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Improving intermediate temperature performance of Ni-YSZ cermet anodes for solid oxide fuel cells by liquid infiltration of nickel nanoparticles

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HIGHLIGHTS

- Ni-YSZ electrodes can be effectively liquid infiltrated with nickel nanoparticles.
- TPB of the Ni-YSZ substrate and infiltrated nickel can be quantified and compared.
- Liquid infiltration of nickel nanoparticles improves Ni-YSZ electrode performance.
- Performance improvement increases as temperature is reduced from 800 °C to 600 °C.

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ABSTRACT

Liquid infiltration of NiO followed by reduction to form Ni nanoparticle catalysts in solid oxide fuel cell (SOFC) can produce a high density of electrochemical reaction sites. In recent years, electrode architectures utilizing porous oxide substrates with ionic conductivity or mixed ionic-electronic conductivity and connected networks of nickel produced by liquid infiltration have become a popular approach to improve SOFC anode catalytic performance, especially for operating temperatures less than 800 °C. However, infiltrated nickel structures suffer from poor durability, demonstrating significant loss in performance during the first 100 h of use. In contrast, traditional Ni-yttria stabilized zirconia (Ni-YSZ) cermet SOFC anodes exhibit long-term performance stability. However, Ni-YSZ cermet anodes have micron sized structures, and consequently have a significantly lower density of electrochemical reaction site density than infiltrated nickel structures, which have dimensions of around 100 nm. In this study, the performance impact of liquid phase infiltration of nickel nanoparticles into Ni-YSZ cermet anode supported SOFCs is studied by measuring the electrochemical behavior of infiltrated cells at 800 °C, 700 °C, and 600 °C, and comparing them to the performance of an uninfiltrated cell. Durability of the nanoparticles after electrochemical testing is also assessed using a method for quantifying particle statistics from fracture cross sections.

1. Introduction

Liquid phase infiltration of catalysts into porous ceramic substrates is commonly used in solid oxide fuel cell (SOFC) electrodes. The catalysts are used to perform a variety of functions, such as improving catalytic performance of the anode and cathode as well as improving the tolerance of electrodes to various impurities [1–5]. Liquid phase infiltration is especially attractive due to its simplicity and low additional cost. Nickel nanoparticles can be infiltrated into an anode ceramic scaffold, which is itself an ionic conductor or a mixed ionic-electronic conductor (MIEC). When a purely ionic conducting scaffold is used, the infiltrated nickel nanoparticles must form a connected network to provide a pathway for electron conduction in the anode. It has been reported that this approach has many advantages, including: significant reduction in the molar fraction of Ni needed, enhanced tolerance to redox cycling, and very fine feature sizes of the deposited Ni [1,5–12]. In nickel-yttria stabilized zirconia (YSZ) SOFC anodes, electrochemical reactions can only occur at triple phase boundaries (TPBs), one-dimensional regions where the gas phase, the ionically conducting phase, and the electronically conducting phase all meet. The fine feature sizes of infiltrated nickel networks are often on the order of 0.1–1 μm, creating a high TPB density of 10–30 μm μm^{-3} [1,2]. This higher density of electrochemically active reaction sites leads to an improved initial performance of the SOFC [9]. However, the performance of infiltrated nickel anodes drops quickly during operation, often within the first few days of exposure to high temperature. This has been

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attributed to the rapid coarsening of the infiltrated Ni nanoparticles [11–14].

In comparison, traditional Ni-YSZ cermets (formed by tape casting layers of mixed NiO and YSZ particles and then laminating layers to the desired thickness) have stable performance over long periods of operation [15,16]. However, the catalytic performance of traditional anodes is lower than the initial performance of the infiltrated nickel electrodes, because tape cast cermets have Ni particles that are on the order of 1 μm, leading to TPB densities between 1 and 10 $\mu m\,\mu m^{-3}$ [17–21]. The poorer catalytic performance of tape cast anodes are exacerbated at lower temperatures, where the electrode charge transfer kinetics are slower [5,22–25]. Liquid infiltration of tape cast Ni-YSZ cermets combines the benefits of long term stability of Ni-YSZ cermets, and the high catalytic activity of Ni infiltration. Various other more complex methods have been attempted to stabilize infiltrated nickel structures, usually involving co-infiltration of an oxide phase [2,26]. However, the behavior of simple Ni infiltrated Ni-YSZ anodes have not been fully investigated, and is the subject of this study. The stability of the infiltrated Ni nanoparticles and their impact on electrochemical performance at 800 °C, 700 °C, and 600 °C was observed using a new quantitative method based on image analysis of fracture cross sections. The performance (as measured by the current – voltage (I-V) characteristics) of the Ni-infiltrated cells was compared to that of uninfiltrated cells at different temperatures.

2. Factors affecting anode polarization

By comparing the performance of cells with infiltrated anodes to identical cells without anode infiltration, any changes in cell performance can be directly attributed to changes in anodic contributions to the overall cell polarization. Anode polarization losses can be separated into two components: anodic concentration polarization due to resistance of mass transfer through pores, and anodic activation polarization due to the charge transfer resistance at electrochemical reaction sites. Anode infiltration will impact both these components.

Anode infiltration with Ni nanoparticles is expected to increase anodic concentration polarization because the volume fraction of pores in the anode is being traded for additional nickel volume fraction. The slight reduction in the size of pores will decrease both the molecular gas diffusivity as well as the Knudsen gas diffusivity. Gas diffusion in SOFC anodes can be modeled using the Dusty Gas Model, which includes both molecular and Knudsen diffusion [23,27–29]. Qualitatively, it is clear that decreasing molecular and Knudsen diffusion rates will increase anodic mass transfer resistance. This is the most immediately obvious negative impact of anode infiltration.

The quantification of the positive effect of liquid infiltration on anodic activation polarization is not as straightforward. Activation polarization in SOFCs is usually modeled by the Butler-Volmer equation [22,23,28,30]. This approach does not provide a first-principle methodology to connect cell microstructure with electrochemical performance. It has been experimentally observed that increased catalytic site density (TPB length) reduces activation polarization in the anode [20]. This simple explanation is adequate for this study because no new materials with potentially different characteristics are being introduced. Introducing Ni nanoparticles in a Ni-YSZ anode increases the electrochemical reaction site density for the same set of anode materials for the infiltrated and uninfiltrated cells. Finally, the temperature dependence of anodic activation polarization is much stronger than that of anode concentration polarization. Thus, the relative importance of the two anodic components of the overall cell polarization will vary significantly with changing temperature.

3. Experimental methods

3.1. Infiltration of button cells

Button cells were purchased from Materials and Systems Research, Incorporated (Salt Lake City, UT). The cells comprised of an 800 μm thick, 2.74 cm diameter NiO-YSZ anode supporting layer, a more finely structured 12 μm thick NiO-YSZ anode active layer (AAL), a 10 μm thick dense YSZ electrolyte, a 15 μm thick and 1.70 cm diameter lanthanum strontium manganite (LSM)-YSZ cathode active layer, and a 50 μm thick LSM cathode current collector layer. The electrochemically active area of the cell, determined here by the cathode diameter, was 2.275 cm^2.

All cells were prepared for infiltration and testing by pre-reducing the NiO-YSZ anode to Ni-YSZ. To reduce the anode, cells were mounted between two alumina tubes and protected using mica gaskets, with light spring load on the alumina tubes to ensure good contact between the tubes and cell. The assembly was placed in a tube furnace and heated to 800 °C at 1 °C min^{-1} with air flowing at 1000 sccm on the cathode side. After equilibrating for 30 min at 800 °C, forming gas (95% Ar – 5% H_2) was introduced on the anode side at 300 sccm for 12 h, with air continuing to flow on the cathode side. The cell is then cooled at 1 °C min^{-1} with gas flowing continuing on both sides.

The Ni-YSZ anodes were infiltrated using repeated cycles of vacuum impregnation of an aqueous nickel nitrate solution followed by drying and decomposition of $Ni(NO_3)_2$ to NiO at higher temperature. The aqueous 4 M $Ni(NO_3)_2$ solution was prepared by mixing 23 g nickel nitrate (Chemsavers, 99.9%+), 1.8 ml Triton-X 100 surfactant (Talas), and 20 ml distilled water at 90 °C. The solution was impregnated into the reduced anode in a vacuum flask at 5 mbar absolute pressure. Excess liquid on the surface of the anode was wiped off to avoid blocking pores for the next round of infiltration. The infiltrated cell was heated to 100 °C at 2 °C min^{-1} and held for 20 min to evaporate the water, then heated to 320 °C at 2 °C min^{-1} and held for 20 min to decompose the infiltrated $Ni(NO_3)_2$ to NiO. For cells used in this study, the above infiltration procedure was repeated five times.

3.2. Electrochemical testing

To prepare for testing, metallic meshes were attached to the electrodes for use as electrical contacts using conductive inks. A nickel mesh current collector (Alfa Aesar, 99.5%) with nickel lead wires (Alfa Aesar, 99.5%) was adhered to the anode using nickel ink (Fuel Cell Materials). A silver mesh current collector (Alfa Aesar, 99.9%) with silver lead wires (Alfa Aesar, 99.9%) was adhered to the cathode using silver ink (Alfa Aesar). The cell was then loaded into the electrochemical test stand, shown schematically in Fig. 1, between an Al_2O_3 tube and a machined Al_2O_3 plate with mica gaskets above and below the cell. A K-type thermocouple was fed inside the cathode side gas inlet tube to measure cell temperature during testing. The whole assembly was then compressed between the aluminum end plates using springs attached to the Al_2O_3 alignment rods on both the cathode and anode sides. A sealing glass paste (Fuel Cell Store) was applied around the edges of the cell to ensure a complete gas seal.

The assembly was heated to 850 °C at 1 °C min^{-1} with forming gas flowing on the anode side at 300 sccm and air flowing on the cathode side at 1000 sccm. The furnace was held at 850 °C for 12 h to cure the glass paste, and then brought to the 800 °C at 1 °C min^{-1}. Cells were tested using a Parstat 2273A potentiostat and impedance analyzer (Ametek, Inc.) with a Kepco power booster. Cells underwent an electrochemical pretest procedure with 3% H_2O – 97% H_2 flowing on the anode side at 300 sccm and 1000 sccm of air flowing on the cathode side. Electrochemical pretesting involved monitoring the open circuit voltage for 24 h to ensure good sealing, and applying galvanostatic current of 0.5 A cm^{-2} for 24 h to stabilize cell performance. Stable cell performance was verified by three repeated identical I-V scans. All I-V scans were conducted galvanodynamically at a rate of 5 mA s^{-1}.