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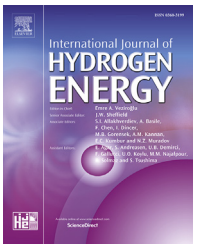

Improving sulfur tolerance of Ni-YSZ anodes of solid oxide fuel cells by optimization of microstructure and operating conditions

Muhammad Taqi Mehran [a], *Muhammad Zubair Khan* [b,c], *Seung-Bok Lee* [b,c], *Tak-Hyoung Lim* [b,c], *Sam Park* [d], *Rak-Hyun Song* [b,c,*]

[a] *Department of Chemical Engineering, School of Chemical and Materials Engineering (SCME), National University of Sciences and Technology (NUST), H-12, Islamabad 44000, Pakistan*

[b] *Fuel Cell Research Center, Korea Institute of Energy Research (KIER), Yuseong-gu, Daejeon, 34129, Republic of Korea*

[c] *Department of Advanced Energy and Technology, Korea University of Science and Technology (UST), Yuseong-gu, Daejeon, 34113, Republic of Korea*

[d] *Department of Mechanical Engineering, University of Louisville, 332 Eastern Parkway, Louisville, KY, USA*

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ABSTRACT

In this study, we propose an improvement in the sulfur tolerance of nickel-yttria stabilized zirconia (Ni-YSZ) anodes for solid oxide fuel cells (SOFCs) by simultaneously employing optimized operating conditions and microstructural modifications. An electrolyte supported SOFC is operated at 20 ppm H_2S impurity at 750 °C for 20 h degradation and 10 h recovery test. The current cycles with a higher amplitude and small pulse time during the constant current operation are beneficial for the mitigation of sulfur poisoning. The effect of humidity on the sulfur degradation of Ni-YSZ anode is also studied. The synergetic effect of microstructure modification and current cycling conditions improves the sulfur tolerance of Ni-YSZ anode. It has been found that, when an anode with a modified microstructure by infiltrated CeO_2 and Yb_2O_3 nanoparticles is operated on 20 ppm H_2S poisoned gas at 10% relative humidity and the optimum pulsed current cycling conditions, about 7 times less degradation of the SOFC performance is observed. This study shows that at lower H_2S concentration, a stable operation of a SOFC with minimum degradation can be achieved with the combination of optimization of operating conditions and modification of the anode microstructure.

Introduction

Solid oxide fuel cells (SOFCs) are known for their potential to convert the chemical energy of fuel into electricity at very high efficiency. Due to its high-temperature operation, SOFCs also offer fuel flexibility and can utilize various conventional carbon/hydrocarbon based fuels such as natural gas, liquefied petroleum gas (LPG), kerosene, and non-conventional fuels such as hydrogen [1–4]. However, the conventional fuels

* *Corresponding author*. Fuel Cell Research Center, Korea Institute of Energy Research (KIER), Yuseong-gu, Daejeon, 34129, Republic of Korea.
E-mail address: rhsong@kier.re.kr (R.-H. Song).

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contain sulfur impurities at very small (ppm) levels as an odor or from the natural sources of the fuel. The SOFC anode is usually based on Ni-YSZ cermet and the Ni catalyst in the anode is poisoned quickly by sulfur containing fuels (even in trace amounts); resulting in performance loss and shortening the lifetime of the SOFC [5–11].

In order to understand the nature of sulfur poisoning in SOFC, extensive studies have been conducted both theoretically and experimentally [11–15]. The previous studies have shown that Ni-YSZ anode is poisoned in the presence of sulfur by two processes. The first process is physical/chemical adsorption of sulfur onto the Ni catalyst particles in the SOFC anode. The adsorbed sulfur blocks the active sites of the catalyst involved in the electrochemical oxidation of the fuel, resulting in a rapid increase of the anode overpotential. The second process involves sulfidation of the anode material, due to the reaction between the Ni-based anode material and sulfur, resulting in severe degradation in catalytic activity [14]. At lower concentrations of sulfur (0–20 ppm), sulfur adsorption and desorption mechanisms are dominant; but, if the sulfur concentration is >20 ppm, the oxidation of Ni and/or formation of Ni_3S_2 becomes the leading cause of poisoning of the SOFC anodes [14]. Strategies for the mitigation of sulfur-related degradation in SOFCs include using sulfur tolerant anode materials and optimization of the operating conditions [16].

Many researchers have investigated the effect of various operating conditions on the sulfur poisoning of SOFCs. It was found that the operating temperature (above 650 °C) significantly influences Ni-YSZ anode degradation and sulfur poisoning is decreased by increasing the temperature [9,17]. High current density was also found to enhance the mitigation of sulfur poisoning [13]. The adsorbed sulfur atoms on the Ni sites combine with the O^{2-} ions from the electrolyte at the triple phase boundary (TPB) and convert to SO_2 by the following reaction:

$$S_{(ad)} + 2O^{2-} = SO_{2\,(g)} + 4e^{-} \quad (1)$$

At high current density, the oxygen-ion flux increases through the YSZ electrolyte and regenerates the Ni sites for further electrochemical reaction. The oxidation of adsorbed sulfur and regeneration of Ni sites in the anode was termed "electrochemical volatilization" by Yokokawa and this process can be used to recover the anode from sulfur poisoning [18,19]. During the SOFC operation on sulfur contaminated fuels, the reactions of chemical and electrochemical depositions of sulfur on Ni compete with the electrochemical volatilization reaction (Eq. (1)). When the deposition reaction becomes dominant, the degradation proceeds rapidly, and vice versa [20]. Yamada et al. reported that by shifting the electrode potential, the sulfur-poisoned anode of the SOFC can be recovered and the poisoning can be prevented to some extent [7]. However, they maintained that by shifting the electrode potential, the metallic Ni preserves its catalytic properties for some time until a new layer of S atoms adsorbs again on the Ni sites. It was suggested by Yamada et al. that the potential shift of the anode electrode should be frequently performed [7]. Wang et al. studied the surface regeneration process for a sulfur poisoned Ni surface by H_2O and O_2 using first principle simulations [21,22]. They found that the presence of water also assists in the regeneration of Ni and SOFCs operating at higher humidity show better long-term performance in sulfur-poisoned conditions [12].

In this study, three different methods, which have synergetic effect on sulfur tolerance of Ni-YSZ anodes, were utilized and tested in order to improve the sulfur stability of Ni-YSZ anodes. In the first method, the operating conditions of the SOFC, with low H_2S concentration fuel, were optimized by exploiting the electrochemical vitalization of the adsorbed sulfur onto the Ni catalysts site. Electrochemical vitalization was achieved by applying high current cycles at various conditions. The effect of different parameters on sulfur degradation of the SOFC and how employing cyclic current can be helpful in improving sulfur tolerance was studied. In the second method, the optimum humidity conditions for the fuel to decrease the sulfur poisoning during operation was determined. In the third method, the Ni-YSZ anode was modified by incorporation of the nano-catalyst CeO_2/Yb_2O_3 via infiltration. A uniform coating of infiltrated catalyst was achieved and it was shown that the addition of CeO_2/Yb_2O_3 catalyst enhanced sulfur tolerance of the Ni-YSZ anode. The synergic effects of different parameters can be explored to improve sulfur tolerance of SOFC anodes [23]. We have studied that the synergetic effect of microstructural modification and current cycling conditions leads to improved sulfur tolerance of the Ni-YSZ anode. The optimized conditions for current cycles, relative humidity, and microstructural modifications were determined through a series of experiments including long-term electrochemical stability testing and electrochemical impedance spectroscopy. It was shown that, at lower concentrations of sulfur impurity (H_2S < 20 ppm), the sulfur tolerance of Ni-YSZ anodes was significantly improved when using a combination of current cycles and incorporation of nano-catalysts.

Experimental

Preparation of single cells

Fig. 1(a) shows the schematics of the electrolyte supported, button-type SOFC, single cell used in this study. A mixture of NiO-YSZ with weight ratios of 60:40 were used for the anode functional layer (AFL). The powders of NiO (Fuel Cell Materials, USA) and YSZ (TZ-8Y, Tosoh, Japan) were ball milled with ethanol for 48 h. After drying and sieving, the powders were mixed with a solvent (α-terpinol) and binder (a mixture of α-terpinol and ethyl cellulose) to produce AFL pastes. The paste was then screen printed on YSZ substrate (Fuel Cells Materials, USA) and subsequently pre-heated and sintered at 350 °C for 3 h and 1350 °C for 5 h in air, respectively. The cathode ink was prepared by mixing LSM (Fuel cell materials, USA) and YSZ (Fuel cell materials, USA). The thickness of the anode layer was 28–30 μm. The cathode layer was also screen printed and sintered at 1250 °C for 2 h. The active area of the cell was 0.5 cm^2. Silver mesh and wires were used as current collectors for both electrodes while Ni and LSCo pastes were applied at anode and cathode side, respectively, to reduce contact losses [24–26]. To prepare the button cells with

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