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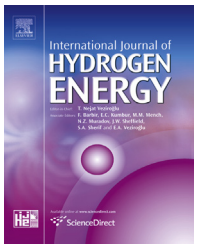

The effect of electrode infiltration on the performance of tubular solid oxide fuel cells under electrolysis and fuel cell modes

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ABSTRACT

The electrochemical performance of two different anode supported tubular cells (50:50 wt% NiO:YSZ (yttria stabilized zirconia) or 34:66 vol.% Ni:YSZ) as the fuel electrode and YSZ as the electrolyte) under SOFC (solid oxide fuel cell) and SOEC (solid oxide electrolysis cell) modes were studied in this research. LSM ($La_{0.80}Sr_{0.20}MnO_{3-\delta}$) was infiltrated into a thin porous YSZ layer to form the oxygen electrode of both cells and, in addition, SDC ($Sm_{0.2}Ce_{0.8}O_{1.9}$) was infiltrated into the fuel electrode of one of the cells. The microstructure of the infiltrated fuel cells showed a suitable distribution of fine LSM and SDC particles (50–100 nm) near the interface of electrodes and electrolyte and throughout the bulk of the electrodes. The results show that SDC infiltration not only enhances the electrochemical reaction in SOFC mode but improves the performance even more in SOEC mode. In addition, LSM infiltrated electrodes also boost the SOEC performance in comparison with standard LSM–YSZ composite electrodes, due to the well-dispersed LSM nanoparticles (favouring the electrochemical reactions) within the YSZ porous matrix.

Introduction

The Ni–YSZ/YSZ/LSM–YSZ system, where Ni–YSZ forms the porous composite fuel electrode and LSM ($La_{1-x}Sr_xMnO_{3-\delta}$)–YSZ the porous composite oxygen electrode, has been the most studied and fabricated SOFC system to date [1,2]. Fabrication of a conventional Ni–YSZ fuel electrode requires high temperature sintering (~1400 °C) and reduction (900–1000 °C) [3]. The LSM oxygen electrode is usually exposed to a lower sintering temperature (max. 1250 °C) to prevent reaction between YSZ and LSM which results in the formation of poorly conducting phases such as $La_2Zr_2O_7$ and $SrZrO_3$ [4]. The high temperature sintering of SOFC electrodes will eventually lead to significant grain growth and a corresponding loss of surface area and electrochemical activity in the electrode phases.

Infiltration/impregnation (of generally nitrates) has been established as an important method in the development of

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high performing electrodes giving them a suitable microstructure for oxygen reduction or fuel oxidation. Infiltration can enhance the catalytic activity (via fine dispersed particles), and ionic and/or electronic conductivity (via connected particles) of fuel cell electrodes leading to a cell power boost. In addition, the high active surface area of the infiltrated particles enables a reduced operating temperature, improving cell stability and reliability [5–7]. The lower particle size and higher surface activity of the infiltrates is a result of a comparatively low heat treatment temperature needed to decompose the nitrates and form the final phases versus the conventional high sintering temperatures for composite electrodes.

Infiltrating LSM into a porous YSZ structure has been previously carried out by various SOFC groups [8–13]. Improvement in the cell performance due to enhanced triple phase boundary (TPB) length and catalytic activity compared to the traditional composite LSM–YSZ cathode has been reported. Infiltration of a ceria-based catalyst into the Ni–YSZ anode also increases the TPBs for hydrogen oxidation and the ionic conductivity leading to improved electrode performance [14–17] as well as coverage of Ni particles by the infiltrate thereby lowering its sintering and agglomeration [3,17]. Ceria infiltration has also been shown to improve sulphur tolerance of the Ni–YSZ anode to a significant extent [18].

In addition to the importance of fuel cells in the production of electricity, an efficient and economic way for hydrogen production is to use a solid oxide electrolysis cell (SOEC). In fact an SOEC is a reversible fuel cell in which steam is fed to the cathode where it is converted to hydrogen fuel [19,20]. This method consumes much less electrical energy compared to conventional water electrolysis for the production of hydrogen. High temperature steam electrolysis has been recently demonstrated using microtubular cells [21–23]. Moreover, application of infiltrated electrodes for SOEC is a relatively new topic with few reported studies to date. More recently, Yang et al. [24] showed that LSM infiltrated porous YSZ has a lower area specific resistance compared with a conventional LSM–YSZ composite electrode under SOEC mode testing. In addition, cells with LSM infiltrated electrodes have demonstrated stable performance under SOEC operation. Chen et al. [25] have shown that GDC impregnated LSM is an effective anode for high temperature SOECs. This same research group also showed that LSM infiltrated electrodes exhibited high electrocatalytic activity and good stability under SOEC operating conditions, and concluded that the high stability is related to the microstructural stability of infiltrated LSM nanoparticles due to the effect of LSM lattice shrinkage under SOEC polarization [26].

In addition, Li et al. [27] also reported on SOEC cells with Ni infiltrated composite cathodes based on LSCM ($La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$). They found that the loading of Ni improves the current density by approximately 20% and, in addition, the combination of infiltrated nickel and redox-stable LSCM also improved the stability of the cathode. Finally, researchers from the Watanabe group prepared SOEC fuel electrodes using a highly dispersed nickel-SDC catalyst [28,29]. They found that the Ni-dispersed SDC fuel electrode gave the highest performance at 17 vol.% nickel loading due to effective enhancement of the reaction rate by increasing the active reaction sites and lowering the electronic resistance. The authors measured a cell consisting of a Ni-dispersed SDC fuel electrode, ScSZ electrolyte, SDC interlayer and LSC as the oxygen electrode and obtained 1.13 V at -0.5 A cm^{-2} and 900 °C under 60% RH (relative humidity) of steam. From our knowledge, there is no report in the literature about the effect of ceria infiltrated nanoparticles into the fuel electrode for electrolysis applications.

In this manuscript, the effects on the electrochemical performance of tubular fuel cells of LSM ($La_{0.80}Sr_{0.20}MnO_{3-\delta}$) infiltration into porous YSZ at the oxygen electrode and, in addition, SDC ($Sm_{0.2}Ce_{0.8}O_{1.9}$) infiltration into the Ni–YSZ fuel electrode, are studied in both SOFC and SOEC modes.

Experimental procedure

The anode supported cells studied in this paper were fabricated by slip casting of a NiO–YSZ anode support followed by dip coating of a thin YSZ electrolyte and a thin porous YSZ layer for cathode infiltration. LSM was infiltrated into the thin porous YSZ layer of both cells to form the cathode and SDC was infiltrated into the NiO–YSZ anode support of the second cell.

In order to produce a suitable slip for casting the anode supported cells, YSZ powder (TZ-8Y, 8 mol% Y_2O_3, Tosoh) was calcined at 1500 °C for 3 h, cooled and mixed with 50 wt% NiO powder (Baker Chemicals) and water at a powder:water ratio of 1:1. The mixture was then milled at 120 rpm for 72 h in a plastic bottle with 5 mm zirconia balls. Additional water was added after milling to adjust the solid loading of the final suspension to 40%. The pH of the slip was set to 4.0 using 2% hydrochloric acid. In order to generate high porosity, 30 vol.% graphite (Sigma Aldrich <325 mesh) was incorporated into the slip following pH adjustment, and then the suspension was mixed for 15 min prior to slip casting.

To create the tubular support, the slip was cast into a plaster mold (previously prepared from a tubular mandrel) and left for about 1 min, after which the excess slip was quickly poured out. The wet tube was then dried at room temperature for 1 h. The resulting drying shrinkage facilitates removal of the green tube. The green tube was further dried at 100 °C in an oven, heated at 700 °C for 1 h to oxidize all the graphite, and then pre-sintered under air at 1150 °C for 3 h. Further details regarding the fabrication of thin porous supports via slip casting and the parameters affecting tube thickness during casting are discussed elsewhere [30,31].

The electrolyte and the thin porous YSZ layer formulas and dip coating procedure are explained in Ref. [32] and Refs. [32,33], respectively. The LSM ($La_{0.80}Sr_{0.20}MnO_{3-\delta}$) cathode and also SDC ($Sm_{0.2}Ce_{0.8}O_{1.9}$) infiltration methods are addressed in Ref. [33]. In this manuscript the anode supported cells without and with infiltrated SDC are referred to as “Tube 1” and “Tube 2”, respectively.

For the electrochemical experiments, platinum mesh was tightly placed inside the tube to provide electrical contact between the fuel electrode and the Pt lead wire. Pt wires were used for current collection at the oxygen electrode side, and LSM paste (terpineol-based) was used to improve current collection. Subsequently, the cell and electrical leads were