

In Situ TGA Measurements During High Temperature Air Exposure of Reverse-Biased Ni Anodes

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Ni-yttria-stabilized zirconia (YSZ) based anode supported cells are the current state of the art for solid oxide fuel cells (SOFCs), due to their low overall cell ohmic resistivity, since the most resistive components can be very thin. Ni-YSZ cermet anodes also have the advantages of ease of fabrication, high porosity, chemical and physical stability in reducing environments, and very good electrocatalytic activity for hydrogen oxidation.¹ However, when air enters the hot (600-1000°C) anode chamber, e.g., during system malfunction or shutdown, NiO, which has a ca. 65% larger volume than Ni, rapidly forms, causing severe cell degradation by cracking the electrolyte.^{2,3} NiO subsequently reduces back to Ni upon returning to a normal (H₂) operating environment and therefore this sequence of events is commonly referred to as a “redox” cycle.

One approach⁴ that we investigated earlier to overcome this problem was to apply a cathodic bias to the anode during air exposure to reduce any NiO that forms, i.e., $\text{NiO} + 2\text{e}^- \rightarrow \text{Ni} + \text{O}^{2-}$, while O₂ is produced at the other electrode. In a prior investigation,⁵ electrolyte-supported cells were used, since it is difficult to completely coat the YSZ electrolyte with a counter electrode, thus leaving areas of the anode unprotected. However, no physical evidence was seen of cracking in these cells, as the electrolyte layer is so thick. Thus, the known⁶ decrease in area specific polarization resistance (R_p) that occurs after a redox cycle was tracked. This showed that⁵ the anode did not appear to be protected from oxidation under a constant negative potential bias (up to -350 mV), as the R_p improved after air exposure (from 11 to 8 Ω·cm²), but was protected when a constant negative current (as low as -6.5 mA cm⁻²) was used. In fact, the cell then deactivated (from 2 to 2.5 Ω·cm²), suggesting that other degradation mechanisms may have been countering the improved performance normally observed during a redox cycle. Overall, however, the results were inconclusive.

In the present work, a novel cell test apparatus was developed to track the extent of Ni anode oxidation by *in situ* mass measurements, all under high temperature conditions, in various gases, and under electrochemical control. The apparatus can operate in a half-cell configuration (both electrodes in the same gas environment) in a Setaram 16 thermogravimetric analyzer (TGA). In this way, the mass of the cell could be monitored during a reverse bias experiment to determine conclusively the extent of protection of Ni from oxidation under a negative bias in air.

Figure 1A shows that, when a -500 mV bias is applied, the cell is not protected. While the cell appears to be gaining some mass with the potential applied, in actual fact, the TGA mass is just “drifting”. However, as the potential was increased to -1500 and -3000 mV in Figure 1B and C, respectively, it can be seen that the anode is being increasingly protected by the bias. The mass gain is only 80% and 60% of that for the unbiased cell, respectively, and in both cases, as soon as a N₂ environment is returned to the TGA/cell chamber, the NiO in the anode that formed very quickly reduces to Ni.

The best protection is achieved when using a -50 mA (-130 mA cm⁻²) applied current in air, as seen in Figure 1D. Under these conditions, only 30% of the Ni in the anode

layer was oxidized. It is noted, however, that the mass does not stop increasing, even in this most protected case. As the mass increases, the potential slowly increases to compensate for the slow increase in cell resistance (i.e., due to NiO slowly replacing the more conductive Ni).

It appears that the cell is protected more effectively by the application of a constant negative current, thus slowing Ni oxidation, while under an applied negative potential, the IR drop is quite large such that it is difficult to polarize the anode to sufficiently negative potentials. Further work is currently underway to determine which regions within the Ni-YSZ anode support layer are being protected, i.e., only in the electrochemically active zones near the electrolyte or throughout the anode microstructure.

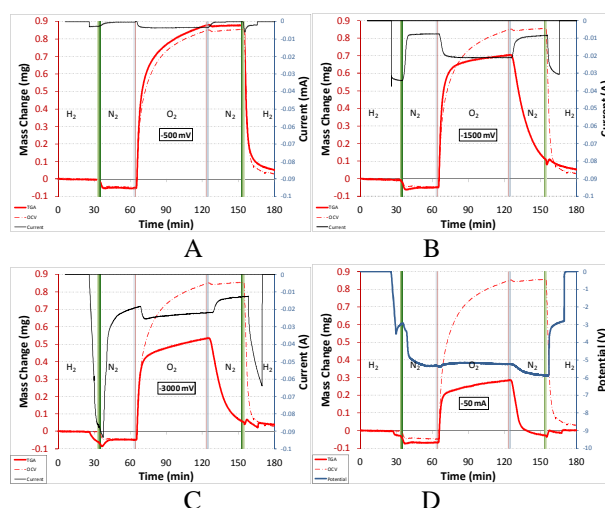


Fig. 1. Cell mass gain (red) during reverse bias compared with when no bias was applied (red hatched), also showing measured current (black) at (A) -500 mV, (B) -1500 mV, and (C) -3000 mV and (D) potential (blue) at -50 mA.

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