

Short communication

## Electrochemical performance of IT-SOFCs with a double-layer anode

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### Abstract

A new type of anode with double layers, composed of an outer layer Ni-CeO<sub>2</sub> (about 0.5 mm) with relatively large porosity and pore size and an inner layer adjacent to the electrolyte Ni-SDC (about 120 μm), was developed for direct utilization of methane fuel in low-temperature solid oxide fuel cells (SOFCs) with thin-film SDC electrolytes. Cells with this novel anode were fabricated using a tri-layer co-pressing technique. This anode microstructure is believed to lower the anodic concentration polarization when using methane as fuel. Impedance measurements show that the anode polarization resistance of the cell with the novel anode in H<sub>2</sub> is only 0.02 Ω cm<sup>2</sup> which is lower than a conventional Ni/SDC anode. However, it is about 0.2 Ω cm<sup>2</sup> lower when using methane as fuel, which is consistent with the results of electrochemical measurements, inferring that the novel anode shows a relatively high catalytic activity towards methane than the conventional anode. The stability of the cell with the novel anode at 600 °C when using methane as fuel was also studied.

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**Keywords:** IT-SOFC; Two-layer anode; Polarization; Co-pressing

### 1. Introduction

Solid oxide fuel cells (SOFC) will undoubtedly find widespread use in the conversion of chemical to electrical energy because of their high efficiency, low pollution, low cost and flexibility in the choice of fuels [1]. Conventional SOFCs are usually operated at high temperature (1000 °C), which causes many problems for materials and fabrication techniques. So it is desirable to lower the operating temperature to 500–800 °C. However, lowering the operation temperature causes an increase in electrode polarization, especially for the cathode. When using hydrocarbon as fuels, anodic polarization in electrochemical oxidation becomes severe.

Cabrera et al. [2] reported that cerium oxide is used as a catalyst in a wide variety of reactions involving the oxidation, or partial oxidation, of a hydrocarbon. Ceria is also noted for its ability to resist carbon deposition and to catalyze the combustion of carbon. Catalytic activity of rare-earth doped ceria for

butane is much lower than that of undoped ceria according to the results of McIntosh et al. [3]. So it is possible that CeO<sub>2</sub> can be adopted as an anode material for SOFCs. In fact, the ionic conductivity of pure CeO<sub>2</sub> is so low that it will introduce a large anodic polarization, which can be greatly reduced by doping, for example, with samarium. Based on the concept of a multi-layer anode [4], a novel anodic microstructure is proposed (see Fig. 1). The anode is composed of two layers: the outer layer is Ni-CeO<sub>2</sub> with a relatively large porosity and pore size, which acts as a current collector, and at the same time, for gas transport and catalyzing the oxidation of methane. The inner layer adjacent to the electrolyte is Ni-SDC, which is used to catalyze the reactions of the other unreacted species. When methane is supplied to the anode, the reaction between CeO<sub>2</sub> and CH<sub>4</sub> can be expressed as [5]:



The produced CO and H<sub>2</sub> can be oxidized to CO<sub>2</sub> and H<sub>2</sub>O at the second layer by O<sup>2-</sup> coming from the cathode. Contact of the reduced CeO<sub>2</sub> with CO<sub>2</sub> or H<sub>2</sub>O produced CO or H<sub>2</sub>,

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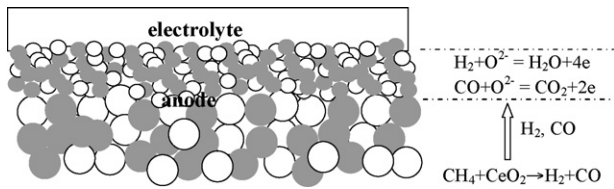
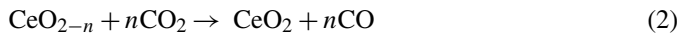


Fig. 1. Schematic of the double-layer anode.

respectively, regenerates the original  $CeO_2$  [5]:



In this work, cells with a two-layer anode were fabricated using a tri-layer co-pressing technique. The preliminary electrochemical performance was measured.

## 2. Experimental

### 2.1. Sample synthesis

$NiO$ ,  $CeO_2$  and SDC ( $Ce_{0.8}Sm_{0.2}O_{1.9}$ ) powders were prepared using the glycine-nitrates-process (GNP). The primary  $NiO$  powder was calcined at  $850^\circ C$  for 4 h,  $CeO_2$  and SDC powders were calcined at  $600^\circ C$  for 2 h, respectively. Then,  $NiO$  and  $CeO_2$ ,  $NiO$  and SDC powders were mixed mechanically in a certain proportion (mass ratio: 65:35), respectively.

### 2.2. Single cell preparation and testing

Single cells with two-layer anodes using a SDC electrolyte were prepared using a dry press [6,7]. The anode layer near the electrolyte is  $NiO$ -SDC (about  $120 \mu m$  thick), the outer layer is  $NiO$ - $CeO_2$  (about  $0.5 mm$  thick). The anode and electrolyte triple-layer were then co-fired at  $1350^\circ C$  in air for 5 h to densify the SDC film. A slurry consisting of SDC + 70 wt%  $Sm_{0.5}Sr_{0.5}Co_3O_3$  and a binder was then applied to the electrolyte by screen-printing, which was subsequently fired at  $950^\circ C$  in air for 2 h to form a porous cathode. For comparison, single cells with a conventional anode that is  $NiO$ -SDC (about  $0.5 mm$  thick) were also prepared. Experimental conditions were controlled to be exactly the same.

The single cell was sealed on an alumina tube with silver paste. Electrochemical characterizations were performed at temperatures from  $500$  to  $600^\circ C$  under ambient pressure. Fuel cell performance was measured with a SOFC test system previously described [8]. Hydrogen (3%  $H_2O$ ) and methane were used as fuel and stationary air as oxidant. The microstructure of the anodes was examined with a scanning electron microscope (SEM, Hitachi X-650). AC impedance was measured at open cell circuit in the frequency range from  $0.01 Hz$  to  $100 kHz$  using a CHI600A electrochemistry analyzer.

## 3. Results and discussion

Shown in Fig. 2 is the cross-sectional view of the double-layer anode. The two-layer anode and the electrolyte are bonded strongly to each other and are homogeneous in thickness. The

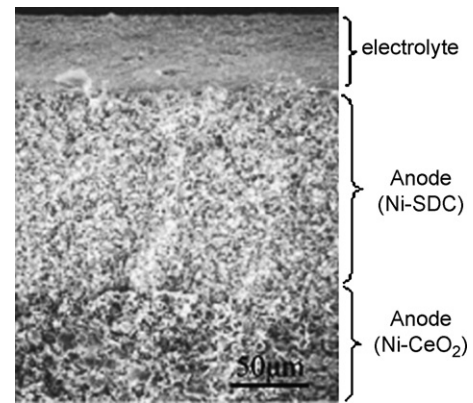


Fig. 2. SEM micrograph of the cross-sectional view of double-layer anode.

electrolyte is relatively dense with thickness about  $40 \mu m$ . The anode is porous. The  $Ni$ -SDC anode layer is about  $120 \mu m$  thick. The particle and pore size in the  $Ni$ - $CeO_2$  layer is larger than that in the  $Ni$ -SDC layer, which benefits the transportation of the gaseous reactants and product. Consequently, anodic polarization should be reduced. On the other hand, the anode–electrolyte cermet is flat after sintering, indicating that the shrinkage ratio of the anode and electrolyte matches well.

Impedance for cells with two-layer anode and ordinary anode were measured at open cell voltages at  $600^\circ C$  using  $H_2$  (3%  $H_2O$ ) and methane as fuels. The measurement was performed using a two-electrode configuration. Results are shown in Fig. 3. In these spectra, the diameter of the depressed semicircle corresponds to the total interfacial polarization resistance of the anode ( $R_a$ ) and cathode ( $R_c$ ). As the cathodes and fabrication processes of the two cells are the same, and they were tested in the same conditions, we can deduce the difference of the anodic interfacial polarization resistance of cells with different anodes from the total interfacial polarization resistance of the anode and cathode. As shown in Fig. 3a, the interfacial polarization resistance of the cell with a two-layer anode is  $0.20 \Omega cm^2$  when using  $H_2$  as fuel, which is similar to that with a conventional anode ( $0.22 \Omega cm^2$ ). However, when the cells were operated under methane (see Fig. 3b), the anodic interfacial polarization

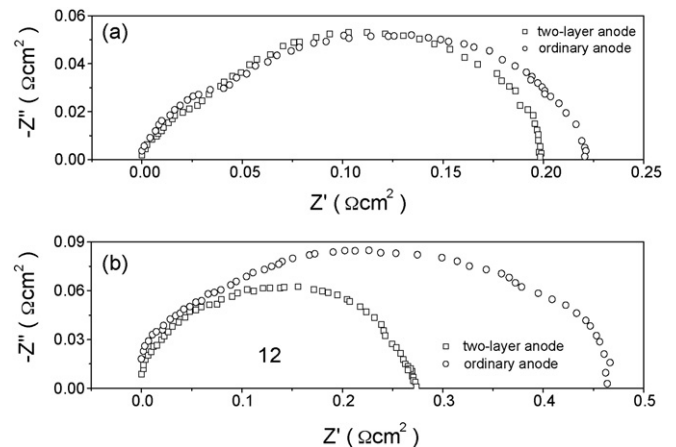


Fig. 3. Impedance spectra at  $600^\circ C$  for the single cells with two-layer anode and conventional anode under: (a) hydrogen and (b) methane.

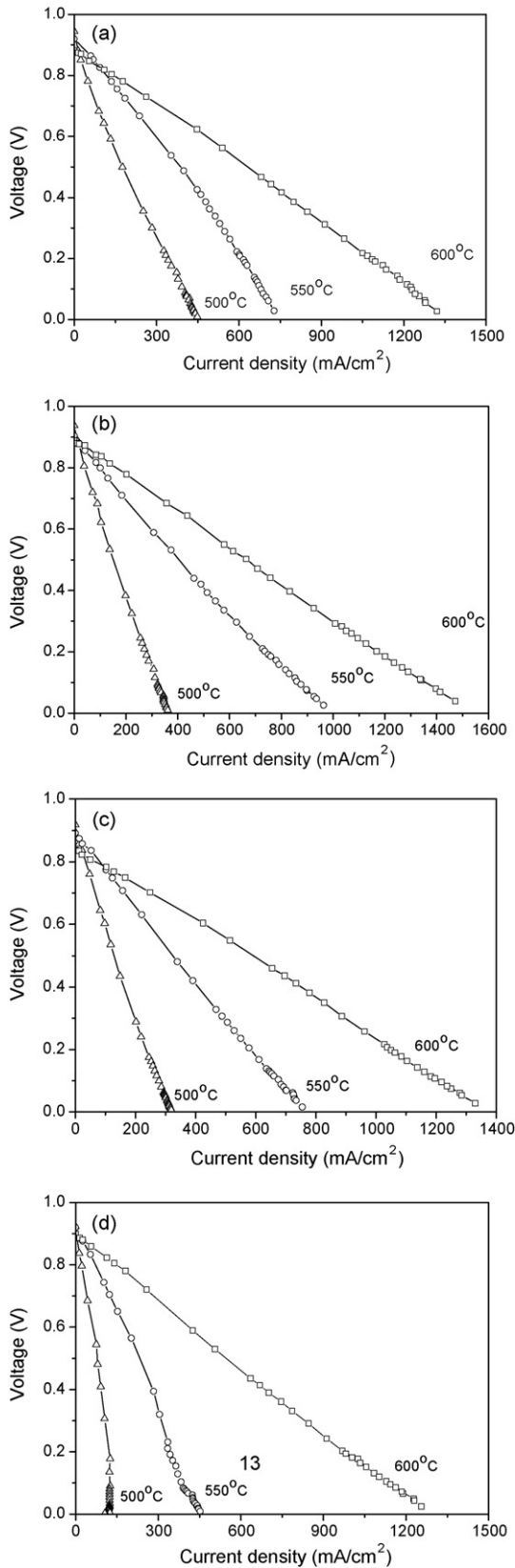


Fig. 4. Temperature dependence of the cell voltages on current densities at 500–600 °C for the single cell: (a) with two-layer anode in H<sub>2</sub>, (b) with conventional anode in H<sub>2</sub>, (c) with two-layer anode in CH<sub>4</sub> and (d) with conventional anode in CH<sub>4</sub>.

resistance of cell with two-layer anode is about 0.2 Ω cm<sup>2</sup> lower than that with the conventional anode, which infers that the two-layer anode shows a higher catalytic activity towards methane than the conventional one.

Shown in Fig. 4 are the voltages as a function of current densities for cells with double-layer and conventional anodes in hydrogen and methane, respectively. Their open circuit voltages (OCVs) were about 0.94 V at 500 °C and decreased with temperature. The OCVs are consistent with those reported for ceria-based cells operating at these temperatures [9–11]. The relatively lower OCVs are believed to be due to the electronic conductivity induced by partial reduction of the ceria electrolyte. In Fig. 4d, changes in slope of the polarization curves are observed at low temperature (500–550 °C) below 0.4 V which is caused by mass transfer limitations. While in Fig. 4a–c, there is no obvious change. SEM photographs of the two-layer anode show that porosity and pore size of Ni-CeO<sub>2</sub> layer is larger than that of the Ni-SDC layer, which is similar to the conventional anode. It is well known that mass transfer or diffusional limitations involving electrode pores could cause concentration overpotentials. So it can be deduced that the anodic concentration polarization of the cells with a two-layer anode is lower than that of the cells with a conventional anode when using methane as fuel.

Fig. 5 displays the maximum power densities as a function of temperature for cells with a two-layer anode and an ordinary anode when using hydrogen (3% H<sub>2</sub>O) and methane as fuels, respectively. Results show that the maximum power densities for the cell with different anodes under hydrogen are similar, indicating that the catalytic activity of the two-layer anode to hydrogen is similar to that of the conventional anode, although a large amount CeO<sub>2</sub> was used in the two-layer anode instead of SDC, whose electrical conductivity is much larger than the former. However, when using methane as the fuel, differences in the maximum power densities are obviously large. This can be attributed to the catalytic activity of pure CeO<sub>2</sub> on hydrocarbon being higher than that of SDC in the conventional anode [3],

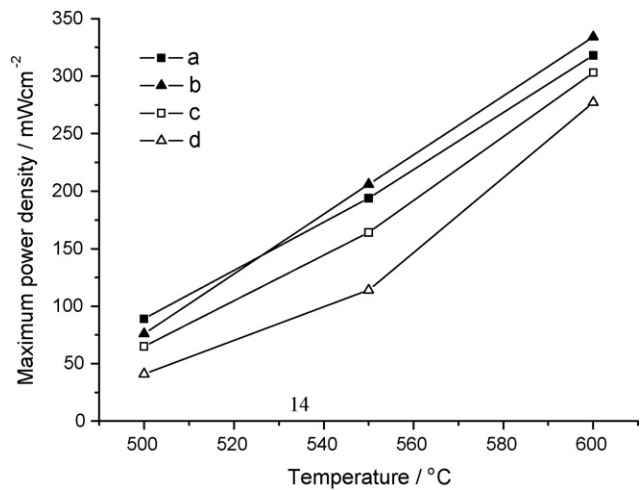


Fig. 5. Temperature dependence of the maximum power densities at 500–600 °C for the single cells: (a) with two-layer anode in H<sub>2</sub>, (b) with conventional anode in H<sub>2</sub>, (c) with two-layer anode in CH<sub>4</sub> and (d) with conventional anode in CH<sub>4</sub>.

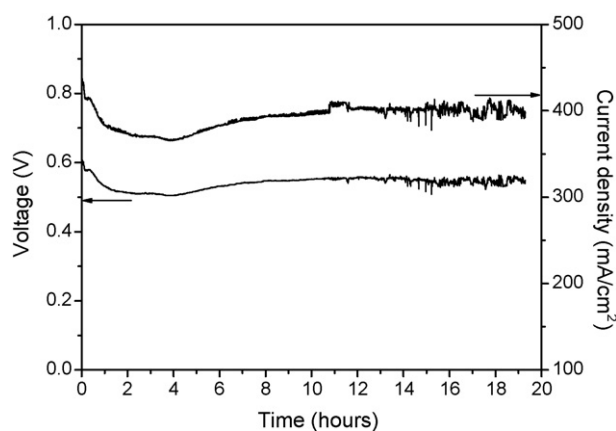


Fig. 6. Stability of the single cell with two-layer anode operated at 600 °C with methane as fuel.

which may reduce the activation energy of hydrocarbon fuel oxidation, as a result, the anodic activation polarization decreases and the power density of the cell increases accordingly.

Fig. 6 gives the stability of the cell with two-layer anode at 600 °C when using methane as fuel. During the first 2–3 h, the voltage and current density decrease gradually, then begin to rise to the initial level. The first decrease may correspond to the initial stage:  $\text{CeO}_2$  catalyzes methane to  $\text{CO}$  and  $\text{H}_2$ , at the same time,  $\text{CeO}_2$  is reduced. With the increase of amount of the reduced  $\text{CeO}_2$ , the speed of oxidization of methane is decreased, as a result, the voltage and current density decrease. With the oxidization of  $\text{CO}$  and  $\text{H}_2$  at the second anode layer, the produced  $\text{CO}_2$  and  $\text{H}_2\text{O}$  can oxidize the reduced  $\text{CeO}_2$ , enabling catalytic activity again. Once these reactions form a continuous process, the performance of the cell began to recover. During the final hours, the voltage and current density showed a relatively large fluctuation. Carbon deposition on the anode, by reaction of the cathode with carbon dioxide in the air, may be the reason. Further studies need to be carried out to verify this.

#### 4. Conclusions

Cells with a novel anode were fabricated and the performance was tested under  $\text{H}_2$  (3%  $\text{H}_2\text{O}$ ) and  $\text{CH}_4$ . The anode consisted

of two layers, the first layer was  $\text{Ni-CeO}_2$  with a relatively large porosity and pore size and thickness of about 0.5 mm; the second layer near the electrolyte was  $\text{Ni-SDC}$  with a thickness about 120  $\mu\text{m}$ . This anode microstructure can reduce the mass transfer limitations in the anode when using methane as fuel. Impedance spectra showed that the anodic interfacial polarization resistance of the cell with a novel anode in  $\text{H}_2$  was similar to that with an ordinary anode. However, it was about  $0.2 \Omega \text{ cm}^2$  lower when using methane as fuel. Electrochemical measurements also showed that trend, implying a relatively higher catalytic activity towards methane. In the stability test, decrease of the voltage and current density during the first 2–3 h could be attributed to the lag of recovery of the catalytic activity of  $\text{CeO}_2$ . Carbon deposition may be the reason for the fluctuations during the last hours.

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