Journal of Power Sources 395 (2018) 185–194

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Performance and stability of large planar solid oxide fuel cells using phosphine contaminated hydrogen fuel

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HIGHLIGHTS

- Planar SOFC stack repeat unit tested using Haynes 242 interconnect.
- SOFC stack repeat unit operated at 800 °C with 10 ppm PH_3 in dry H_2 fuel.
- Degradation rate due to PH_3 was 3×10^{-3} mV·h^{-1} at 800 °C after 440 h of testing.
- Lower degradation than previous reported levels for small-scale testing.

ARTICLE INFO

Keywords:
Solid Oxide Fuel Cells (SOFC)
Gasification
Coal syngas
Anodes
Contaminants
Thermodynamic analysis

ABSTRACT

Coal syngas, a potential fuel for SOFCs, contains impurities like PH_3, which rapidly degrade Ni-based SOFC anodes. Past research showed significant reconstruction of Ni anodes in button cells with degradation rates of ~0.5 mV·h^{-1}. It is not evident that these rates correspond to actual stack applications due to major differences in fuel utilization and delivery. Herein, a single planar repeat unit with an active area of 32.64 cm^2 is constructed using a Haynes® 242 manifold. The cell operates at 800 °C using dry H_2 with and without 10 ppm PH_3. The cell employs a co-flow configuration with a fuel utilization of 12.5%. The performance of the cell is evaluated over 440 h by voltage-current measurements and electrochemical impedance spectroscopy. The post-run analysis of the contaminated cell is conducted via XRD, XPS and SEM. The degradation rate for the cell is found to be 3×10^{-3} mV·h^{-1}, which is far lower than that reported previously. The cell shows low evidence of significant PH_3 poisoning and there is no reconstruction of the Ni-anode microstructure, as seen in button cell testing. Some basic electrochemical and thermodynamic modeling, and microstructural/chemical characterization are presented and related to the cell's relatively stable performance observed in this work.

1. Introduction

The fuel flexibility in Solid Oxide Fuel Cells (SOFCs) is an important benefit of the technology, where not only hydrogen may be used as fuel, but also various light hydrocarbon and syngas fuels. However, trace impurities in these alternative fuels have been shown to poison the typical Ni-YSZ (yttrium-stabilized zirconia) cermet anode material. Low levels of species that escape a gas clean-up system upstream of the anode can cause significant damage.

Many researchers have investigated the effects of phosphine in syngas mixtures on Ni-YSZ anodes. They have shown that phosphorus has an immediate and irreversible effect on the SOFC anodes when tested in a small "button cell" configuration. Xu et al. [1] determined the degradation rate for 10 ppm of PH_3 in hydrogen and coal syngas to be ~0.46 mV·h^{-1} when the cell was operated at a constant load of 0.5 A·cm^{-2} at 800 °C. The most significant observation of Xu's work was the extensive reconstruction of the anode microstructure. The microstructure showed almost a complete closure of the pore structure with the nickel phosphide phase. Chen et al. [2] observed similar results with the additional observation of a previously unidentified YPO_4 phase when the cell was operated in PH_3 contaminated syngas fuel that was not observed at the Ni-YSZ triple-phase grain boundary when the cell was operated in PH_3 contaminated H_2 fuel. Trembly et al. [3] also reported that Ni_5P_2 was produced on the Ni-YSZ anode surface when

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https://doi.org/10.1016/j.jpowsour.2018.04.105
Received 10 January 2018; Received in revised form 27 April 2018; Accepted 30 April 2018
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tested in a PH_3 containing fuel. Marina et al. [4] observed a delay in the degradation of cell performance upon exposure to 2–5 ppm PH_3, and also noted the formation of nickel phosphide phases on the nickel metal current collector and in the Ni-YSZ composite anode. Degradation was assigned to changes in the current collector [5–7]. Zhi et al. [8] reported slightly different results, where Ni-YSZ half cells were exposed to a higher concentration of PH_3 (20 ppm). The post-mortem analyses by x-ray diffraction (XRD) indicated the presence of nickel phosphate and zirconyl phosphate phases instead of the nickel phosphide phase [5]. Marina et al. [4] tested anode and electrolyte-supported button cells at temperatures of 700–800 °C with syngas containing 0.5–10 ppm PH_3. The electrolyte-supported cells degraded quickly and the degradation rate did not exhibit dependence on temperature or current density.

The works discussed above all employed a button cell configuration in their tests, which is indicative of a circular shaped planar cell with a small active area (1–2 cm^2). This is different than the square planar cells used in commercial SOFC stacks, which are typically greater than 30 cm^2 in active area. These smaller cells can be useful in laboratory tests, since they limit difficulties in cell fabrication, electrode/interconnecting and sealing. Unfortunately, their performance is not necessarily indicative of industrial scale applications, especially since the local temperature, mechanical stresses, fuel/oxygen concentration, and gas flow characteristics at the electrodes may be drastically different due to the size and manifold approach for the cells. With this in mind, one notable difference is the gas flow arrangement, where the fuel is typically impinged perpendicular to the electrode surface for the button cells. The larger planar cells in a fuel cell stack utilize a cross-flow or co-flow fuel delivery configuration over the electrodes. These practical differences between button cells and larger planar cells require further investigation since the temperature, fuel and steam concentration will vary as a function of distance across the planar cell due to the difference in gas flow orientation. This aspect not only affects local performance across the cell, but also affects the manner and mechanism of degradation. This is very important as it relates to the electrode degradation as a function of fuel impurities, where a different path to failure may be identified compared to that shown for button cell testing.

In this paper, we report extended testing of a commercial electrolyte-supported SOFC with a Ni-YSZ cermet anode using H_2 fuel containing 10 ppm of PH_3. The electrodes had a thin layer of platinum contact paste to ensure a seamless connection to the metal manifold which were used to draw the current from the cell. The current-voltage and electrochemical impedance spectroscopy measurements were intermittently performed during the constant loading in order to monitor the performance of the SOFC as a function of loading time. Post-mortem analyses of the contaminated cell were conducted by SEM, XRD, and XPS, which provided chemical and microstructural characterization of the anode material as functions of loading and spatial position across the cell. These results are contrasted to previous reports [1] and thermodynamic/kinetic modeling.

2. Experimental

2.1. SOFC materials and testing setup

The SOFCs in this study were 10 cm × 10 cm in size and were produced by NexTech Materials, Ltd. (Lewis Center, OH). The cells were electrolyte-supported with an active area of 32.64 cm^2. For these cells, the anode electrode was ~50 μm thick with a NiO-GDC/NiO-YSZ composite composition (where GDC is $(Ce_{0.9}Gd_{0.1})O_2$). The cathode electrode was 50 μm thick with a LSM/LSM-GDC composite composition (where LSM is $(La_{0.8}Sr_{0.2})MnO_3$). The electrolyte had a Hionic™ support (scandia-doped zirconia composite electrolyte) with a thickness of ~150 μm.

The manifolds were machined from Haynes® 242, a Ni-Mo-Cr alloy, with one gas inlet and one gas exhaust tube of Inconel® 601 per manifold. These materials were chosen because of their high-temperature strength, thermal expansion characteristics, oxidation resistance, and corrosion resistance. Each manifold had 10 channels machined on their interface that were 4 cm long, 3 mm wide, and 1.5 mm deep. The gases flowed parallel across each cell face rather than perpendicular to the cell face (which is typical of the button cell testing). The SOFC was mounted between the two manifolds with two high-temperature mica sheets per electrode that acted as gaskets to seal the assembly.

Platinum mesh (Alfa Aesar, 99% purity), 50 mm × 50 mm in size, served as the current collector at each electrode and was attached to the electrodes using platinum contact paste. The contact paste in this work was synthesized by mixing ~90 wt% Pt powder (99.9%, Technic Inc., Cranston, RI) with Johnson Matthey ink vehicle (product 63-2). Platinum wires 0.25 mm in diameter (with silver wire extensions to reach the outside of the furnace) were used as voltage taps for the electrical measurements in a four-point configuration. These wires were attached to the cell using the same platinum paste. The platinum paste was used instead of Ni contact paste, so that the phosphine would only interact with the nickel in the anode and the manifold. Once fully assembled, the SOFC repeat unit was loaded into the furnace and a force of 17.9 kPa was applied on top of the stack by means of an alumina tube that extended out of the testing furnace. Alicat Scientific mass flow controllers (MC Series) were used to control the fuel, air, and nitrogen flow rates and the controllers all possess an accuracy of ± 0.8% of the reading and 0.2% of the full scale.

2.2. SOFC reduction protocol and electrochemical testing

The SOFC was heated from room temperature to 800 °C at a rate of 1 °C·min^{-1}. During the heating period, the anode was purged with N_2 at 100 SCCM and the cathode was purged with air at 100 SCCM. Upon reaching 800 °C, the N_2 flow rate at the anode was reduced to 99 SCCM while starting the gradual introduction of the H_2 fuel at 1 SCCM, while the cathode was maintained at 100 SCCM of air. Over a period of four hours, the N_2 flow to the anode was gradually decreased from 99 to 0 SCCM and the H_2 flow rate was gradually increased from 1 to 100 SCCM to reduce the nickel in the anode from NiO to Ni. During testing, the air was fed at 300 SCCM to the cathode and H_2 with 10 ppm of PH_3 was purged at 200 SCCM to the anode.

The cell was loaded to a constant current density of 100 mA·cm^{-2}. The constant current load was supplied using TDI load cell (Model SDL 1103). This current density corresponds to a fuel utilization of 12.5% for the given active area of the cell. The fuel utilization represents a fraction of the total fuel input. The voltage at this current density was continuously monitored.

During the PH_3 poisoning tests, the concentration of the phosphine in the H_2 fuel both in the feed tube and exhaust was measured periodically by means of a photoionization detector (MultiRAE Plus) with the UV lamp set to 10.6 eV. The device was calibrated using isobutylene, as instructed by the manufacturer and a correction factor was applied for the phosphine. In this work, the PH_3 monitoring was performed for the first 24 h only, which will be discussed later.

Once a particular test was completed, the furnace was cooled to ambient temperature at a rate of 1 °C·min^{-1}. While cooling, air was purged to the cathode at 50 SCCM and a 50/50 N_2/H_2 mix was purged to the anode at 50 SCCM. Upon reaching ambient temperature, the manifold assembly was withdrawn from the furnace and the fuel cell was quickly removed from the manifold. The cell was immediately vacuum sealed and taken to a glovebox where it was stored in a dry nitrogen environment until post-mortem characterization. This was done to preserve the sample from potential air and moisture contamination.

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