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Electrochemical Manufacturing for Energy Applications

by

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Editor's Note: For 2022, NASF-AESF Foundation Research Board has selected a project on electrodeposition toward developing low-cost and scalable manufacturing processes for hydrogen fuel cells and electrolysis cells for clean transportation and distributed power applications. This report introduces the project and outlines the work to be undertaken.

Introduction and review of literature

Solid oxide fuel cells (SOFCs) are electrochemical devices that generate electricity by direct conversion of chemical energy of fuels (H_2 , CO , CH_4 , etc.) through electrochemical reactions. They have enormous potential for commercial applications given their high efficiency, high energy density and fuel flexibility.¹⁻⁴ In general, SOFCs consist of three major components, namely two porous composite electrodes, referred to as the fuel electrode (anode) and air electrode (cathode), and a dense electrolyte layer.⁵ SOFCs are powered by redox reactions of oxygen and fuel at the three-phase boundary (TPB), where the gas phase, electron-conducting phase, and ionic-conducting phase collide to form the electrochemical reaction.^{6,7} The fuel is oxidized at the fuel electrode (anode) side. The anode electrode assists the fuel adsorption and catalyzes the oxidation reactions by the combination with oxide ions to bring forth the electron for the electric current. The reduction of oxygen produces oxygen ions at the cathode site. These oxygen ions diffuse through the dense layer of solid electrolyte to the anode. The electrons are then liberated to the outer circuit, *i.e.*, the cathode side, to complete the energy generation circle. It is therefore critical to have porous structures for the enhancement of catalytic activity in the anode electrode.^{8,9}

To serve this purpose, the nickel-yttria-stabilized zirconia (Ni-YSZ) has been found to be the most effective anode electrode for intermediate-temperature SOFCs that operate below $800^\circ C$.¹⁰ Nickel is stable under reducing conditions and able to react as a catalyst to promote the fuel oxidation process. Furthermore, in amalgamation with the porous YSZ structure, Ni facilitates the conduction of oxide ions in the electrode component. Thus, Ni-YSZ is preferred for use in single cell SOFC construction. Therefore, it is critical to choose the appropriate manufacturing method for producing the porous anode electrode.^{11,12} On the other hand, the cathode occupies the other side of the anode while sandwiching the electrolyte, controls the whole cell that influences the performance of the output system.

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The performance of the cathode however, can be degraded by poisoning and corrosion issues caused by external contaminants, such as oxidants from the surrounding air which contains pollutants. For example, long-term exposure to carbon dioxide and humidity in the air during the operating cycle may lead to corrosion of the cathode.¹³ The most frequent type of material used in SOFC applications is perovskite (calcium titanate, CaTiO₃), while the most common electrode is strontium-doped lanthanum manganite (LSM). The high conductivity of LSM-based electrodes up to 100 S/cm at 600°C and the well-matched coefficient of thermal expansion with the YSZ electrolyte are two benefits. To avoid the degradation of the cell, it is also suggested that the components of the fuel cycle should be compatible, so that thermo-mechanical stress is minimized for optimal SOFC performance.¹⁴ Therefore, it is critical to select the appropriate fabrication method for integrating electrolyte and cathode electrode elements.

The electrolyte should be adequately densified to prevent fuel/oxidant gas leakage to the electrodes and to lower the resistance to oxygen ion transport in the electrolyte. To prevent losses due to leakage current, it is expected that the electronic conductivity of the electrolyte to be lower as well. Flaws, pinholes and other defects are the potential reasons for the drastic reduction of the electrochemical performance of the fuel cell. To reduce the manufacturing defects and ensure high density, the sintering step of the electrolyte is, therefore, vital. The YSZ electrolyte can be sintered in the temperature range of 1300-1500°C.¹⁵ The density of the electrolyte is a critical factor in maximizing the electrical conductivity of the electrolyte. The nominal electrical conductivity of the SOFC electrolyte should be in the range of 2.4×10^{-2} S/cm for practical applications.¹⁶ Because of the compatibility and low chemical reactivity with YSZ, as well as their similar coefficients of thermal expansion, LSM is more commonly used for the oxygen electrode.

To date, a variety of manufacturing techniques such as extrusion,¹⁷⁻¹⁹ isostatic pressing,^{17,20} tape casting^{21,22} and slip casting^{23,24} have been adopted to fabricate porous anode material. In these conventional processes, the pores are generated by mixing the anode powder with pore-formers and burning out the pore-formers during the sintering process. These pores are generally distributed in a random manner in the anode substrate,^{25,26} resulting in a significant number of isolated pores not being interconnected. This limits the gas diffusion in Ni-YSZ supports of SOFCs.²⁷⁻²⁹ Additionally, this random distribution of pores leads to higher tortuosity of the anode, which is not a favorable condition for the gas diffusion in the electrodes.³⁰

To overcome this problem, a freeze-casting technique can be beneficial to create a functionally-graded support with pore channels formed by the ice crystal growth.^{31,32} Freeze-cast structures exhibit several advantages, including low tortuosity and high porosity that enables rapid gas diffusion. Apart from these properties, freeze-cast electrodes and supports offer low polarization resistance, high electrochemical performance and facilitate catalyst infiltration, as they have straight pore channels.³³ Wei, *et al.*³⁴ reported the fabrication of metal supports for SOFC with vertically aligned porous structures using the freeze-casting technique. The freeze-casted planar single cells developed by the NASA Glenn Research Center using the freeze-casting method have exhibited a significantly high specific power density of 1.0 kW/kg due to the low tortuosity of acicular pores in the anode support.³⁵ Frequently, several planar freeze-cast fabricated fuel cells have been reported in recent years.³⁴⁻³⁸ However, low thermocyclic durability and slow startup times are several common issues for planar solid oxide fuel cells.

In our research, a directional freeze-casting method will be implemented to prepare porous anode scaffolds of YSZ, and Ni will be deposited inside the open pore structures by electrodeposition. Traditionally, Ni-YSZ anodes are fabricated by a powder metallurgy process through mechanical mixing of NiO and YSZ, which is subsequently followed by sintering at temperatures from 1300 to 1500°C and reduction in a hydrogen-rich atmosphere. This method requires a large amount of Ni (greater than 30 vol%) to achieve sufficient electronic conductivity. Additionally, the process involves high temperature reduction in hydrogen, which itself an energy intensive process, and thus, increases the cost of fabrication. Therefore, the proposed method of fabricating Ni-YSZ anode cermet will not only be cost effective but also will be energy efficient. Electrodeposition of Ni into the porous YSZ scaffolds might also be effective to enhance the electrochemical activity of the electrodes through the deposition of catalytically active nanoparticles and minimizing the cell's ohmic resistance through the formation of a thin-film electrolyte. This technique can also hinder the current leakage or chemical interaction between functional layers by depositing thin buffer layers.³⁹ Additionally, infiltration by electrodeposition will allow a wider range of composition, in particular for metals that cannot be processed at high temperatures such as copper.

Framework for Fabrication of Ni-YSZ Anode Cermet

The proposed framework for the fabrication of Ni-YSZ cermet is shown in Fig. 1 below.

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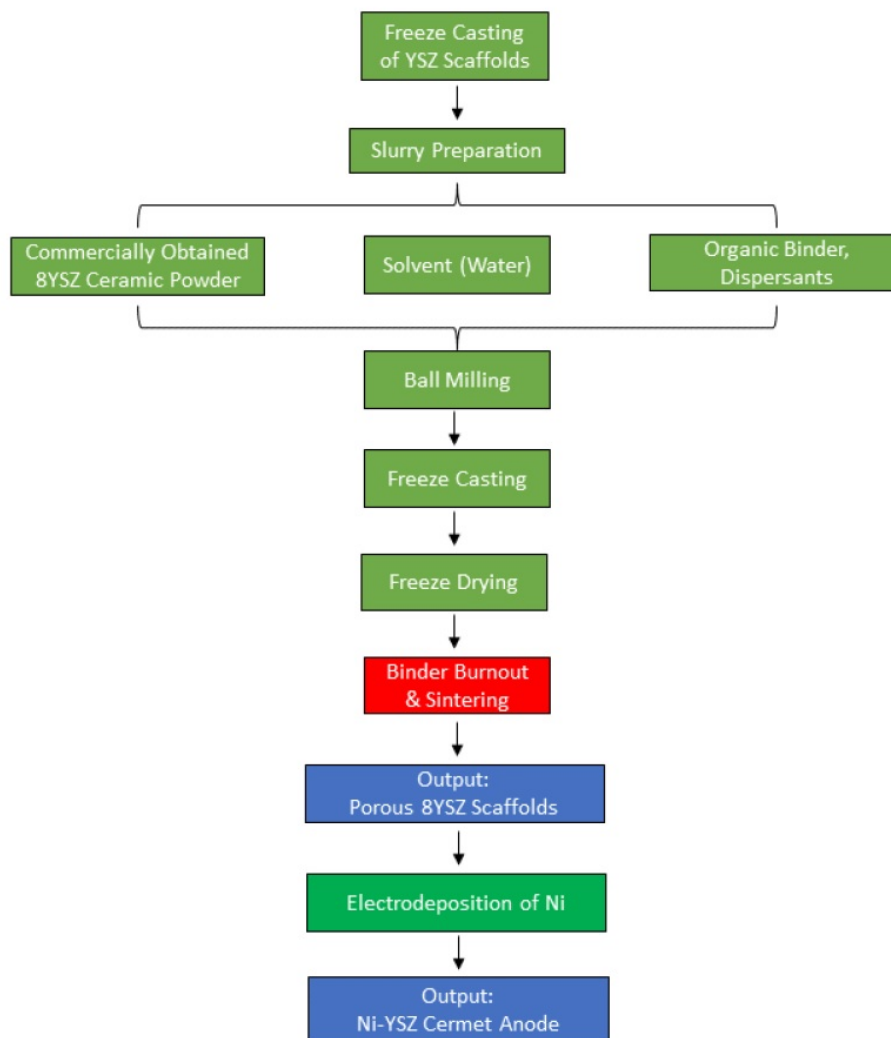


Figure 1 - Framework for the fabrication of Ni-YSZ SOFCs anode electrode

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Early in his career, he received the Young Investigator Research Program grant from the Air Force Office of Scientific Research to design high-performance materials inspired by bone that can reinforce itself under high stress. This critical research can be used for aircraft and other defense applications, but also elucidate the understanding of bone diseases like osteoporosis.

He also earned the Junior Faculty Research Award as an assistant professor at the University of Texas-Dallas School of Engineering.