>4</sub>, there is no obvious disordered carbon peak in the CO deposited carbon Raman spectra. The CO deposited carbon is mainly in regular crystal graphitic carbon structure and rarely in amorphous carbon structure.

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## 1. Introduction

Solid oxide fuel cells (SOFCs) are well known for their fuel flexibility and tolerance to carbon monoxide, besides their high efficiency, low environmental impacts and system simplicity for stationary or mobile applications [1]. Nickel based cermet anode (e.g. Nickel/yttrium-stabilized zirconia (Ni/YSZ) anode, Ni/scandium-stabilized zirconium (ScSZ) anode) is the most commonly used SOFC anode material ascribe to the advantages of Ni in high electronic conductivity, high catalytic activity and good thermal stability at high temperature [2–4]. However, the Ni metal is also a catalyst of carbon deposition reactions in SOFC anode when fueled with CH<sub>4</sub> or CO [5,6]. The carbon deposition reactions include: the methane cracking reaction as shown in Eq. (1), the reverse Boudouard reaction as shown in Eq. (2), and the reduction of carbon monoxide as shown in Eq. (3), respectively [7–9].



The deposited carbon will occupy the Ni surface reaction active sites, and then deteriorate the catalytic activity of Ni cermet electrode [10]. And the anode pore structure can be damaged by deposited carbon [11], which further accelerates the SOFC anode performance degradation.

Extensive researches have been focused on the SOFC anode carbon deposition process and carbon deposition inhibition strategy for CH<sub>4</sub> and other types of hydrocarbon fuels. Existed researches in published literature are mainly focused on the kinetics of hydrocarbons internal reforming [12–14], the impact of carbon deposition on the anode microstructure [15] and the effects of carbon deposition on cell performance [16], inhibition of carbon deposition by optimizing the operating condition and by adding different elements (CeO<sub>2</sub>, CuO) in SOFC anode [16,17], etc.

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However, it should be noted that compared with the studies in CH<sub>4</sub> carbon deposition characteristics on Ni/YSZ anode, relative few studies have been focused on the CO carbon deposition characteristics on Ni/YSZ anode. Due to the difference of reaction routes between CH<sub>4</sub> and CO carbon depositions, the deposited carbon morphology and inhibition strategies are quite different [18–21]. Therefore, it is important to clarify the characteristics of CO carbon deposition on the Ni surface and to experimentally test the effects of operating conditions on CO carbon deposition degree on the Ni surface.

In this paper, the carbon deposition behavior of CO/CO<sub>2</sub> fuel on an Ni/YSZ porous anode support button cell has been experimentally investigated with various discharging time, operation temperature and fuel component (CO/CO<sub>2</sub>). Then, the deposited carbon on the anode cross-sections was characterized by an X-ray photoelectron spectroscopy (XPS) and a Raman spectrometer. The XPS and Raman spectra were deconvoluted using pure Gaussian peaks with the same maximum bandwidths. Finally, the comparative analysis of the CH<sub>4</sub> and CO deposited carbon morphology and microstructure have been obtained.

## 2. Experiments

### 2.1. Anode-supported button cell

An anode-supported SOFC button cell made by SICCAS (Shanghai Institute of Ceramics, Chinese Academy of Sciences) was employed. It consists of a Ni/YSZ anode support layer (680 μm), a Ni/scandium-stabilized zirconium (ScSZ) anode active interlayer (15 μm), a ScSZ electrolyte layer (20 μm), and a lanthanum strontium manganate (LSM)/ScSZ cathode layer (15 μm) [22]. The cathode layer is 1.4 cm in diameter and all other layers are 2.6 cm in diameters. The anode support layer and active layer were prepared by mixing nickel oxide (NiO) powder (Inco Ltd., Canada) with 8 mol% YSZ powder (Tosoh, Japan) and with ScSZ powder (Zr<sub>0.89</sub>Sc<sub>0.1</sub>Ce<sub>0.01</sub>O<sub>2-x</sub>, Daiichi Kigenso Kagaku Kogyo, Japan) respectively. The powders were mixed at 50 wt% NiO and 50 wt% stabilized zirconia (YSZ or ScSZ). The electrolyte substrate was a dense film of ScSZ powder. All the ceramic powders were homogenized in a planetary mill with methyl ethyl ketone and ethanol (dispersant) to slurries. Besides, rice starch, polyvinyl butyral, polyethylene glycol and dibutyl o-phthalate were added into the anode layers slurries, which were used as pore former, binder and plasticizer. After being vacuumed for 2 min, the ScSZ, NiO–ScSZ and NiO–YSZ slurries which were used to form electrolyte, anode active and support layers, were cast onto the glass plate by tape casting in sequence. After drying overnight at room temperature, the multilayer tape was detached and co-sintered at 1400 °C in air for 4 h. Then the button cells were cut out from the whole sintered plate. Therefore, the anode and electrolyte layers of all cells were fabricated in one time, which compensates the performance differences caused by cell to cell variations in fabrication to a certain extent. The cathode material was similarly made into paste by mixing LSM (Inframatt Advanced Materials, USA) and ScSZ powders in a mass ratio of 50:50. Then, the paste was screen-printed onto the ScSZ layer of button cell and sintered at 1200 °C for 3 h to form the cathode. The button cells were cut directly from one large cell plate so the anode and electrolyte layers of all cells were fabricated at the same time; thus eliminating the anodic material differences caused by cell to cell variations in experimental tests. Before testing, silver paste was reticulated on the anode and cathode surface by screen-printing for current collection. A test setup was constructed to provide the experimental condition for the button cell operation on carbon monoxide fuel [22].

### 2.2. Experimental conditions and procedures

The experiments focused on the impacts of temperature, discharging time and anode gas compositions on the anodic carbon depositions. A mixture of CO/CO<sub>2</sub> was used as the fuel of SOFC button cell and the cell was kept discharging at 0.7 V. The detailed descriptions of the experimental conditions are shown in Table 1.

Before carbon deposition experiments, pure H<sub>2</sub> was fed into the chamber for 1 h to fully reduce the Ni anode and later Ar was used as purging gas for 1 h. During the actual testing, the flowrates of both fuel and oxidant (pure O<sub>2</sub>) were kept at 100 ml min<sup>-1</sup>. Finally, the cell was cooled down to ambient using Ar (150 ml min<sup>-1</sup>) and H<sub>2</sub> (3 ml min<sup>-1</sup>) as protecting gas. Here, about 2% H<sub>2</sub> was added to maintain a reducing atmosphere in the anode chamber to prevent oxidation of the carbon deposited in the anode. Following three cases were used as control experiments for the comparisons between carbon deposition characteristics of CH<sub>4</sub> and CO. (Table 2).

After the tests, the surface morphology and elemental distribution in the anode cross-sections were characterized using a scanning electronic microscope (SEM) and an energy dispersive spectrometer (EDS) with an electron probe microanalyzer (JSM-6460, JEOL, Tokyo, Japan). The surfaces of the anode cross-sections were analyzed by an X-ray photoelectron spectroscopy (XPS) (PHI Quantera, ULVAC-PHI, Kanagawa, Japan) with a monochromatic Al Kα ( $h\nu = 1486.7$  eV) X-ray source. To avoid any influence of carbon contamination during the sample transfer and handing, all the sample surfaces were peeled 1.2 nm by an electron gun before characterization. The spot size for analysis was 300 μm × 300 μm. To compensate for the surface-charge effects, the binding energy scale was calibrated with reference to the binding energy of O1s at 530.2 eV. The survey scans were acquired between 1200 and 0 eV. Concurrent region sweeps for O1s, Ni2p, Zr3d, Y3d, and C1s were also obtained. The elemental surface composition was calculated using the transmission values with relative sensitivity factors specific for the instrument equipped with an Al source. The deposited carbon on the anode cross-sections was measured by a Raman Spectrometer (RM2000, Renishaw, New Mills, UK). The excitation line was provided by an Ar<sup>+</sup> laser at 515 nm. The Raman spectra were acquired in the range of 1000–1800 cm<sup>-1</sup>.

## 3. Results and discussion

### 3.1. Characterization of anode carbon deposition

Fig. 1 shows the SEM micrographs of the anode cross-sections for CH<sub>4</sub> 800 °C and CO 8 h cases. The SEM micrographs and surface element distribution maps of the anode cross-sections for the CH<sub>4</sub> carbon deposition have been reported in detail in the previous paper [23]. It is difficult to investigate the morphological nature of the CO and CH<sub>4</sub> deposited carbon on the anode surface in

**Table 1**  
Experimental conditions for the anode carbon deposition.

Cases	Temperature (°C)	Discharging time (h)	Anode gas compositions (%)	
			CO	CO <sub>2</sub>
CO 0.5 h	750	0.5	90	10
CO 2.0 h	750	2.0	90	10
CO 8.0 h	750	8.0	90	10
CO 90%	750	8.0	90	10
CO 50%	750	8.0	50	50
CO 10%	750	8.0	10	90
CO 750 °C	750	8.0	90	10
CO 800 °C	800	2.0	90	10
CO 850 °C	850	2.0	90	10

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