



Short communication

High performance Ni–Sm₂O₃ cermet anodes for intermediate-temperature solid oxide fuel cells

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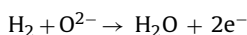
ABSTRACT

A novel anode consisting of Ni and Sm₂O₃ with negligible oxygen-ion conductivity was developed for intermediate-temperature solid oxide fuel cells (SOFCs). Its triple phase boundary length is pretty small compared with the conventional Ni-samaria doped ceria (SDC) anode, of which SDC is one of the electrolytes having high oxygen-ion conductivity. Even so, single cells with Ni–Sm₂O₃ anodes generated peak power density of 542 mW cm⁻² at 600 °C, comparable to, if not higher than those with the Ni–SDC anodes when the same cathodes and electrolytes were applied. In addition, Ni–Sm₂O₃ exhibited lower interfacial polarization resistance than Ni–SDC. The high electrochemical performance, which might be related to the high catalytic activity of Sm₂O₃ and the unique microstructures of the Ni–Sm₂O₃, suggests a viable alternative to the conventional anodes for SOFCs.

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1. Introduction

Solid oxide fuel cells (SOFCs) have the potential to produce electricity with high efficiency [1]. The fuel is electrochemically oxidized at the anode according to the following reaction:



Therefore, the catalytic properties of the anode to fuel oxidation reaction are of great importance [2,3]. In addition, the anode must provide paths for the transport of oxygen ions, electron, and gas since the reaction takes place where the three species are available [4]. Beside its low cost, nickel is a very good electronic conductor and an excellent electrocatalyst for the electrochemical oxidation for hydrogen and hydrocarbons. So, the anodes are usually based on porous composites of Ni with oxygen-ion conducting ceramics such as yttria-stabilized zirconia (YSZ) or doped ceria (DCO) [1]. The use of YSZ in the anode serves several purposes, one of which is to supply a conductive network for oxygen ions. In this way an extended region of triple-phase-boundary (TPB) is formed, where electrons, oxygen ions, and the gas phase can meet and react. The electrochemically active zone thus expands up to 10–20 μm from the physical electrolyte–anode interface due to the ionic transport in the YSZ network [5]. As a result, the fuel cell performance is greatly improved and the interfacial polarization

resistance is substantially reduced by YSZ incorporation [6]. The involvement of DCO can further enhance the performance of the Ni anodes due to the reason that DCO has higher oxygen ion conductivity and higher catalytic activity than YSZ [7]. In principle, the performance improvement is more significant for an oxygen-ion conductor with higher conductivity [8]. Comparative studies of the anode materials with different levels of the oxygen ionic transport, such as Ni–Zr_{0.85}Y_{0.15}O_{1.93}, Ni–Ce_{0.9}Gd_{0.1}O_{2-δ}, Ni–Ce_{0.6}Gd_{0.4}O_{2-δ}, Ni–La_{0.75}Sr_{0.25}Cr_{0.97}V_{0.03}O_{3-δ}, and Zr_{0.71}Y_{0.12}Ti_{0.17}O_{2-δ}, confirmed that increasing ionic conductivity leads to lower values of the total polarization resistance [9].

However, as sharp contrast to the principle that high performance is directly associated with high ionic conductivity, this work reports a composite anode consisting of Ni and Sm₂O₃, which is a non-conductive oxide. Although the conductivity of Sm₂O₃ is negligible compared with that of DCO, the interfacial polarization resistance of Ni–Sm₂O₃ is even lower than that of Ni-samaria doped ceria (SDC) when the fuel cells are operated at 600 °C. This result suggests new materials and/or alternative viability for the development of SOFCs.

2. Experimental

The powders involved in this work including Sm₂O₃, Sm_{0.2}Ce_{0.8}O_{1.9} (SDC), NiO and Sm_{0.5}Sr_{0.5}CoO₃ (SSC) were synthesized via a glycine nitrate method. Taking the synthesis of Sm₂O₃ as an example, a solution containing Sm³⁺ (1 mol L⁻¹) was prepared by dissolving Sm(NO₃)₃ in distilled water. After adding

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glycine, the solution was heated till self-combustion occurred. The resulted ashes were calcined at 800 °C for 2 h to form Sm_2O_3 powders. The synthesis of other powders was described in detail in our previous work [10]. Sm_2O_3 ceramics were obtained via dry-pressing the powder into pellets with 15 mm in diameter under 300 MPa and then sintered at 1250 °C for 5 h. The conductivities of the Sm_2O_3 ceramics were measured at temperatures from 500 to 800 °C using two-probe impedance spectroscopy.

Single cells consisting of SDC electrolytes, Ni– Sm_2O_3 anode substrates, and SSC–SDC cathodes were fabricated with a dry pressing process [11]. Anode powders (NiO and Sm_2O_3 with a weight ratio of 65:35) were prepared by mixing and grinding NiO and Sm_2O_3 with an agate mortar and pestle. 15 wt.% of starch was added as the pore former. Green bodies consisting of NiO– Sm_2O_3 substrates and SDC electrolytes were formed by co-pressing the anode powder and SDC powder uniaxially under 300 MPa. The bi-layer pellets with dense electrolytes were formed by co-firing the green bodies at 1250 °C in air for 5 h. For comparison, single cells with Ni–SDC anodes were also fabricated with the same process as employed in preparing those with Ni– Sm_2O_3 anodes. The cathodes were then screen-printed onto the other side of the electrolytes and the fabricating process was kept as consistent as possible so that identical cathodic polarization resistance can be achieved. The thickness of the electrolytes and the anodes of the two cells are about 35 μm and 0.4 mm, respectively.

The cells were sealed onto an alumina tube with silver paste (DAD-87, Shanghai Research Institute of Synthetic Resins). Humidified (3% H_2O) hydrogen was used as the fuel with a flow rate of 50 mL min^{-1} and ambient air as the oxidant. An Electrochemical Workstation (IM6e, Zahner) was used to characterize single cells. The current–voltage curve was obtained by using a galvanostat mode and the electrochemical impedance spectra were measured under open circuit conditions in the frequency range from 0.1 Hz to 1 MHz. The microstructure was observed via a scanning electron microscope (SEM, JSM-6700F, JEOL).

3. Results and discussion

Fig. 1 shows typical current–voltage curves for single cells with Ni– Sm_2O_3 anodes. At 600 °C, the cell exhibited open-circuit voltage (V_{oc}) of 0.853 V, which is close to those reported for H_2 /air fuel cells with SDC electrolytes and Ni–SDC anodes. The reported values were 0.850 V [12], 0.88 V [13], and 0.85 V [15] when SSC–SDC cathodes were fabricated with various methods. The closeness in V_{oc} suggests that Ni– Sm_2O_3 anodes exhibit electrochemical activity as high as those of Ni–SDC composites. Low electrode performance would cause low V_{oc} using mixed-conducting electrolytes such as

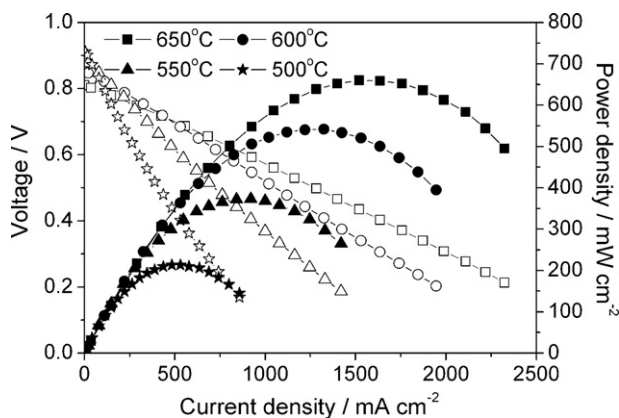


Fig. 1. I – V curves for the single cell with Ni– Sm_2O_3 anode at different temperatures when humidified (3% H_2O) hydrogen and ambient air were used as the fuel and oxidant, respectively.

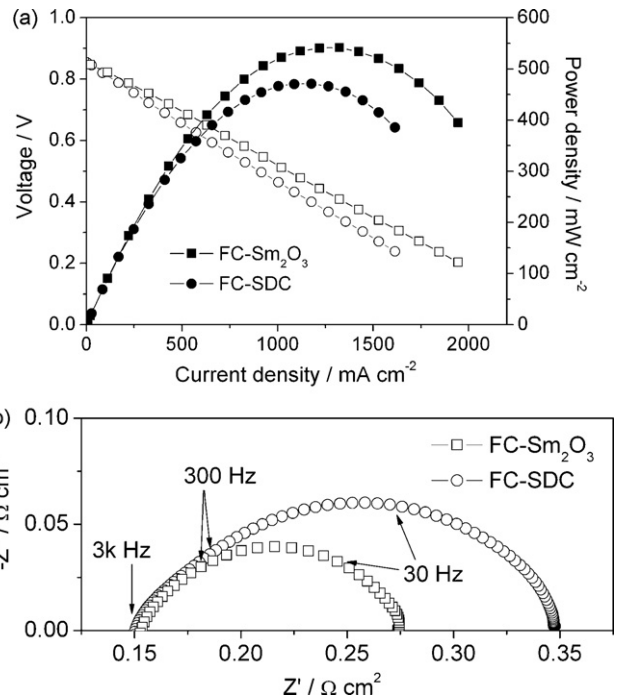


Fig. 2. (a) I – V curves for the single cells with Ni– Sm_2O_3 and Ni–SDC anode at 600 °C and (b) impedance spectra measured under open circuit conditions.

doped ceria with elevated temperature [13,14]. The peak power densities are 660, 542, 372, and 213 mW cm^{-2} at 650, 600, 550, and 500 °C, respectively. The power densities are also comparable to the reported values for fuel cells with Ni–SDC anodes and SDC electrolytes of similar thickness. For example, using $\sim 30 \mu\text{m}$ thick SDC as the electrolytes, the peak power densities at 600 °C were 399 mW cm^{-2} [12], 397 mW cm^{-2} [15], and 491 mW cm^{-2} [16], respectively. To make direct comparison, single cells with Ni–SDC anodes were prepared using identical process as those with Ni– Sm_2O_3 anodes. For convenience, the single cells with the Ni– Sm_2O_3 anode and the Ni–SDC anode are referred as FC– Sm_2O_3 and FC–SDC, respectively. Fig. 2 shows the comparison of performance measured at 600 °C. The curve for the cell voltage and power density as a function of current density demonstrates that FC– Sm_2O_3 exhibits better performance than FC–SDC. Since the cathodes and electrolytes of the two cells are exactly the same, the difference in performance should originate from the variation of the anode. Fig. 2b shows impedance spectra measured under open circuit conditions. The total interfacial polarization resistance (R_p), which is derived from the difference between low and high frequency intercepts with the real axis, shows a smaller value of 0.118 Ωcm^2 for FC– Sm_2O_3 than that for FC–SDC, 0.199 Ωcm^2 . Due to the difficulty to separate the anodic polarization resistance (R_a) from R_p for anode-supported cells, it is reasonable to consider that the variations in R_p are only derived from the anodes. The small R_p , high V_{oc} , and high power density demonstrate that Ni– Sm_2O_3 composites show good enough electrochemical behavior as the anode of intermediate-temperature SOFCs. Further, the electrochemical performance is even better than that of the Ni–SDC anodes.

The performance of a Ni–cermet anode depends directly on the conductivity and catalytic activity of the ceramic component. The conductivity of Sm_2O_3 was thus measured with Sm_2O_3 pellets, which had 98% of the theoretical density. The conductivity of Sm_2O_3 is three orders of magnitude lower than that of SDC at 500–800 °C. For example, the conductivities of Sm_2O_3 at 600 °C are 4.0×10^{-6} and $5.2 \times 10^{-6} \text{ S cm}^{-1}$ in humidified hydrogen (3% H_2O) and air, respectively, far lower than the value of SDC, $8.6 \times 10^{-3} \text{ S cm}^{-1}$. Therefore, the Sm_2O_3 matrix in the Ni– Sm_2O_3 anode has a neg-

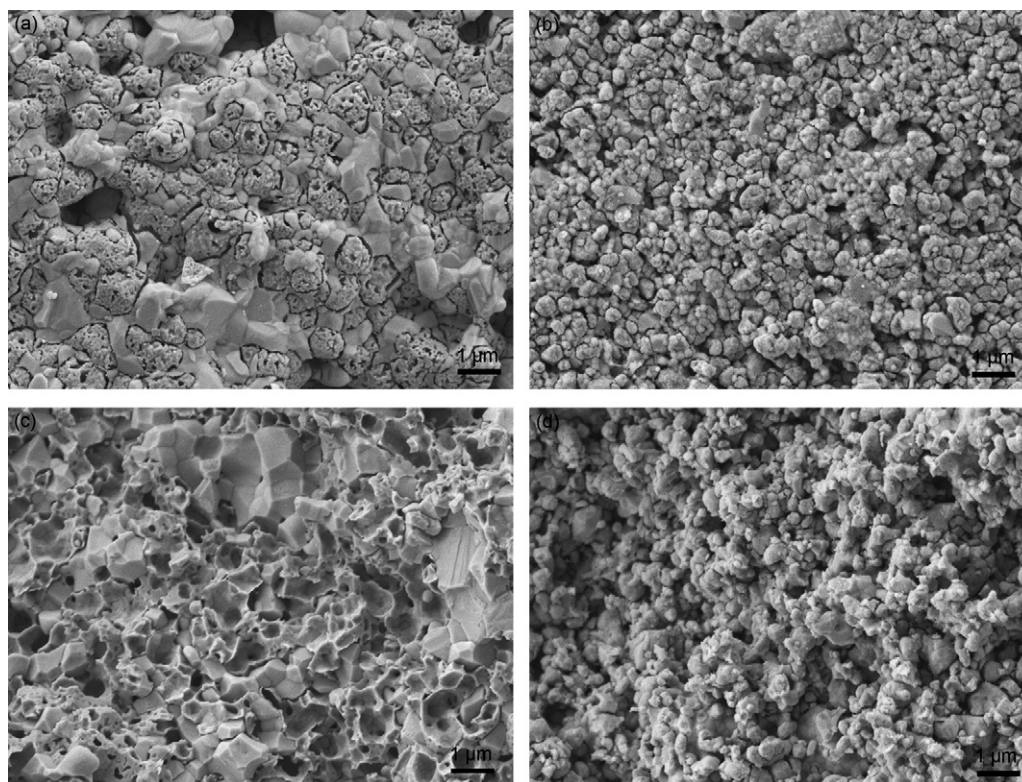


Fig. 3. SEM micrographs of the Ni-Sm₂O₃ anode for: (a) surface and (c) cross-section; and of the Ni-SDC anode for: (b) surface and (d) cross-section.

ligible ionic conductivity and TPB is thus limited to the physical interface between the electrolyte and Ni-Sm₂O₃ anode. Accordingly, it is reasonable to consider that the high performance of Ni-Sm₂O₃ anode is only related to the high catalytic activity of the anode. Sm₂O₃ have been demonstrated to be a promising oxidative catalyst [17], which might be the reason for the excellent electrochemical behavior of the Ni-Sm₂O₃ anode. In addition, the microstructure characteristics of Ni-Sm₂O₃ composites are quite different from those of Ni-SDC. Fig. 3 shows the SEM pictures for the surface and cross-sectional microviews of the two composites. The Ni-SDC anode that composed of submicron particles displays porous microstructures, which are very similar to those reported in the literatures, and the compact Ni and SDC particles cannot be easily identified from each other [18]. On the contrast, the Ni-Sm₂O₃ shows remarkably different microstructures. The Ni particles are porous themselves and can be visibly distinguished from the well-developed Sm₂O₃ particles. It seems very likely that the joining between the Ni and Sm₂O₃ particles is very strong. In addition, the Ni particles form an interconnecting network, which is cooperated tightly with that of Sm₂O₃. Therefore, besides the catalytic property of Sm₂O₃, the unique microstructure might be a reason for the high performance of the Ni-Sm₂O₃ anode since the anode performance is very dependent on its microstructure [19]. Note that no solid-state reaction took place between Sm₂O₃ and Ni or NiO during fabrication and measurement as investigated with X-ray diffractometry (XRD, Philips X'pert PROS diffractometer). EDX result also showed that no obvious solid-state diffusion occurred between ceria and samaria at the electrolyte/anode interface.

4. Conclusions

We have demonstrated that the single cells with the Ni-Sm₂O₃ anode exhibited high performance when hydrogen was used as the fuel. Comparing with Ni-SDC anodes which have large TPB length, the electrochemical reaction in the Ni-Sm₂O₃ anode should be

constricted to the physical interface between the electrolyte and anode since Sm₂O₃ has extremely low conductivity. The high performance might be due to the electrocatalytic activity of Sm₂O₃ and the unique microstructure of the anodes. Although the catalytic activity deserves further investigation in details, this result would provide a new thinking approach to design and develop the anodes of SOFC.

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