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# Electrochemical performance and carbon deposition of anode-supported solid oxide fuel cell exposed to H<sub>2</sub>–CO fuels

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## ABSTRACT

H<sub>2</sub>–CO mixtures were fed to anode-supported solid oxide fuel cell (SOFC) Ni-YSZ/YSZ/GDC/BSCF to investigate the cell electrochemical performance and carbon deposition on the anode. Reasonable power density ( $\sim 0.8 \text{ W cm}^{-2}$ ) was achieved with different H<sub>2</sub>–CO ratios as fuels. By analyzing the electrochemical impedance spectroscopy (EIS) data, it was found that the medium frequency resistance increased with the increasing CO content, which indicated it was most likely associated with the anode charge transfer process. When ratio of H<sub>2</sub>:CO was around 2, CO mainly participates in the water gas shift reaction; and with the increasing CO content in the mixtures, CO also partly was involved in electrochemical oxidation. The cells could operate stably for all H<sub>2</sub>–CO mixtures about 10 h without failure at a constant current of  $50 \text{ mA cm}^{-2}$ . After the cells were tested, no carbon deposition was observed for the pure CO case, but with the presence of H<sub>2</sub>, carbon was observed. This phenomenon proves that the presence of H<sub>2</sub> in H<sub>2</sub>–CO mixtures promotes carbon deposition of CO. We firstly explored the carbon deposition area and found that carbon formation occurred only on the anode surface, which might be mainly caused by CO reduction reaction due to shifting the reaction equilibrium towards reverse syngas formation.

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## Introduction

Solid oxide fuel cells (SOFC) are one of the most flexibility and high efficiency energy conversion devices which directly convert the chemical energy of fuels, such as natural gas,

hydrogen, syngas and biogas, into electrical energy without the restrictions of Carnot cycle [1,2]. Currently, the metal oxide composites are the commonly used anode materials, especially Ni-YSZ (8% mol Y<sub>2</sub>O<sub>3</sub> stabilized ZrO<sub>2</sub>) cermet and Ni-based cermet anodes, e.g. Ni-ScSZ (Sc<sub>2</sub>O<sub>3</sub> stabilized ZrO<sub>2</sub>) and Ni-GDC (Gd<sub>2</sub>O<sub>3</sub> stabilized CeO<sub>2</sub>) anode [3–5], ascribing to

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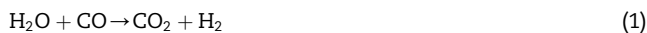
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its structure stability, high electronic conductivity and high catalytic activity for the hydrocarbon fuels electrochemically oxidized. The ceramic phase supports the Ni particles, provides a thermal expansion coefficient (TEC) match to the electrolyte (e.g. YSZ, GDC), and inhibits coarsening of the Ni at the operating temperature.

The hydrocarbon fuels can be reformed to syngas (mainly H<sub>2</sub> and CO mixtures) which can be directly electrochemically oxidized in the SOFC anode chamber [6]. Pure CO can also undergo direct electrochemical oxidation in the SOFC anode [7]. However, the oxidation is very complex when H<sub>2</sub> is introduced to CO [8–10]. Jiang et al. [11] studied the cell performance of anode-supported SOFC under different H<sub>2</sub>–CO ratios. The results showed that water gas shift reaction as shown in Eq. (1) played a major role in the anode reactions, and a high cell performance could be maintained by producing additional H<sub>2</sub> through this reaction. However, Sukeshini's [10] results indicated detrimental effects of H<sub>2</sub>O on CO oxidation and the water–gas shift reaction was not observed. Thus, the electrochemical process and mechanism of H<sub>2</sub>–CO mixtures in Ni-YSZ anode is still debatable and understanding the oxidation of H<sub>2</sub>–CO mixtures is particularly important for designing optimized electrodes.

Another issue in using H<sub>2</sub>–CO mixtures as fuel of SOFC is that the metal of Ni metal is easily deactivated by carbon formation due to excellent catalyst activity for C–H bonding breaking [9,12]. The carbon deposition in the Ni cermet anode may occur through the reversible Boudouard reaction as shown in Eq. (2) and the reaction of CO hydrogenation as shown in Eq. (3), respectively [13]. The carbon deposition rate increases when H<sub>2</sub> is added to CO [14] due to the CO hydrogenation.



The deposited carbon will cover the surface of the Ni catalyst, occupy the active sites of Ni surface reaction and deteriorate the catalyst activity of Ni, then restrict and block the pores of anode or stop current generation by blocking the triple-phase boundary (TPB). Thus, it is important to study the carbon deposition in the Ni-YSZ anode. There are substantial efforts focusing on the strategy of solving carbon deposition through exploring new anode materials and novel electrode structures [6,13,15–21]. However, the performance of state of the art anode materials is less than that of conventional Ni-YSZ anode-supported SOFC with a thin electrolyte film.

Thus, this work focuses on the electrochemical oxidation of H<sub>2</sub>–CO mixtures and the possibility of carbon deposition on the Ni-YSZ anode. Moreover, the cell stability at low current density (50 mA cm<sup>2</sup>) condition was investigated.

## Experimental details

Gd<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>2-δ</sub> (GDC) and Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3-δ</sub> (BSCF) were synthesized by an EDTA-citrate complexing sol–gel process.

Stoichiometric amounts of Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O were dissolved in distilled water followed by the addition of citric acid and EDTA. The pH value of the solution was around 6 with the help of ammonia with the molar ratio of total metal ions: EDTA: citric acid of 1:1:2. The mixture was heated on a hot plate at 90 °C to evaporate the solvent resulting in a transparent gel, which was pre-fired at 240 °C for 12 h and further calcined in air at 800 °C for 5 h. The BSCF powder was calcined in air at 1000 °C for 5 h. NiO-YSZ anode substrate was fabricated by tape-casting [22] and then fired at 1100 °C for 2 h. The YSZ (Tosho, Japan) film was deposited on NiO-YSZ substrate by spray coating, then co-fired at 1400 °C for 5 h in air, obtaining a dense YSZ electrolyte film. The GDC barrier fired at 1300 °C for 3 h was also deposited on the NiO-YSZ/YSZ half-cell using the same method to prevent the reaction between YSZ electrolyte and the BSCF cathode. Finally the BSCF cathode was deposited on the GDC surface followed by sintering at 950 °C for 2 h in air. Ag paste was selected as the current collector and the cathode active area was 0.48 cm<sup>2</sup>.

The single cell was sealed on an Al<sub>2</sub>O<sub>3</sub> tube using silver paste (DAD-87, Shanghai Research Institute of Synthetic Resins, Shanghai, China). The cell was reduced in-situ at 700 °C for several hours using humid hydrogen (~3% H<sub>2</sub>O) and then the temperature was held at 800 °C. Performances of the cells were analyzed using a self-assembly four-probe set-up PAR-STAT2273 advanced electrochemical system. Different ratios of H<sub>2</sub>–CO mixtures (100 mL min<sup>-1</sup> at standard ambient temperature and pressure) were used as fuel and ambient air as cathode atmosphere. I–V curve and Electrochemical Impedance Spectroscopy (EIS) of the single cell were measured at 800 °C under different H<sub>2</sub>–CO ratios. The EIS ranged from 0.01 Hz to 1 MHz with amplitude of 20 mV in Open Circuit Voltage (OCV). The cell resistance was determined by fitting the EIS data using Zview software. The single cell was tested at a constant current density of 50 mA cm<sup>-2</sup> for 10 h at 800 °C under different H<sub>2</sub>–CO mixtures and voltage was measured. Then the cells were cooled down to room temperature under Ar atmosphere.

The anode surface and cross-sections microstructure of the cells after testing were characterized by field emission scanning electron microscope (FE-SEM, JEOL, Japan) equipped with an energy dispersive X-ray spectroscopy (EDS, Oxford X-Max 80SDD). Raman spectrometer (LabRAMHREvolution, HORIBAJobinYvonS.A.S HORIBA, France) was used to probe the deposited carbon on the surface of the Ni-YSZ anode. The Raman spectra were acquired in the range of 1200–1800 cm<sup>-1</sup>.

## Results and discussion

### Thermodynamics equilibrium calculation

The thermodynamic conditions of carbon formation at various H<sub>2</sub>–CO ratios were evaluated by using Factsage 6.0. Fig. 1 shows the carbon deposition regions and demarcation lines at different temperature. It is assumed that graphite is the only condensed phase, since there is no significant difference of demarcation lines for the two condensed phases (graphite and carbon nanofibers) at high temperature (>600 °C) [23]. The carbon-formation boundary lines tend to the linear connection between CO and H<sub>2</sub> with increasing

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