Recent Advances in Coal Gas Impurity Interactions with SOFC Anodes

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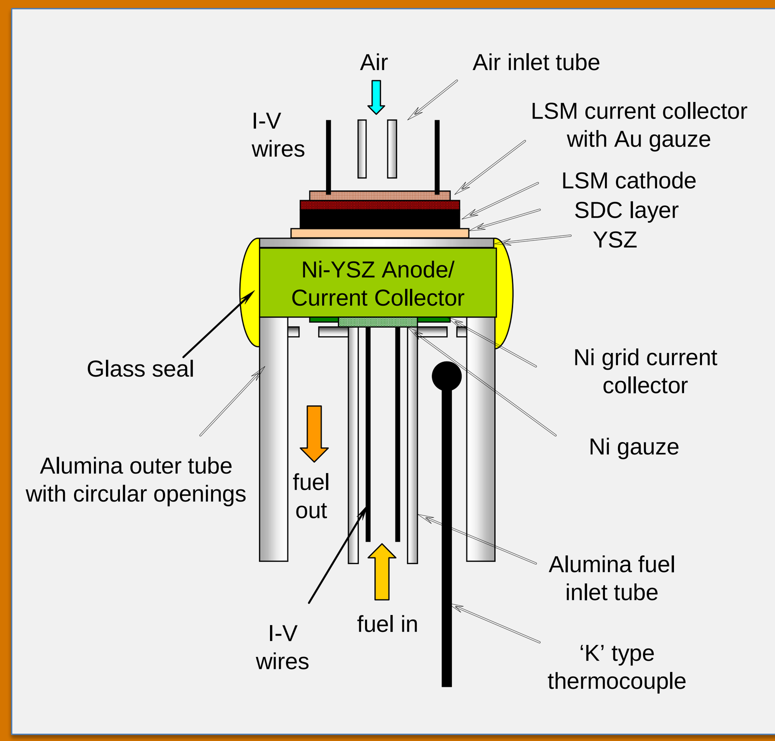
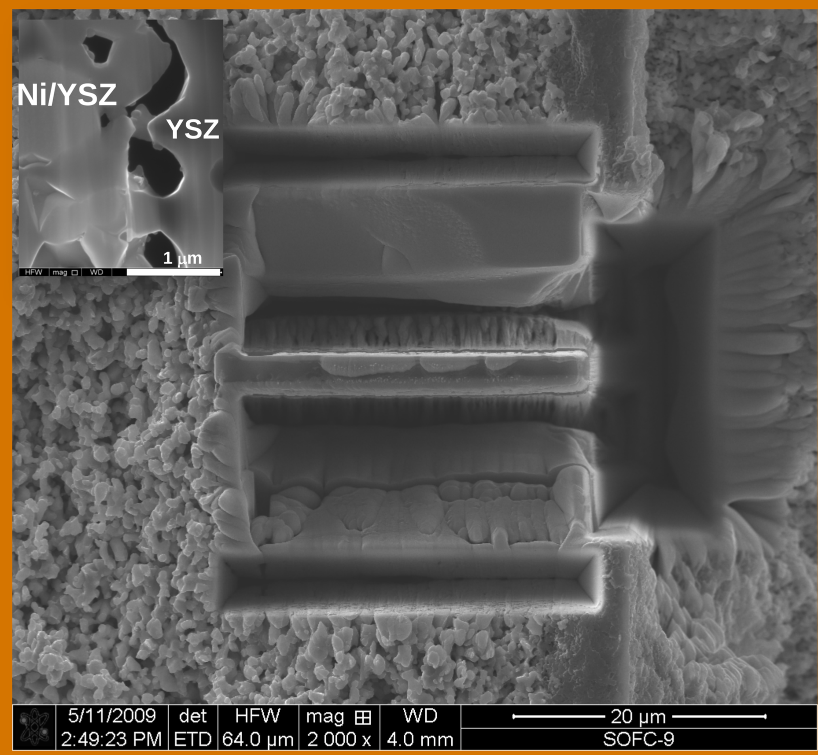
Purpose and Approach

- Evaluate effect of coal gas impurities (As, Cl, P, Sb, Se) on Ni/YSZ SOFC anode performance and predict SOFC stack life
- Button cell testing: electrolyte-supported cells – more rapid response to coal gas contaminants; anode-supported cells – typical of architectures used by SECA industrial SOFC development teams
- Varied impurity concentration, temperature, reaction time, fuel utilization, and current density
- Coupon tests to determine penetration rate and nature of impurity/Ni interactions
- Post-test analyses by SEM/EDS, SEM/WDS, FIB/SEM, TEM, EBSD, XPS, Auger spectroscopy, Tof-SIMS
- Thermochemical modeling of Ni/impurity interactions in coal gas

Eight button cells installed per box furnace, with individual gas flow controls; 6 furnaces

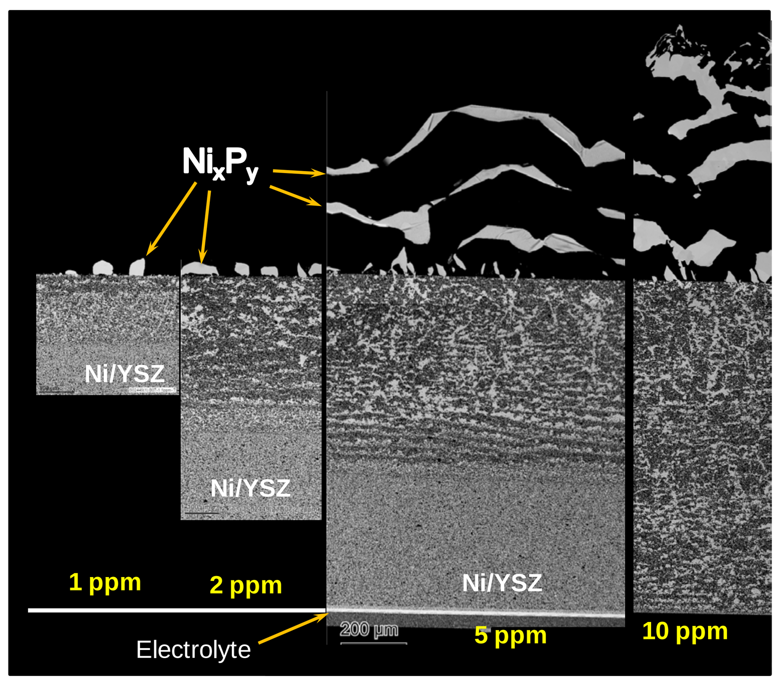


Schematic of button cell test stands

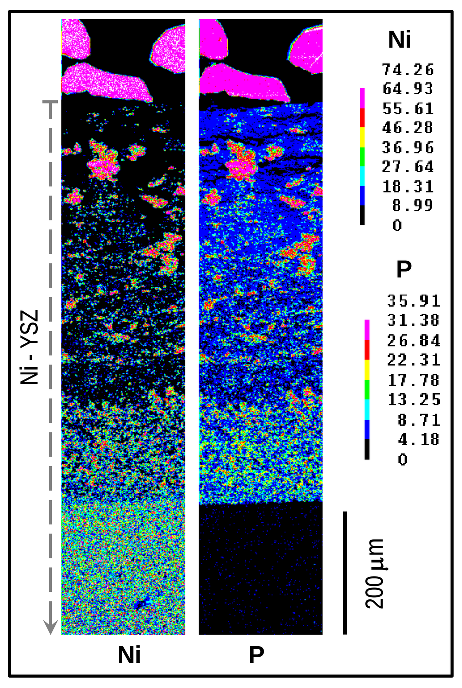


Focused ion beam (FIB) workstation for TEM sample preparation

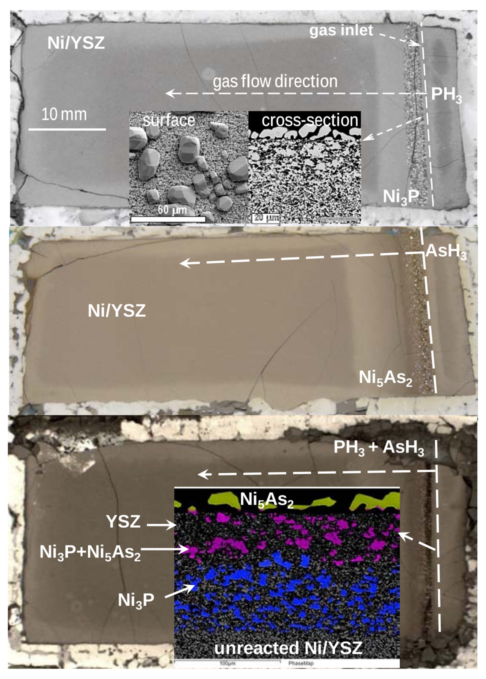
Results



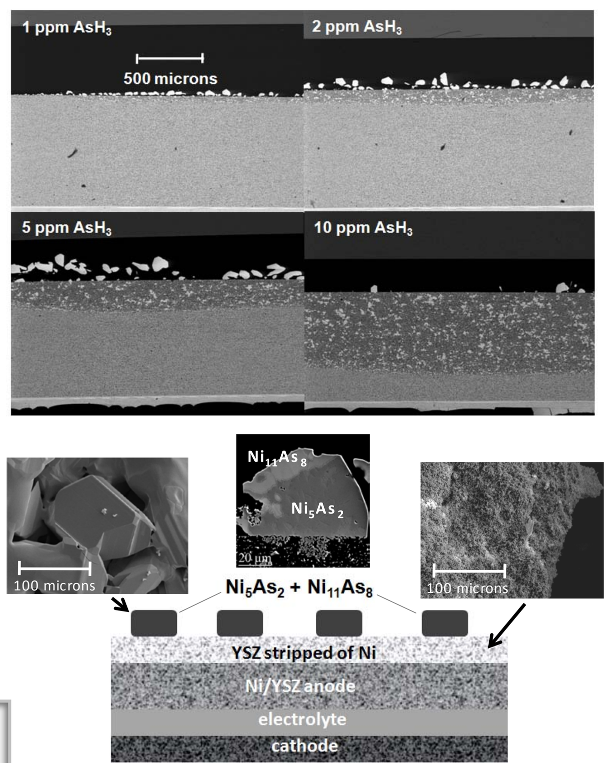
Button cells after 1000 h cell test at 700°C in synthetic coal gas with PH_3. Ni and Ni_xP_y are light grey, YSZ is dark gray, pores are black. Not converted Ni/YSZ is seen in 1-5 ppm cells. All Ni was converted to NiP_x during a test with 10 ppm PH_3.



Ni/YSZ anode after 1700 hr tests with 2 ppm PH_3 at 750°C. WDS data showing all phosphorus is associated with Ni, not with zirconia.

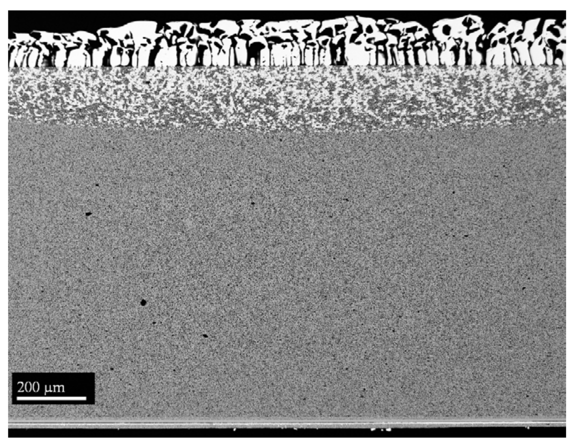


Ni/YSZ coupons after exposure to synthetic coal gas containing 0.5 ppm PH_3, AsH_3, or PH_3+ AsH_3 flowed lengthwise across the coupon for 500 hours. Phosphorus and arsenic are completely captured within a short distance from the gas inlet.

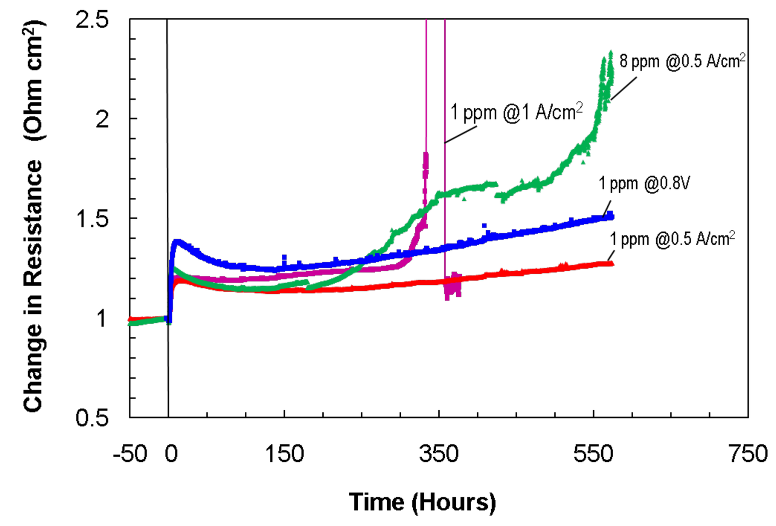


Button Ni/YSZ anode-supported cells after 480 h exposure to coal gas containing AsH3 at 800°C and proposed degradation mechanism.

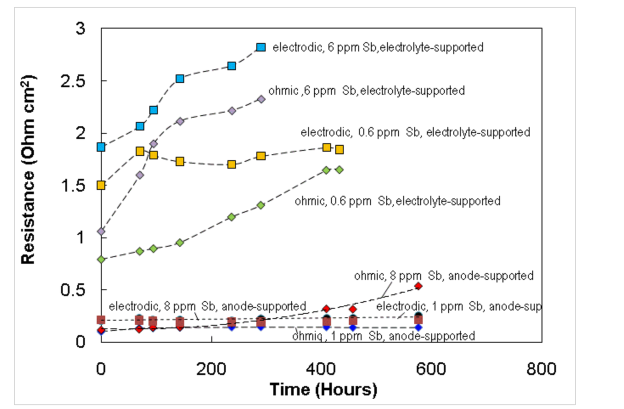
I. Phosphorus and arsenic were found to interact strongly with nickel resulting in the formation of multiple second phases (Ni_5As_2, $Ni_{11}As_8$, Ni_3P, Ni_5P_2, $Ni_{12}P_5$, Ni_2P), depending on temperature, contaminant concentration, reaction time. Loss of electrical connectivity in the anode support was the principal mode of cell failure, as nickel was converted to nickel arsenide or nickel phosphide that migrated to the surface to form large grains. Phosphorus and arsenic concentrations of ~10 parts per billion or less are estimated to result in acceptable rates of fuel cell degradation.



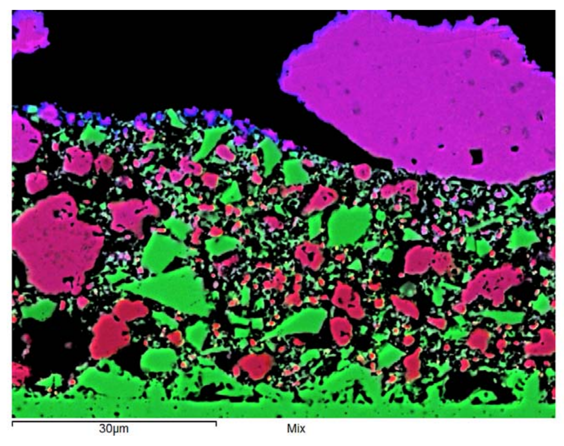
Ni/YSZ anode-supported cell after 600 h exposure to hydrogen containing 1 ppm Sb at 800°C.



Anode-supported cell performance during exposure to hydrogen containing Sb at 800°C.

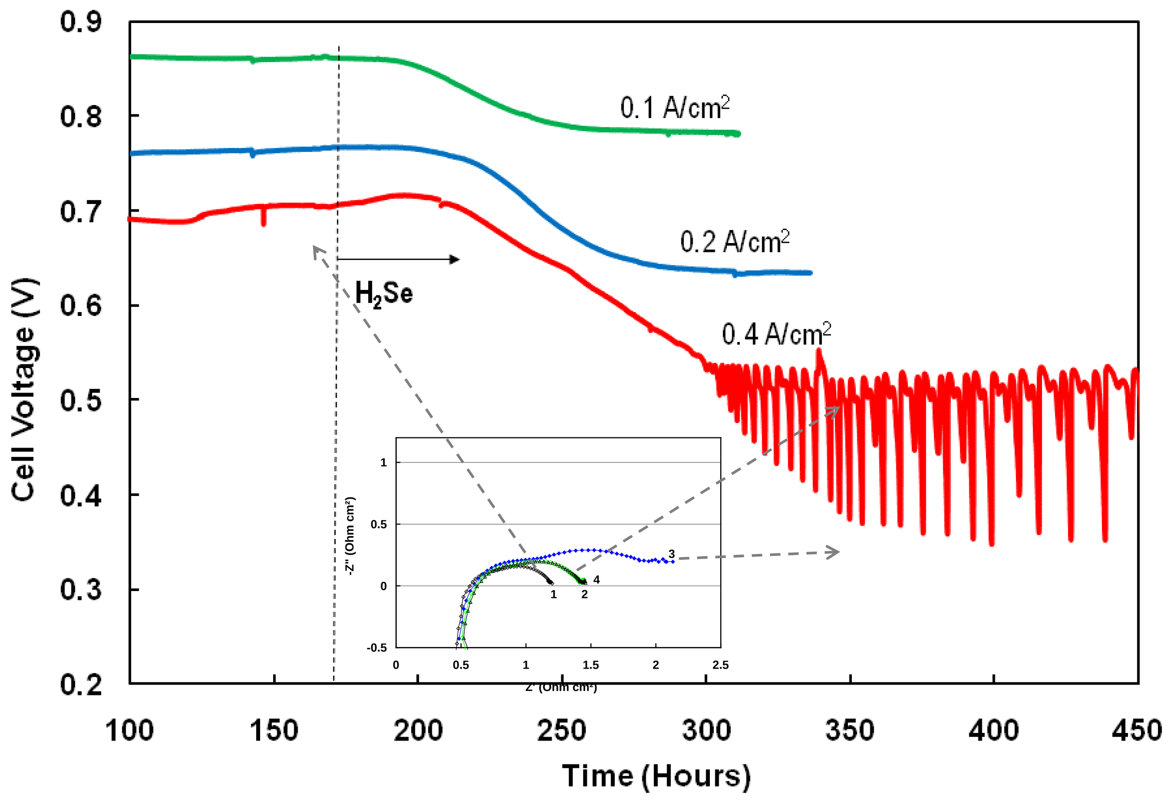


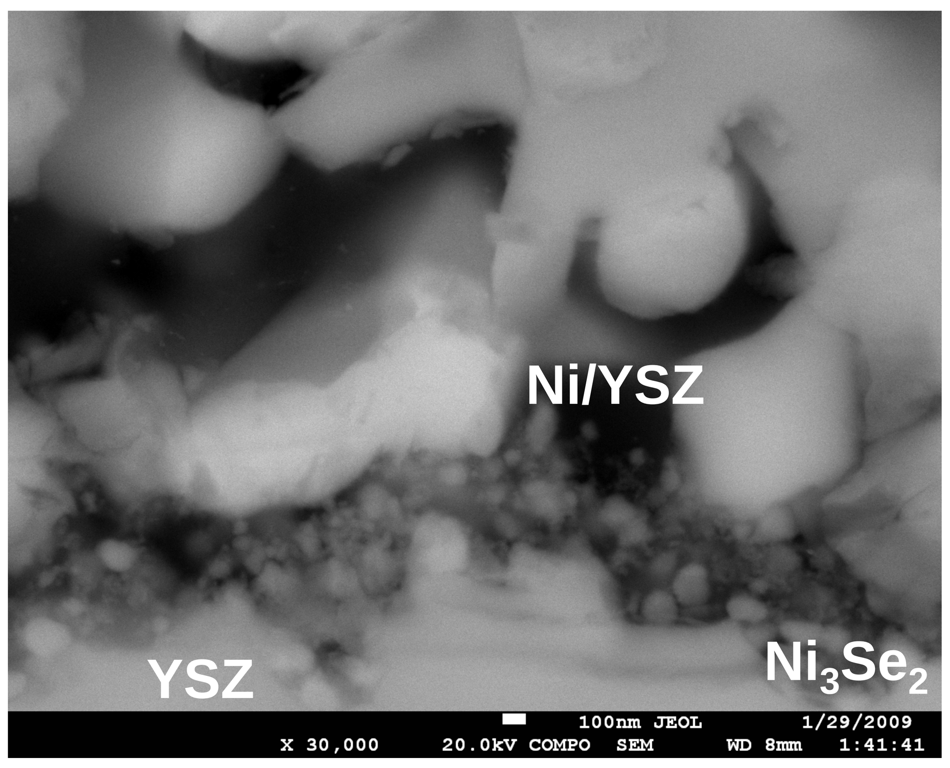
Electrodic and ohmic resistances of anode-supported and electrolyte-supported cells during exposure to hydrogen containing Sb at 800°C.



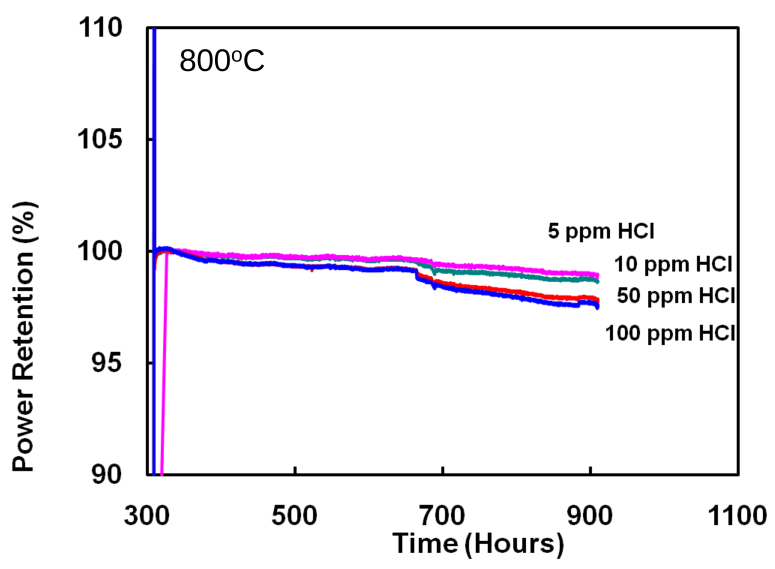
Ni/YSZ anode of electrolyte - supported cell after 423 h exposure to hydrogen containing 1 ppm Sb at 800°C. Green is YSZ, red is Ni-Sb solid solution (<2 at% Sb), magenta is Ni-Sb.

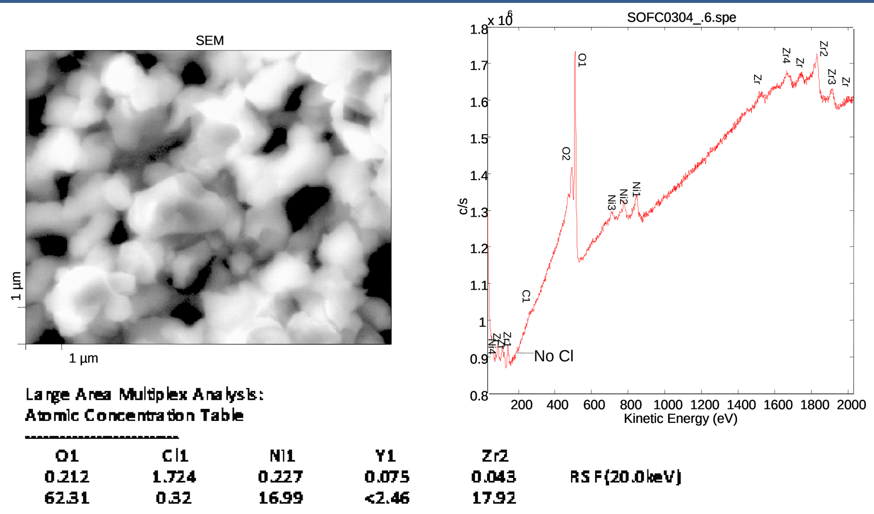
II. Antimony interacts with nickel to form Ni_3Sb, Ni_5Sb_2, and NiSb. Initial Ni passivation by Sb followed by loss of electrical connectivity in the anode support are consistent with cell degradation observations.





III. Sulfur and Selenium Nickel-sulfur and nickel-selenium interactions were found to be much weaker than those with arsenic or phosphorus, and no second phases were detected in the temperature range 600-800°C when less than 10 ppm of the contaminant was present. However, Ni/YSZ anode performance loss was substantial, with rapid increases in the area specific resistance of 40-300% and decreases in power output of 10-70 %. Selenium poisoning was found to be similar to sulfur poisoning, possibly affecting the rate of the electrochemical reaction by selenium atoms blocking the active sites at the triple-phase boundary. Whereas cells recovered nearly completely from sulfur exposure within a few hundred hours, recovery from selenium exposure under otherwise identical conditions was not full. At higher polarization losses, oscillatory behavior was observed, where cell performance fell rapidly and then regained the activity. At even higher polarization losses irreversible cell failure occurred in the presence of as little as 0.5-1 ppm of H_2Se. Ni-Se phase was found at the anode-electrolyte interface.





Auger spectra obtained on the Ni/YSZ anode support cross section after testing in coal gas with 50 ppm of HCl at 800°C.

IV. Hydrogen chloride SOFCs showed low to minimum reversible degradation in the presence of 200 ppm or less of hydrogen chloride. No formation of new solid phases was observed and no microstructural changes were noticed.

Summary

Phosphorus and Antimony: Strongly reacts with Ni to form a series of Ni-P or Ni-Sb solid phases. Performance losses due to surface adsorption at the active interface and to loss of electrical percolation in the anode support.
Arsenic: Strongly reacts with Ni to form a series of nickel arsenide solid phases. Performance losses primarily due to loss of electrical percolation in the anode support.
Sulfur: Reversible performance degradation due to surface adsorption at the active interface. No solid phase formation with nickel at expected concentrations.
Selenium: Partially reversible performance degradation due to surface adsorption at the active interface at low overpotentials. Cell failure because of nickel selenide formation at at high overpotentials and/or high fuel utilizations is likely.
Chlorine: Minimal reversible degradation.

Acknowledgements

Support from the U.S. Department of Energy, National Energy Technology Laboratory (NETL) through Solid-State Energy Conversion Alliance (SECA) program is gratefully acknowledged. PNNL is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RL0 1830. The authors appreciate SEM analyses performed by JP McKinley and AL Schemer-Kohrn and SEM sample preparation by CE Chamberlin.

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