Interactions of Ni/YSZ Anodes with Coal Gas Contaminants

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Goal: Establish Maximum Acceptable Coal Gas Contaminant Concentrations

Part of a coordinated study involving:

- Randy Gemmen, Kirk Gerdes, NETL
- Gopala Krishnan, SRI International
- Stephen Sofie, MSU
- Jason Trembly, RTI
- PNNL team

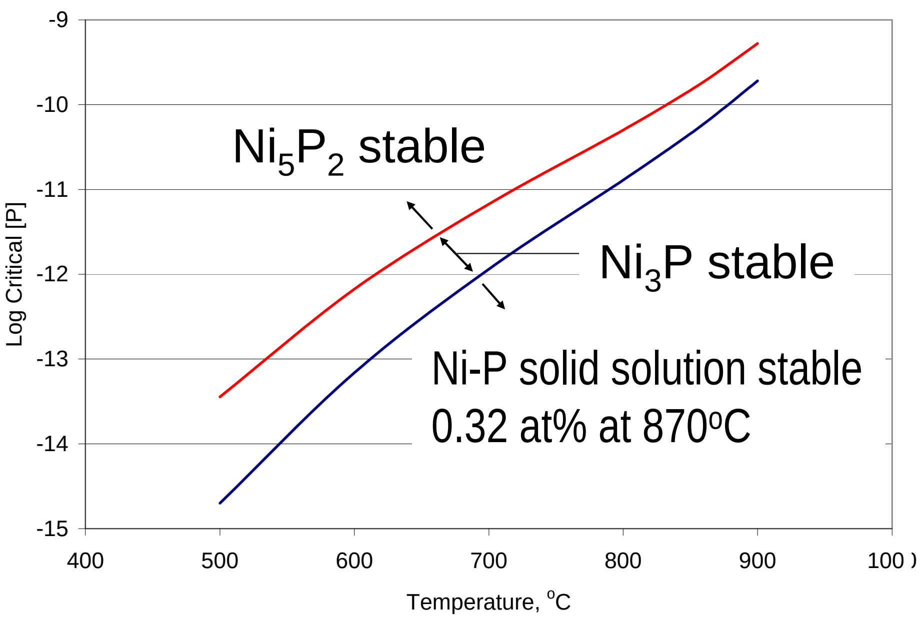
Approach

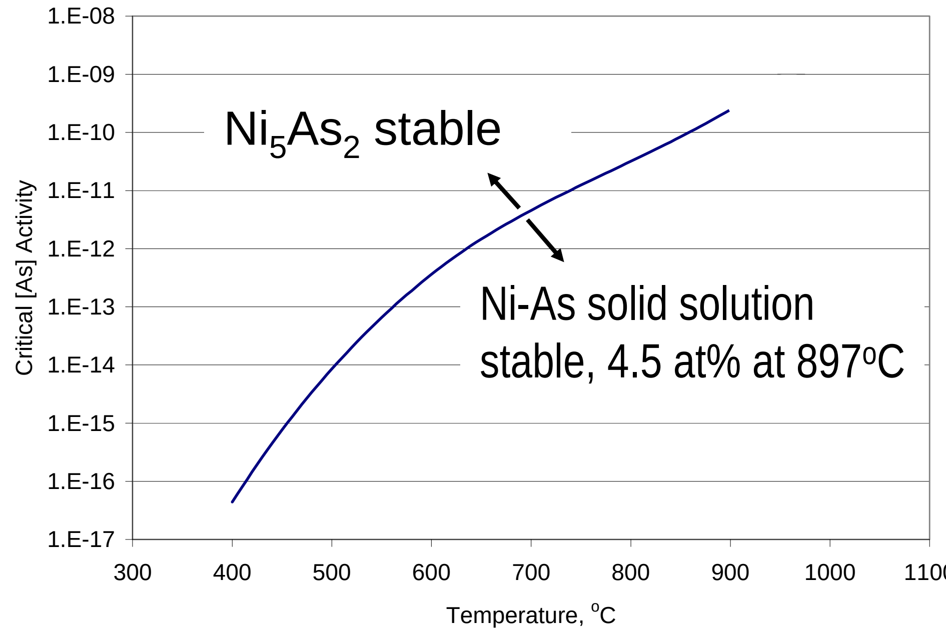
- Thermodynamic assessment of coal gas contaminant - Ni phase equilibria
- Button cell testing of Ni interactions with coal gas contaminants. Parameters addressed included contaminant concentration, temperature, reaction time, fuel utilization, and current density
- Post-test analyses to determine the composition and extent of nickel modification
- Coupon tests in flow-through and flow-by arrangements to determine penetration rate and nature of contaminant/Ni interactions – companion to button cell tests

Summary

- Phosphorus and arsenic interact strongly with Ni and are nearly completely captured by the anode
- One degradation mode involves loss of electronic percolation due to nickel phosphide and nickel arsenide formation, grain growth, and inducement of micro-fractures within the anode support
- Electrochemical degradation may be very low if an electrical pathway to the active interface is maintained ("shadowing effect" for strongly interacting contaminants)
- Nickel conversion to the active interface by P and As results in significant degradation
- Selenium poisoning occurs quickly, similar to but slower than sulfur, and reaches steady state performance

Phosphorus and Arsenic: Very Strong Interactions with Nickel





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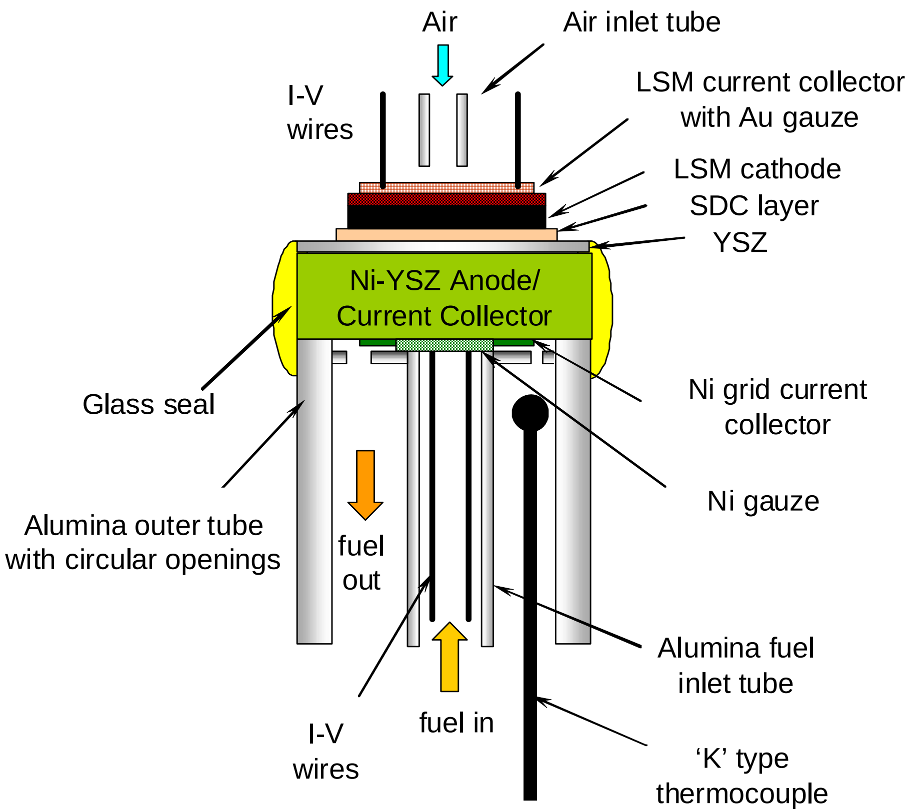
Schematic of Button Cell Test Stands



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

- Ni/YSZ anode-supported cells
- Electrolyte supported cells with 30 μm Ni/YSZ anode (from Fuel Cell Materials, NexTech)

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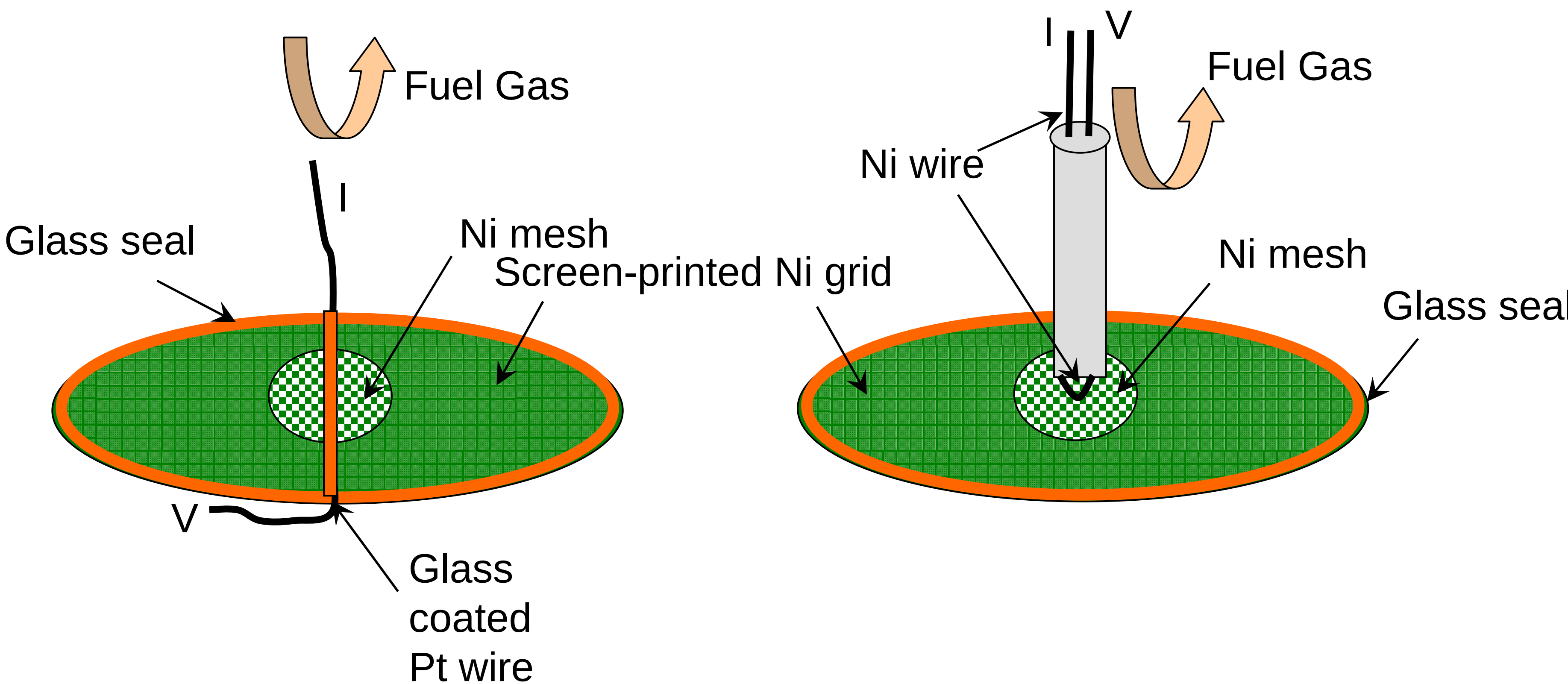
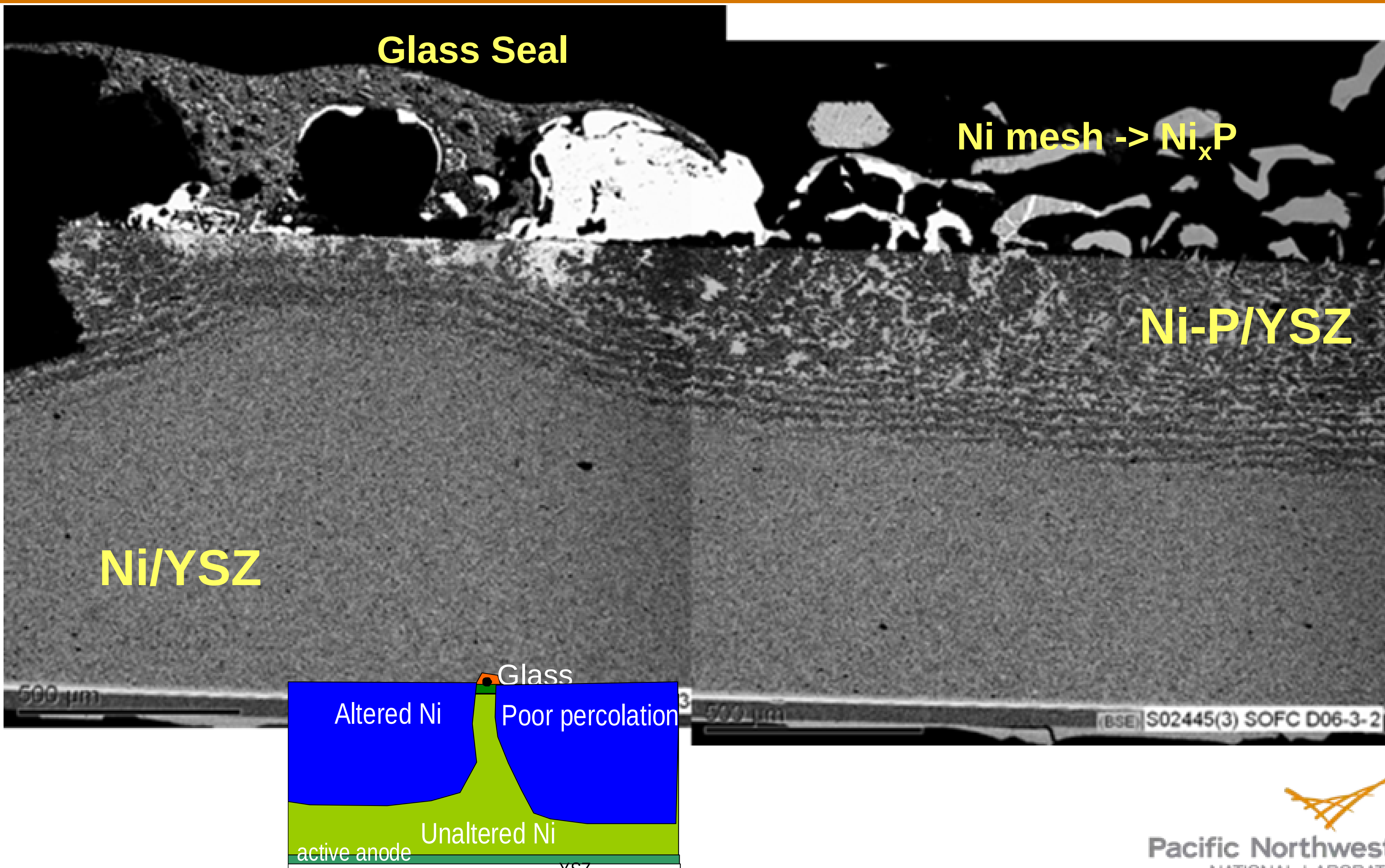
Current Contact Method Important in Degradation Studies

Glass Coated Contact　　Single Point Contact



Pt and Ni wire instability
affected some earlier results

Anode after Exposure to 5 ppm of PH_3 in Coal Gas for 790 hours at 700ºC



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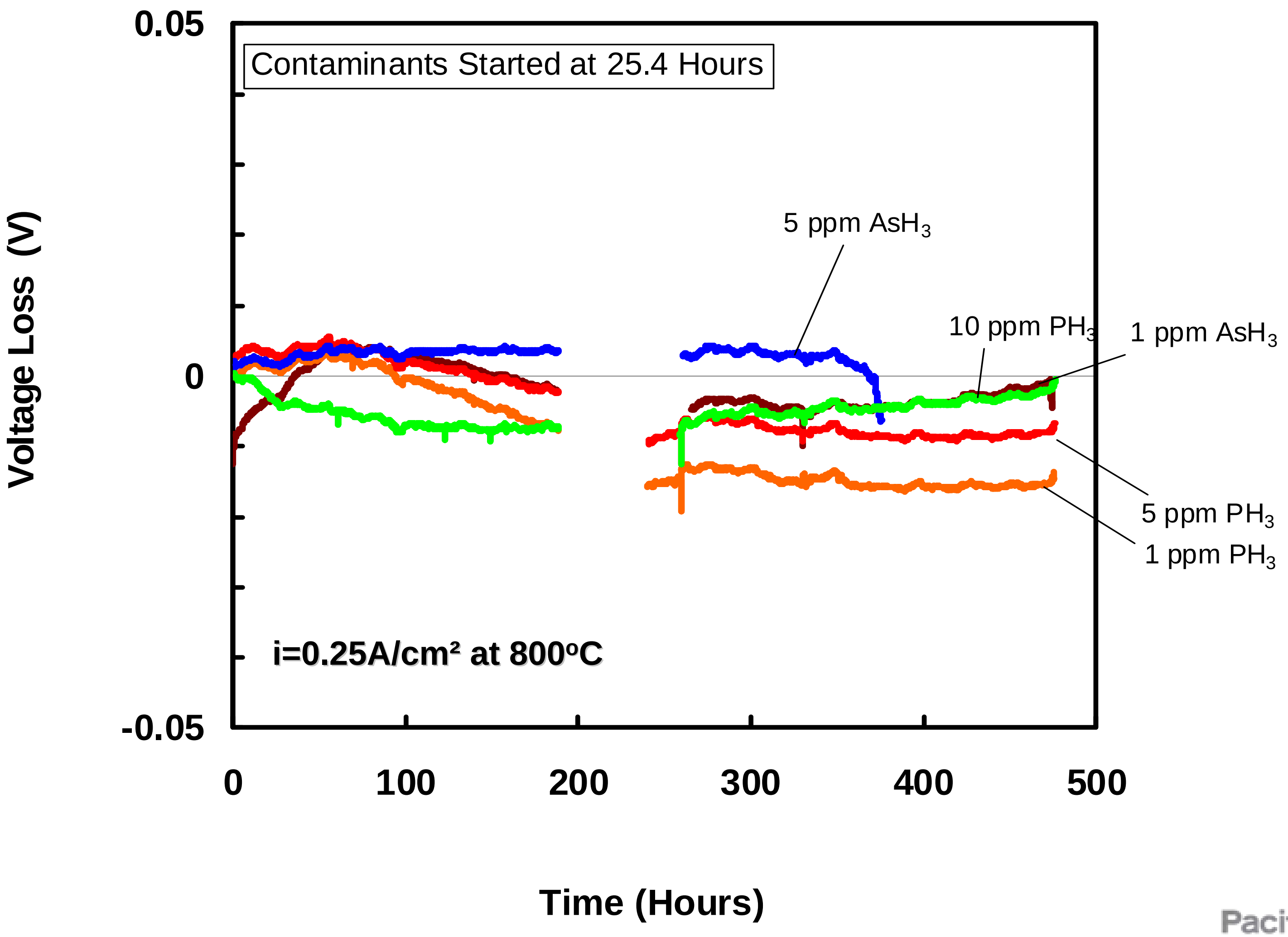
Glass Coated Contacts:
Minimal Effect of PH_3 or AsH_3 on Cell Performance



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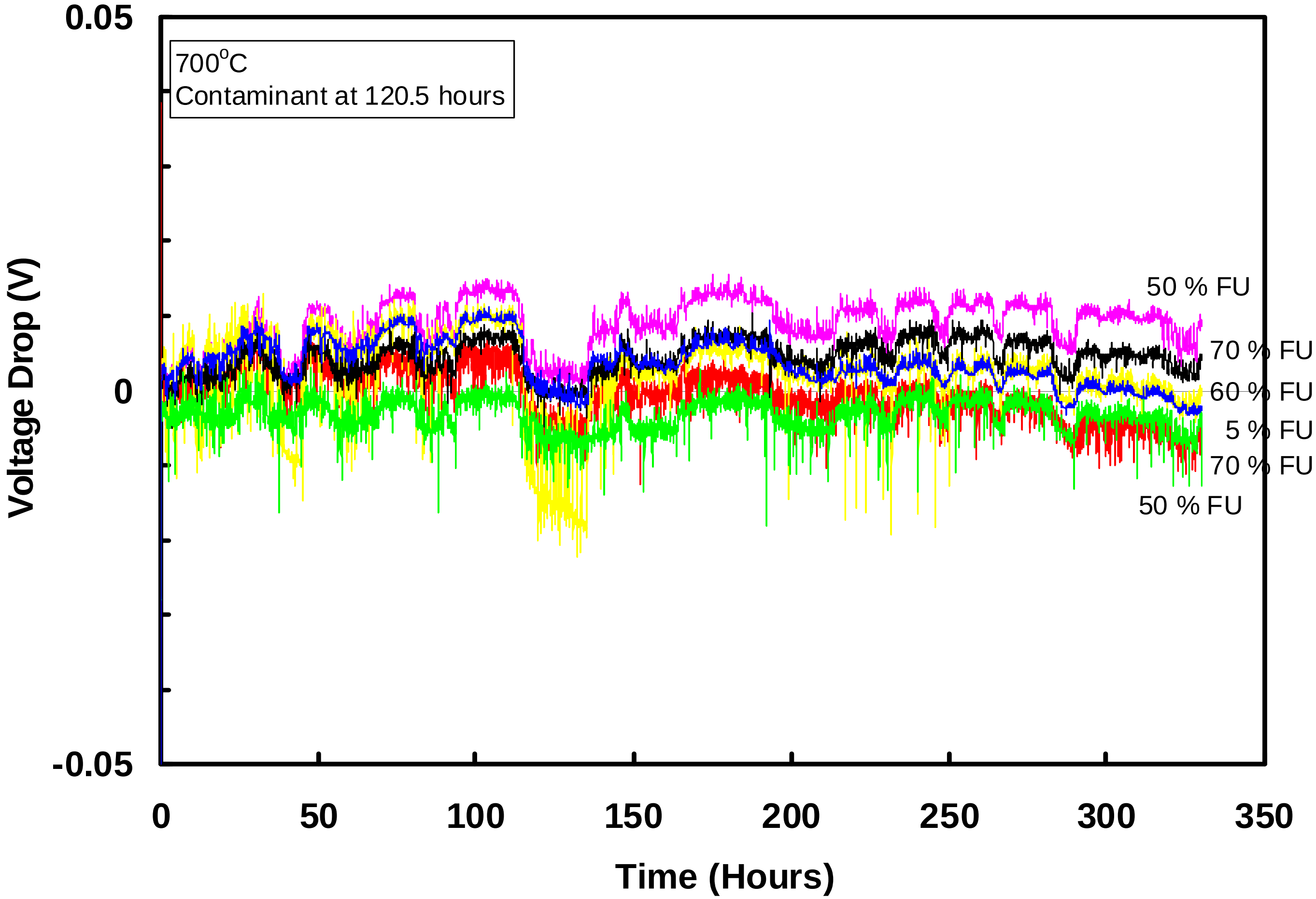
Low Degradation Rates at Different Fuel Utilizations* at 700°C with 1 ppm of AsH_3



* Fuel utilizations were adjusted by adding oxygen to the coal gas mix

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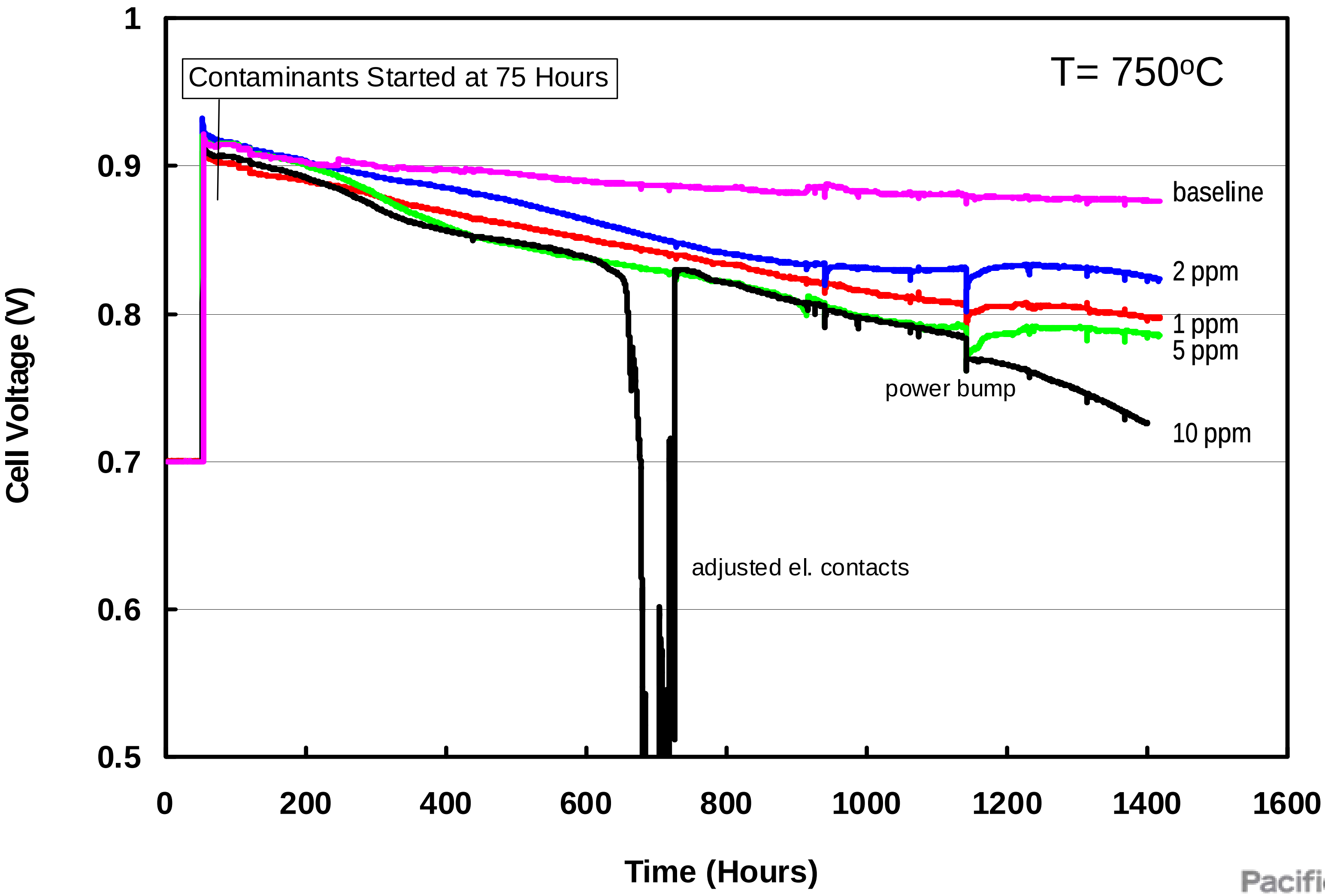
Single Point Contact Tests with PH_3: Electrical Percolation Losses More Visible



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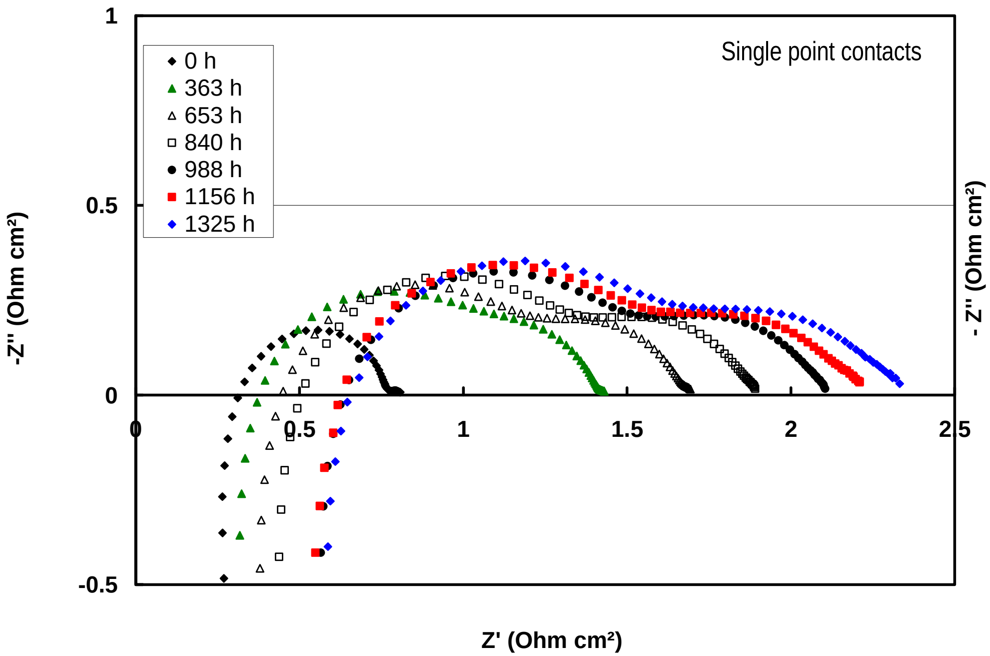
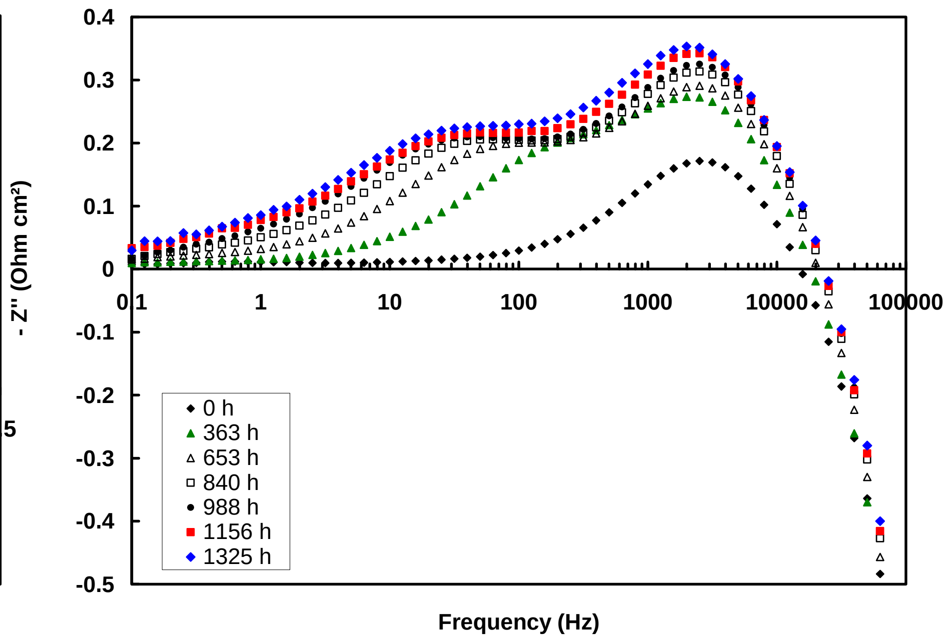
Single Point Contact: Impedance Spectra of Anode-Supported Cell at 750ºC in Coal Gas with 5 ppm of PH_3





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

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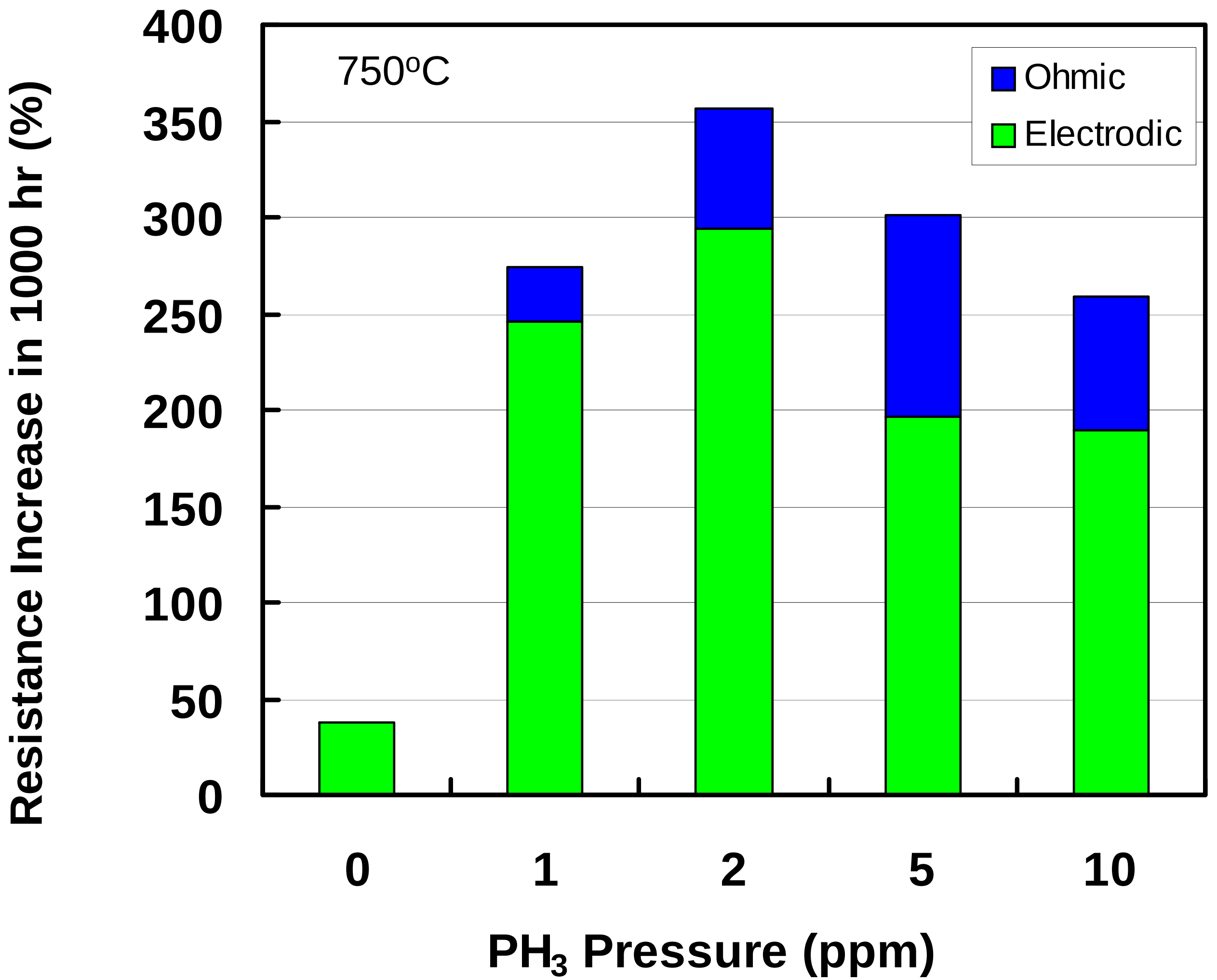
Single Point Contact: Ohmic Losses Increase More Rapidly with Exposure than Electrodic Losses



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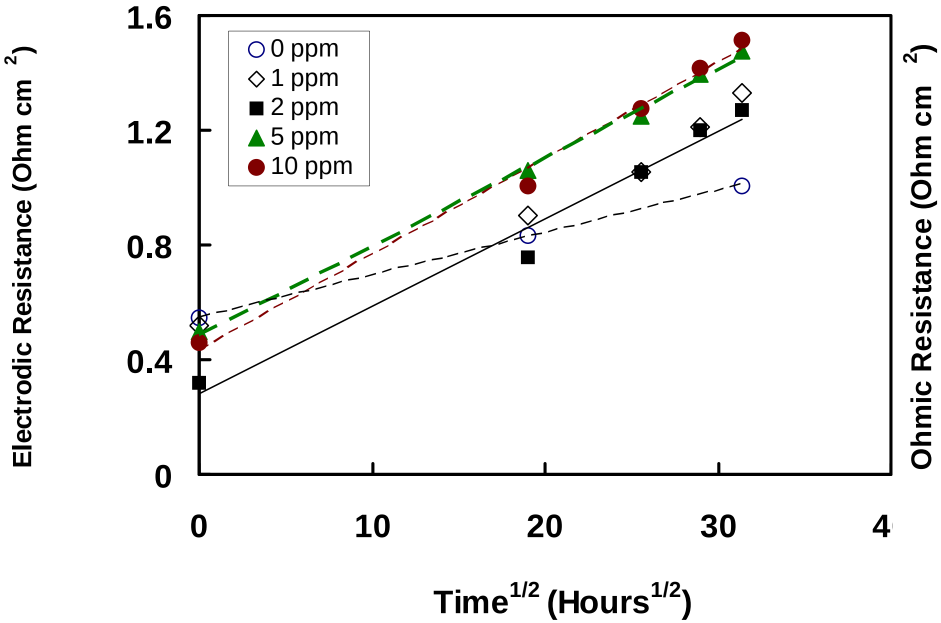
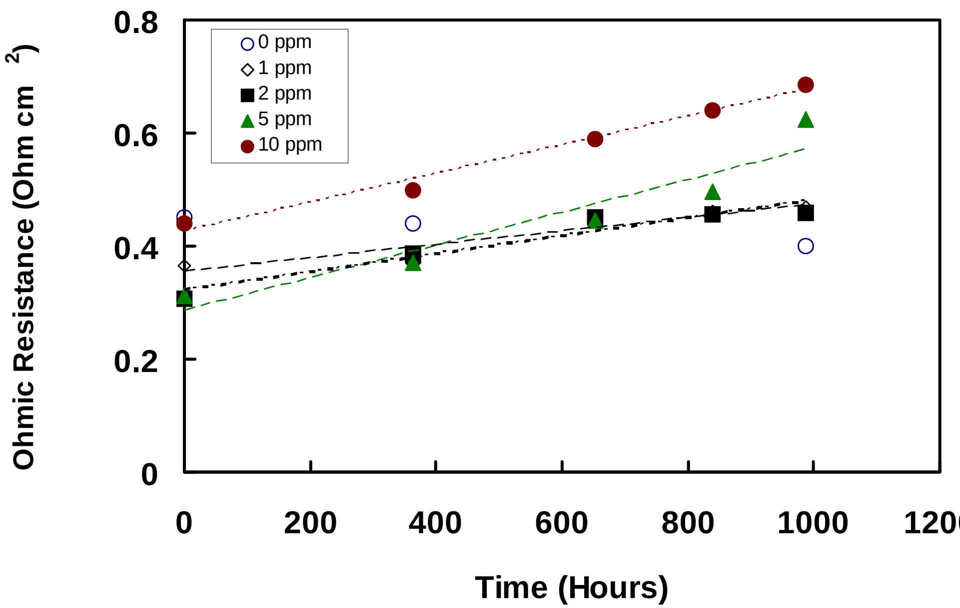
Ohmic Resistances Increase Linearly with Time of Exposure, Electrodic with Time$^{1/2}$





Ohmic and electrodic resistances calculated from the impedance spectra obtained at 750°C at a bias current of 0.1A/cm² in coal gas with 1, 2, 5 and 10 ppm of PH_3.
Single point contact test configuration.

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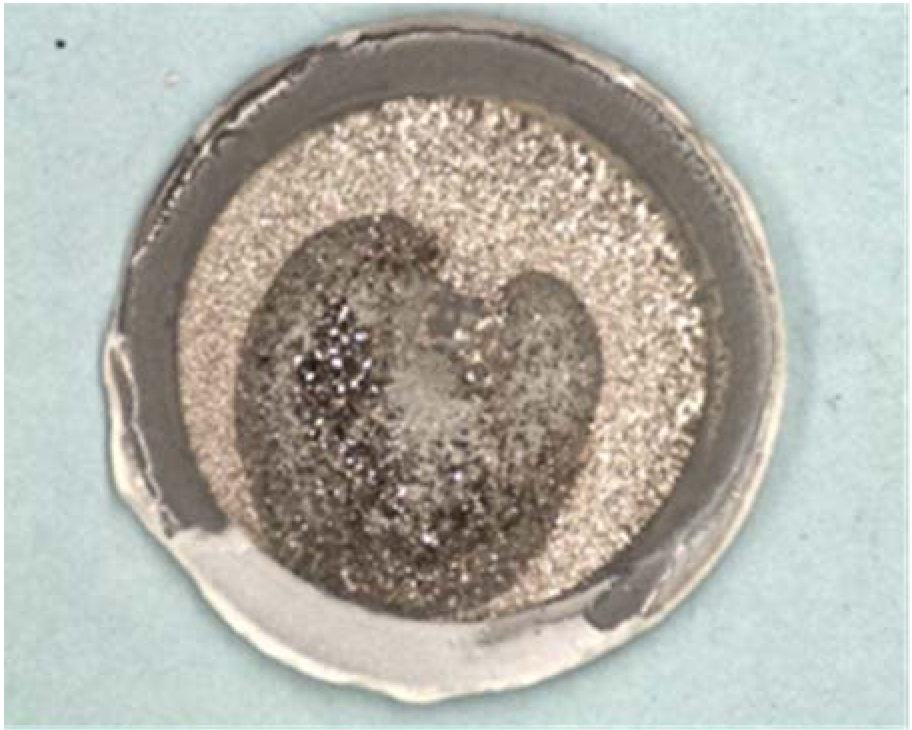
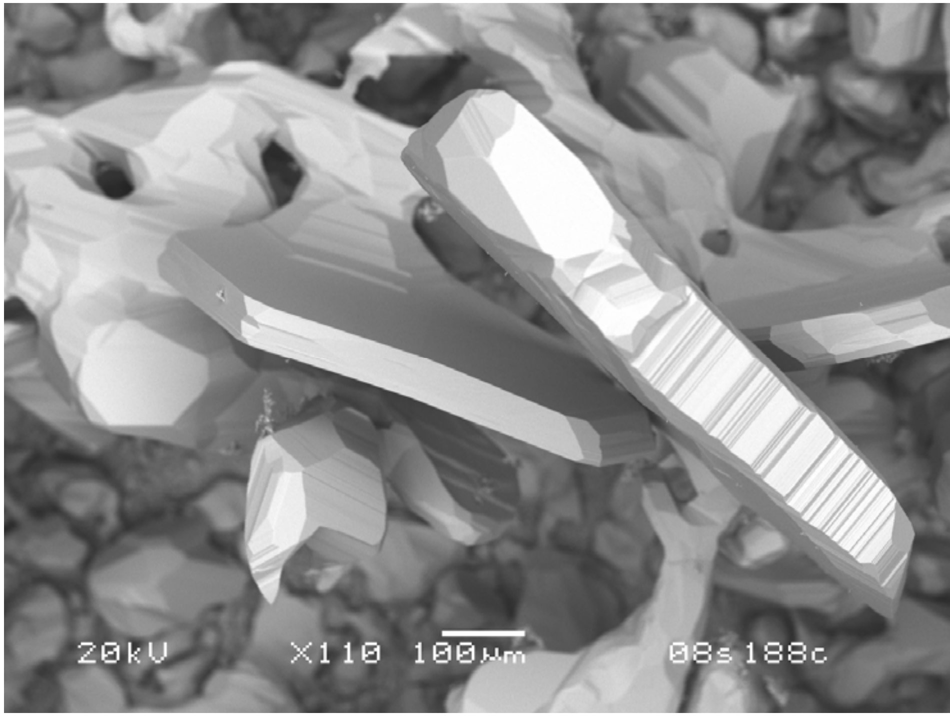
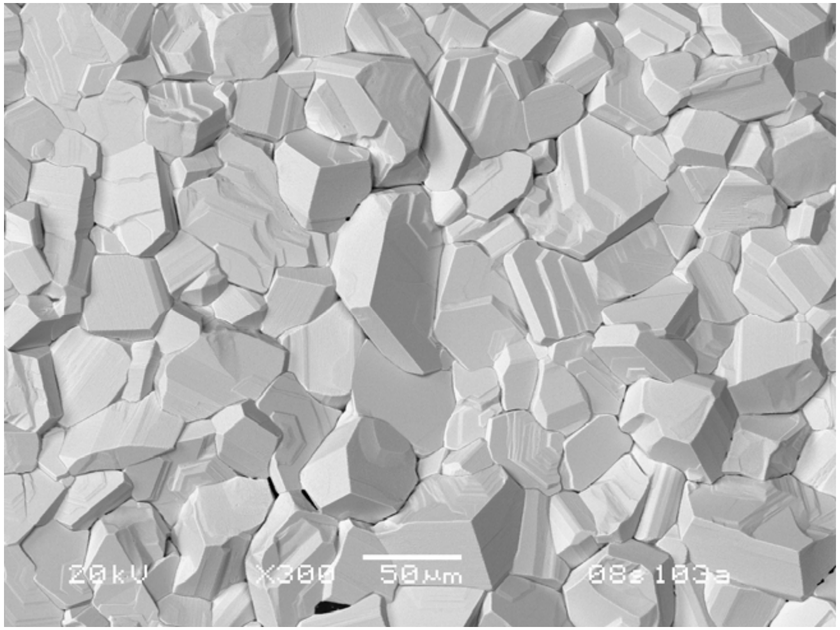
Extensive Re-crystallization in the Upper Part of the Cell





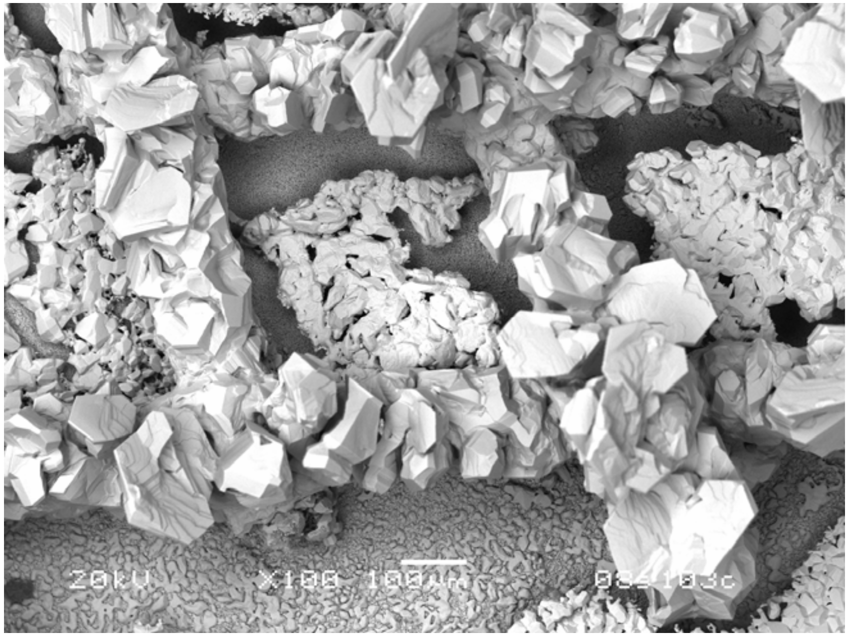
800°C, 770 hours with 5 ppm PH_3

Anode Current Collector Surface after 357 Hour Test in Coal Gas with 2 ppm of PH_3, 1 ppm of AsH_3, and 1 ppm of H_2S at 800°C



Ni_3P - Ni_5As_2

No Ni-S (by SEM/EDS)



Ni mesh corroded to form Ni_3P and Ni_5P_2

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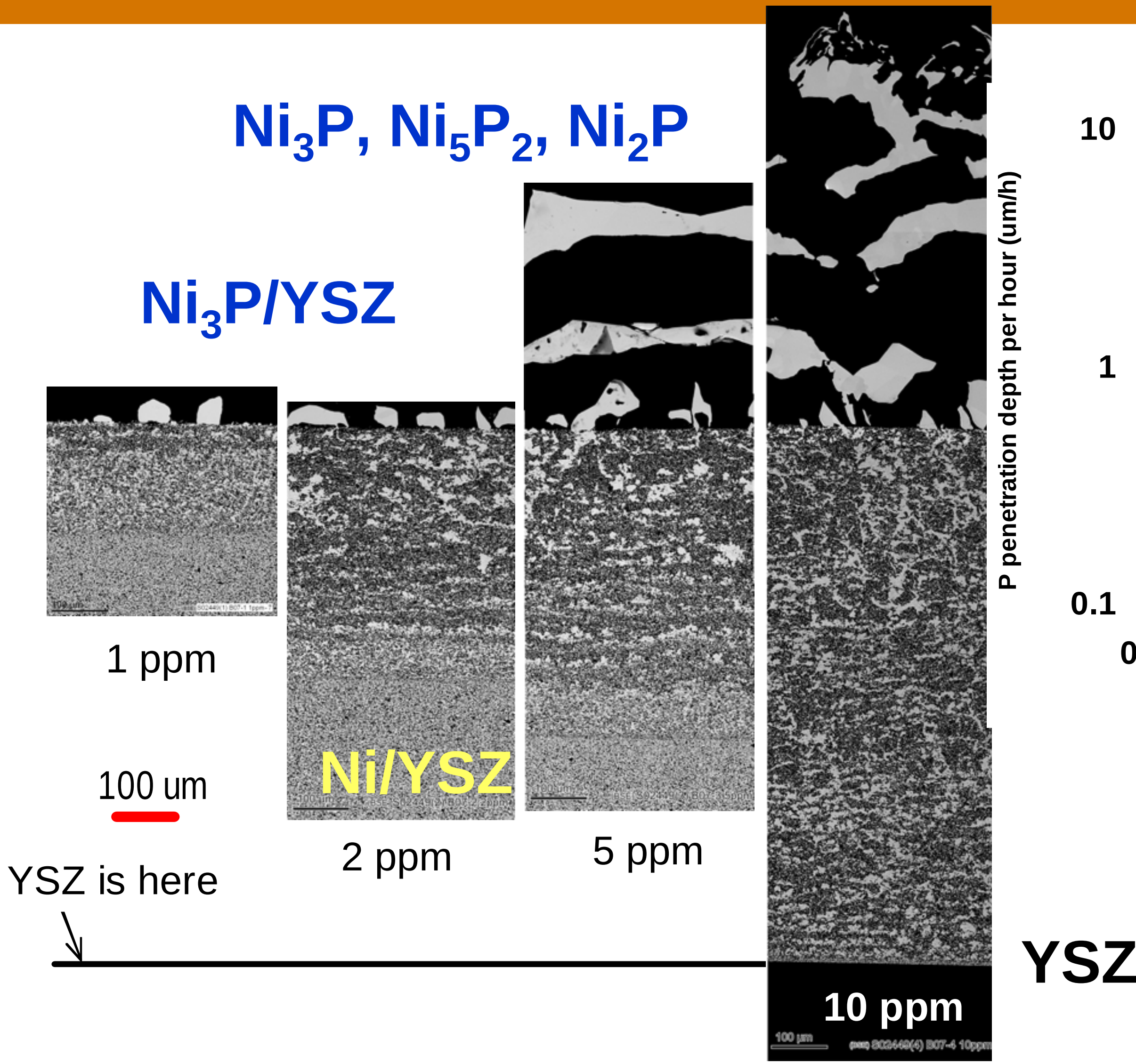
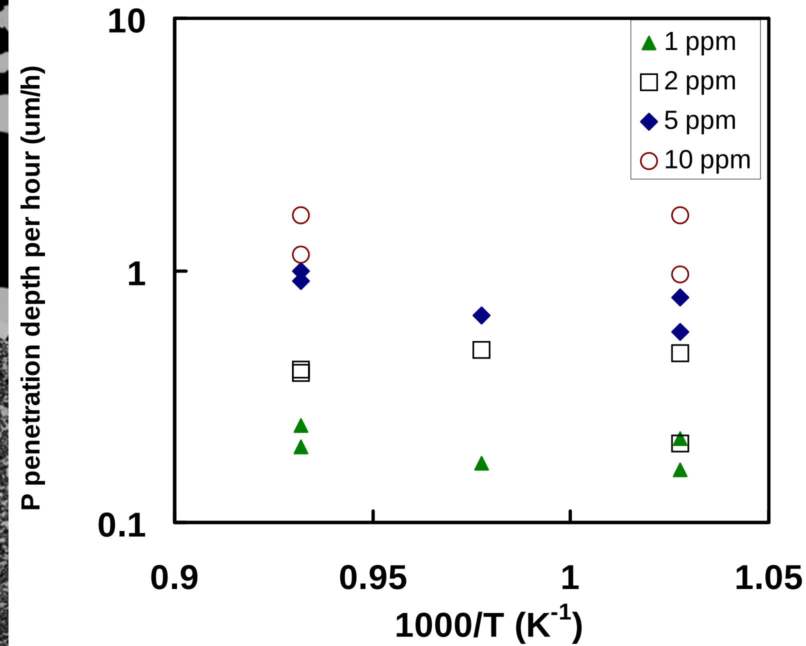
Anode-Supported Cells after 990 Hour Test at 700°C with 1, 2, 5 and 10 ppm of PH_3 in Coal Gas





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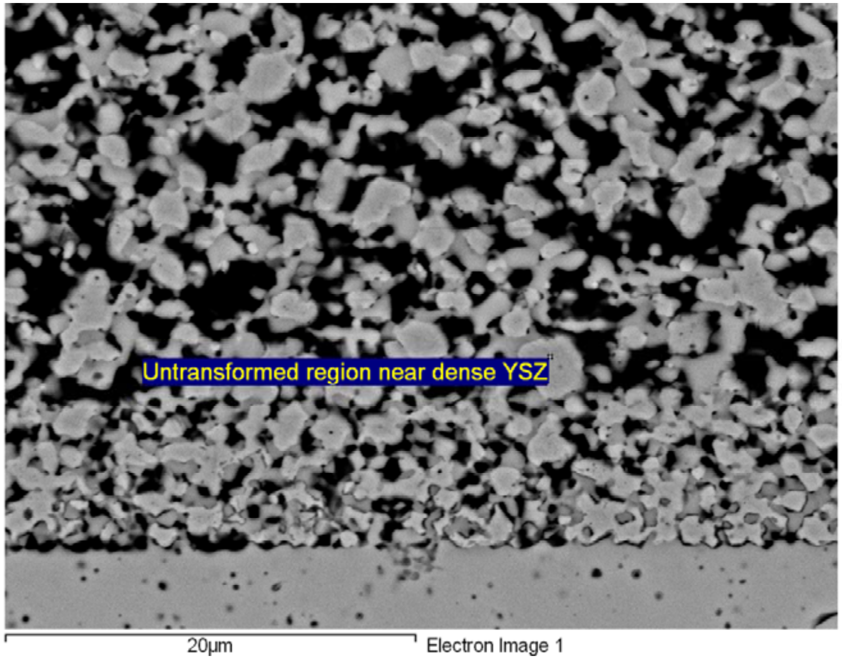
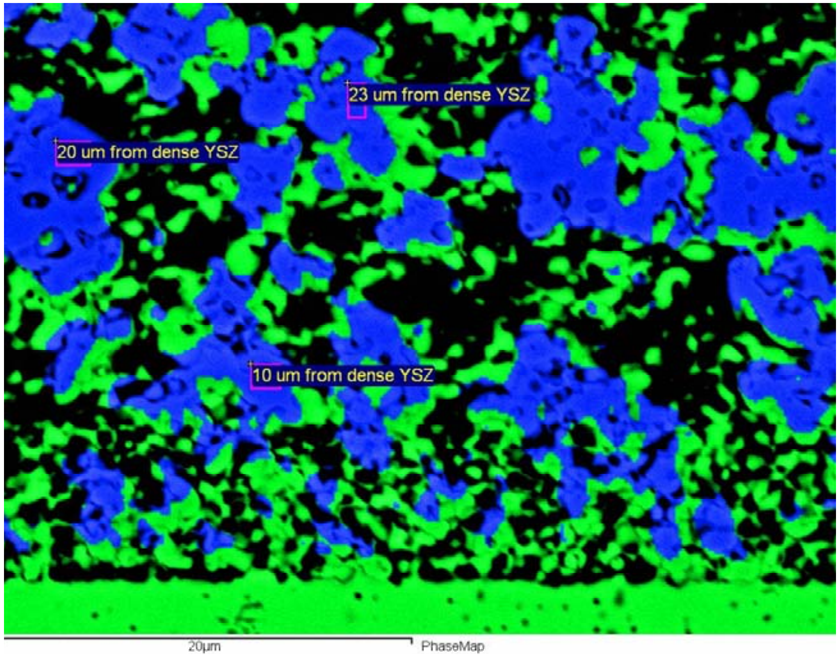
Active Interface of an Anode-Supported Cell after 1000 h Test at 700ºC with 10 ppm of PH_3

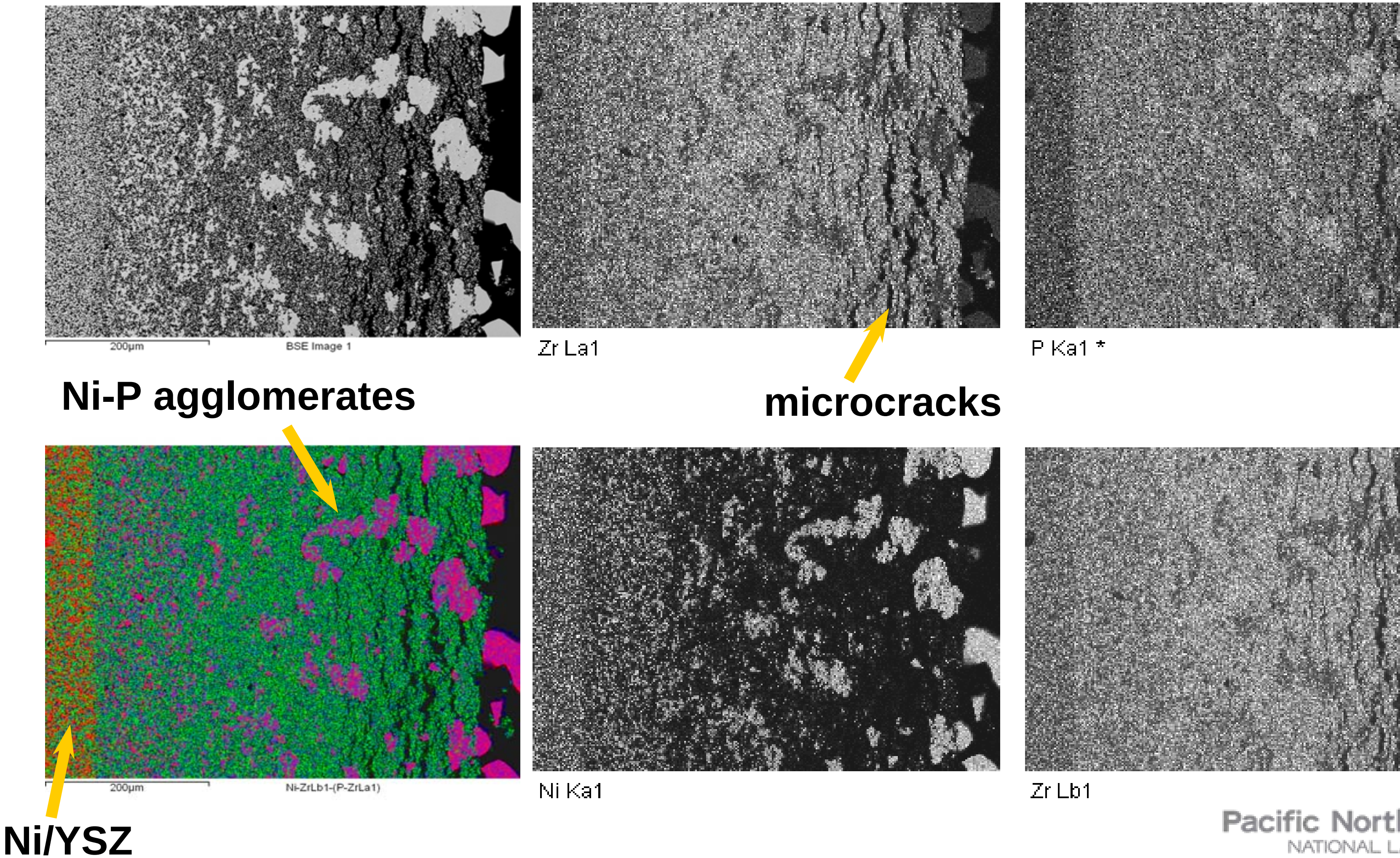


Unreacted interface

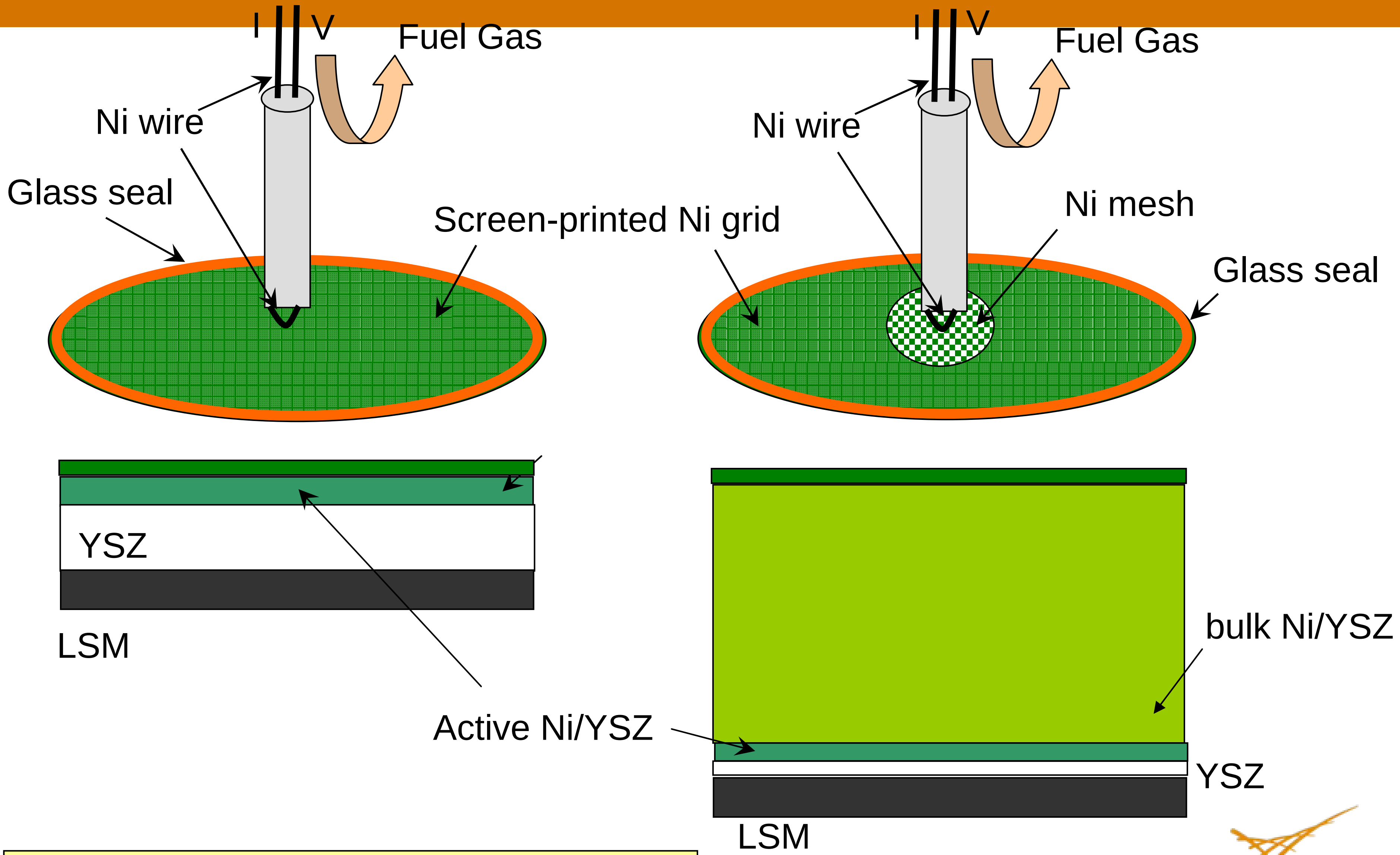


Complete conversion of nickel to Ni-P showing extensive coarsening

Elemental Maps of Bulk Ni/YSZ after 1000 hour Test at 700°C with 5 ppm of PH_3



Electrolyte-Supported Cell   Anode-Supported Cell



The same configuration for both cell types

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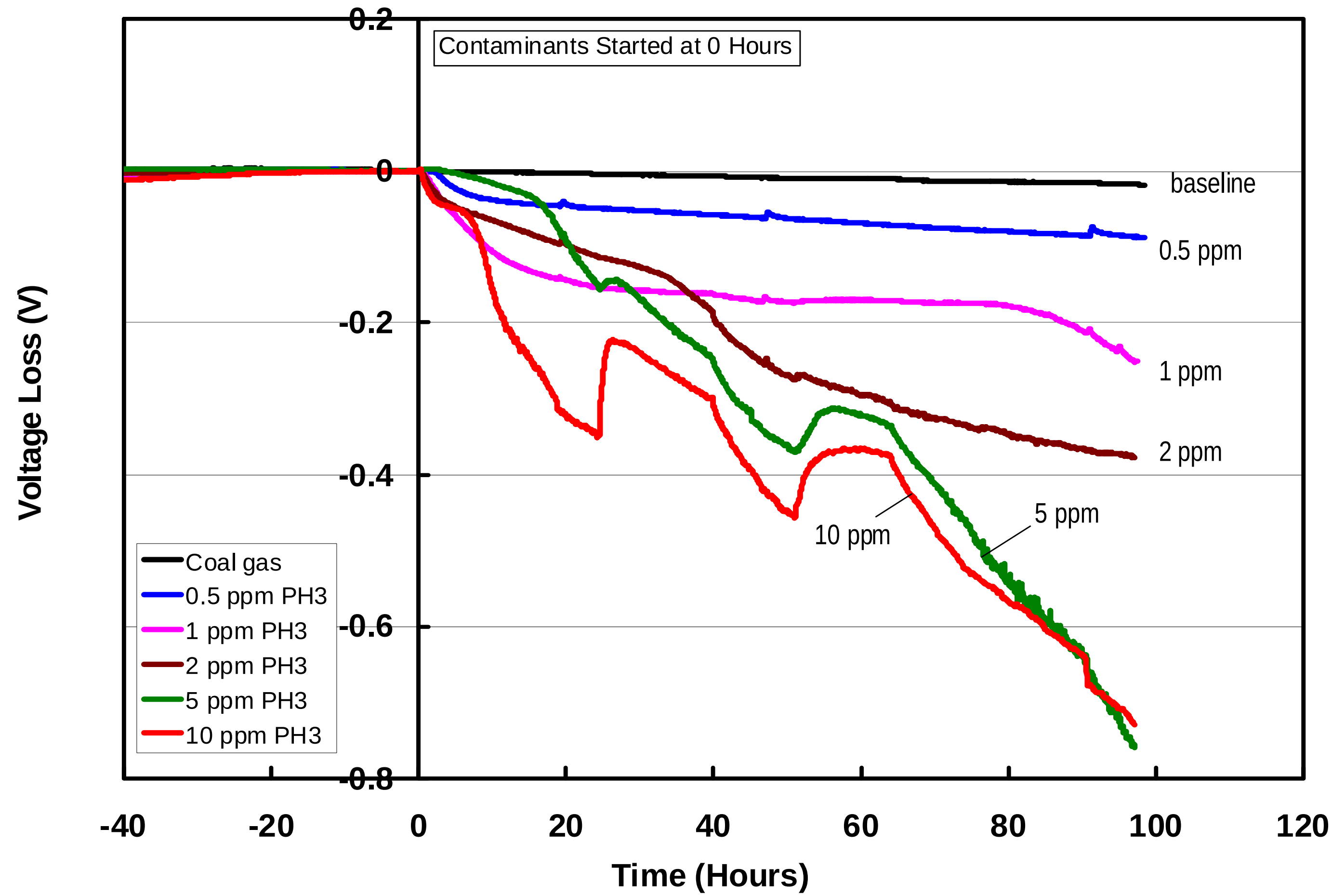
Electrolyte Supported Cell
Voltage Losses in Coal Gas with PH_3 at 800ºC



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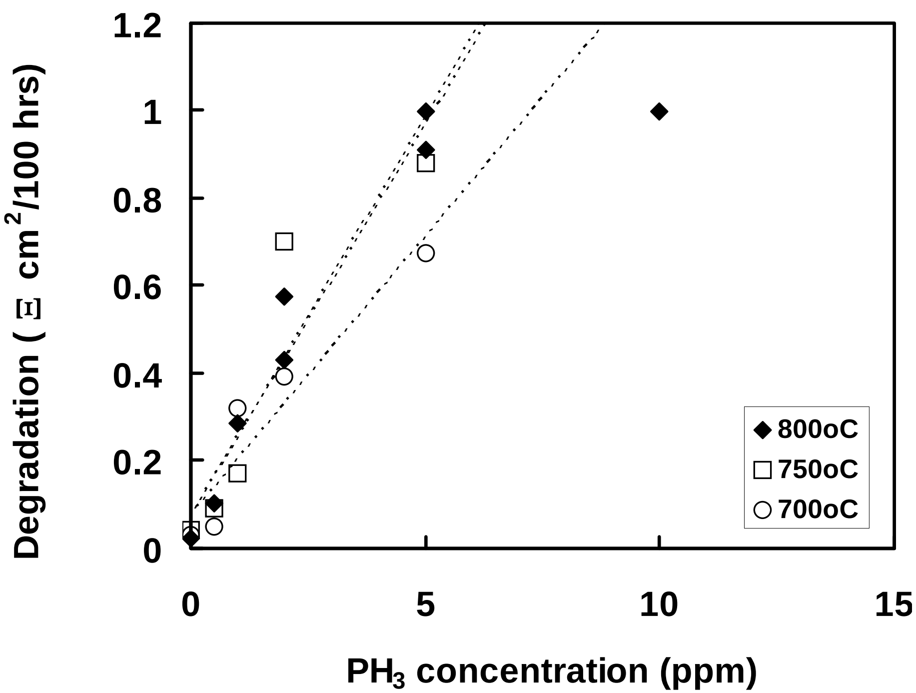
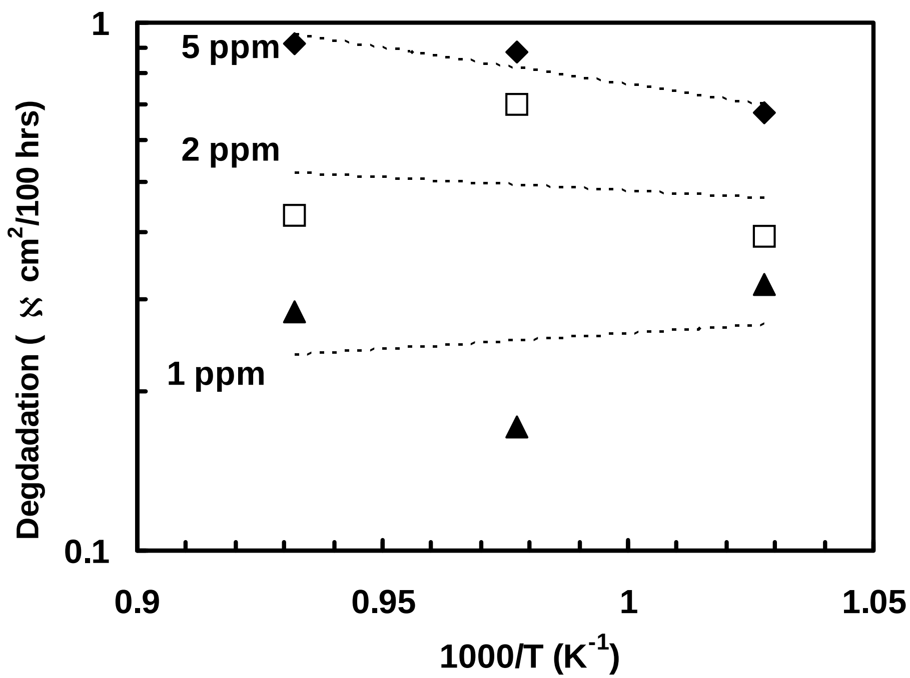
Electrolyte-Supported Cell Degradation Rate with Phosphorus





- Higher degradation rate at higher pPH_3
- No clear temperature dependence in this range

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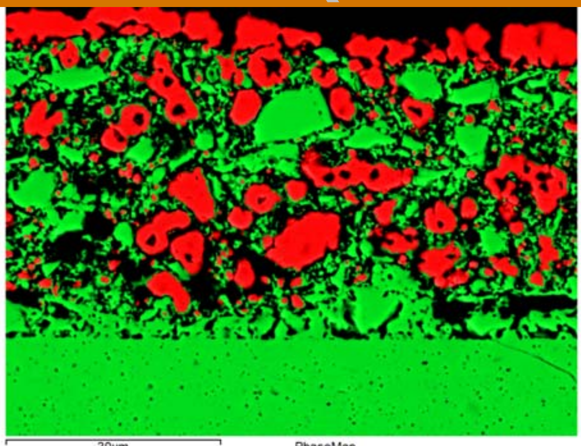
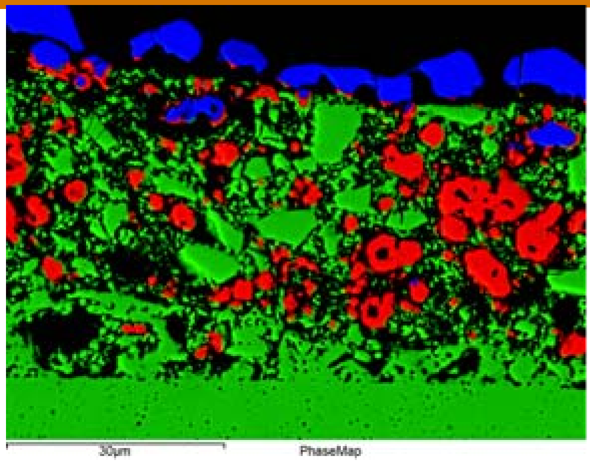
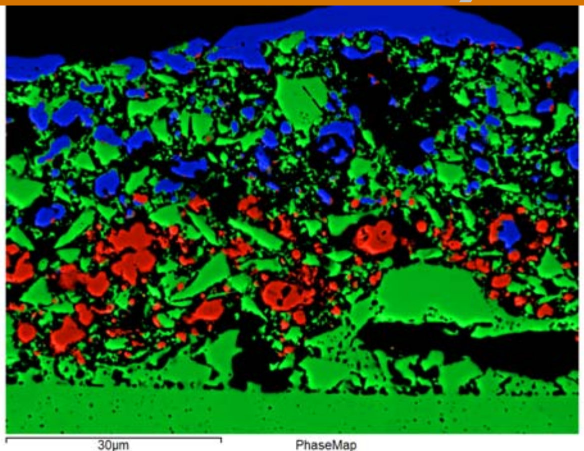
Ni/YSZ after 100 Hour Test in Coal Gas at 800^{o}C (Ni – Red, YSZ – Green, Ni-P – Blue)



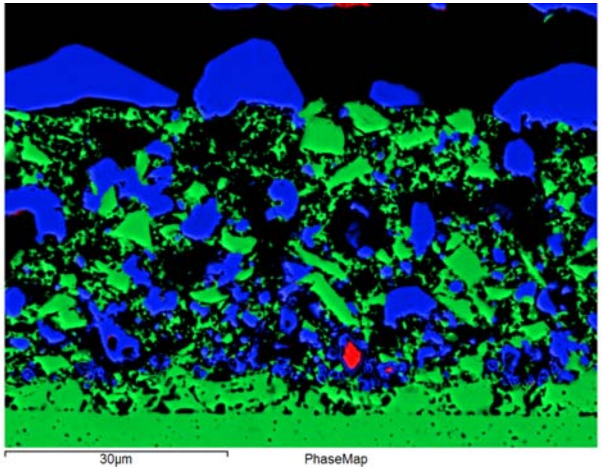
No contaminants



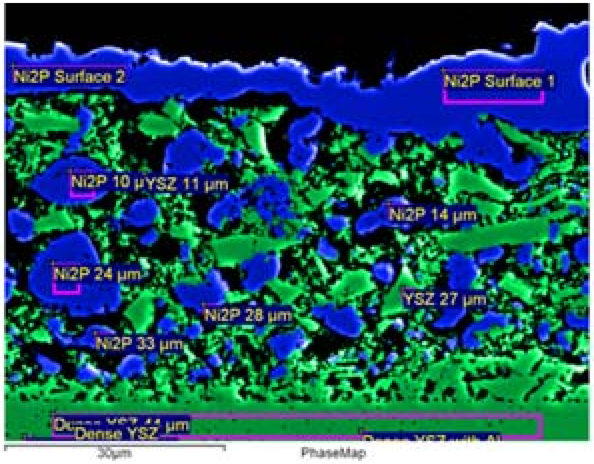
0.5 ppm PH_3



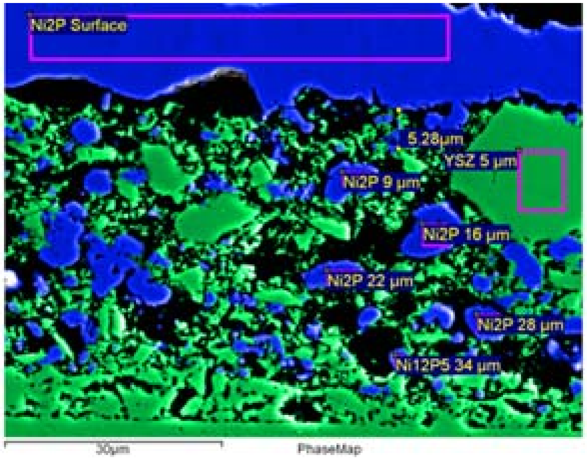
1 ppm PH_3



2 ppm PH_3



5 ppm PH_3



10 ppm PH_3

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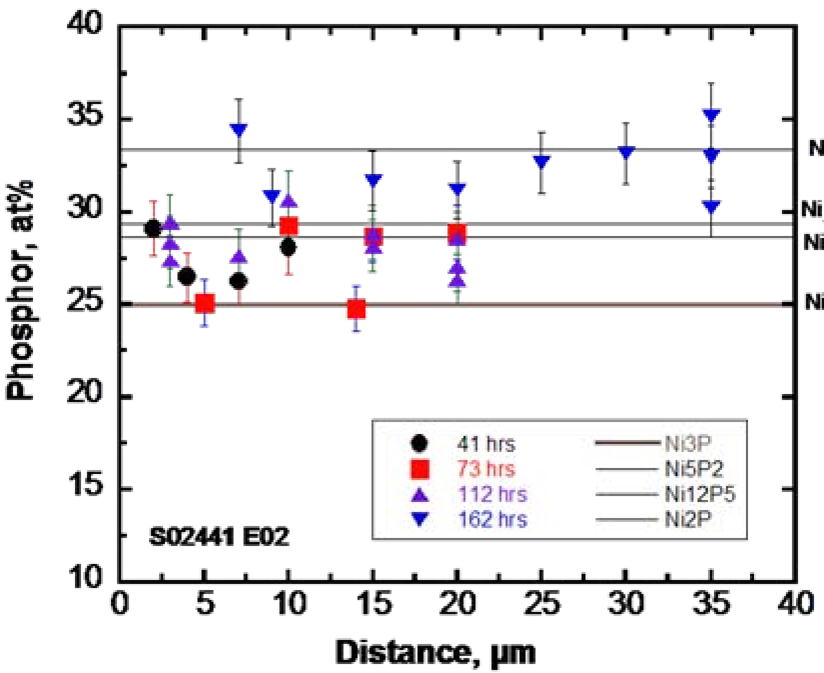
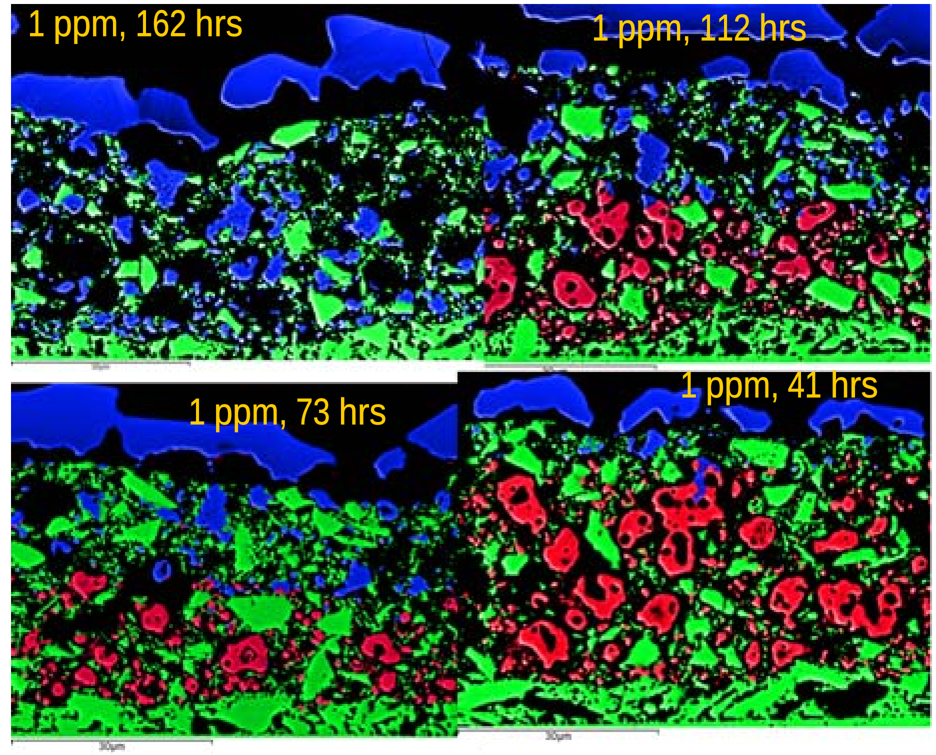
Time Dependence for the YSZ Supported Cells after Exposure to 1 ppm of PH_3 at 800°C (Ni-Red, Ni-P – Blue, YSZ – Green)





Moved towards higher order Ni-P phases with increased exposure

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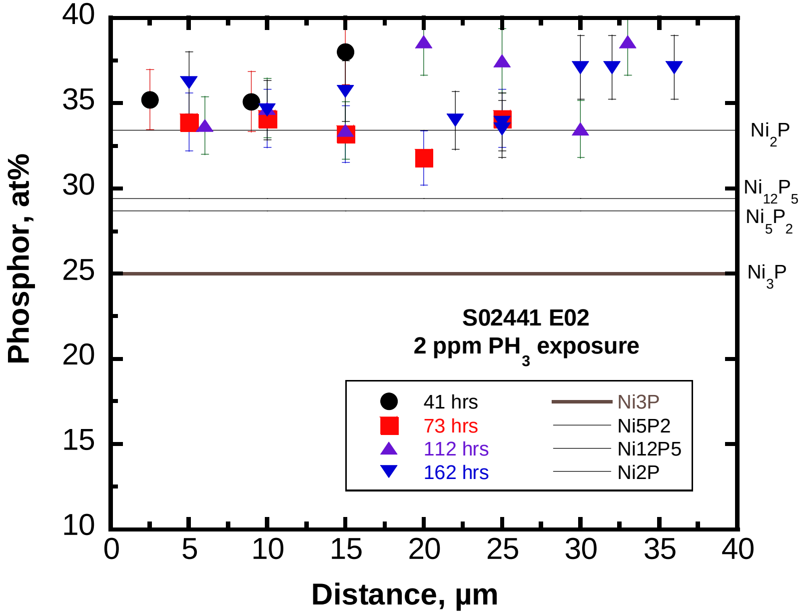
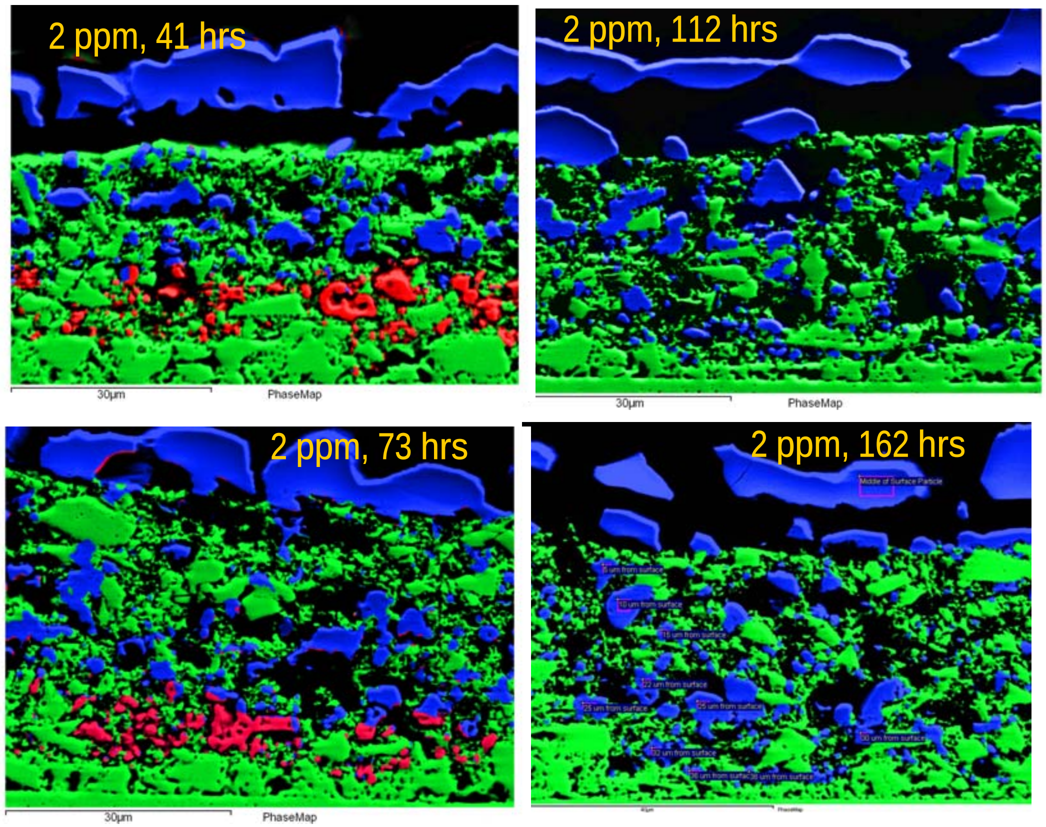
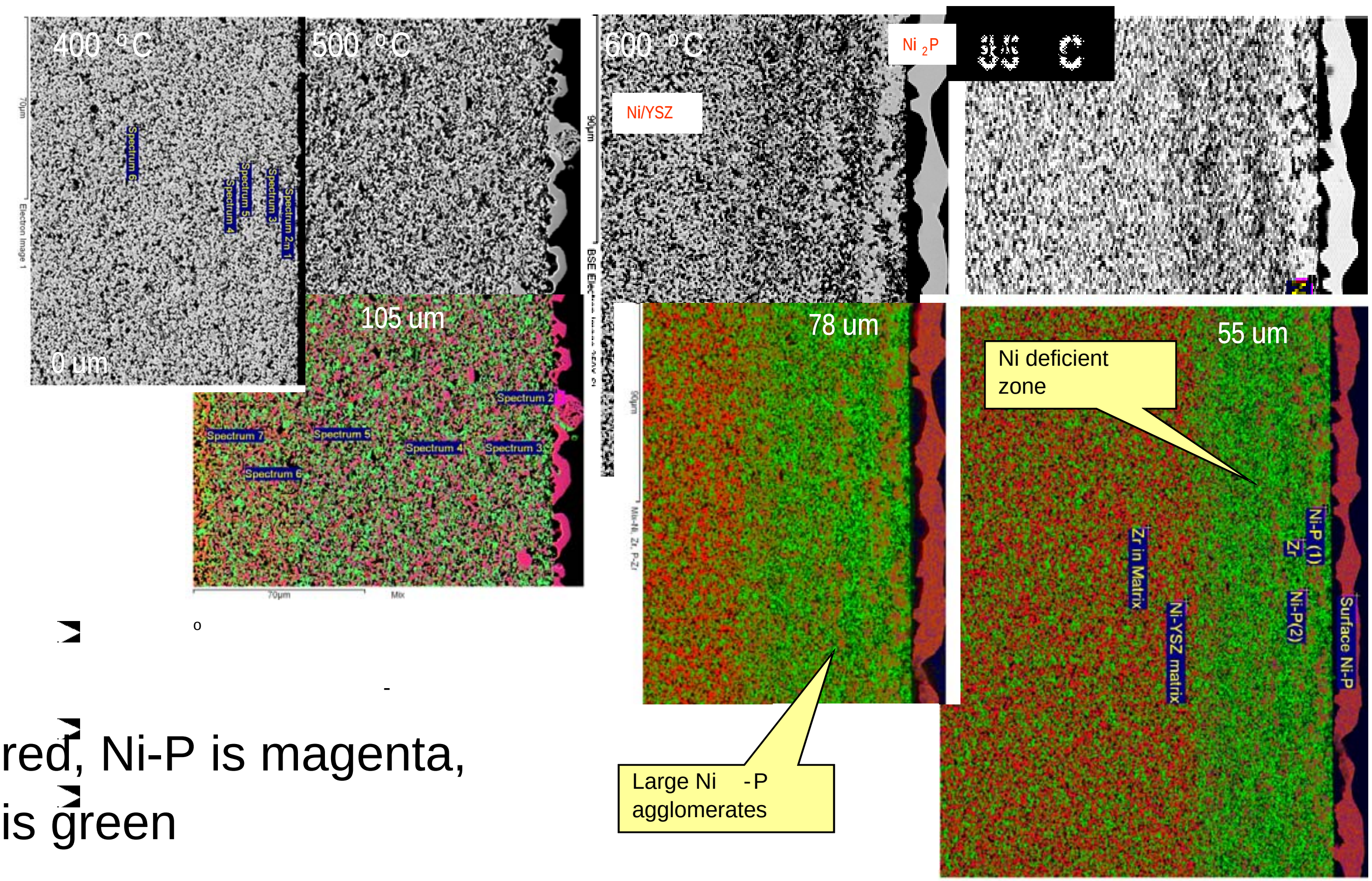
Time Dependence for the YSZ Supported Cells after Exposure to 2 ppm of PH_3 at 800ºC (Ni-Red, Ni-P – Blue, YSZ – Green)





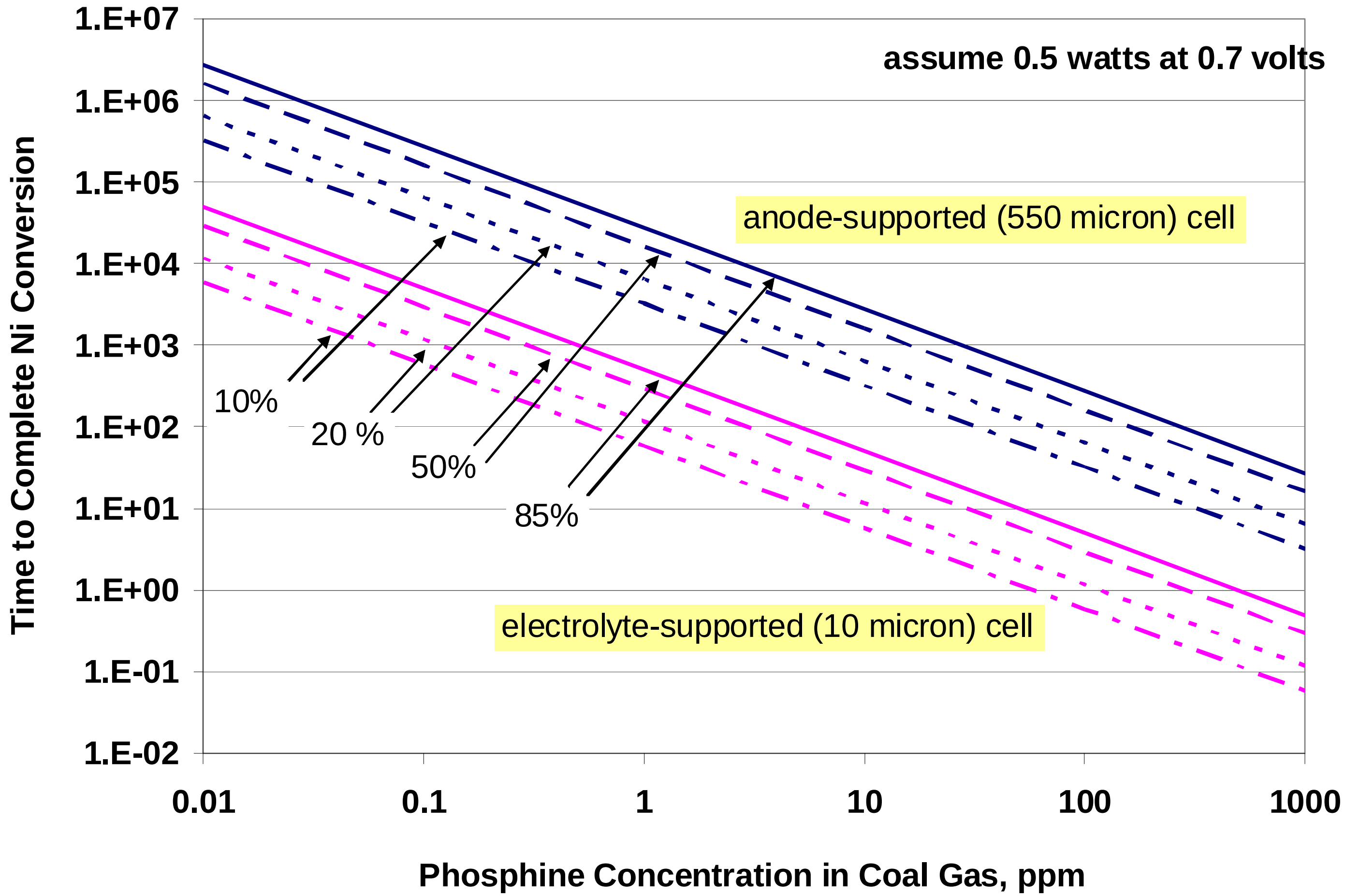
At highest exposures, observed mixture of Ni_2P and Ni_5P_4

Anode-Support Coupon Test in Flow Through Configuration Shows Ni Redistribution (no current collector)



Ni is red, Ni-P is magenta, YSZ is green

How Long Does It Take to Consume Nickel?



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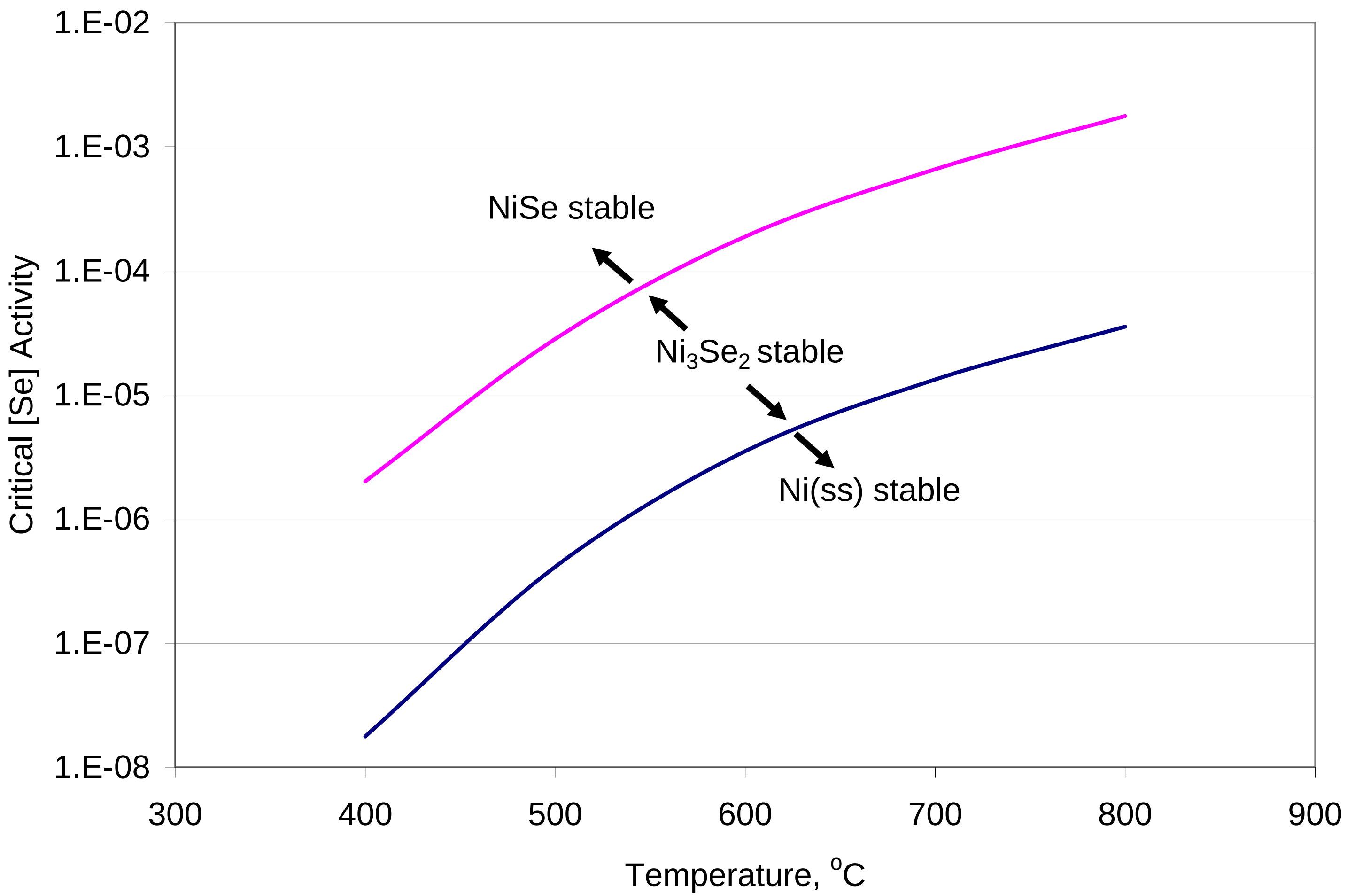
Much Higher Se Concentration Needed to Form Nickel Alteration Phase



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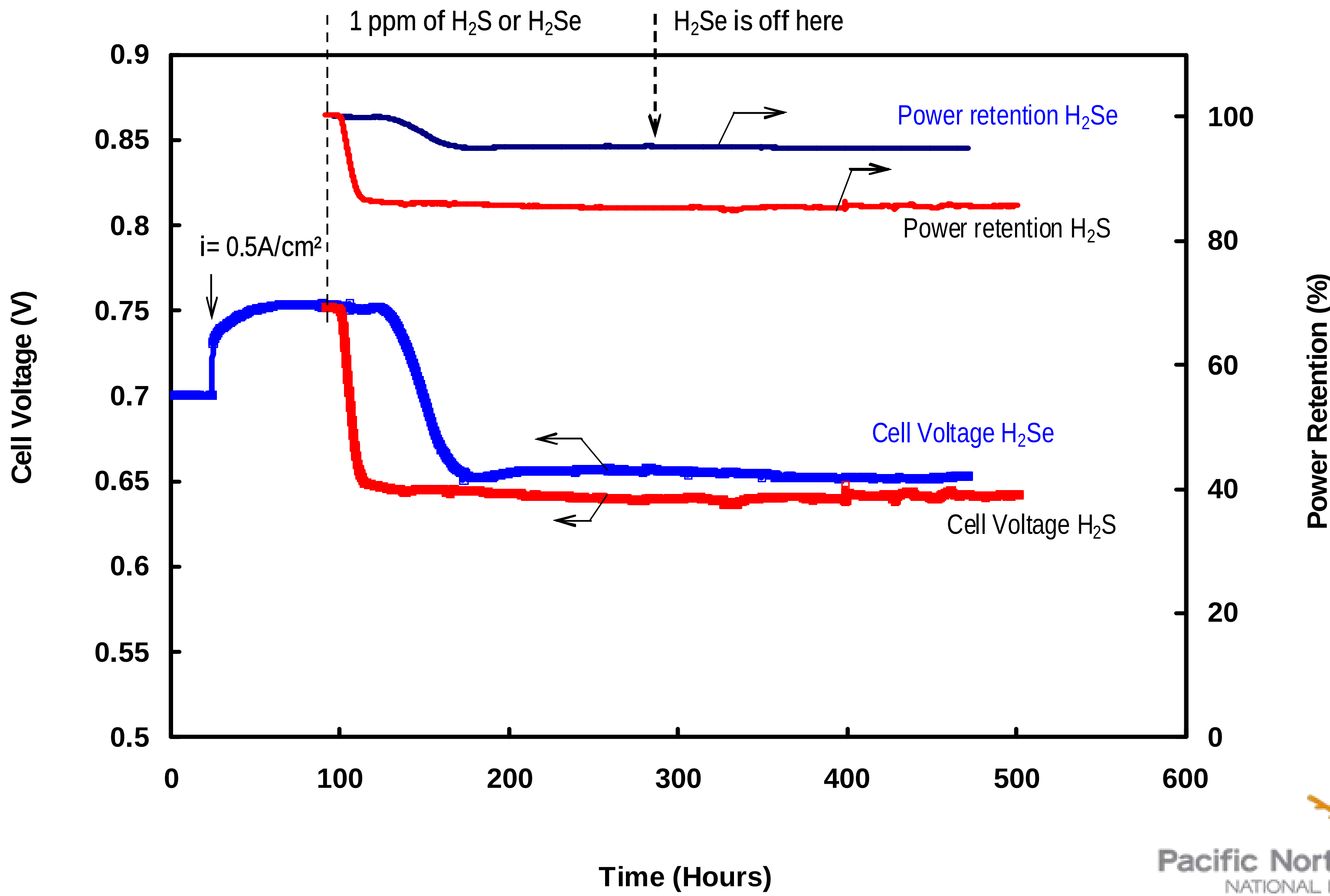
Effect of 1 ppm of Hydrogen Sulfide or Hydrogen Selenide on Anode Supported SOFC at 800ºC



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Acknowledgements

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- Helpful discussions with Briggs White, Wayne Surdoval and other members of the coordinated team are gratefully acknowledged.

- J Templeton, J Bonnet, B McCarthy contributed to cell fabrication.

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