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Effect of PH_3 poisoning on a Ni-YSZ anode-supported solid oxide fuel cell under various operating conditions

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ABSTRACT

The Ni-YSZ anode-supported solid oxide fuel cell (SOFC) can generate electrical power by using coal-derived syngas as the fuel. However, trace contamination of phosphine (PH_3) in the syngas can cause irreversible degradation in cell performance. A series of tests at 10 ppm PH_3 in the fuel gas was carried out under a variety of operating conditions, viz, with/without electrochemical reaction in syngas and with/without H_2O in H_2 fuel at 750 °C, 800 °C and 850 °C. The poisoning effects were evaluated by both electrochemical methods and chemical analyses. The post-mortem analyses of the SOFC anode were performed by means of XRD, SEM/EDS, and XPS. The results show that the degradation rate is larger at the higher cell working temperature using syngas with PH_3 in a 200 h test though PH_3 is more reactive with Ni in the anode at lower working temperature and produces a secondary nickel phosphide (Ni_xP_y) phase. The dominant compositions of Ni_xP_y on the cell anode are Ni_5P_2 with the presence of H_2O, and $Ni_{12}P_5$ without the presence of H_2O. The production of Ni_xP_y can be generated on the cell anode using syngas or dry H_2 fuel with 10 ppm PH_3 contaminant. Further, the appearance of Ni_xP_y phases is independent of the electrochemical reactions in the cell.

1. Introduction

The poisoning effect on the Ni-YSZ anode-supported cell using snygas fuel has been investigated at 800 °C in previous papers [1,2]. This paper will explore the poisoning effect for variations of the SOFC working temperature and fuel compositions. Several researchers have reported the effects of PH_3 in syngas mixtures and H_2 fuel on Ni-YSZ anodes, and nickel phosphide (Ni_xP_y) compounds were identified as products on the Ni-YSZ anode surface [3,4]. But it is unclear whether or not the formation of Ni_xP_y is related to SOFC working temperature, electrochemical reactions or H_2O present in the reactions.

In this paper, we report extended tests on commercial SOFC button cells with Ni-YSZ composite anodes in a syngas mixture and dry H_2 both containing 10 ppm PH_3. The current collector is arranged to expose the central part of the anode to the fuel gas mixture without any intervening metal grid or metal paste. Periodic evaluation of impedance assesses the ohmic and polarization resistances during the experiment. Extensive post-mortem analyses by SEM, XRD and XPS are used to evaluate the chemical and microstructural changes in the anode. These results are compared to the previous reports and to thermodynamic predictions.

2. Experimental methods

2.1. SOFC and test setup

In this study, commercial anode-supported solid oxide button cells and Ni-YSZ cermet discs manufactured by Materials and Systems Research Inc. (MSRI) were used. The detailed description of the cell composition, structure, dimensions and cell contact configuration has been reported in a previous paper [1]. Mass flow controllers were employed to control the flow rates of H_2, CO, CO_2, N_2/PH_3 (1000 ppm PH_3 in a balance of nitrogen) and air separately. A temperature-controlled humidifier was used to adjust the H_2O concentration of the simulated coal syngas fed to the anode. The total syngas (30% H_2, 26% H_2O, 23% CO and 21% CO_2) and dry H_2 fuel flow rate was kept constant at approximately 200 standard cubic centimeters per minute (sccm) and the air-flow rate was held at approximately 300 sccm. For syngas fuel, the anode fuel transfer lines were heat-traced to over 120 °C so that water condensation between the humidifier and furnace was prevented. CO, CO_2 and PH_3 were injected downstream of the anode humidifier close to the furnace into a ceramic (Al_2O_3) inlet tube to ensure that all trace species in the stream reached the anode of the SOFC

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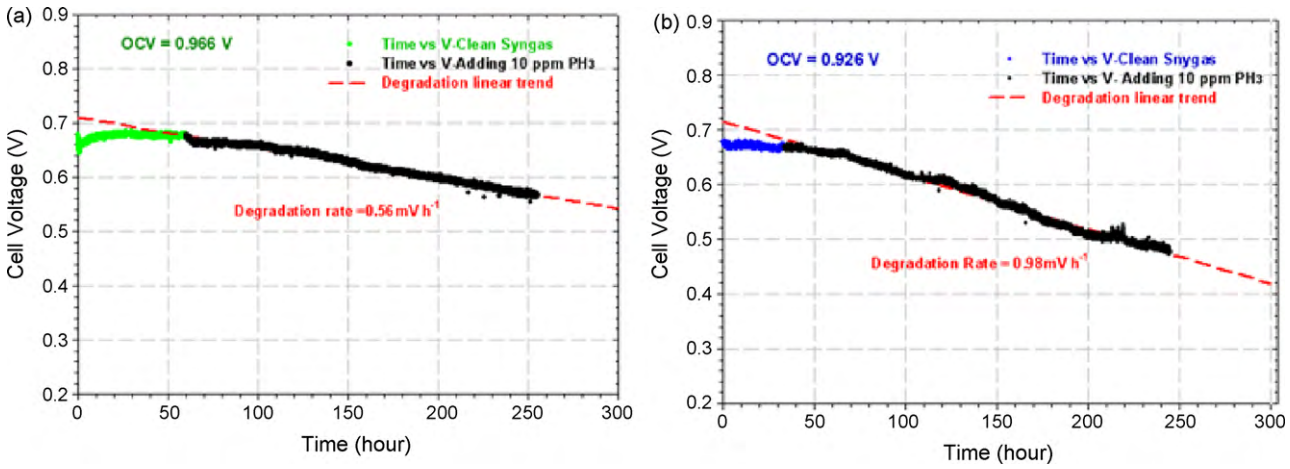

Fig. 1. The cell voltage versus time under 0.5 A cm^{-2} load operating on syngas before and after adding 10 ppm PH_3 at (a) 750 °C and (b) 850 °C.

in a minimum amount of time. For the test with dry H_2 fuel, the H_2 by-passed the humidifier, was mixed with PH_3 close to the furnace and then delivered to the cell anode or Ni-YSZ cermet disc.

2.2. Electrochemical testing of the SOFC

The cell tests followed the same procedure which was described in the previous paper [1]. To investigate the temperature-related effects for the PH_3 poisoning, the cells were further tested with syngas fuel at 750 °C and 850 °C. The cell OCVs were recorded and showed reasonable agreement with the theoretical values at specific temperatures. The cell OCV, voltage under 0.5 A cm^{-2} load and degradation rates for all the tests have been recorded. Impedance spectra were taken periodically during cell testing after adding PH_3. The impedance spectra were collected using a Solartron SI 1260 impedance/gain-phase analyzer with AC amplitude of 20 mV at frequencies ranging from 100 kHz to 0.1 Hz. To inspect whether or not the PH_3-poisoning effects on Ni-YSZ anode were related to the electrochemical reactions, a Ni-YSZ cermet disc (without electrolyte and cathode) was tested at 850 °C by loading syngas with 10 ppm PH_3 on one side of the Ni-YSZ cermet disc while the other side was sealed by a mica membrane which prevented air from reaching this surface. After each cell test was completed, the anode side was purged with 80% N_2 and 20% H_2 while being cooled to room temperature in about 4 h. This purge minimized the exposure of the cell anode to ambient air. To investigate the correlation between PH_3-poisoning effects and H_2O present on the cell anode, one cell was run under 0.5 A cm^{-2} load, and a second cell was kept at OCV when using dry H_2 fuel for about 120 h at 800 °C. The cell impedances were taken periodically during the testing.

2.3. Morphology, chemical and thermodynamic analyses

The microstructure and chemical composition of the cell anode were examined with a Hitachi S-4700 SEM/EDS. To determine the composition of the anode, an XRD (Panalytical X'Pert Pro PM-3040) with a Cu K-alpha radiation source (1.54060 Å), and an XPS (PHI 5000 VerasProbe XPS Microprobe) with a monochromatic Al K-alpha radiation source (8.34118 Å) were employed. Thermodynamic analysis was carried out with the FACTSAGE 5.4 software package.

3. Experimental results

3.1. The poisoning effect of PH_3 in syngas at 750 °C and 850 °C

After accounting for a slight change in cell performance during the initial break-in period (loading at a constant current density of 0.5 A cm^{-2}), the cell voltage under load was stable over 24 h in coal syngas. Following the introduction of 10 ppm PH_3, the cell performance quickly starts to degrade (Fig. 1). Both cells were run for about 200 h after adding 10 ppm PH_3. The average cell degradation rates under 0.5 A cm^{-2} constant current density are 0.56 mV h^{-1} for the 750 °C case and 0.98 mV h^{-1} for the 850 °C case. The performance loss is nearly double at the cell working temperature of 850 °C than that at 750 °C. These two "as-received" MSRI cells were made in the same batch which means the cells have the same

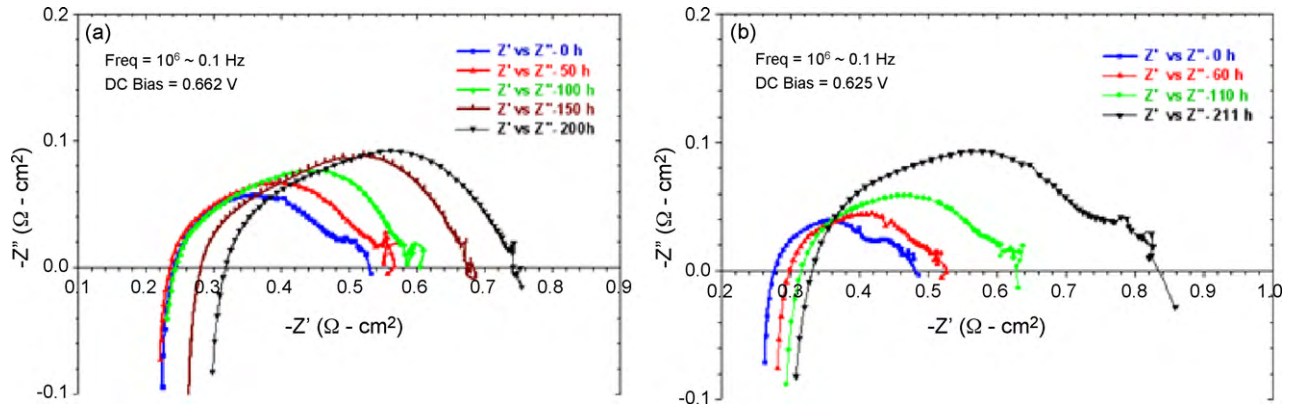

Fig. 2. The normalized impedance spectra of the cells in syngas before and during exposure to 10 ppm PH_3 at (a) 750 °C and (b) 850 °C.