A Study of H_2S and PH_3 Effects on Alternative Anodes for Solid Oxide Fuel Cells

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Background

Part 1: SMM Anode for PH_3 Tolerance

- Recent studies have shown that nickel-based anodes degrade rapidly in the presence of ppm levels of phosphine (PH_3). Phosphine can cause loss in the cell performance primarily by:

  - Ni catalyst fouling due to formation of secondary phases
  - Changes in cell micro-structure (Ni migration to anode surface etc.)

- The objective of this work is to identify an oxide anode that shows tolerance to PH_3.

- $Sr_2MgMoO_{6-\delta}$ (SMM)* powder was synthesized and fuel cell tests were conducted in syngas, H_2, and H_2 containing 10 ppm PH_3 on electrolyte-supported cells.

Part 2: Ni/GDC Anode for H_2S Tolerance

- H_2S has also been shown to degrade the standard Ni/YSZ anode. The Ni/GDC anode however can withstand ppm levels of H_2S without irreversible harm to the cell.

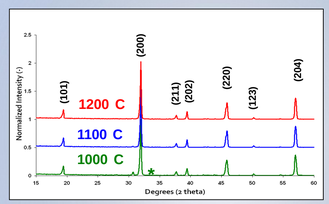
- The emphasis of this work was on the development and testing of a Ni/GDC anode with a GDC barrier layer at the active interface for evaluation of H_2S tolerance.

* Y. H. Huang, R.I. Dass, J.C. Denyszyn, J.B. Goodenough, J. Electrochem. Soc. 153 (2006) A1266.

Cell Fabrication

Powder Synthesis for SMM Fuel Cells

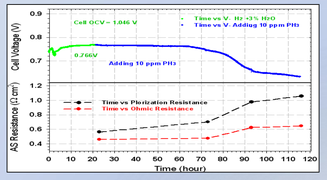
- The SMM powder was made via a solid-state synthesis method.
  - $SrCO_3$, MgO, MoO_3 was used as raw materials.
  - Calcination was completed at 1200°C for 4 hours.
  - BET surface area = 4.711 m^2/g.

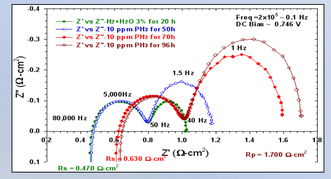


Architectures for SMM and Ni/GDC Fuel Cells

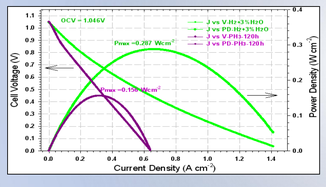
SMM Cell	Ni/GDC Cell
SMM/GDC – 40 µm thickness	Active Anode - 50/50 wt % NiO/GDC – 10 µm
Barrier Layer – GDC – 5 µm	Current Collection – 70/30 wt % NiO/GDC – 40 µm
Electrolyte – YSZ (8 mol % Y) – 100 µm	Barrier Layer – GDC – 5 µm
Active Cathode - LSM/GDC – 10 µm	Electrolyte – YSZ (8 mol % Y) – 100 µm
Cathode Current Collector- LSM – 40 µm	Active Cathode - LSM/GDC – 10 µm
	Cathode Current Collector- LSM – 40 µm

Experimental Results for the SMM Anode

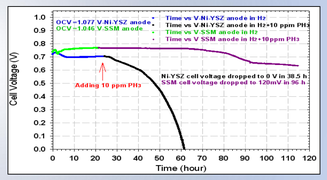




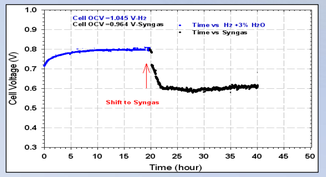
- Cell showed stability in wet H_2 for ~20 hrs. Upon adding 10 ppm PH_3, cell remained stable for ~40 hrs (1 mV drop). However, after 40 hrs in PH_3, increases in both series and polarization resistances occurred to the cell resulting in a loss in cell performance.



- PH_3 reduces cell power density by almost 46% after 100 hours exposure.

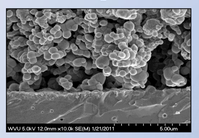


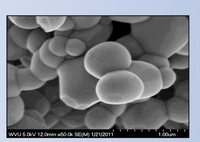
- SMM exhibits much better tolerance to PH_3 than the standard Ni/YSZ anode.



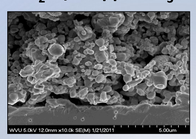
- The ultimate goal is to be able to run this cell on coal derived syngas. Initial results indicate a stable cell in syngas for 20 hrs upon switching the fuel stream from wet H_2 to syngas. The cell however exhibits relatively low performance in syngas compared to wet H_2.

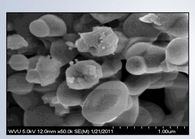
H_2



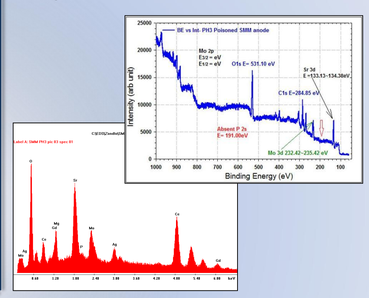


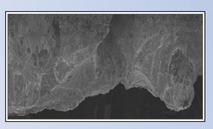
H_2 w/ 10 ppm PH_3





EDS/XPS of Poisoned Anode Interface

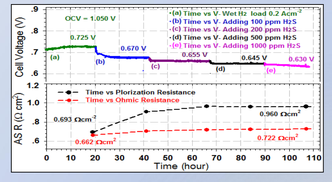




- The analysis detected a slight presence of phosphorus at the interface. Unlike the Ni/YSZ anode, changes to the anode microstructure are minimal and degradation of the cell is initially attributed to densification of the contact paste as well as possible cell de-lamination upon the introduction of 10 ppm PH_3.

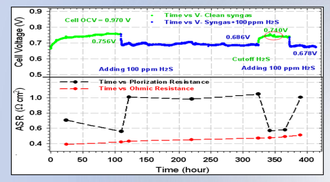
- XPS indicates a lack of P2s peak at the active interface.

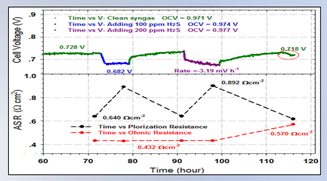
Experimental Results for the Ni/GDC Anode



- The Ni/GDC cell operated in wet H_2 with increasing levels of H_2S. In this fuel, the cell remained stable to 500 ppm H_2S, during a 20 hr testing interval. In 1000 ppm H_2S, the cell potential dropped almost 15 mV in 20 hrs.

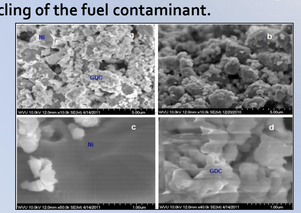
- The ohmic resistance of the cell slowly increased during each level of H_2S, whereas the polarization resistance increased most during the initial adsorption process and then remained stable thereafter.



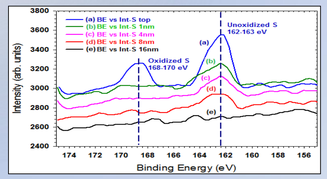


- The Ni/GDC anode operating in syngas with and without 100 ppm H_2S. Cell exhibited stability under these conditions and also did not degrade from cycling of the fuel contaminant.

- The cell did not however maintain stability in 200 ppm H_2S in syngas. The degradation rate of 3.19 $mVhr^{-1}$ suggests that 100 ppm was the limit for this cell in syngas.



- SEM images of (a) poisoned Ni/GDC the anode interface, (b) clean reduced Ni/GDC anode interface, (c) Ni particle in the anode interface and (d) GDC particle in the anode interface.



- Depth profile of the XPS spectra on the H_2S poisoned cell Ni surface. Oxidized S peak at 169-170 eV is only significant on the top Ni surface. Unoxidized S peak is detectable at 8 nm depth of Ni surface.

Future Work

SMM Anode

- Perform thermodynamic calculations to determine what (if any) reactions are anticipated between P and the anode constituents.

- Verify the behavior of the cell in response to 10 ppm PH_3 and run this cell in fuel containing both H_2S and PH_3 contaminants.

- Apply this cell to full size (10 x 10 cm) planar fuel cells for investigation of degradation rates using various flow configurations.

Ni/GDC Anode

- Determine degradation rates as a function of hydrogen and oxygen partial pressures to determine what fuel composition and contaminant levels are most suitable for operation.

- Identify the role of the barrier layer in tolerance of H_2S.

Acknowledgements

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