Journal of Power Sources 196 (2011) 7182–7187

Contents lists available at ScienceDirect

Journal of Power Sources

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

The effect of current density on H_2S-poisoning of nickel-based solid oxide fuel cell anodes

E. Brightman[a,*], D.G. Ivey[b], D.J.L. Brett[c], N.P. Brandon[a]

[a] *Department of Earth Science and Engineering, Imperial College London, London SW7 2AZ, UK*
[b] *Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, Canada T6G 2V4*
[c] *Department of Chemical Engineering, University College London, Torrington Place, London WC1E 7JE, UK*

ARTICLE INFO

Article history:
Received 30 June 2010
Received in revised form
24 September 2010
Accepted 29 September 2010
Available online 7 October 2010

Keywords:
Solid oxide fuel cell
Sulphur poisoning
Ceria
Ni–GDC
Electrochemistry
Impedance spectroscopy

ABSTRACT

Sulphur-containing impurities can have a damaging impact on nickel-based SOFC anode performance even at sub-ppm concentrations, but the electrochemical mechanism of this interaction is not fully understood. In this work, three-electrode cells of Ni-$Ce_{0.9}Gd_{0.1}O_{1.95}$/YSZ/$(La_{0.8}Sr_{0.2})MnO_{3-x}$ have been used to obtain new electrochemical data on the sulphur poisoning behaviour of Ni-based SOFC anodes operating at different current densities in the temperature range 700–750 °C. The three-electrode arrangement enabled direct measurement of anode overpotential, with concurrent impedance measurement to provide detail into the electrochemical processes occurring at the anode during sulphur poisoning.

The initial, stepwise degradation on exposure to 0.5 ppm H_2S caused an increase in anode polarization resistance, which was almost entirely recoverable on removal of H_2S. Operation at higher current density was found to result in a smaller increase in anode polarization resistance. It is proposed that this initial poisoning behaviour is caused by adsorbed sulphur inhibiting surface diffusion of H atoms to active sites.

Exposure to 1 ppm and 3 ppm levels of H_2S led to an observed secondary degradation which was also recoverable on removal of sulphur. This degradation was caused by an increased ohmic resistance, and was more severe at higher temperatures. The authors discuss possible explanations for this behaviour.

1. Introduction

Sulphur-containing impurities are present in most fuels suitable for solid oxide fuel cells (SOFC). Sulphur is known to be a poison to nickel and other catalysts [1–8], but it is expensive to remove completely, and the effects of sulphur on SOFC anodes are not yet fully understood. There have been many previous studies, mostly on Ni–YSZ anodes with H_2/H_2S fuel mixtures, across a wide range of H_2S concentrations (0.05 ppm to several thousand ppm) and temperatures (600–1000 °C) [3,8,9]. The most important trends to draw from these studies are that the extent of sulphur poisoning increases with sulphur concentration, and decreases at a given concentration with increasing temperature. The most interesting and relevant conditions applicable to state-of-the-art SOFCs with partially desulphurized fuel are for pH_2S around 0.1–10 ppm and temperatures between 700 and 800 °C. These conditions may be applicable for a commercial SOFC operating on natural gas that has been passed through a simple desulphurizer unit, or where breakthrough of sulphur impurity arises from desulphurizer failure.

Several researchers have used d.c. polarization techniques to show that within the above operating range there is an initial reversible (or partially reversible) degradation step over a number of minutes when H_2S is first introduced, followed by a much slower irreversible degradation over several hours [3,10]. Impedance spectroscopy has also been used to show that the drop in cell power output is attributable to an increase in anode polarization resistance [3,11]. This is consistent with a mechanism involving adsorption of S on the Ni surface causing blockage of active sites for H adsorption and oxidation.

Cheng et al. [12] have shown that the increase in anode polarization resistance, rather than the drop in cell power output, should be used to describe the extent of sulphur poisoning when investigating the influence of cell voltage or current. If the drop in power output is used, then there is an apparent contradiction in the effect of potential or current density on the extent of poisoning, depending on whether the cell is operated under galvanostatic or potentiostatic control.

For longer-term (several hours or more) exposure to a sulphur-containing fuel, a slow irreversible increase in ohmic resistance is sometimes observed [3,8]. This has been suggested to arise from bulk nickel sulphide formation, such as Ni_3S_2, which would cause a drop in conductivity of the anode. However, thermodynamic calculations have shown that under usual SOFC operating condi-

---

[*] Corresponding author. Tel.: +44 207 594 9980; fax: +44 207 594 7444.
E-mail address: e.brightman07@imperial.ac.uk (E. Brightman).

0378-7753/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2010.09.089

tions, i.e., $pH_2S < 100$ ppm at $T > 600\,^\circ C$, Ni_3S_2 would spontaneously decompose to Ni and H_2S [13]. The authors have recently reported observations of surface reconstruction of Ni grains induced by S adsorption [14], causing step formation, which may be indicative of S dissolution in the surface of Ni.

Nickel/gadolinium-doped ceria (Ni-CGO) anodes are of interest for use in intermediate-temperature SOFCs, which have many advantages in terms of manufacturing and operating costs [15]. The effects of sulphur impurities are much more important as temperature is lowered, however, because S adsorbs more strongly on Ni at lower temperatures.

In this work, three-electrode measurements of SOFCs at 700–750 °C using combined electrochemical impedance spectroscopy (EIS) and d.c. potentiometry have been performed to investigate the effect of current density on the increase in anode polarization resistance due to sulphur poisoning for Ni–CGO anodes. Higher current densities were found to give rise to a lower increase in polarization resistance in the presence of sulphur, as well as a faster recovery on the removal of sulphur. The operating temperature and sulphur concentration were also varied and a secondary degradation mechanism was observed over a period of 2–3 h. This is thought to be a result of dissolution of sulphur in the nickel surface forming a barrier to electronic conduction.

2. Experimental

Electrolyte supported button cells in a three-electrode configuration were fabricated with nickel–gadolinium-doped ceria (Ni–CGO) anodes, yttria-stabilised zirconia (YSZ) electrolytes, and lanthanum-strontium-manganate (LSM–YSZ) cathodes and reference electrodes. 8 mol% YSZ electrolyte powder (TZ-8Y, Tosoh, Japan) was uniaxially die-pressed and sintered at 1450 °C for 5 h to give dense pellets 1.25 mm ± 0.05 mm thick and 23 mm diameter. Cermet anodes of 60 wt% NiO:40 wt% $Ce_{0.9}Gd_{0.1}O_{1.95}$ (Fuel Cell Materials, USA) were screen printed and sintered at 1350 °C for 1 h. Cathodes and reference electrodes of 50 wt% $(La_{0.8}Sr_{0.2})MnO_{3-x}$:50 wt% $(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$ (Fuel Cell Materials, USA) were then screen printed and sintered at 1150 °C for 1 h. The electrode geometry used for the anode was a circular disc 11 mm in diameter with a surface area of 0.95 cm^2 and the cathode was an identical circular disc, surrounded by a ring with an internal diameter of 17 mm, and an external diameter of 19 mm. The thickness of the electrodes was in the range 30–70 μm.

The cell was attached to the end of an alumina tube using Ceramabond^{TM} 503 alumina-based ceramic paste (Aremco, USA), with fuel gas supplied through a narrower alumina tube directly to the anode inside the larger tube. The cathode was open to stagnant ambient laboratory air such that oxygen depletion was negligible for the duration of the experiment. Platinum mesh was used for electrical contact, with gold paste on the counter and reference electrodes to improve the surface conductivity, and external tension-springs for contact pressure. The cell temperature was monitored with a type K thermocouple positioned ~5 mm above the surface of the counter electrode. Hydrogen and nitrogen gases were passed through a water bubbler in a temperature-controlled water bath to achieve humidification to ~2% H_2O. The anode was reduced at 800 °C by increasing the H_2 concentration stepwise as follows: 4.9% (30 min), 9.8% (15 min), 14.7% (15 min) and 24.5% (30 min). The furnace was then ramped down to the operating temperature at a rate of 7.5 °C min^{-1}, and the gas composition was changed to 49% H_2, 49% N_2 and 2% H_2O. For the sulphur poisoning experiments the hydrogen was diverted to bypass the water bubbler and the water bath was heated to 35 °C to achieve 4% H_2O in the nitrogen, which, when mixed 50:50 with the fuel gas, gave the desired 2% H_2O. The pure hydrogen was mixed in various proportions with hydrogen containing 10 ppm H_2S, to achieve H_2S concentrations of 0.5, 1, and 3 ppm in 50% H_2, 2%H_2O, and 48% N_2 at a total flow rate of 100 cm^3 min^{-1}.

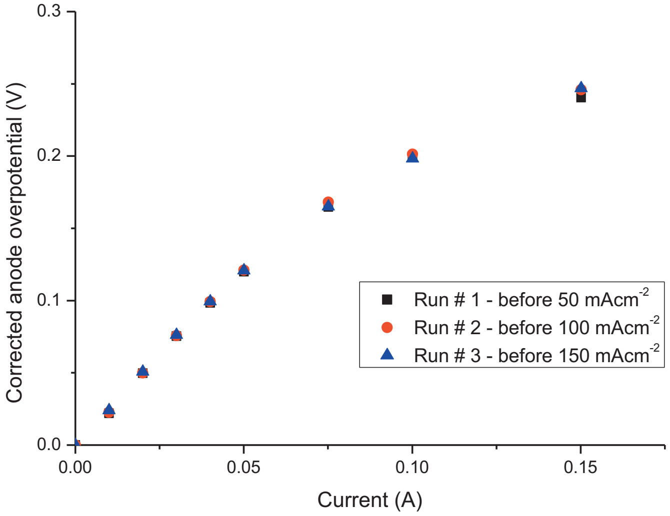

Fig. 1. Polarization performance of test cell for Section 3.1 before each successive H_2S exposure. $T = 715\,^\circ C$, 49% H_2, 49% N_2, 2% H_2O.

Electrochemical impedance measurements and potentiometry were carried out under galvanostatic control using an Autolab PGSTAT302 (Eco Chemie, The Netherlands) with an FRA module. Autolab Nova software v1.5 was used for control and analysis of the measurements.

Cells were first characterized in clean fuel using the overpotential correction procedure described in Offer et al. [16], which involves using EIS to compensate for errors in the measured overpotential due to non-ideal reference electrode geometry. The cells were then held galvanostatically at the specified current density for the poisoning and recovery test. The cell potential was measured every 10 s and impedance was measured every 25 min with an amplitude of 10 mA (r.m.s.) across the frequency range 9.9 kHz to 0.05 Hz for the sulphur poisoning experiments.

3. Results and analysis

3.1. Effect of current density

A cell operated at 715 °C was exposed to 0.5 ppm H_2S in 49% H_2/49% N_2/2% H_2O as described above and recovered in clean fuel successively at three different current densities. The cell was characterized by an i-V measurement with impedance compensation as described in Ref. [16] between each successive poisoning (Fig. 1). The measured performance was consistent with a background degradation rate of <1% over the duration of the test.

An example of the typical impedance spectra measured during the degradation test is shown in Fig. 2(A). The spectra were fitted to an equivalent circuit shown in Fig. 2(B) consisting of a series resistance R_s and two *R-CPE* parallel elements (*CPE* = constant phase element), using Z-View v3.0 (Scribner Associates, USA). It was found that only the low frequency semicircle ($\nu_{max} \approx 1$ Hz) was affected by the presence of sulphur, referred to here as R_p (*LF*), which is consistent with other studies [3,12]. The frequency range of this arc is consistent with the range expected for diffusion-related processes [17].

Current densities of 0.05 A cm^{-2}, 0.10 A cm^{-2} and 0.15 A cm^{-2} were used. The measured cell potential E was converted to give an uncompensated anode resistance between working electrode and reference electrode (here given as the symbol $R_{WE\text{-}RE}$) by the