

Deactivation of Ni/YSZ SOFC Anodes Exposed to CO/H₂ Mixtures

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Introduction

Solid Oxide Fuel Cells (SOFCs) have the potential of converting traditional and alternative fuels more efficiently than other energy conversion devices. Prospective fuels for SOFCs, which operate at temperatures between 973 and 1273 K, include natural gas, propane, gasoline, diesel, methanol, ethanol, and products of the gasification of coal and biomass. Hydrocarbons and alcohols either decompose in the gas phase or react catalytically in this temperature range, resulting in mixtures of H₂, CO, CO₂, H₂O, CH₄, and other species. For example, according to thermodynamic calculations, at 1073 K methanol is decomposed to 63% H₂ and 30% CO, while ethanol gives 57% H₂ and 20% CO [1]. Similarly the exhaust from gasification of coal [2] or biomass [3] will contain significant quantities of H₂ and CO. In this work, we have studied the deactivation of nickel/yttria-stabilized zirconia (Ni/YSZ) SOFC anodes, after exposure to H₂ and CO mixtures at 1073 K, by analyzing the Ni/YSZ electrochemical performance and physical characteristics. Differences in the behavior between systems at open circuit potential, characteristic of the anode not connected to the triple phase boundary, and under polarization were investigated.

Materials and Methods

Ni/YSZ anodes were prepared by ball milling equal quantities (by mass) of NiO powder (Alfa Aesar) and YSZ (Tosoh, TZ-8Y) in ethanol for 48 h. The dried powder was then mixed with terpineol (Alfa Aesar) to form a slurry which was painted on YSZ electrolytes (~0.5 mm) and sintered at 1623 K for 2 h. Platinum was used in the cathode and reference electrodes, which were on the opposite side from the anode, while silver loops were used as current collectors. The cell was fixed to the cell holder with glass paste (ESL 4460) [4]. After reduction at 1073 K in 10% H₂ in He for 1 h, the anodes were exposed to various CO/H₂ mixtures (0/100, 25/75, 50/50, 75/25, and 100/0) for 6 h, with a fixed current of 0 (OCP) or 10 mAcm⁻². Cell performance was measured with cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) at 0 h, 3 h and 6 h. After testing, the gas was switched to helium and the system cooled. Temperature programmed oxidation (TPO) experiments were performed after testing the cells to quantify any carbon deposits. For TPO, a stream of 10% O₂ in He (50 ml/min) was passed over the sample while increasing the temperature to 1173 K at 10 K/min. The effluent gas was analyzed using a mass spectrometer (Cirrus 200 Quadrupole). To study the morphology of the carbon deposited on the anodes, the samples were broken and the cross sections were observed with a scanning electron microscope (Philips XL30 ESEM).

Results and Discussion

All cells were characterized electrochemically with dry hydrogen before testing with the CO/H₂ mixture and in each case an OCP equal to ~1.2 V was obtained. The maximum currents obtained in the CV measurements decreased as the CO content of the feed stream

increased. Nevertheless, exposure to 100% CO resulted in the least amount of deposited carbon at OCP and with anodic polarization (Figs. 1 and 2a). In fact, essentially no carbon was deposited when the cell was operated with a current density of 10 mA/cm². In contrast, the exposure of the cell to CO/H₂ mixtures resulted in enhanced carbon deposition, and operating with a current density greater than zero had little effect (Fig. 2b) on the amount of carbon deposited, which is in contrast to the effect of current density when CH₄ is the fuel [4]. Potentially the presence of hydrogen may be assisting the dissociation of adsorbed CO and, thus, promoting carbon formation. Increasing the percentage of H₂ above 25%, reduced the carbon formation and resulted in carbon that was more reactive (Fig. 1); that is, the peaks in the TPO spectra shifted to lower temperatures. The presence of an increased concentration of H₂ in the gas phase will result in more adsorbed hydrogen, which subsequently decreases the number of surface sites for CO adsorption and carbon formation. Under anodic polarization, more water will be formed through electrochemical oxidation as the concentration of H₂ increases. Studies are ongoing to fully elucidate the relationship between H₂, CO and deposited carbon and to relate these results to those obtained previously with CH₄ and H₂ mixtures [4, 5].

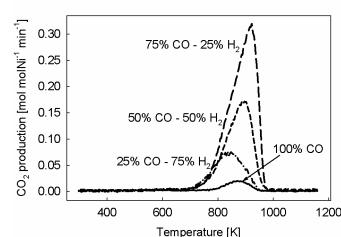


Fig. 1. TPO spectra of Ni/YSZ anodes exposed to CO/H₂ mixtures for 6 h at 1073 K at OCP.

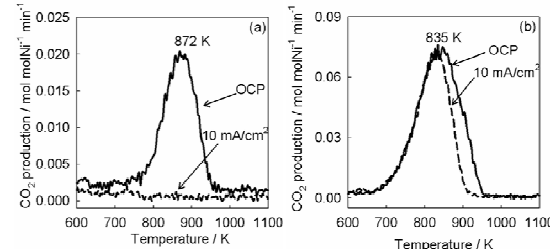


Fig 2. TPO spectra of Ni/YSZ anodes exposed to (a) 100% CO and (d) 25% CO 75% H₂ for 6 h at 1073 K.

Significance

The results of this study have implications for SOFCs operating on syngas. Specifically the performance and electrode stability are influenced by the gas composition, and the mixture of H₂ and CO results in more carbon deposition than using pure CO as a fuel.

References

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