Processing of SOFC Anodes for Enhanced Intermediate Temperature Catalytic Activity at High Fuel Utilization

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Introduction

In an operating SOFC stack, the fuel composition changes along the flow channel over the anode surface because the fuel is electrochemically oxidized and steam is generated. Cell performance loss occurs at high fuel utilization conditions (Fig. 1) due to the loss in Nernst potential, the anodic concentration polarization, and the anodic activation polarization. The loss in Nernst potential is a thermodynamic loss due to high oxygen partial pressure in the H_2O-rich fuel. The anodic concentration polarization can be minimized by decreasing the thickness of the electrode and increasing the anode porosity. The anodic activation polarization becomes significant at high fuel utilization since the water vapor molecules occupy the reaction sites near the TPBs and hinder the fuel oxidation reactions. The drive to decrease the SOFC operation temperatures to an intermediate range (600-800°C) exacerbates the anodic activation polarization. This research will concentrate on decreasing anodic activation polarization at intermediate temperatures and high fuel utilization by increasing the anodic TPB length by infiltration of the anode, thereby increasing the power density of the fuel cells.

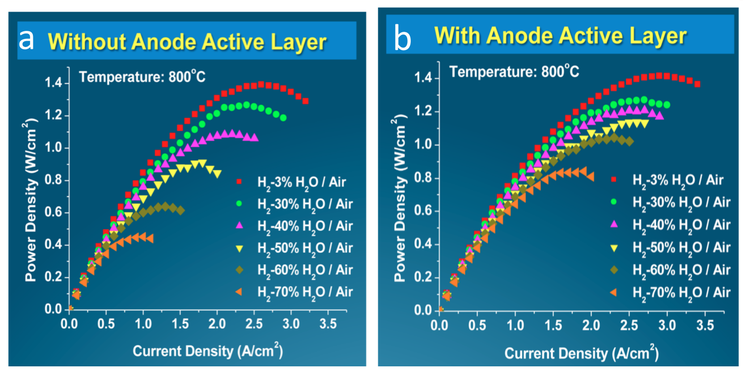

*Fig. 1. a) Reduction of power density with fuel utilization. b) Effect of refining anode microstructure (Yoon et al., J. Electrochem. Soc., **155**, 2008, pp B610).*

Anode Infiltration and Heat Treatment

Infiltration is an effective approach to deposit nano-sized catalyst particles in the electrodes. Depositing 10-100 nm Ni catalyst particles increases the TPB length by 1-2 orders of magnitude over the Ni formed by conventional sintering of YSZ/NiO leading to Ni particles of ~ 1 µm. NiO will be infiltrated using aqueous $Ni(NO_3)_2$ followed by drying, firing and a reduction anneal. The goal is to achieve a sufficiently high loading of NiO that would eventually result in a percolated network of Ni particles within the porous YSZ scaffolding on annealing under reducing conditions. Kishimoto et al. (*J. Power Sources, **199**, 2012, pp 174*) showed that it is possible to control the morphology of Ni particles on YSZ by doping and varying the annealing temperature and NiO thickness (Fig. 2). A surfactant will be added to minimize the interfacial energy between NiO and YSZ to get complete coverage of the YSZ scaffold surface with NiO. The thickness of the NiO can be controlled by the Ni loading of the infiltrate solution. The NiO will then be reduced to Ni by annealing under reducing conditions. The reduction temperature, YSZ doping and NiO thickness will be used to control the agglomeration behavior the particles to maximize neck formation and TPB length. The intermediate operating temperatures (600-800°C) will mitigate against Ni particle coarsening effects as well as Ni loss through volatile $Ni(OH)_2$ vapor formation.

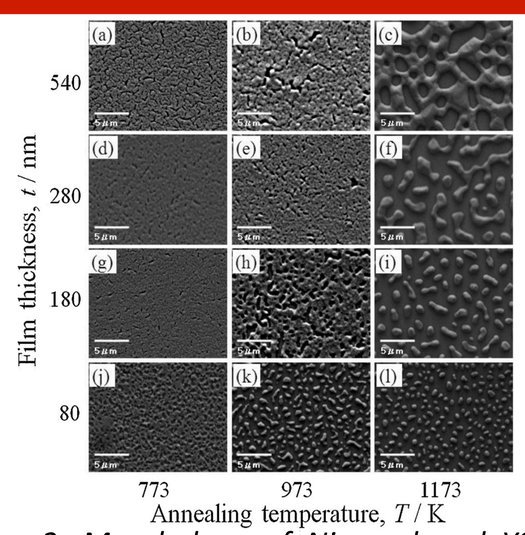

Fig. 2. Morphology of Ni on doped YSZ (Kishimoto et al., J. Power Sources, 2012).

Microstructural Characterization

µ-CT imaging of the anode will be carried out using a Xradia 520 Versa 3-D x-ray microscope, where 3-D images are reconstructed (Fig. 3a) from multiple angular views obtained by rotating the specimen about a fixed axis. The 400nm minimum voxel size allows for a spatial resolution of ~ 1.2 µm. While µ-CT has the resolution to accurately characterize the anode pore structure (of the order of several microns), the Ni particles (in the 10-100 nm range) will be resolved by TEM imaging (Fig. 3c) of cross-sectional samples produced by FIB (Fig. 3b). This will allow examination of the connectivity of the Ni particles, as well as the contact angle between the scaffold and Ni. BU has a FEI Technai Osirus 200KV FEG STEM equipped with EDX and EELS, and a FEI Quanta 3D FEG FIB.

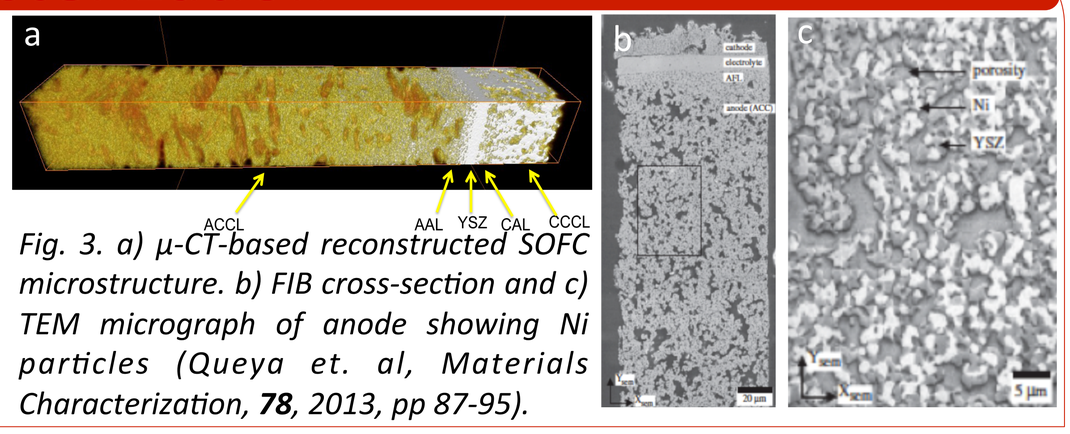

*Fig. 3. a) µ-CT-based reconstructed SOFC microstructure. b) FIB cross-section and c) TEM micrograph of anode showing Ni particles (Queya et. al, Materials Characterization, **78**, 2013, pp 87-95).*

Electrochemical Characterization of Anode

An out-of-cell measurement of the the effective binary diffusivity of H_2-H_2O ($D^{eff}_{H2\text{-}H2O}$) through the porous anode structure will be carried out using the apparatus shown in Fig. 4a, consisting of a YSZ chamber closed off by an oxygen pump on one side and the anode structure on the other. The YSZ chamber wall acts as an oxygen sensor. After equilibration with a given H_2-H_2O atmosphere, oxygen at steady state will be electrically pumped through the YSZ disc into the chamber. The oxygen will react with the hydrogen and will correspondingly decrease the partial pressure of hydrogen and increase the partial pressure of water vapor inside the chamber and establish a partial pressure gradient across the anode sample (Fig. 4b). The steady state current (i) can be related to the flux of hydrogen and water vapor in the opposite directions across the Ni-YSZ sample, leading to the equation: $p^{(i)}_{H2} = p^0_{H2} - (RTl/2FD^{eff}_{H2\text{-}H2O})i$. The effective binary diffusivity can be calculated from a fit to a measured $p^{(i)}_{H2}$ versus i plot (Fig. 4c). For anode catalytic activity measurements, the same anode structure will be deposited on both sides of a solid electrolyte. Impedance spectroscopy will be performed at different H_2/H_2O environments and temperatures to characterize the polarization losses. The polarization resistance of one of the active anode electrodes can be written as: $R_p/2 = RT/2Fi_0 + (RT/2Fi_{as}).(1 + p^0_{H2}/p^0_{H2O})$. Since the anodic saturation current, i_{as}, can be calculated knowing $D^{eff}_{H2\text{-}H2O}$, i_0 (exchange current density) can be directly determined from the measured polarization resistance. The exchange current density is the measure of overall effective catalytic activity of the anode, and is an indicator of the effectiveness of the infiltrated Ni particles.

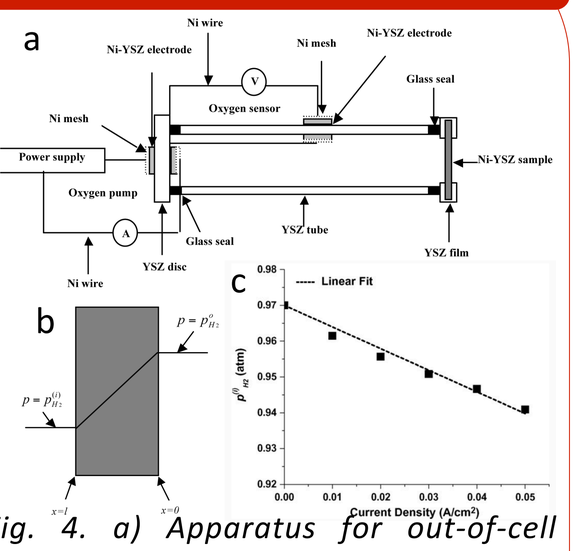

*Fig. 4. a) Apparatus for out-of-cell measurements, b) pH_2 variation across anode, c) Determination of effective diffusivity from pH_2 versus I plot (He et al., J. Power Sources, **195**, 2010, pp 532).*

Proposed Project Outcomes

1. Demonstrate the ability to deposit fine nano-sized connected Ni catalyst particles by infiltration into porous YSZ scaffolds to increase TPB length by 1-2 orders of magnitude.
2. Optimize anode microstructure based on quantitative microstructural characterization, polarization measurements and modeling, to produce SOFC cells that demonstrate a 50% improvement in cell performance at intermediate temperatures (600-800°C) and at high fuel utilization rates (up to 85% water vapor) over cells with conventionally processed anodes, and a 1W/cm^2 power density even at high fuel utilization rates and at intermediate temperatures.