Ni/YSZ Anode Interactions with Antimony, Arsenic, Chlorine, Phosphorus, Selenium, and Sulfur in Coal Gas

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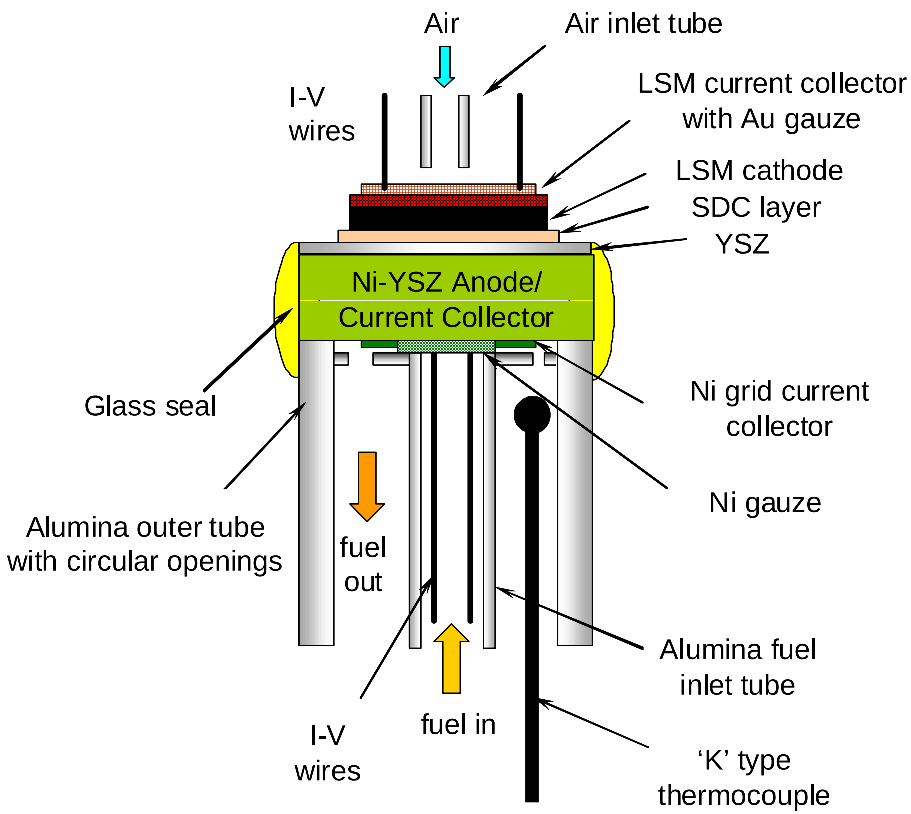
Objective: Establish Maximum Acceptable Coal Gas Contaminant Concentrations

- Button cell testing:
  - Anode-supported cells – typical of architectures used by SECA industrial SOFC development teams
  - Electrolyte-supported cells – more rapid response to coal gas contaminants
  - Test parameters include contaminant concentration, temperature, reaction time, fuel utilization, and current density
- Coupon tests in flow-through and flow-by arrangements
  - To determine penetration rate and nature of contaminant/Ni interactions
- Post-test analyses by SEM/EDS, EBSD, TEM, FIB-SEM, AES, XPS, Tof-SIMS
- Thermochemical modeling of Ni/contaminant interactions in coal gas

Schematic of Button Cell Test Stands



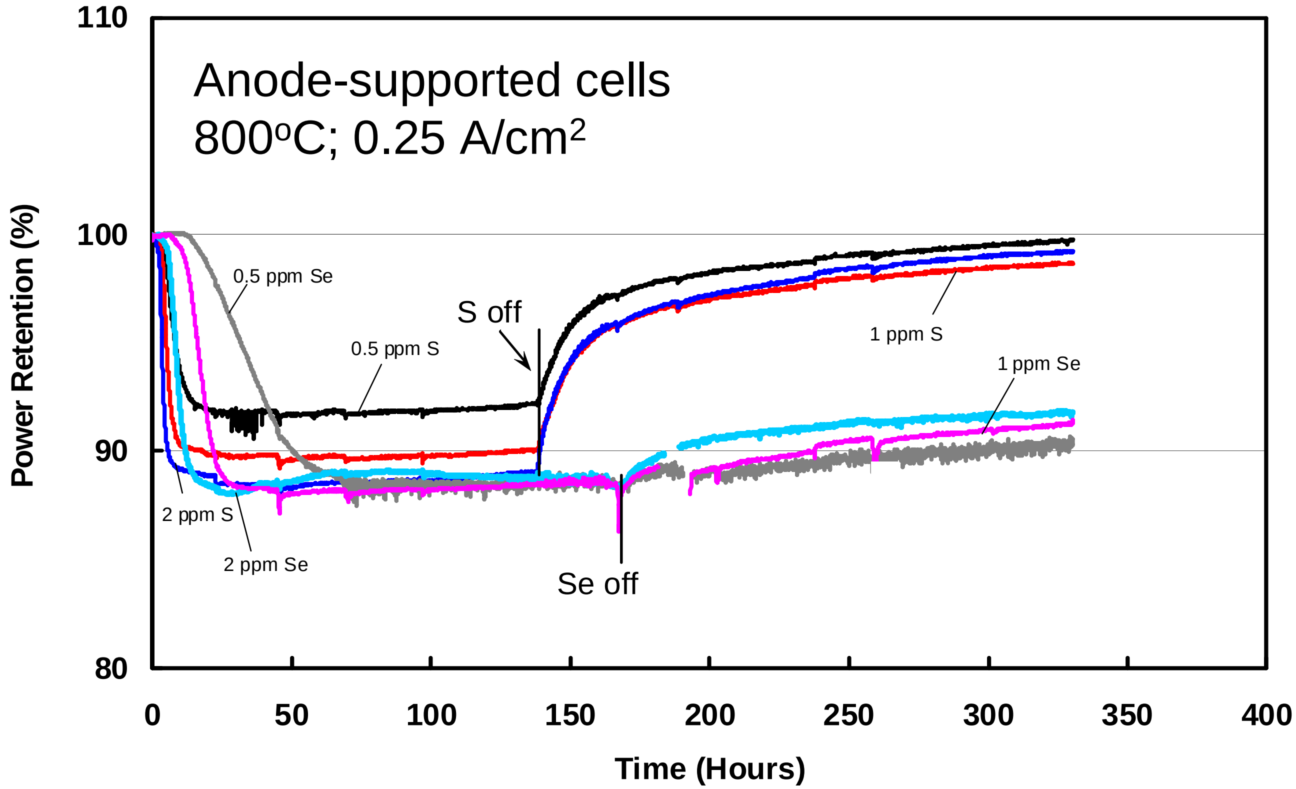
Eight button cells installed per box furnace, with individual gas flow controls

- Ni/YSZ anode-supported cells
- Electrolyte supported cells (*NexTech Materials, Inc*) with 30 μm Ni/YSZ anode

Outline

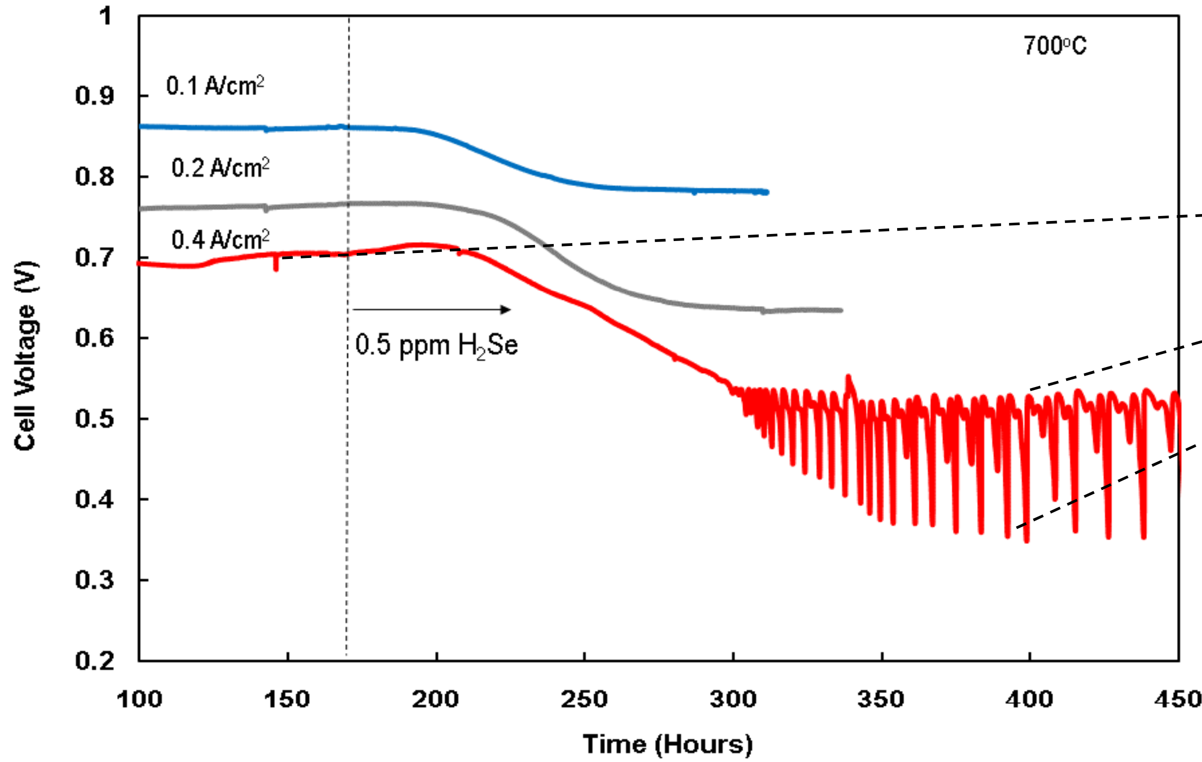
- Selenium and Sulfur – degradation processes affected by local conditions at the active anode/electrolyte interface
- Hydrogen Chloride – minor reversible degradation, without formation of new solid phases
- Arsenic – strong interactions with nickel, resulting in solid phase formation and structural rearrangement
- Phosphorus – also strong interactions with nickel, both solid phase formation and phosphorus surface diffusion to the interface
- Antimony – rapid surface adsorption followed by solid phase formation

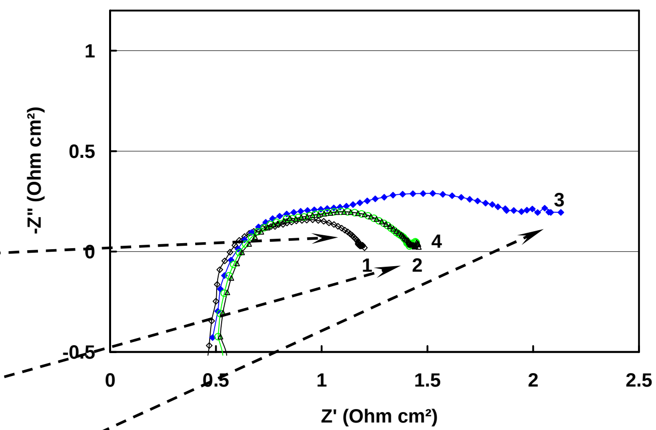
Three Levels of Ni-Se Interactions

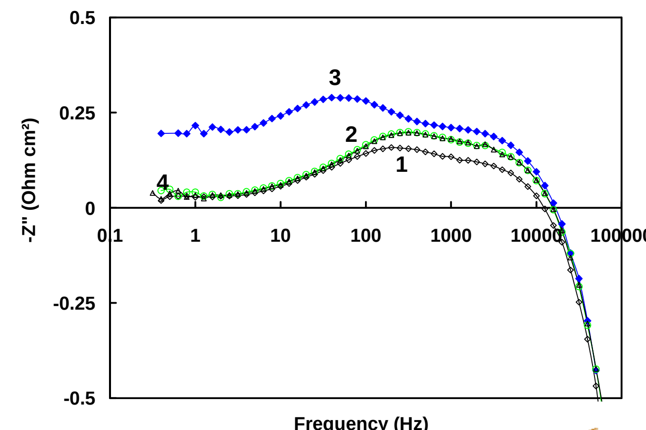


- 1^{st} level: relatively rapid but modest decrease in performance to a new steady state, very similar to effects of sulfur but slower kinetics and less reversible

Ni-Se Interactions: Effect of Overpotential







- 2nd level: at higher polarization losses, oscillatory behavior observed in constant current mode, where cell performance falls rapidly and then regains activity. Oscillations cease if current density is decreased.

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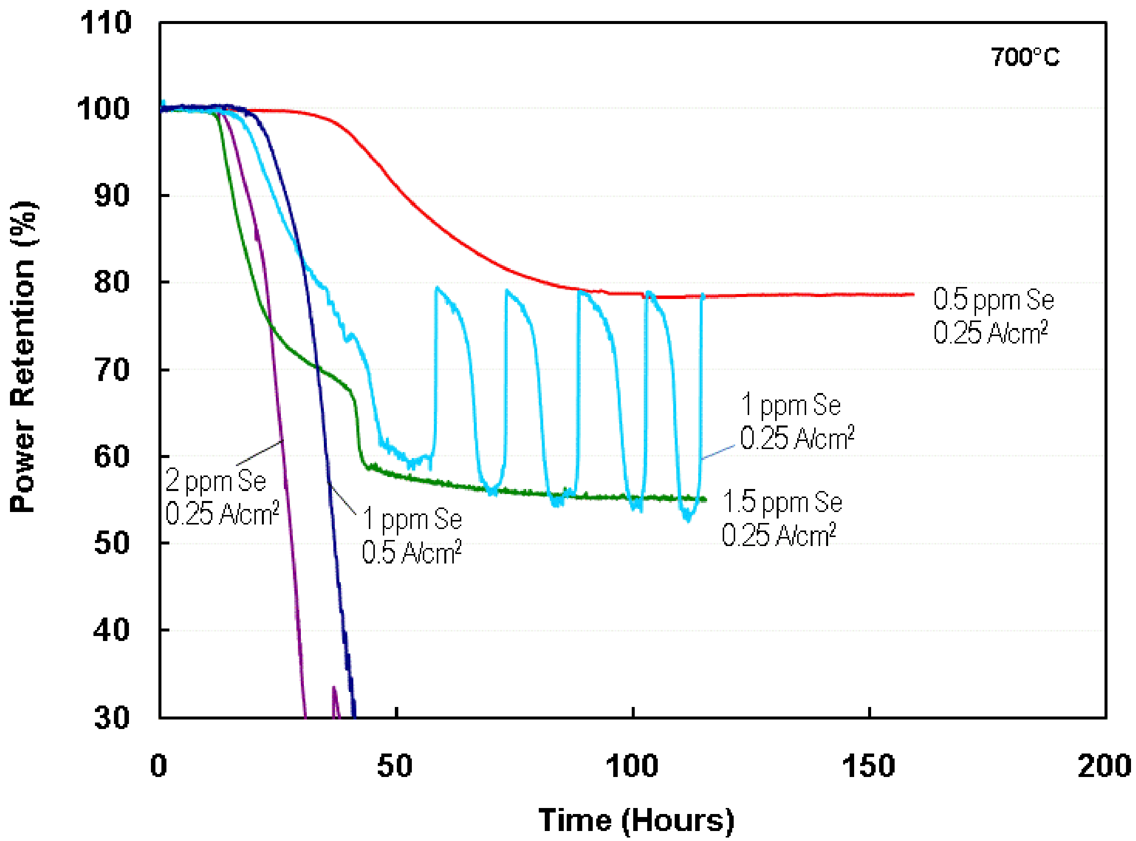
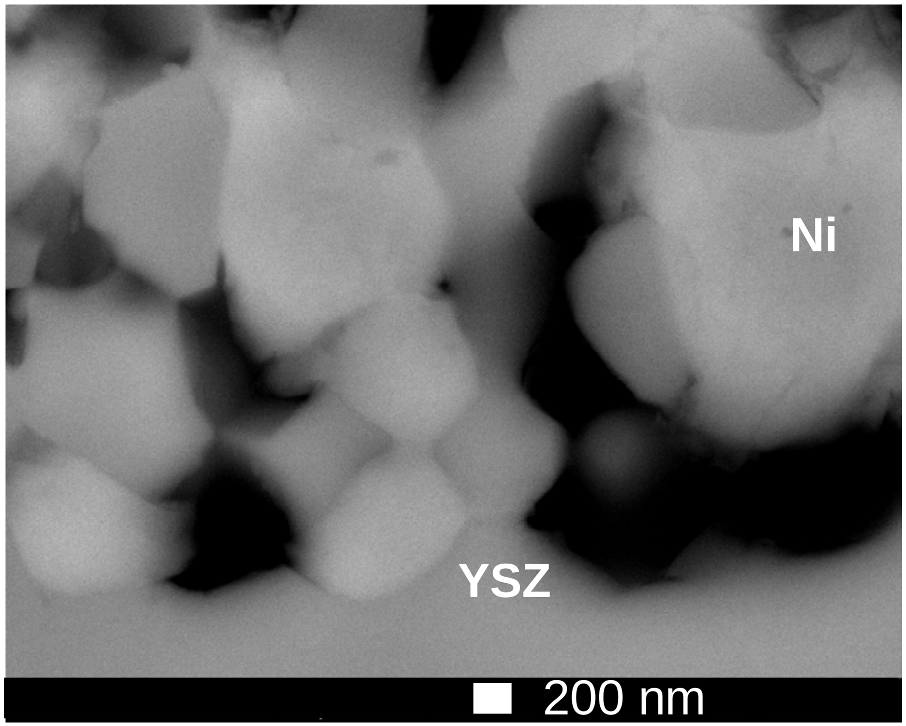
More Degradation at Lower Temperature, Higher Current Density, higher H_2Se Concentration

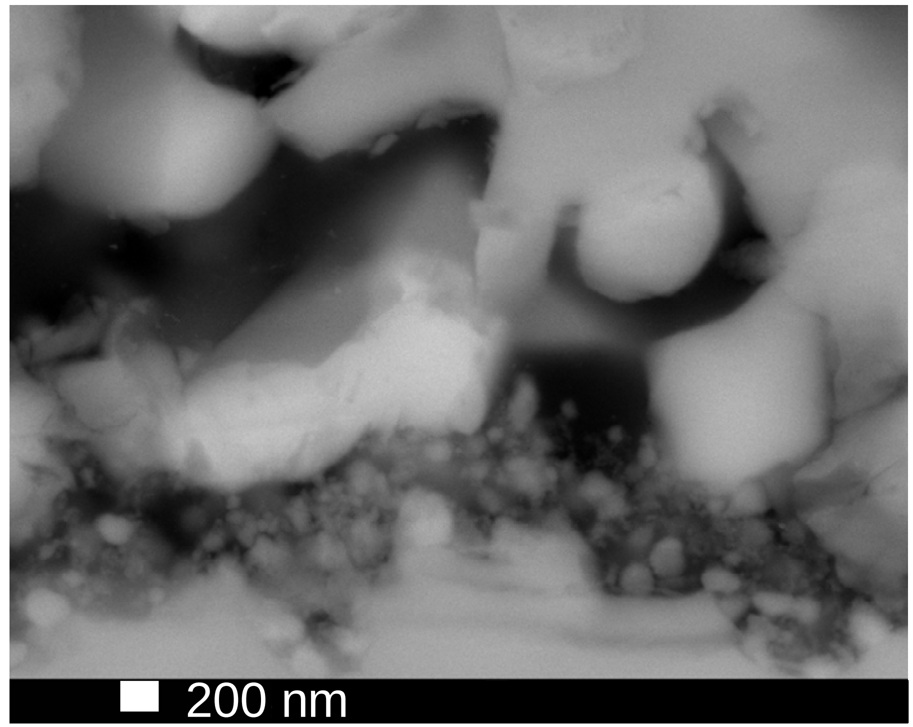


- 3rd level: at even higher polarization losses, irreversible cell failure occurs

Microstructural Changes at the Interface after Exposure to H_2Se

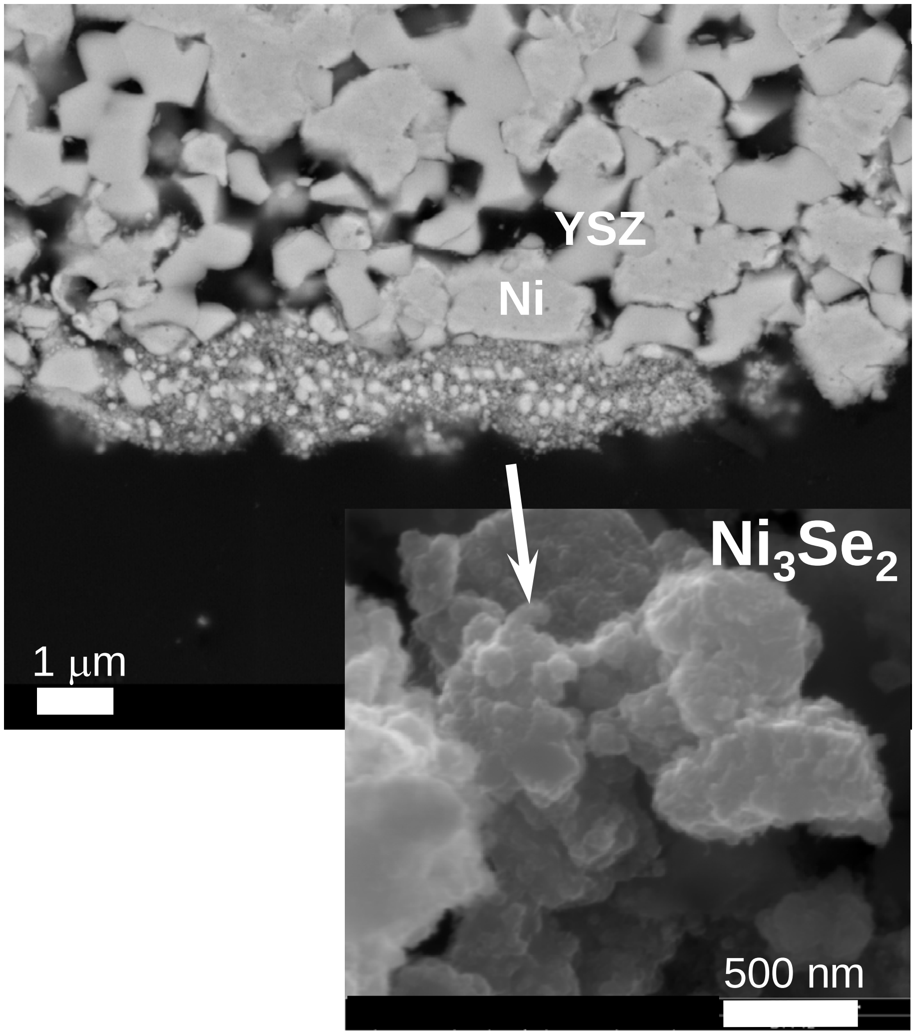


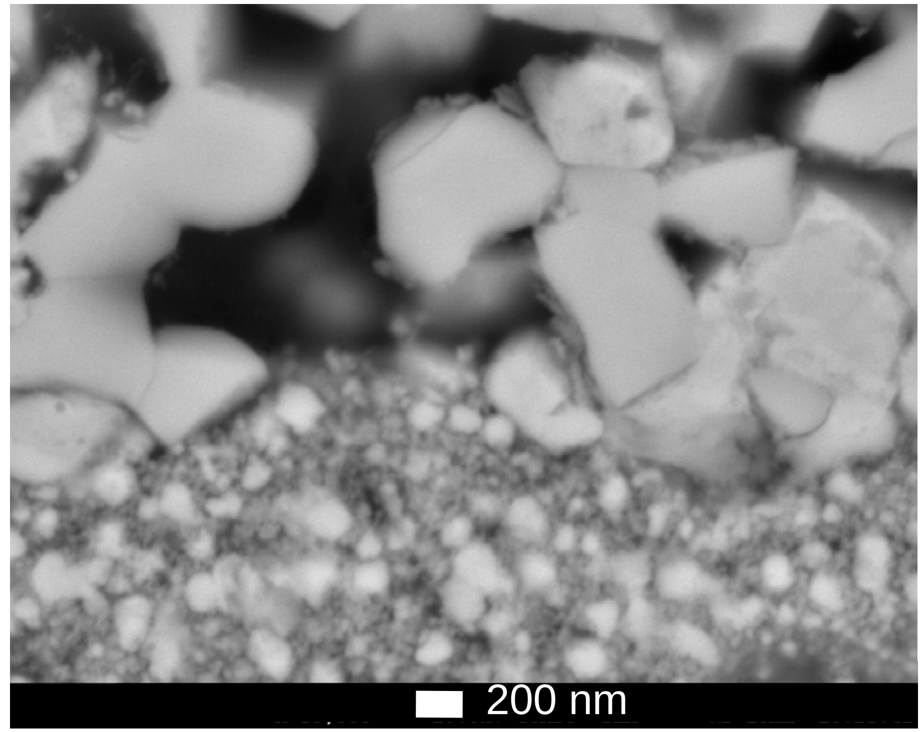
Ni/YSZ –YSZ interface after 160 hour exposure to 1 ppm of H_2S in coal gas at 700^{o}C



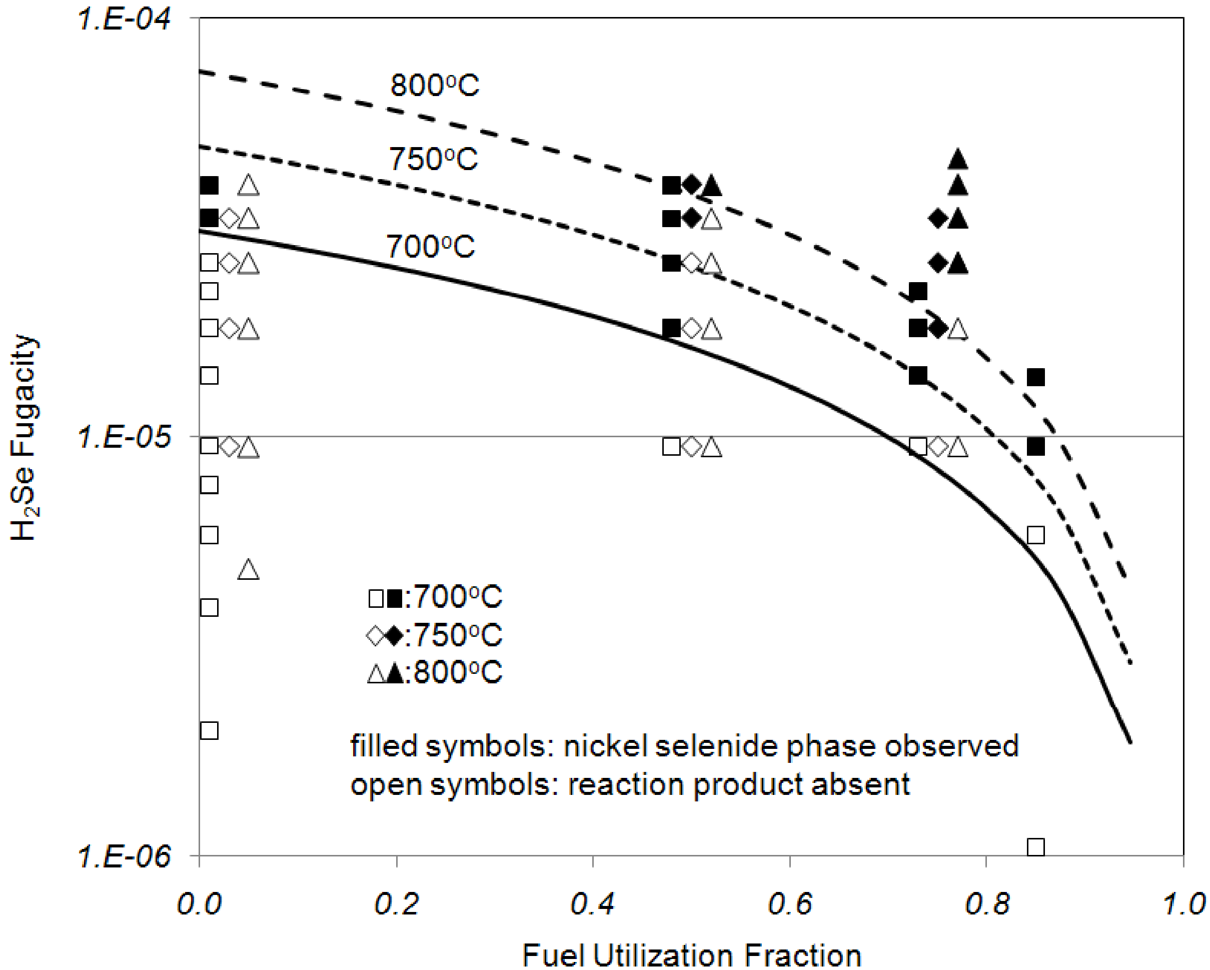
Ni/YSZ –YSZ interface after 160 hour exposure to 1 ppm of H_2Se in coal gas at 700^{o}C

Nickel Selenide Observed at the Anode/ Electrolyte Interface: 650ºC, 0.5 ppm H_2Se





Comparison of Experimental Phase Observations to Calculated Phase Boundary for Ni-Se System in Coal Gas



Second phase is easier formed at the active interface (with a current load) than anywhere else in the cell

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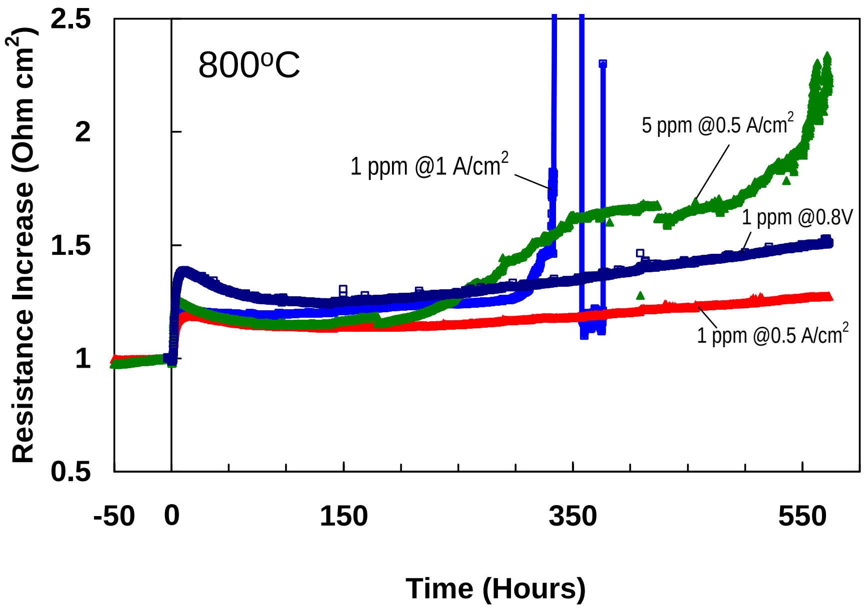
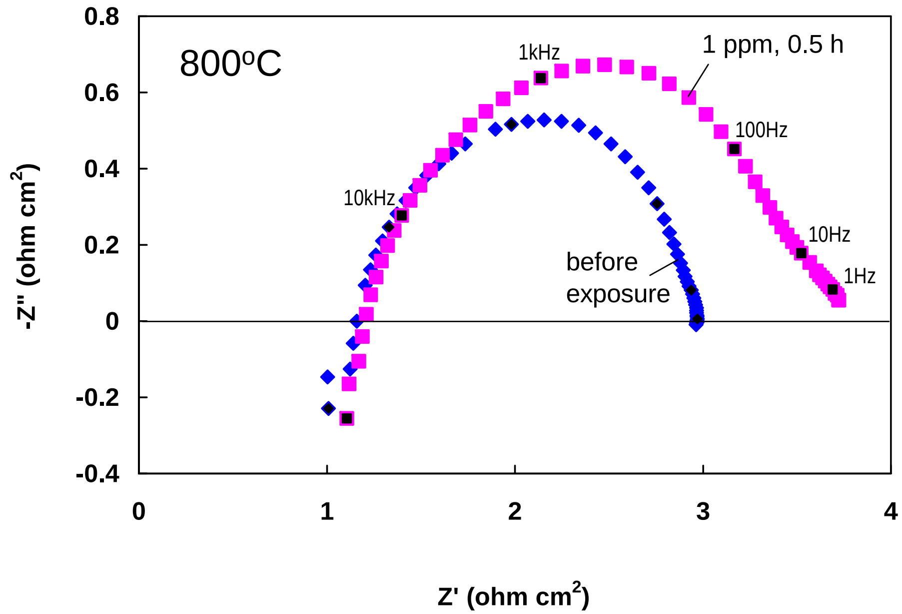
Antimony: Two Levels of Degradation

Anode-supported

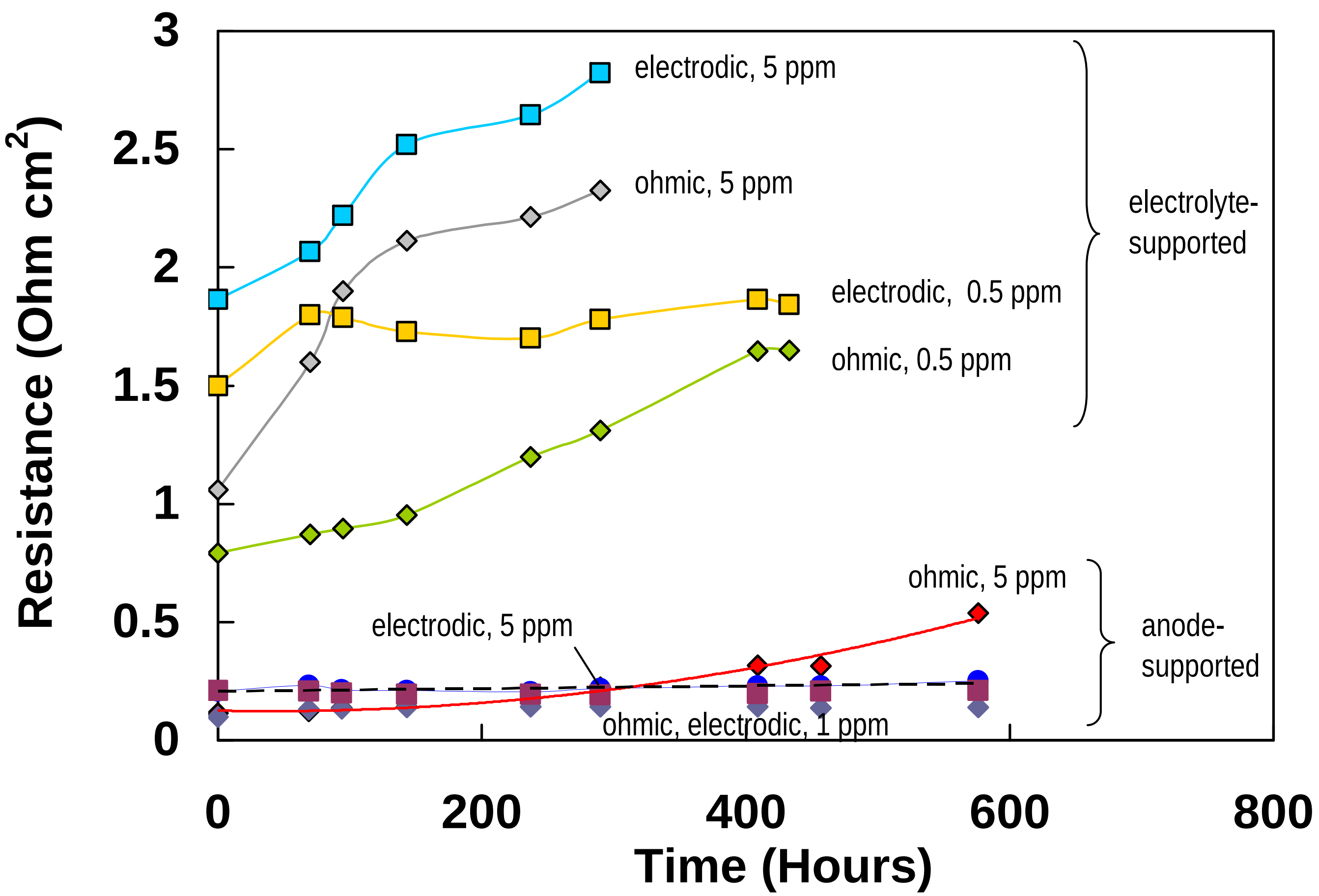


Electrolyte-supported



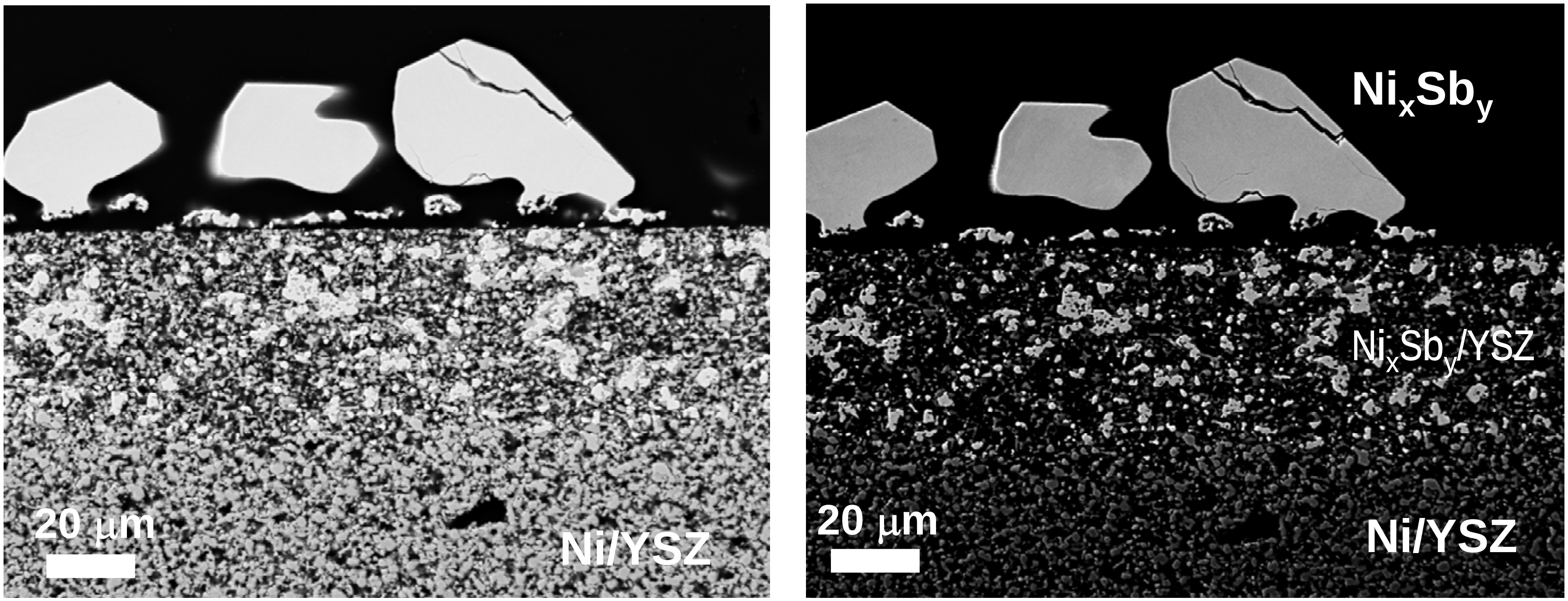
- 1st level: rapid modest decrease in performance to a new steady state, similar to effects of S and Se

Antimony Strongly Interacts with Nickel



- 2nd level: second phase formation, loss of electrical percolation in the anode support

Antimony Strongly Reacts with Nickel to Form new Ni_xSb_y Solid Phases



Anode-supported cell after test with 1 ppm Sb at 800°C for 600 hours

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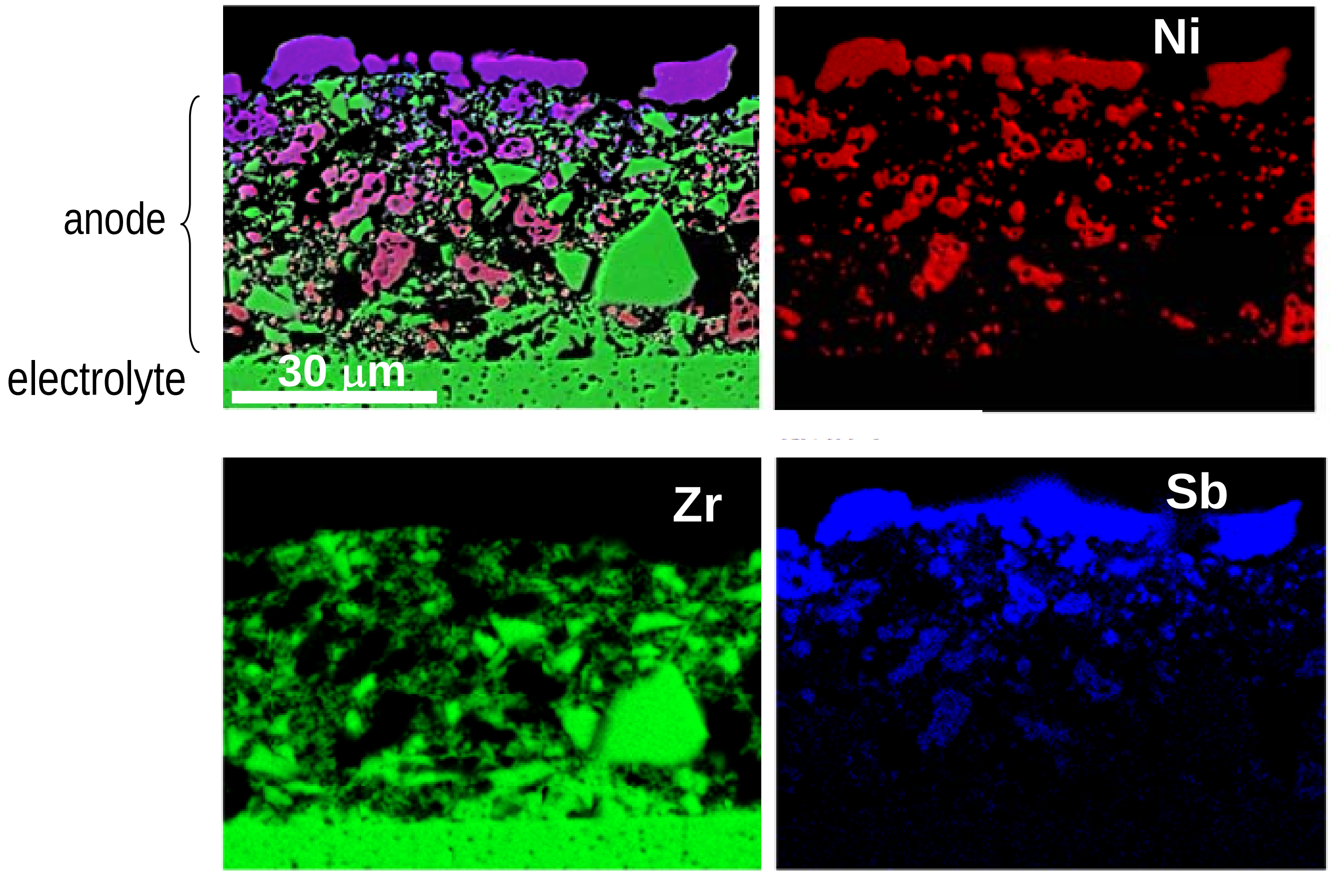
Electrolyte-Supported Cell after Test with 1 ppm Sb at 800ºC for 440 hours



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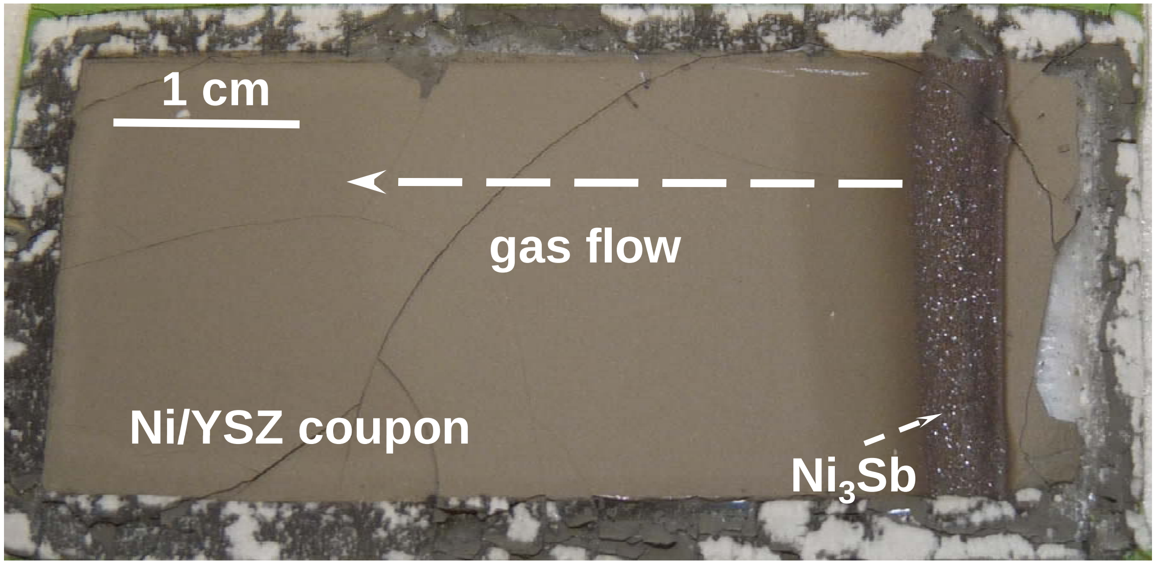
Strong Antimony Interactions with Nickel Results in Non-Uniform Uptake

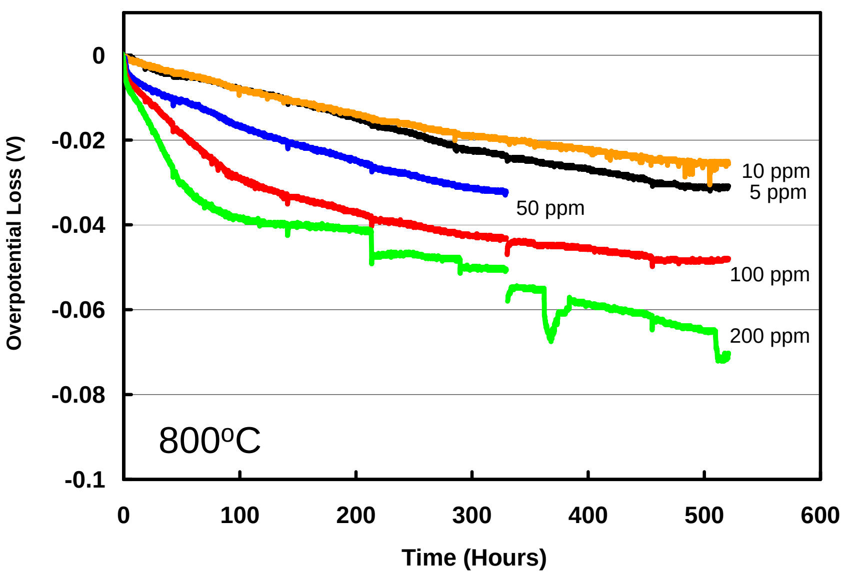
gas inlet

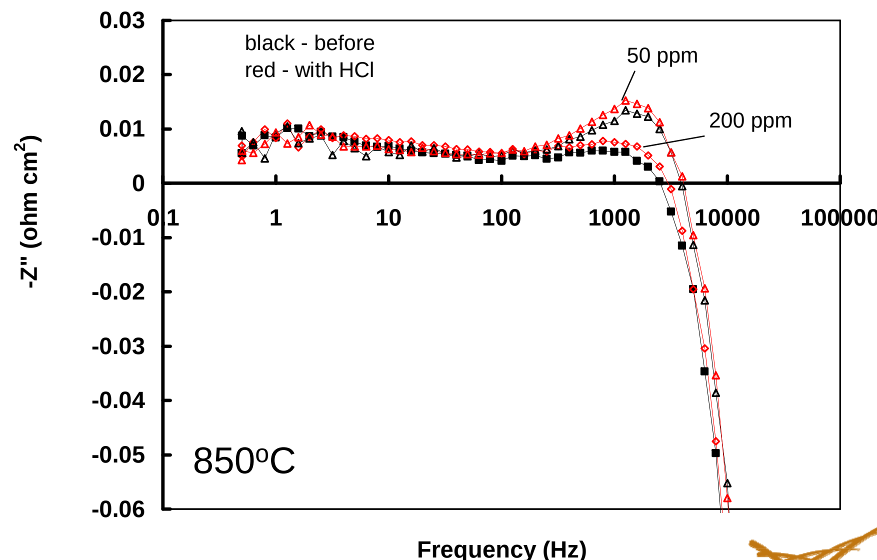


- 1 ppm Sb is captured at the gas inlet forming Ni-Sb secondary phases; 800^{o}C, 100 hours

Nickel-Chlorine Interactions

- Small cell performance degradation due to HCl exposure, primarily due to increases in electrodic resistance; reversible
- Solid nickel chloride phase formation should not occur in coal gas at realistic HCl concentrations





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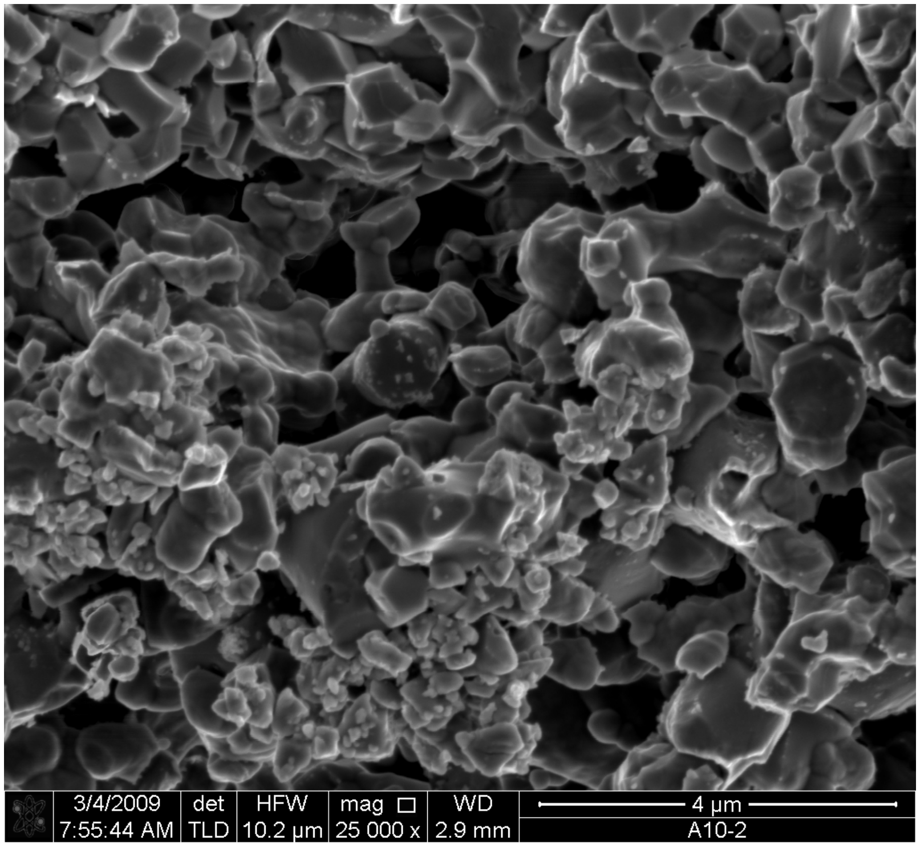
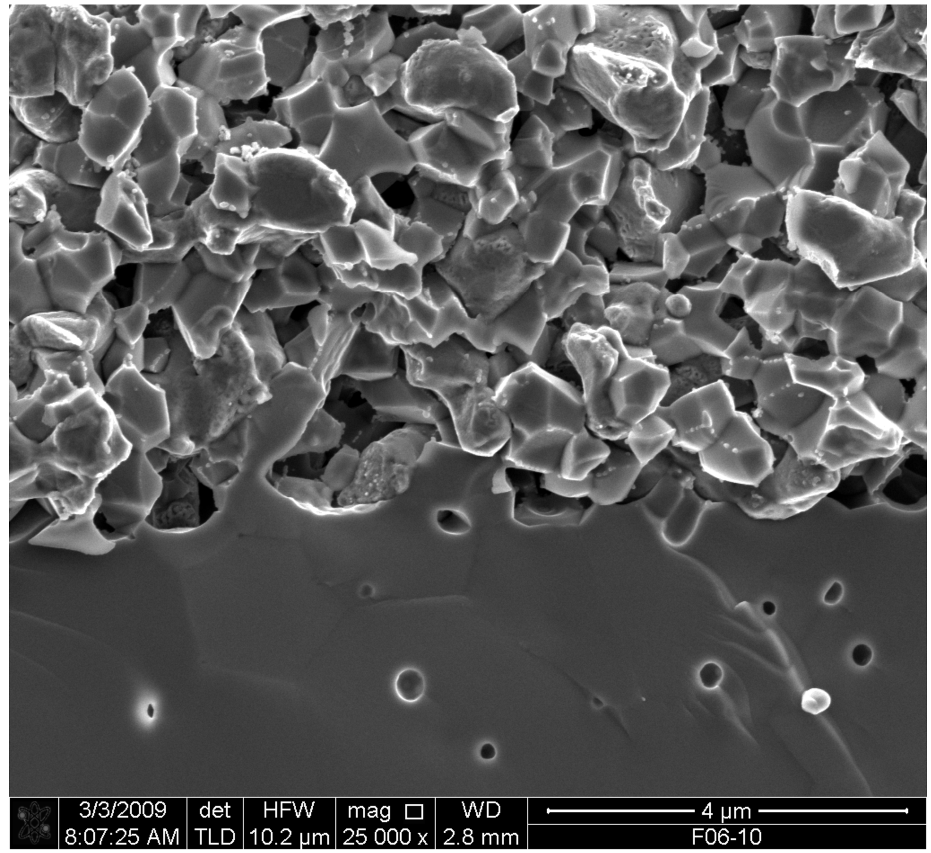
No Changes in Anode Microstructure after Testing in Coal Gas with HCl

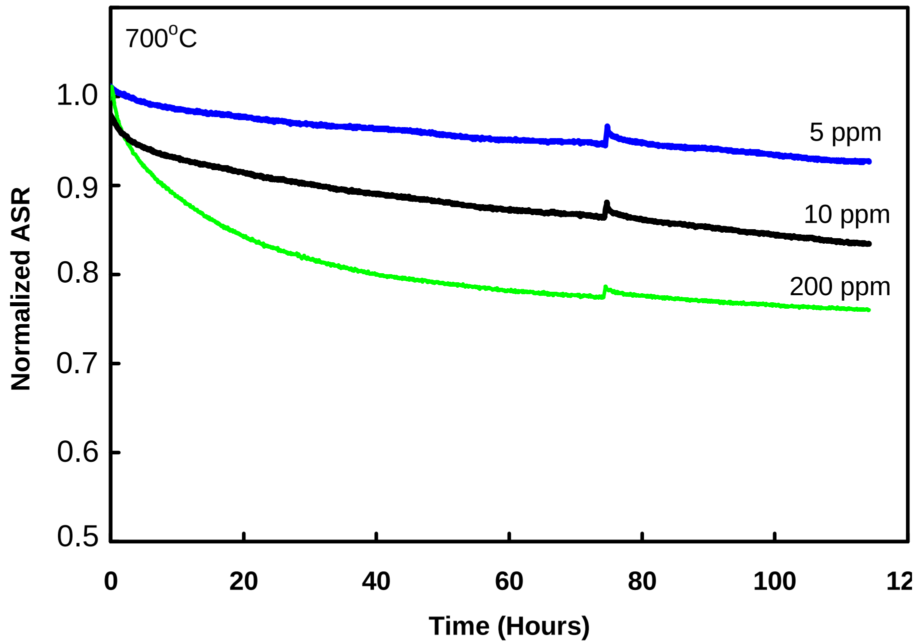


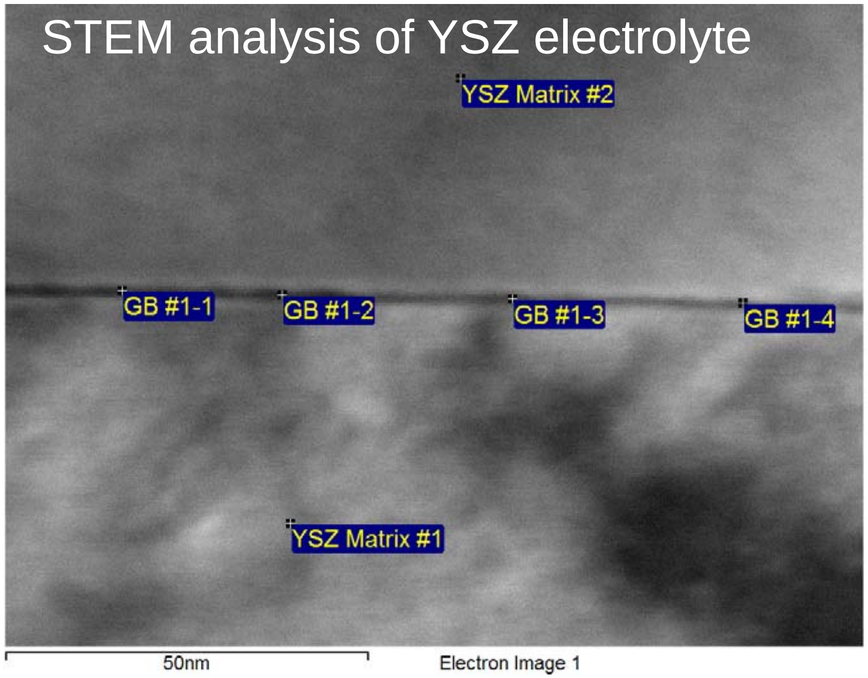
Control cell with no HCl, 800^{o}C



800^{o}C, 450 hrs, 50 ppm HCl

HCl Removes Impurities in YSZ Electrolyte; Grain Boundaries Likely Most Affected





Spectrum	Al	Mn	Y	Zr
GB #1-1	0.27	2.74	12.12	70.82
GB #1-2	0.32	3.59	11.56	71.01
GB #1-3	0.40	3.74	11.25	70.30
GB #1-4	0.52	3.24	11.89	68.92
YSZ Matrix #1	0.00	0.00	10.53	75.91
YSZ Matrix #2	0.00	0.00	10.27	75.92

Visible decreases in ohmic resistance (as determined by EIS) at low temperatures, 700ºC or below

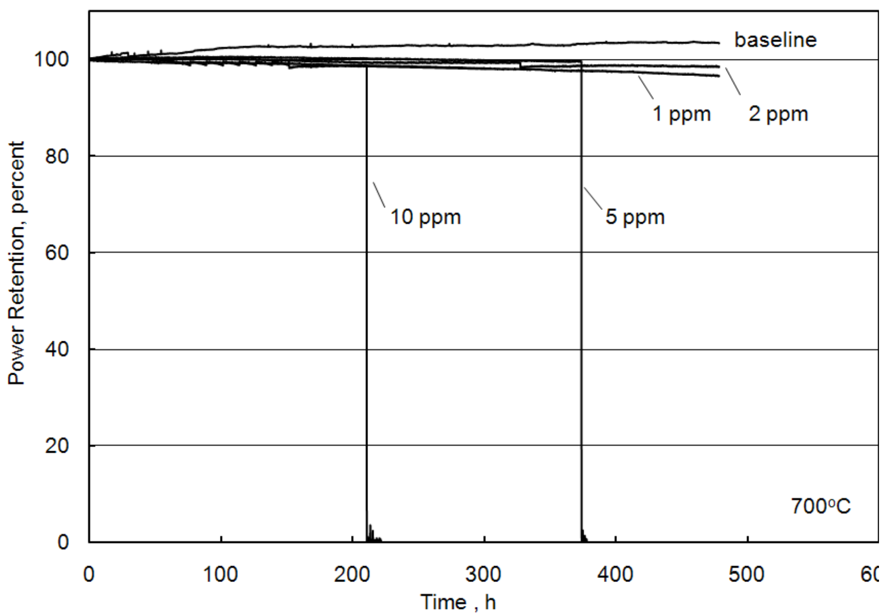
Nickel-Arsenic Interactions

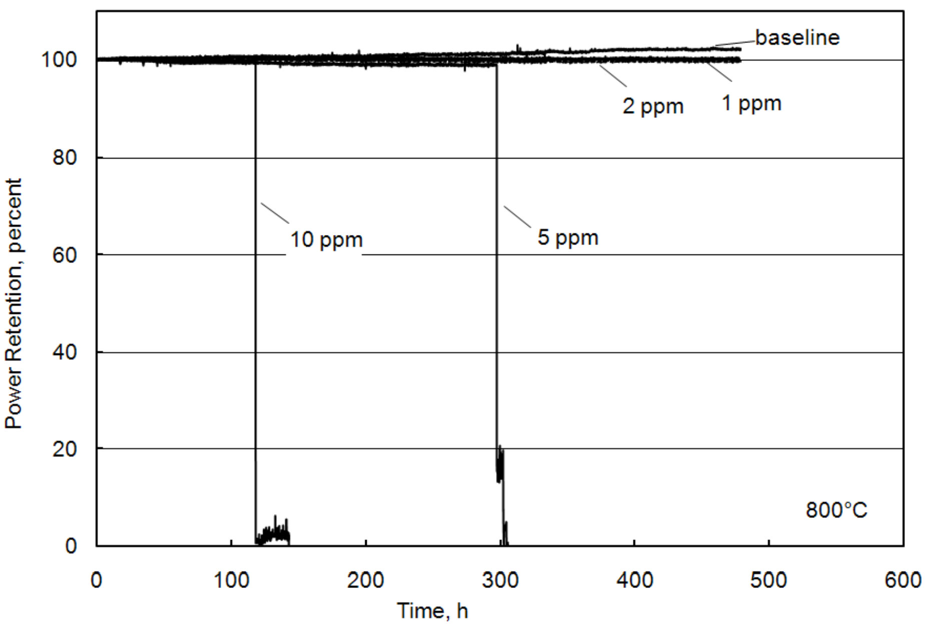
- Forms bulk nickel arsenide phases at arsenic concentrations below 1 ppb in coal gas
- For anode-supported cells, cell failure occurs well before arsenic reaches the active anode/electrolyte; failure is attributed to loss of electrical percolation in the anode support
- For electrolyte-supported cells with a relatively thin anode, poisoning of the active interface was observed

Abrupt cell failure for anode-supported cells in coal gas with arsenic

700ºC

800ºC

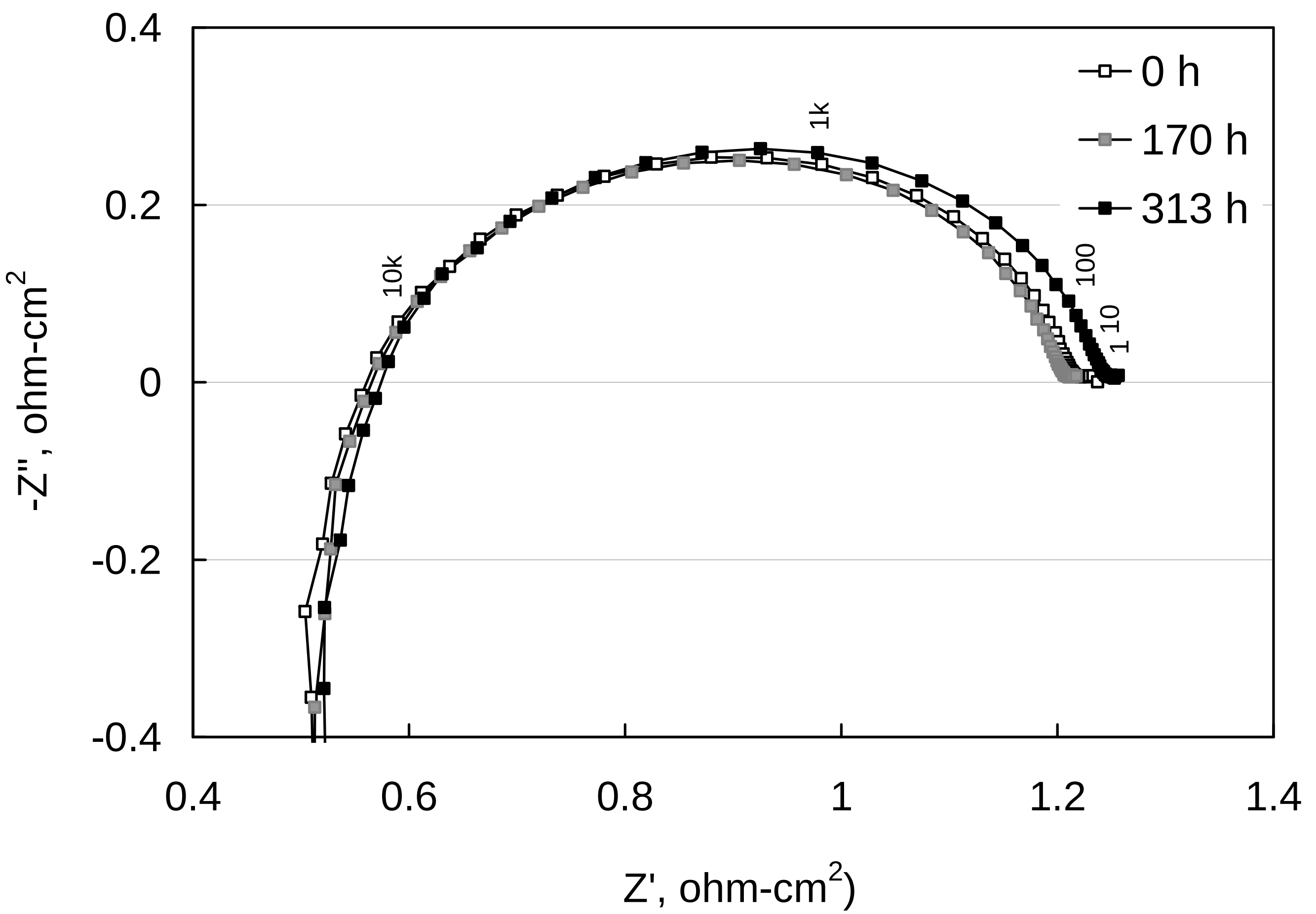




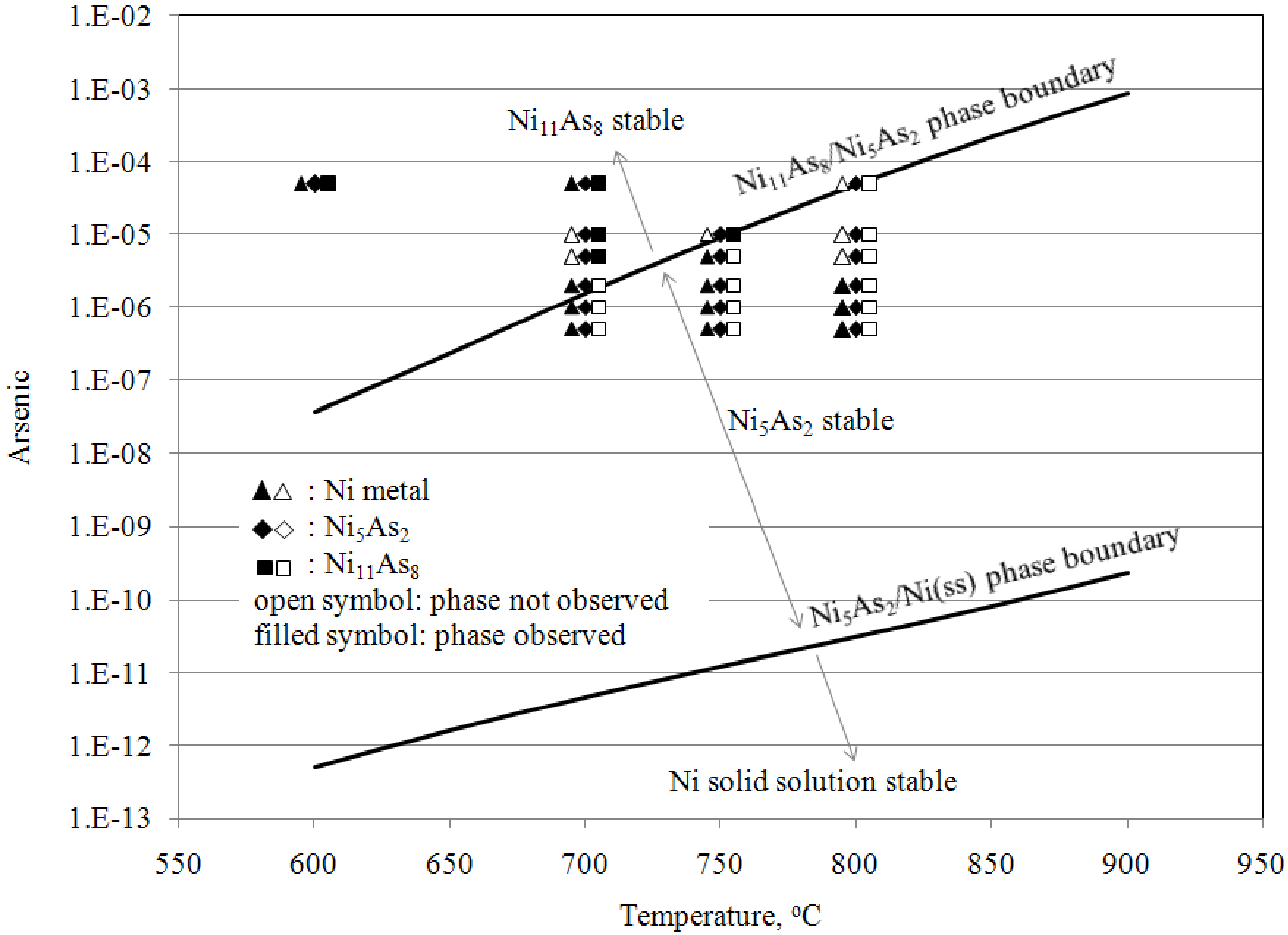
Cell failure occurs well before any evidence of arsenic reaching the active anode/electrolyte interface

Coyle, Marina, Thomsen, Edwards, Coffey, Cramer, Pederson,
J. Power Sources, 193 (2009) 730

Impedance Spectra Reveal no Electrochemical Degradation Prior to Complete Failure



Calculated and Observed Phase Boundaries in the Ni-As System in Coal Gas



Experimental observations consistent with thermochemical modeling

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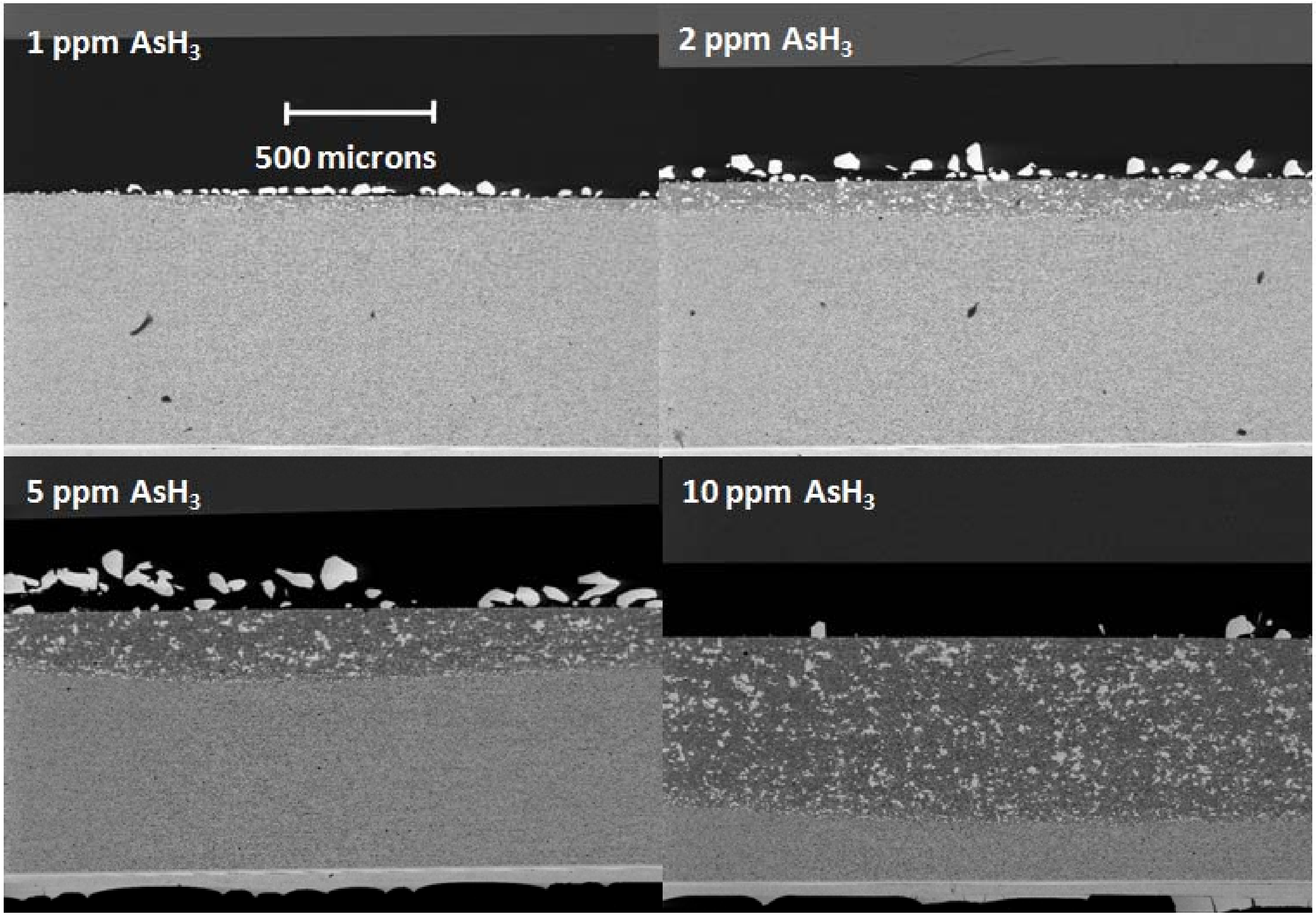
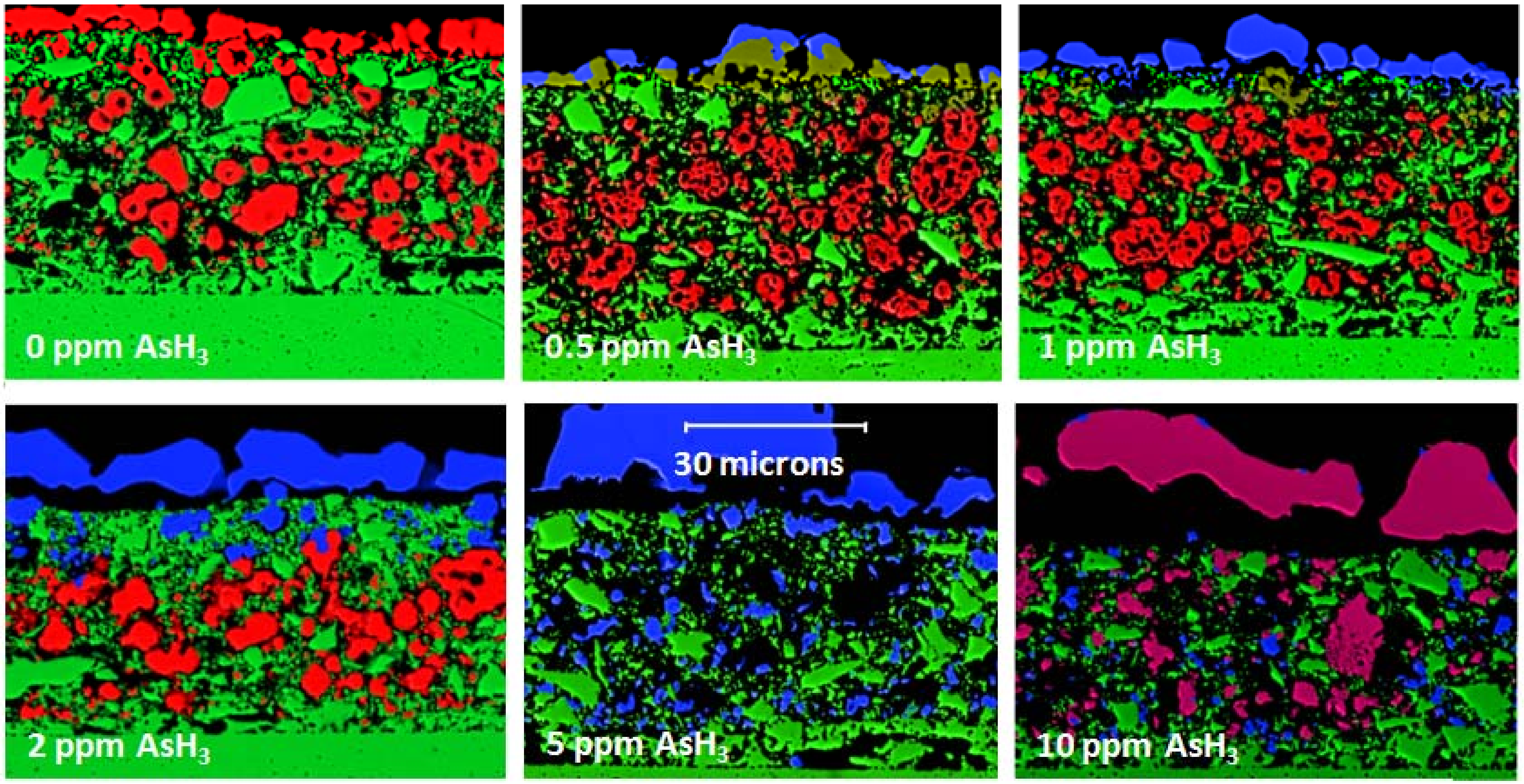
Progressively greater Ni reaction with time, arsenic concentration



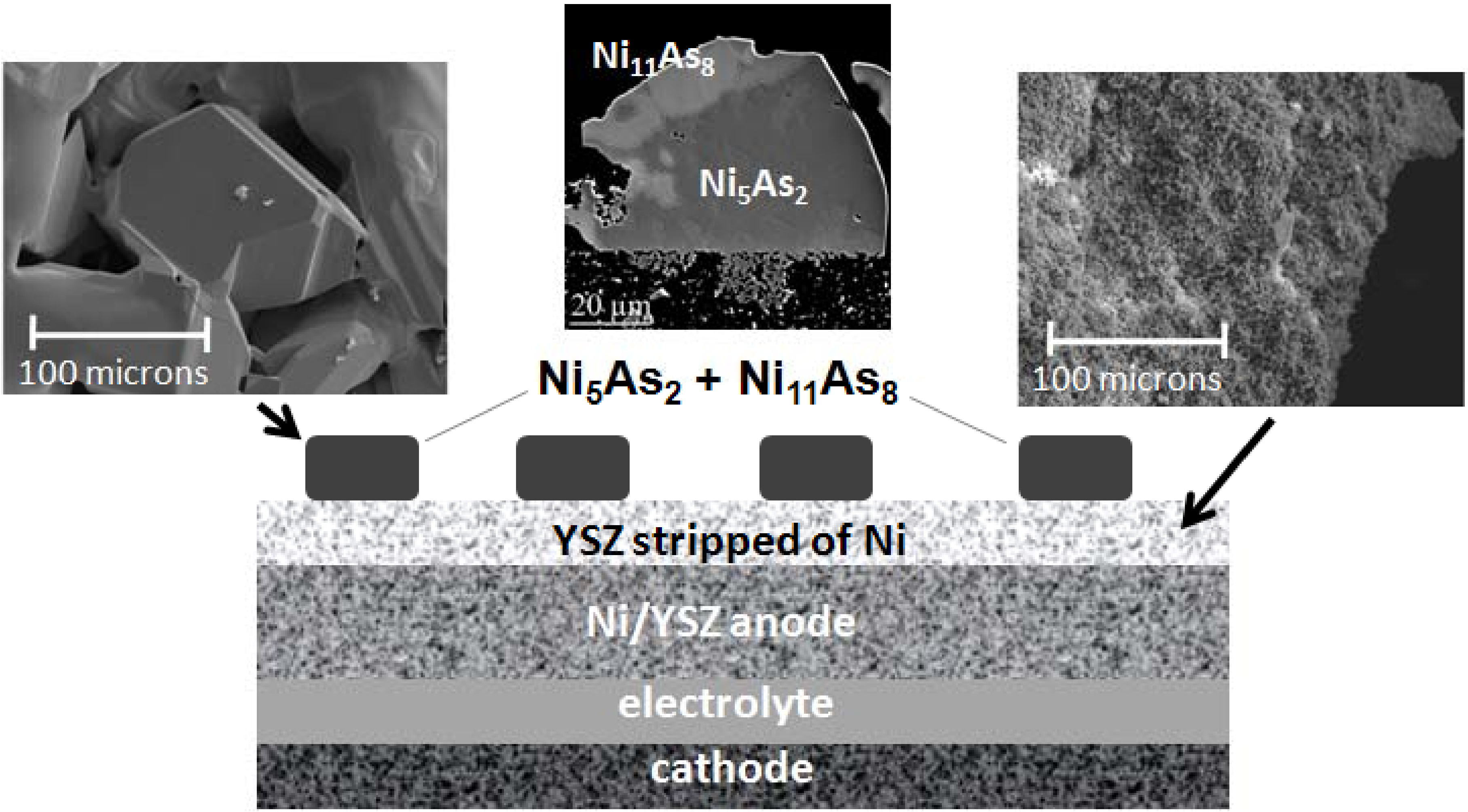
480 hour exposure to coal gas with AsH_3 at 800°C.

Reaction progression for electrolyte-supported cells following 50 h at 700ºC

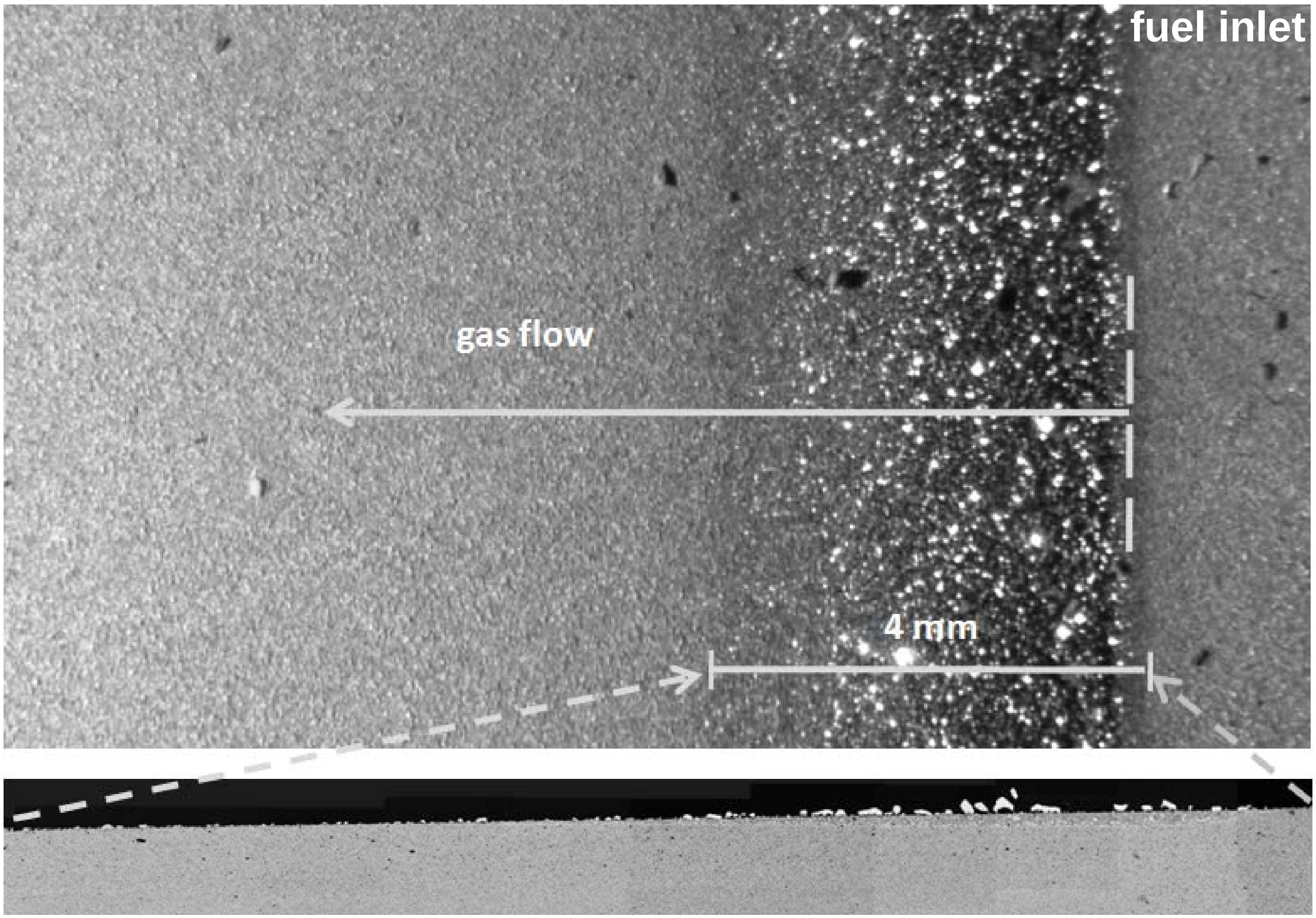


Red: Ni Light Green: YSZ Dark Green: Ni(As) solid solution
Blue: Ni_5As_2 Magenta: $Ni_{11}As_8$

Morphology of Ni/YSZ anode following reaction with As in coal gas

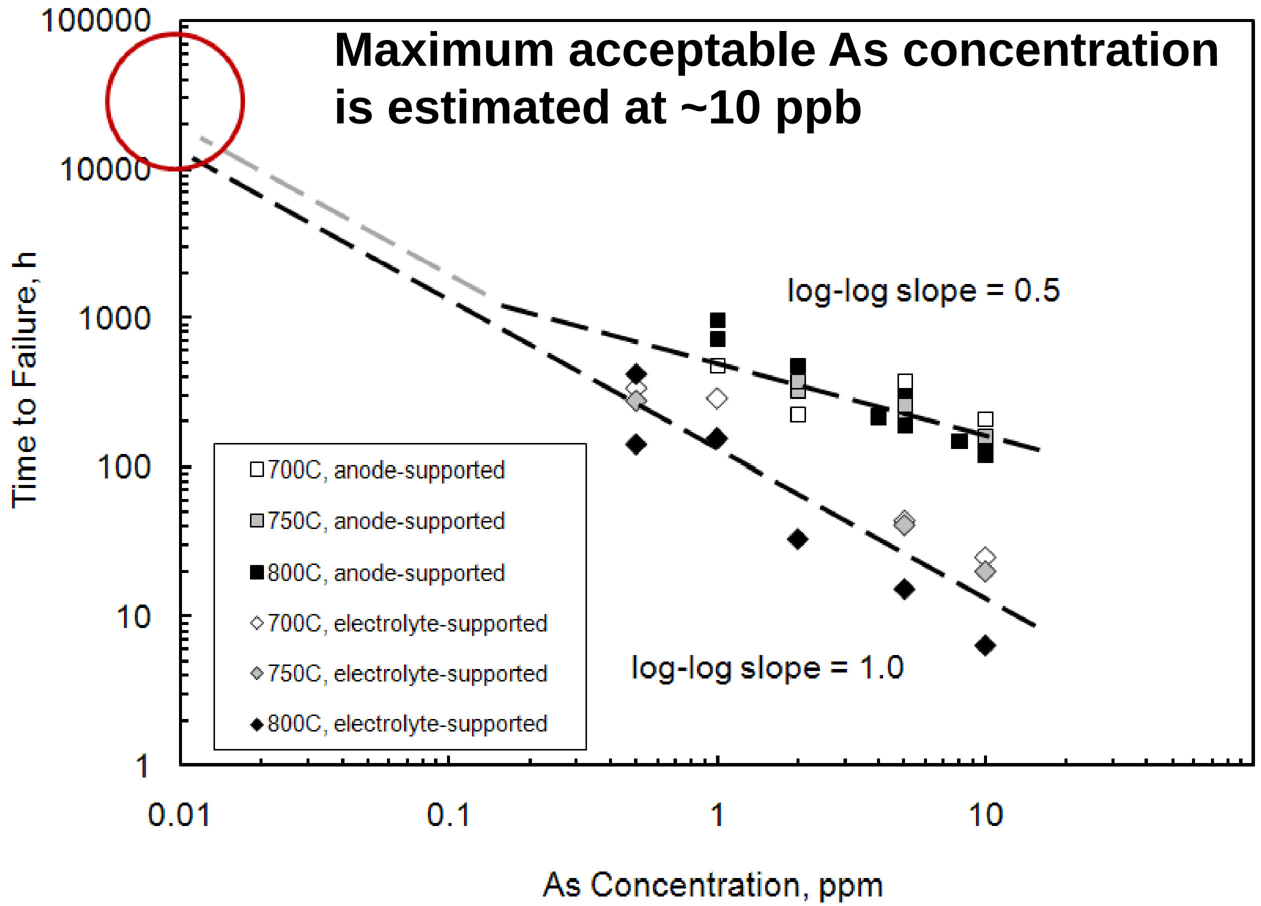


Ni/YSZ Coupon Exposed to Coal Gas with As in Flow-by Arrangement: As Captured within Short Distance of Fuel Gas Inlet



0.5 ppm AsH_3
500 hours
700^{o}C

Time to Failure Linearly Related to As Concentration for Electrolyte-Supported Cells



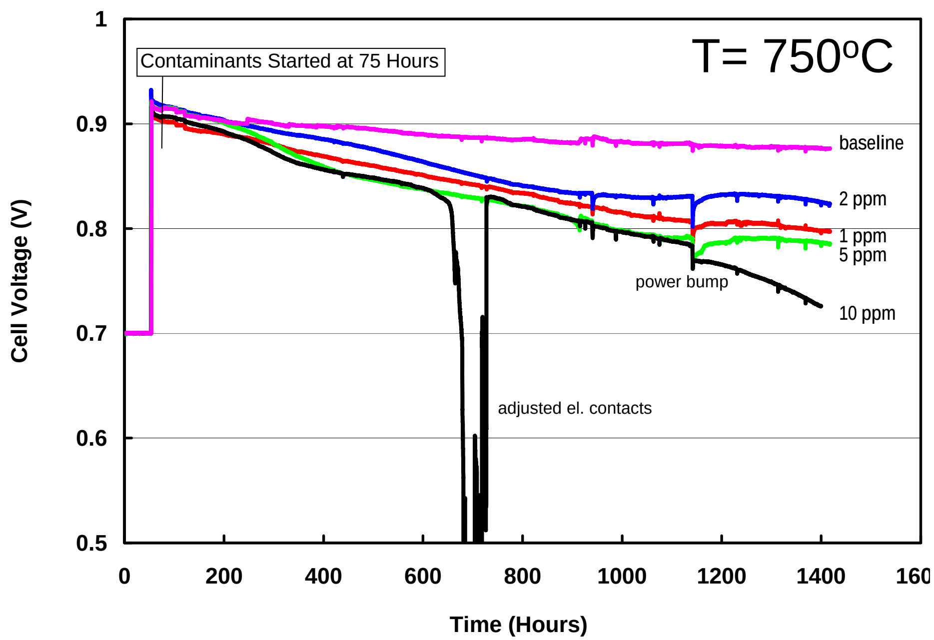
Square root dependence for anode-supported cells is attributed to diffusional processes (coalescence of grains, which disrupt electrical connectivity). At long times and low concentrations, expect both anode and electrolyte-supported cells to show log log slope of 1, where degradation is limited by rate of As delivery.

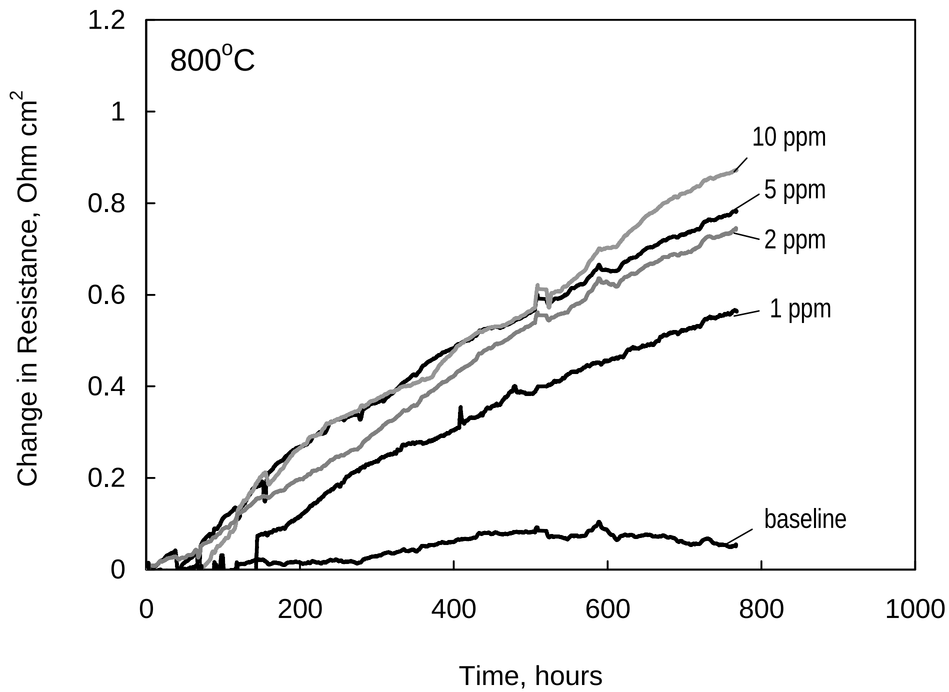
Coyle, Marina, Thomsen, Edwards, Coffey, Cramer, Pederson, *J. Power Sources,* 193 (2009) 730

Nickel-Phosphorus Interactions

- Like arsenic, nickel reacts strongly to form bulk nickel phosphides at concentrations less than ~1 ppb in coal gas
- For anode-supported cells, loss of electrical percolation in the anode support was the principal mode of failure; coalescence of nickel phosphide crystals and the appearance of microcracks in the zirconia support contributed
- For electrolyte-supported cells, migration of phosphorus to the active interface led to poisoning.

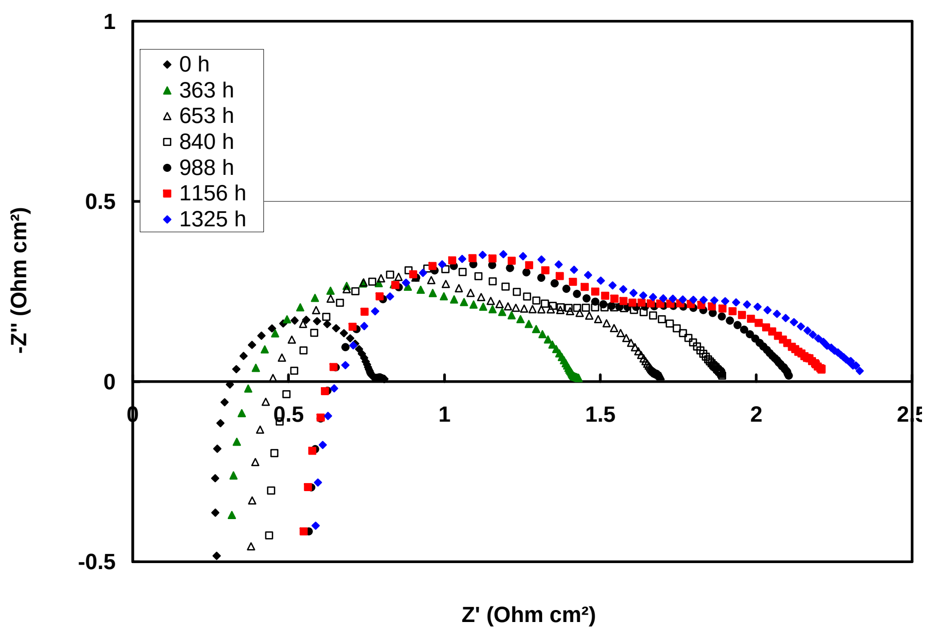
Anode-Supported Cell Tests in Coal Gas with Phosphorus: Degradation Onset More Gradual Than with Arsenic

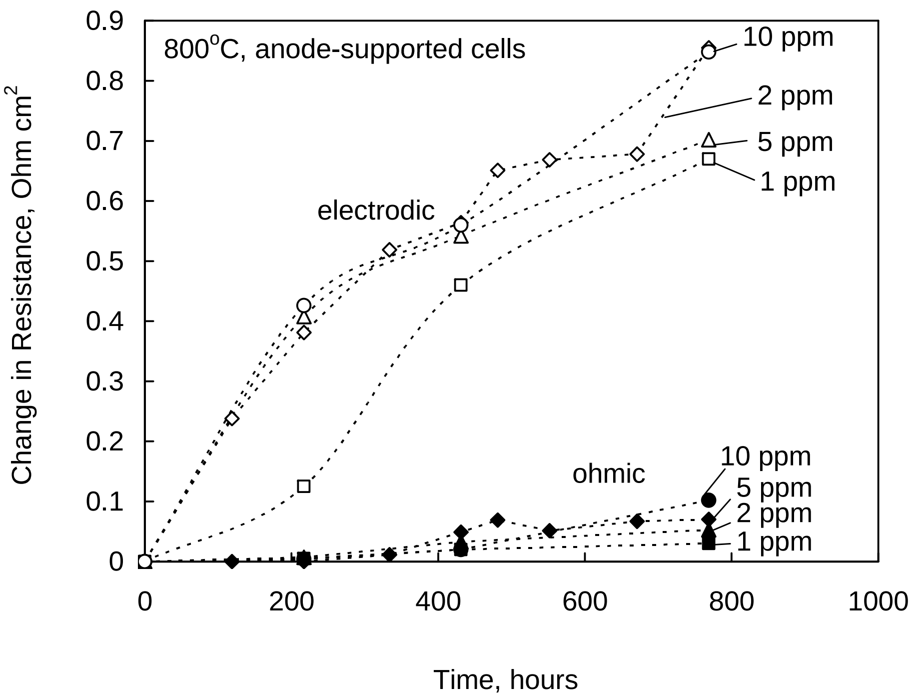




Marina, Coyle, Thomsen et al, submitted to SSI

Impedance Spectra Show Increases in both Ohmic and Electrodic Contributions to Cell Resistance





- New process appears at around 50-100 Hz
- Ohmic and electrodic resistances double after 1000 hours of exposure

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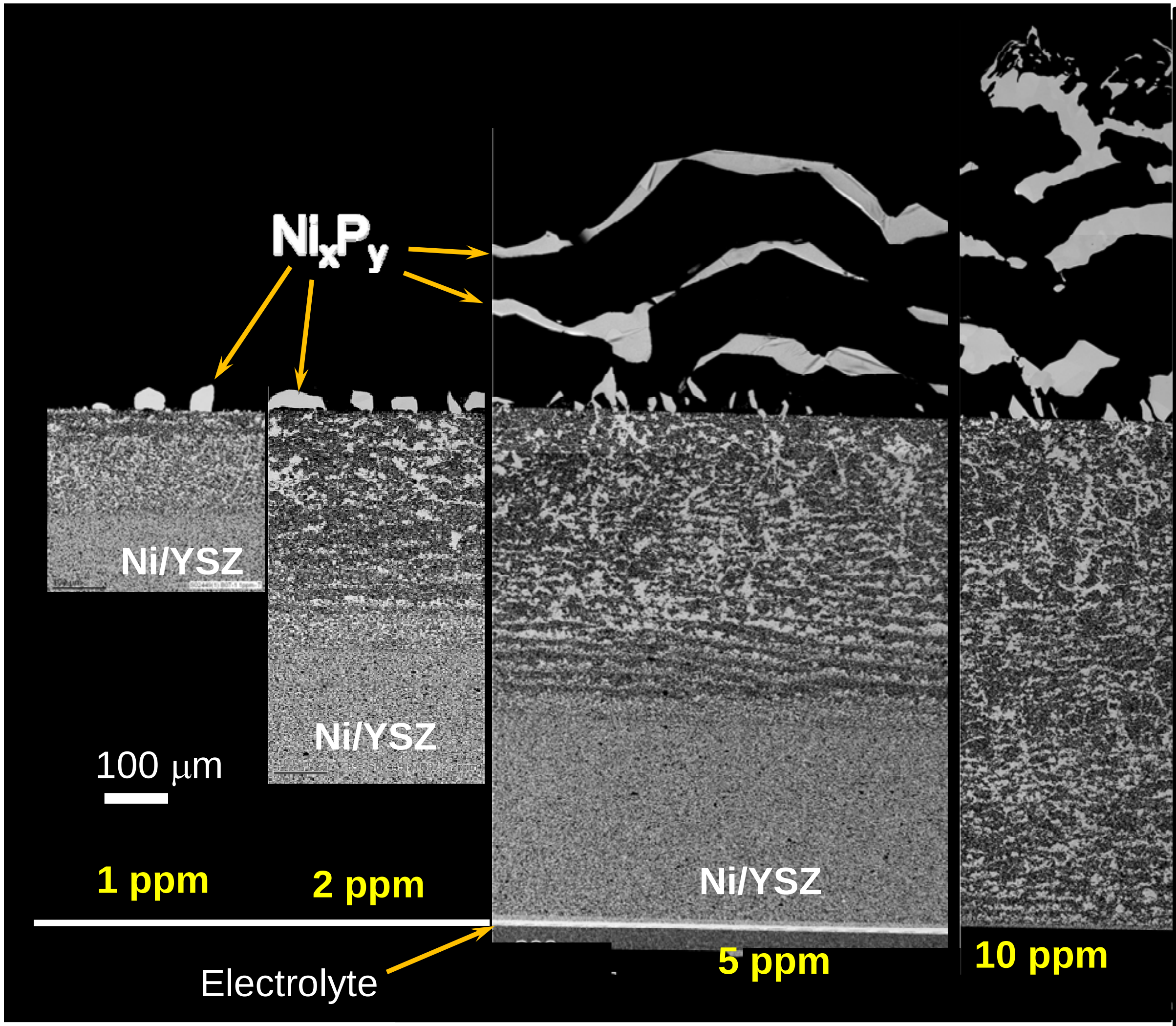
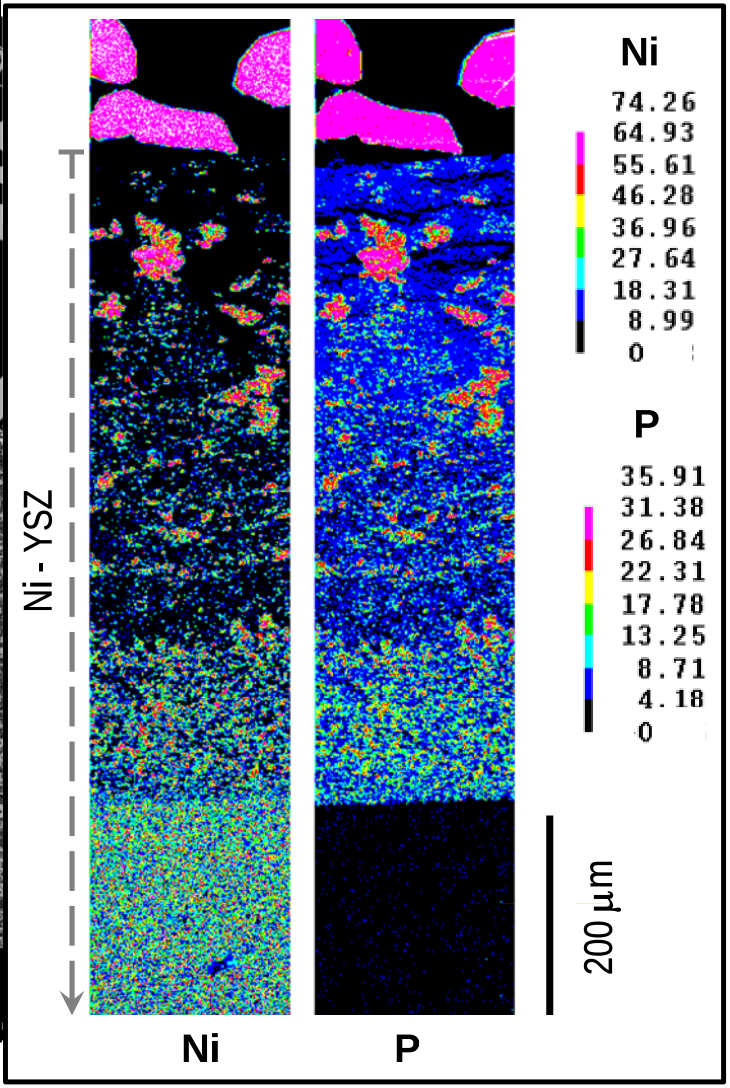
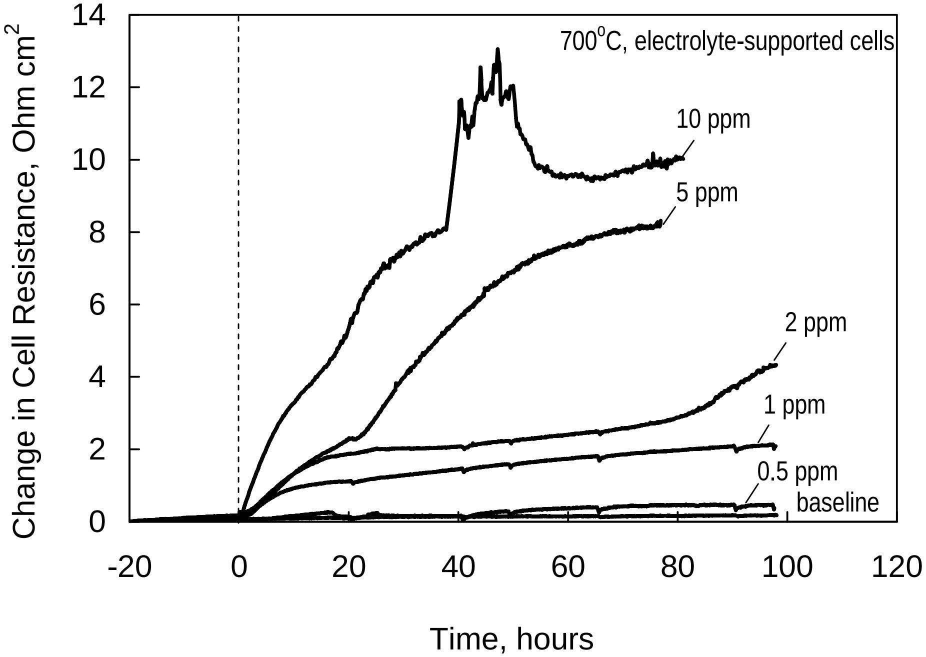
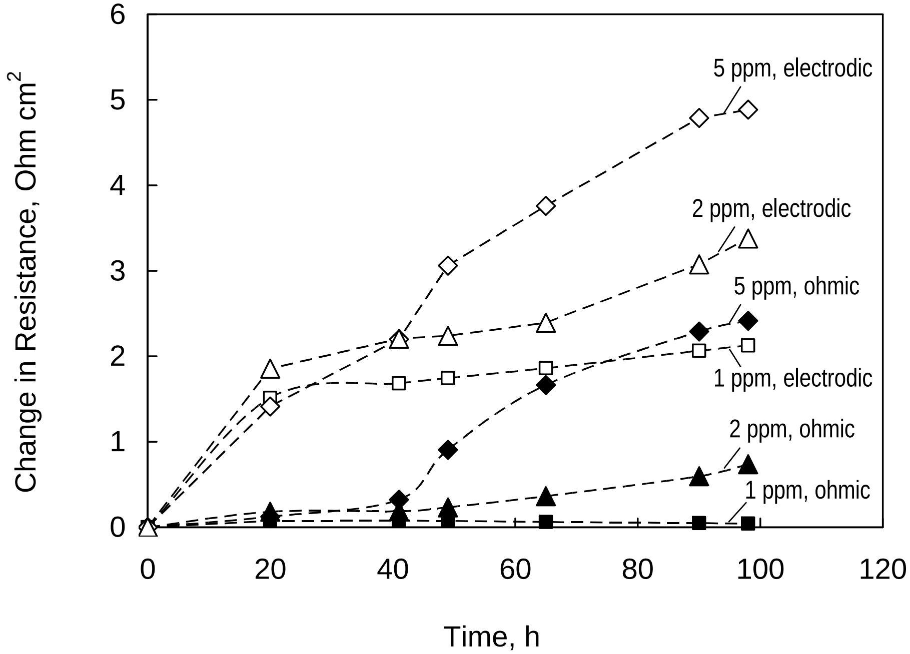
SEM Analysis of Anode-Supported Cells after 1000 hour Tests at 700°C with PH_3 in Coal Gas





Electrolyte Supported Cells in Coal Gas with PH_3 at 700ºC





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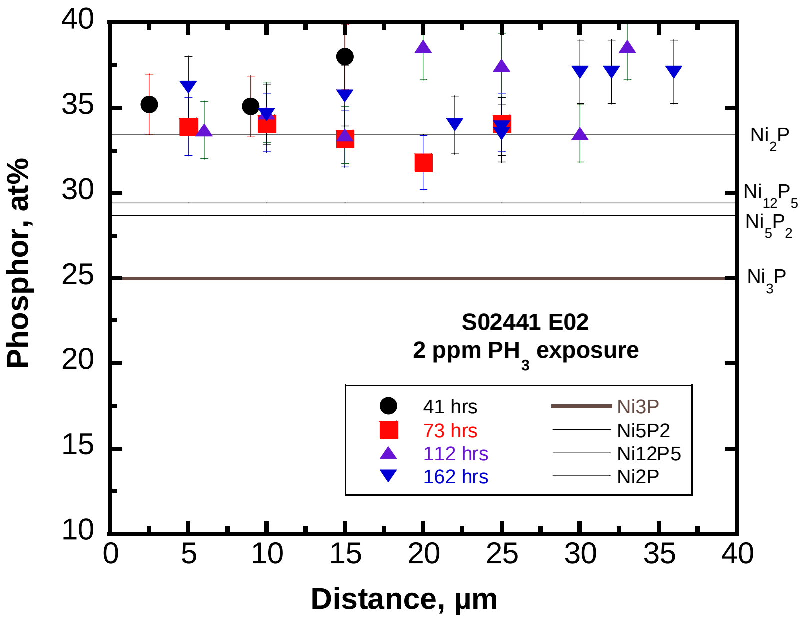
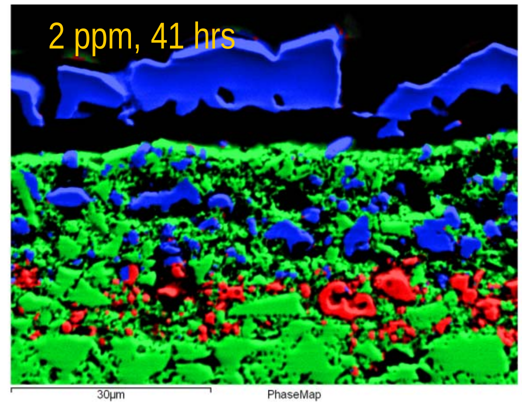
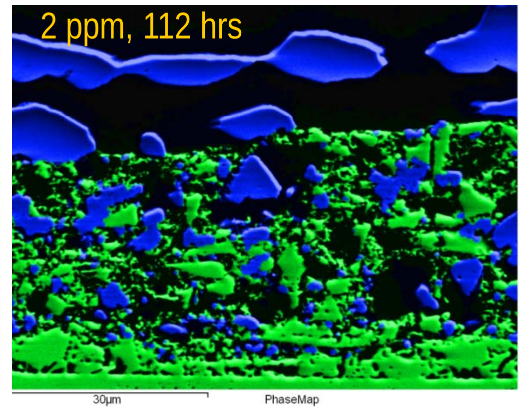
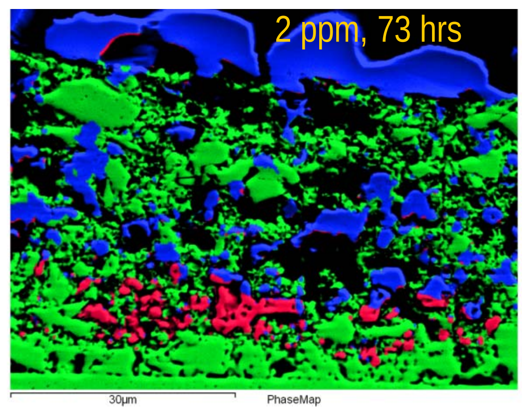
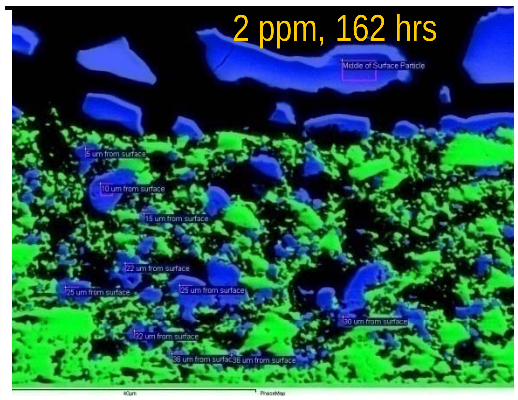
Time Dependence for Electrolyte-Supported Cells after Exposure to 2 ppm PH_3 at 800ºC (Ni-red, Ni-P – blue, YSZ – green)











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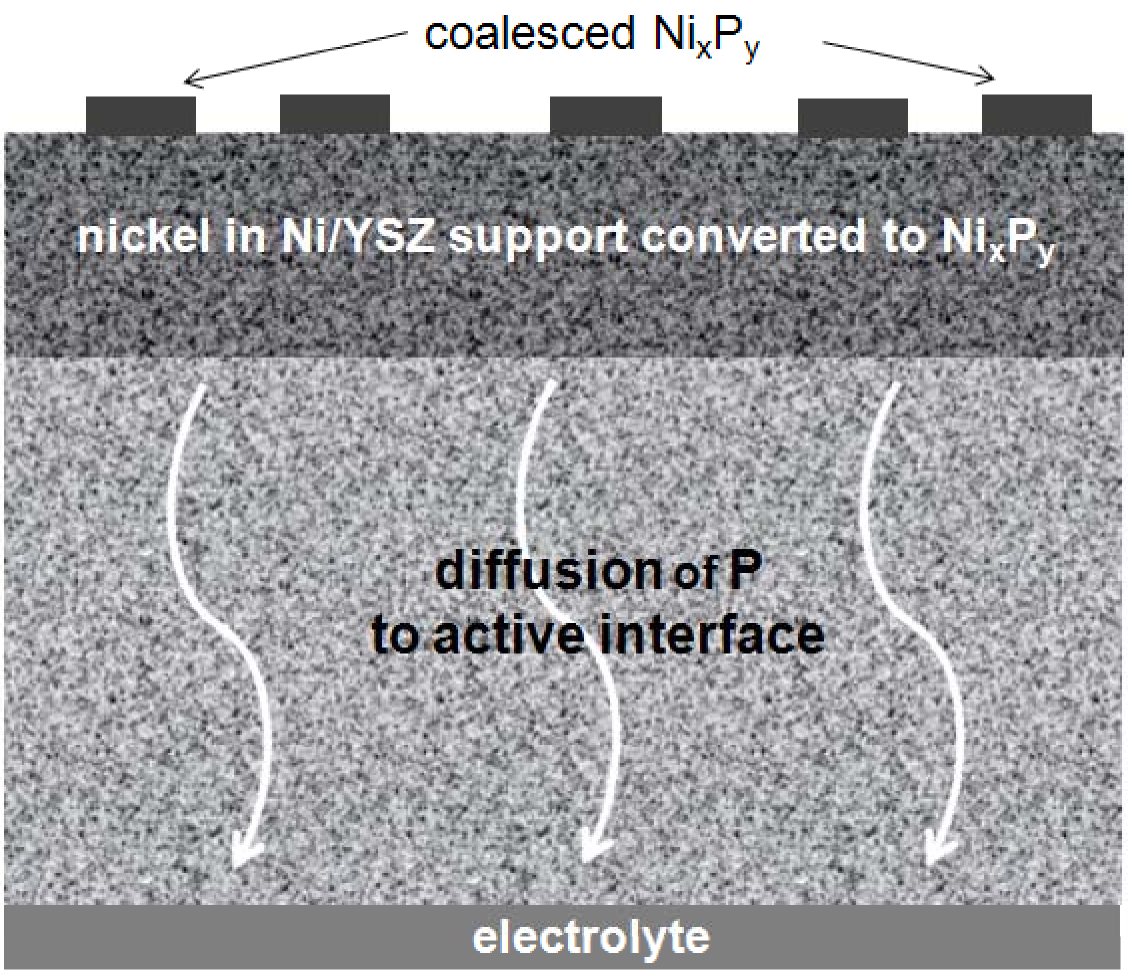
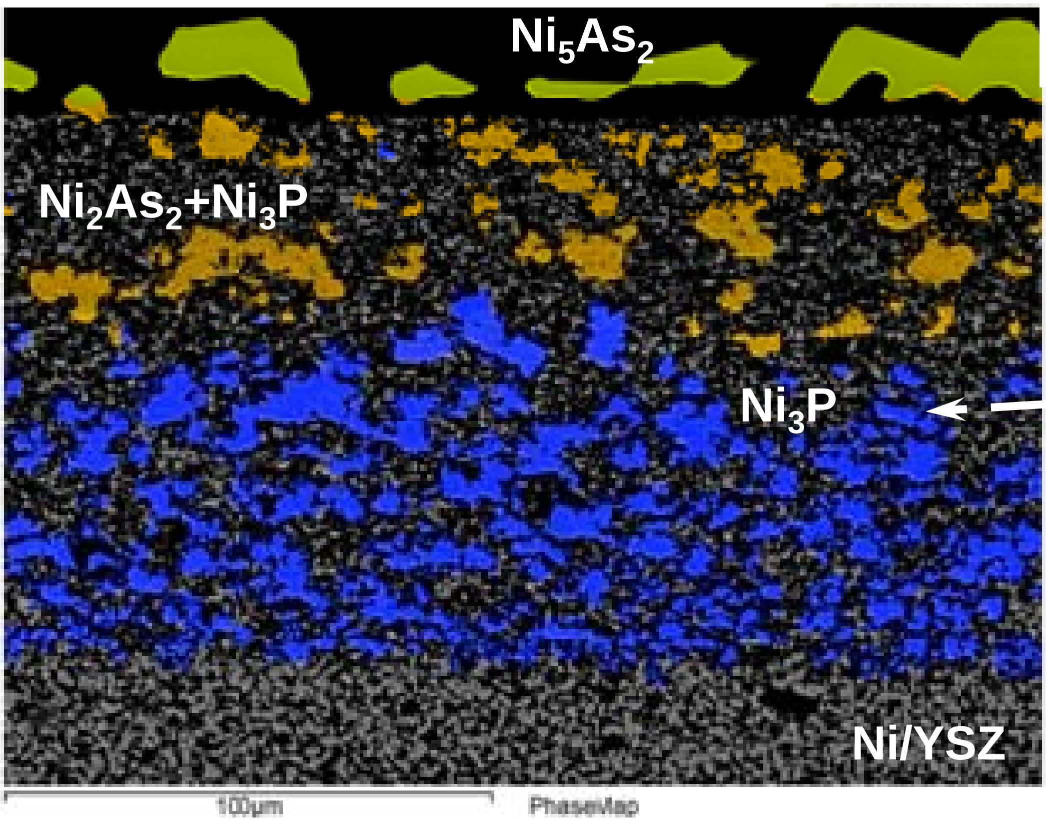
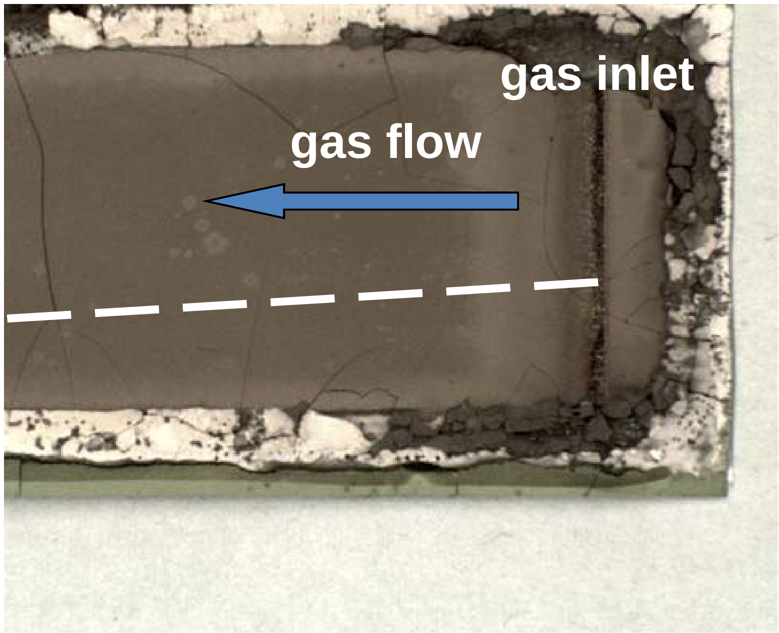
Effect of Phosphorus on SOFC Anode



Ni/YSZ Coupon after 500 Hour Exposure to 0.5 ppm PH_3 and 0.5 ppm AsH_3 at 800ºC





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Summary

- Phosphorus and Antimony

  Strongly react 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 high overpotentials and/or high fuel utilizations is likely.

- Chlorine:

  Minimal reversible degradation.

Acknowledgements

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- We would like to acknowledge NETL management team for stimulating and helpful discussions.

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