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Effective improvement of interface modified strontium titanate based solid oxide fuel cell anodes by infiltration with nano-sized palladium and gadolinium-doped cerium oxide

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ABSTRACT

The development of low temperature solid oxide fuel cell (SOFC) anodes by infiltration of Pd/Gd-doped cerium oxide (CGO) electrocatalysts in Nb-doped $SrTiO_3$ (STN) backbones has been investigated. Modification of the electrode/electrolyte interface by thin layer of spin-coated CGO (400–500 nm) contributed to a significant improvement in performance of the STN backbones and infiltrated electrodes. The improvement is due to the result of CGO enrichment at the interface. The impedance analysis showed that addition of Pd further increased the electrode reaction rate with a factor 10 with respect to the CGO electrocatalysts. Very low electrode polarization resistances of 0.055 Ω cm^2 (after excluding the gas diffusion limitation contribution) and 1.2 Ω cm^2 at 600 °C and 400 °C, respectively, have been obtained in 3% H_2/H_2O. A gradual decrease in polarization resistance was achieved with increasing loading of Pd-CGO electrocatalyst. The microstructural analysis of the infiltrated Pd-CGO electrocatalyst on STN revealed a homogenous coating of Pd and CGO nanoparticles.

1. Introduction

The electrochemical conversion of chemical energy by electro-oxidizing the fuels (hydrogen or hydrocarbons) using solid oxide fuel cells (SOFCs) is a proven technology for sustainable energy production [1]. Development of efficient anodes, cathodes and electrolytes at low temperature ranges are the primary goal for SOFC technological advancements [2]. The loss associated with the ionic conduction in electrolytes is addressed by reducing the thickness to few microns and by using alternative electrolyte materials with higher ionic conductivities. Gd-doped cerium oxide (CGO) electrolyte based fuel cells with Ni-CGO anodes have shown a power density of 1.1 W/cm^2 at 650 °C and increased 3 times with bimodally integrated anode functional layer, as reported by Kang Taek Lee et al. [3,4]. However, the majority of voltage loss in state of the art SOFCs is associated with the overpotential of the electrodes [5,6].

The development of electrodes with low electrode polarization resistance is required to demonstrate the operation of SOFCs at low temperatures (400–600 °C). Blennow et al. studied the redox behaviour and electrochemical characterization of Nb-doped $SrTiO_3$ (STN) as a potential anode for SOFCs [7]. The electrochemical performance of this anode had been improved with the composite of CGO and STN [8]. Marina et al. [9,10] reported the beneficial electrochemical effects of CeO_2-modified (La,Sr)(Ti,Ce)O_3 anodes. Electrode/electrolyte modifications at the interface also facilitate an improvement in electrode performance. A thin layer of Y-doped CeO_2 on either side of anode and cathode yielded high power density in SOFCs, as reported by Barnett et al. [11]. A change in oxygen transport properties was obtained by insertion of dense $La_2NiO_{4+\delta}$ in between electrolyte and porous $La_2NiO_{4+\delta}$ cathode at low temperature (600 °C) [12]. Recently, we reported an improved electrochemical activity for hydrogen oxidation in SOFC anodes with metallic Pd, sputtered at the interface of electrode and electrolyte [13].

The poor electrocatalytic activity of ceramic anodes is the major drawback limiting their application in SOFCs. There are several studies reporting on the possibilities of using Ce-doped $SrTiO_3$ ceramic oxides as potential 'stand-alone' anodes for SOFCs [14–16], however, the studied materials are also limited by catalytic activity. A way to improve anode kinetics in ceramic oxide anodes such as STN is performed by solution infiltration technique resulting in nano-sized electrocatalysts [17]. Nano-structured electrodes will have a very high specific surface area, which is normally associated with high electrochemical performance. Low temperature

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calcination of these infiltrated precursors retains the nanostructure of the percolated electrocatalysts. The possibility of using inexpensive, abundantly available oxides such as tungsten and copper based alternative SOFC anodes by infiltration have recently been reported [18]. Nevertheless, that finding showed higher anode overpotentials, indicative of a need of much better catalysts at low temperature operations of SOFCs (<600 °C). Incorporation of transition metal catalysts in ceramic anodes by infiltration have been widely investigated, in particular Pd addition in doped strontium titanates have shown improved anode performance [19,20–22]. Guntae Kim et al. studied the effect of Pd and CeO_2 in $Y_{0.04}Ce_{0.48}Zr_{0.48}O_2$ and composite $La_{0.3}Sr_{0.7}TiO_3$–YSZ anodes [21]. Shiwoo Lee et al. reported a cell performance of 780 mW/cm^2 at 800 °C that was achieved by an addition of 0.5 wt.% Pd and 5 wt.% CeO_2 in $La_{0.3}Sr_{0.7}TiO_3$ anodes [22]. In a study conducted earlier, we reported the preparation and characterization of efficient ceramic oxide backbones infiltrated with Ni, Pt, Ru or Pd in combination with Gd-doped ceria (CGO) for SOFC anodes [23]. Noble metal catalysts are proven to exhibit excellent catalytic activity for hydrogen oxidation. However, considering the cost and scarcity, it is important to minimize the use of noble metal catalysts. A significant reduction in quantity of noble metals could be made by catalytic precursor infiltration in an electronic conducting ceramic backbone in comparisons to the conventional cermet type anodes [19]. Constituting the majority of the electrocatalyst by cerium oxide (90 wt.%) with minimal quantity of noble metals reduce the cost considerably. CGO has been shown to have a self-limited grain growth [24], which is advantageous for the stability of nano-structured electrodes. It is to be noted that based on the data reported by H. Kurokawa et al., for a cell operating at a power density of 100 mW/cm^2 the cost of metallic Pd (approximate loading of 1 μmol/cm^2) for 1 kW stack is 8.62 USD, while for metallic Pt and Rh the cost is 53.44 and 24.35 USD [19]. Also, based on the current market situation, the Pd price is about half of the price for Pt, which is known among the noble metals for superior catalytic activity towards hydrogen oxidation.

In this article, we report on the effect of CGO interfacial layer in improving the performance of Pd-CGO electrocatalyst infiltrated STN anodes. In order to modify the electrode/electrolyte interface, thin CGO layers were spin-coated on the 120 μm $Sc_{0.1}Y_{0.01}Zr_{0.89}O_{1.895}$ electrolyte tapes (10Sc1YSZ). The coated tapes were heat treated at low temperatures, resulting in the formation of CGO fluorite type structure. The resulted tapes were printed with STN ink and sintered at high temperatures to form the backbone. The resulted CGO modified STN backbone (CMS) was infiltrated with Pd-CGO electrocatalyst to form an active anode. The high performance in the CMS electrode is due to the enrichment of CGO at the interface, resulting in possible enhancement of triple phase boundary and increase of catalytically active sites for hydrogen oxidation. Although it is certainly not the aim of this study to provide an extensive model for the electrode impedances, the clear change in electrode responses, in relation to the preparation methods, gives clear indications towards the underlying mechanisms. We have tried to present these findings in a tentative model. Further, more detailed, studies are necessary to elucidate these highly interesting features.

2. Experimental

2.1. Spin coating of CGO

CGO precursor gel, suitable for spin coating, was prepared by dissolving cerium nitrate ($Ce(NO_3)_3{\cdot}6H_2O$) and gadolinium nitrate ($Gd(NO_3)_3{\cdot}6H_2O$) in a molar ratio Ce:Gd = 0.8:0.2 in ethylene glycol. The detailed characterization of the CGO precursor for spin coating is reported elsewhere [25]. Pre-sintered 10Sc1YSZ tapes (6 × 6 cm^2) were washed with ethanol and heat treated at 300 °C overnight, to remove any organic impurities. A few drops of precursor were added on the tape that was held by a vacuum in the spin coater (Model: WS-400A-8NPP/LITE, Laurell Technologies Corporation). During the spin coating process, initial ejection of excess solvent and subsequent evaporation of the solvents led to a uniform thin coating on the tapes. The thin film deposited on the electrolyte was heat treated at 350 °C for 1 h in air, which burned away the binders and formed a CGO layer of 400–500 nm in thickness.

2.2. Preparation of Pd-CGO infiltrated anodes

The STN powders having the nominal composition $Sr_{0.94}Ti_{0.9}Nb_{0.1}O_3$ were synthesized by a wet chemical method reported in our earlier publication [23]. Backbones of STN were prepared by screen printing an in-house fabricated STN ink on both the sides of CGO-coated ScYSZ electrolyte tapes. The symmetrical cell assembly was first sintered in air at 1200 °C for 4 h and subsequently pre-reduced at 1000 °C in 9% H_2/N_2 for 5 h. The cells were cut into smaller squares having an electrode area of 0.25 cm^2 for use in the electrochemical set-up.

A 0.75 M CGO ($Ce_{0.8}Gd_{0.2}O_{2-\delta}$) precursor solution was prepared by dissolving cerium nitrate ($Ce(NO_3)_3{\cdot}6H_2O$) and gadolinium nitrate ($Gd(NO_3)_3{\cdot}6H_2O$) in water along with a polymer surfactant to improve wetting properties. A precursor solution of Pd-CGO was made by mixing 0.60 M palladium nitrate ($Pd\ (NO_3)_2{\cdot}6H_2O$) in an already prepared CGO solution. Pd-CGO precursor solution contained 10 wt.% of Pd and 90 wt.% of CGO. The STN anodes were prepared by infiltrating a few drops of the precursor solution into the symmetrical cell. Vacuum was applied in order to remove the air bubbles in the porous STN backbone and to facilitate the liquid precursor to coat the backbone surface of the anode homogeneously. After each infiltration, the cells were calcined at 350 °C for 1 h in air. The change in weight after the calcination was recorded after each infiltration. The cell was infiltrated with Pd-CGO in 1, 6 or 9 repetitive cycles to obtain loadings of 0.4, 6, and 10 wt.% in the CGO modified STN backbone. Similarly, for comparison, unmodified STN backbones were infiltrated three times with a CGO precursor [4 wt.% loading, denoted: *STN CGO(3)*] or a Pd-CGO precursor (4.5 wt.% loading, denoted: [STN *Pd-CGO(3)*].

2.3. Microstructural characterization

FEG-scanning electron microscope (SEM SUPRA 35), operated at 5 kV, was employed to characterize the microstructure of the infiltrated anode samples. Few selected samples were also investigated by a transmission electron microscope (TEM) at an accelerating voltage of 300 kV (JEM–3000F). An oxford instruments energy dispersive X-ray spectroscopy (EDS) microanalysis detector with an ultrathin window was used to conduct chemical analysis of samples in scanning transmission electron microscopy (STEM) mode, utilizing the 1 mm probe size. A 100 nm thin TEM lamella was prepared by the use of a FIB-SEM H-bar technique in a Crossbeam 1540XB dual focused ion beam (FIB)/SEM (Carl Ziess) using an optimum method [26].

The crystal structure of the synthesized STN powder and sintered STN symmetrical cells on ScYSZ was verified using XRD (Bruker D8 Bragg-Brentano diffractometer) with Cu Kα radiation.

2.4. Electrochemical characterization

In this study symmetrical cells have been used. This has the advantage that the electrolyte can be very thin (120 μm in our case), thus strongly reducing its contribution to the electrode dispersion. Measurements under bias in a symmetrical cell are meaningless,