



Microstructural variations and their influence on the performance of solid oxide fuel cells based on yttrium-substituted strontium titanate ceramic anodes



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HIGHLIGHTS

- Performances of Y substituted SrTiO₃ anode based electrolyte supported cells with different anode designs were tested.
- The influence of low ionic conductivity of Y substituted SrTiO₃ to cell performance was observed.
- The degradation of Y substituted SrTiO₃ anode based electrolyte supported cells was tried to understand and be controlled.
- A possible mechanism of anode processes was obtained.

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ABSTRACT

Donor-substituted strontium titanates have been widely recognised as alternative anode materials to the state-of-the-art Ni/YSZ cermet in solid oxide fuel cells (SOFCs). Electrolyte-supported SOFCs based on Y_{0.07}Sr_{0.895}TiO₃ ceramic anodes with different microstructural designs were prepared. Ni or Ni with Ce_{0.8}Gd_{0.2}O_{1.9} (CGO) was infiltrated onto the pore walls within the ceramic anode framework as an electrocatalyst for anode reactions. Performances and electrochemical impedance spectroscopy measurements of the cells were analysed in detail to observe the influence of low ionic conductivity of Y_{0.07}Sr_{0.895}TiO₃ to cell performance, to understand how to control the degradation of the cells, and to obtain a possible mechanism for the anode processes. The anode design containing both functional and current collecting layers with sufficient Ni-CGO infiltration is favourable for high power output and low performance degradation.

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1. Introduction

Solid oxide fuel cells (SOFC) are promising electrical power generators because of higher fuel efficiency and lower CO₂ emissions compared to conventional combustion systems and better fuel flexibility than other kinds of fuel cells. However, the state-of-the-art anode material for SOFCs, the Ni/YSZ cermet, shows significant limitations such as low tolerance to re-oxidation (redox) [1–5], high sensitivity to sulphur poisoning [6] and coking [7].

Hence, the development of SOFCs has stagnated on a system level due to the need to integrate additional components to avoid the aforementioned operational handicaps. Among the possible alternative anode materials, donor-substituted SrTiO₃ ceramics have attracted increasing interest during the last few years because of their relatively high conductivity [8–10] and good dimensional stability upon redox cycling [11–13]. Many single cells based on such kinds of anodes have been reported to show promising performances [14–20]. In earlier works of this group [17], anode supported cells (ASCs) based on Y-substituted SrTiO₃ exhibited power output of over 1 W cm⁻² at 800 °C and robustness of surviving in 50–200 redox cycles, while ASCs based on Ni/YSZ cermet cannot survive in even one cycle. Recent developments on a system level [21] further indicate certain prospects for practical

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applications.

Although the robustness of donor-substituted SrTiO₃ ceramics makes them suitable as anode backbones, they have significant weaknesses: The lack of catalytic activity for the oxidation of anode fuels, and the limited ionic conductivity. The former can be compensated by catalyst infiltrations such like Ni and Gd substituted CeO₂, which has been widely and specifically discussed [11,22–24], while for the latter, there is only limited knowledge [25,26]. Although mixing ion-conducting materials with substituted SrTiO₃ anodes seemed to be effective to solve the problem in certain extent [17], the degree to which the low ionic conductivity of donor-substituted SrTiO₃ limits anode performance has not yet been clarified. What's more, most recently some results were published to discuss the long-term stabilities of donor-substituted SrTiO₃ anodes based SOFCs [21,27]. They all showed degradation problems while the explanations were only in assumptions.

Actually, the general understanding of the electrochemical anode processes of donor-substituted SrTiO₃ based cells is still poor. It is known that catalytic sites for oxidation of the fuel gases, electronic pathways, oxygen-ion pathways and fuel gas diffusion pathways are essential for anode reactivity. The Ni/YSZ cermet can fulfil these essential requirements with 3 phases: Ni, YSZ and fuel gas since Ni can act simultaneously as catalyst and electronic pathway. The anode reactions mostly take place along the contact areas of the 3 phases, known as triple-phase boundaries (TPB). However, a donor-substituted SrTiO₃ anode needs 4 phases because none of the phases can cover two essentials at the same time like Ni in the Ni/YSZ cermet, which makes the anode processes of donor-substituted SrTiO₃-based cells more complicated. Very few reports discuss this topic. Hussain et al. [23] considered infiltrated Ni, infiltrated Ce_{0.8}Gd_{0.2}O_{1.9} (CGO) and a Nb-substituted SrTiO₃ (STN) backbone as catalyst, ionic conductor and electronic conductor, respectively, for the anode processes. They claimed that their infiltrated CGO formed a homogeneous film and covered the surface of the STN particles. Although 4 phases contribute to the anode reactions, all of them are always connected to each other, which creates a situation similar to the TPB in the Ni/YSZ cermet. However, most of the reported cells based on donor-substituted SrTiO₃ ceramic anodes do not have such an ideal surface coverage of an ionic conductor. Normally, the catalyst and ionic conductor are located separately from each other on the ceramic backbone. Some of them also show high performance [17,24], although the microstructural arrangements appear less favourable.

In this study, electrolyte-supported SOFCs (ESCs) based on Sr_{0.895}Y_{0.07}TiO₃ (YST) ceramic anodes with different microstructural designs and catalyst infiltrations were prepared to obtain a better understanding of the microstructure-property relationships, explaining how low ionic conductivity of YST will limit anode performance, why there are degradation problems for infiltrated YST based cells and how to control. Based on relative analysis, mechanisms for explaining the anode-processes of infiltrated YST based anodes are also raised.

2. Experimental

Powders of Sr_{0.895}Y_{0.07}TiO₃ (YST) and Sr_{0.895}Y_{0.07}TiO₃ with 10 mol% Ti excess (YST1.10) were prepared by spray pyrolysis. After spray pyrolysis the raw powders were heated up to 900 °C in air for 5 h. The reason for using YST1.10 as anode material is the higher conductivity after mixing with YSZ compared to that of YST–YSZ mixtures, the specific can be found in a former research [28]. Ti-isopropoxide, Y(NO₃)₃·6H₂O and Sr(NO₃)₂ were used as the starting materials. Zr_{0.852}Y_{0.148}O_{1.926} powder (YSZ, Tosoh, Japan) or Zr_{0.887}Sc_{0.113}O_{1.944} (ScSZ, Treibacher, Austria) powder was used for

the ceramic anode composite. They were mixed with YST1.10 in volume ratio of 1:2 by 24 h ball-milling respectively. The phase purities of YST or YST1.10-YSZ powders after sintering at 1350 °C for 5 h in 4% H₂/Ar were checked by XRD using a Siemens D4 diffractometer with Cu K α radiation. Apart from perovskite and/or fluorite no other phases were observed. The specific about powder preparation can also be found in a former publication [28].

Screen printing pastes of YST1.10-YSZ (2:1 in volume)-graphite, YST1.10-ScSZ (2:1 in volume)-graphite or YST-graphite (the YST and YST1.10 powders were pre-calcined at 900 °C) were prepared by mixing the powders with terpeneol and ethyl cellulose. Here graphite was used as a pore former (15% in volume). ScSZ electrolyte discs (34 mm in diameter, 160 μ m in thickness) were prepared in a commercial production line at Nippon Shokubai Ltd., Japan. YST1.10-YSZ-graphite (or YST1.10-ScSZ-graphite) and/or YST-graphite were screen-printed on one side of the discs as the anode functional layer and/or current collector, respectively. After de-binding, the anodes were sintered at 1350 °C for 5 h in 4% H₂/Ar. The porosity of sintered anode current collectors is about 25–30%, ~10 μ m in thickness, while that of anode functional layers is about 30–35%, ~15 μ m in thickness. All layers are well contacted with each other. Afterwards, different amounts of NiO and CGO were impregnated into the anodes by immersing the discs in Ni nitrate or (Ce, Gd) nitrate solutions in vacuum and subsequently heating the discs up to 500 °C. La_{0.8}Sr_{0.2}MnO₃ (LSM)-YSZ and LSM were screen-printed onto the other side of the discs as cathode functional layer and current collecting layer, respectively. The cathodes were sintered in situ at operating temperature during performance testing. Table 1 gives an overview of the different cell types indicating the various amounts of catalysts. A series of cells for each cell type were prepared and tested, typical results are discussed in results and discussion part.

Current–voltage (I–U) measurements of the cells were carried out under different conditions using a self-assembled seal-less testing system. The anode was contacted with a Ni mesh, whereas the cathode was contacted with an Au mesh. A H₂ flow rate of 200 ml min⁻¹ was applied as the fuel gas. A membrane evaporator was used at room temperature to moisten the fuel gas (~10% H₂O). Air at a flow rate of 400 ml min⁻¹ was used on the cathode side. The test rig is described in more detail in a former report [29]. The cells were first heated up to 900 °C and stabilised for over 30 h, mainly to ensure in-situ sintering of the cathode. The cells were then mainly operated at 850 °C. I–U curves were recorded from time to time at different temperatures. Electrochemical impedance spectroscopy (EIS) was measured with a Zahner IM6ex, from 200 kHz to 50 Hz at different electrical loads and 20 mV amplitude.

The prepared YST powders were also uniaxially pressed into pellets (\varnothing 22 mm, 1.3 mm in thickness) and densified in Ar/4% H₂ at 1350 °C for 12 h for measuring the oxygen permeation rate. The samples were cut to a diameter of 14.7 mm and 1 mm thickness and mounted in a home-made quartz glass recipient as described earlier [30]. 250 ml_N min⁻¹ air and 50 ml_N min⁻¹ argon was supplied as feed and sweep gas, respectively. The permeate, i.e. oxygen enriched argon, was analysed using a mass spectrometer (Omnistar, Pfeiffer Vacuum, Germany). At first, the recipient was heated to 1000 °C in order to seal the specimens to the glass compartments using gold rings. After thermal equilibration the oxygen permeation rate was measured in ca. 50 K-steps down to 750 °C.

Microstructures of different cells were investigated by scanning electron microscopy (SEM; Zeiss Ultra55).

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