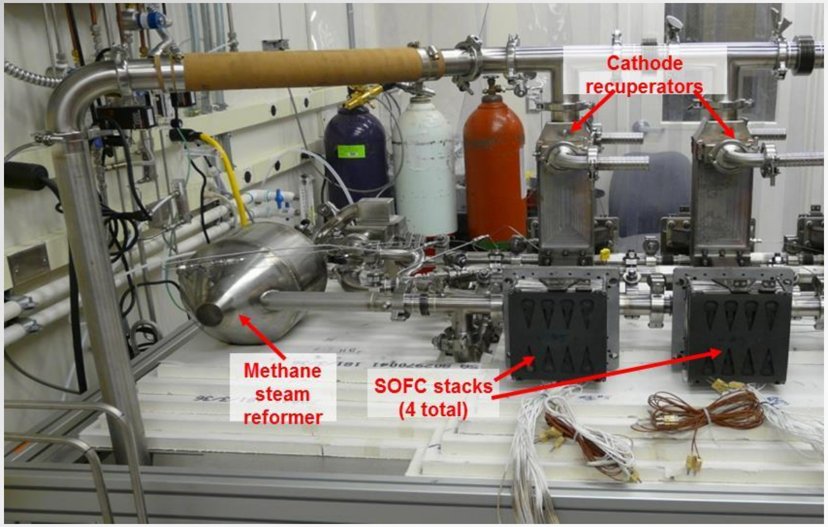
Phosphorus, Sulfur, and Chlorine in Fuel Gases: Impact on High Temperature Fuel Cell Performance and Clean-Up Options



57% net electrical efficiency on methane

8 SOFC cells per furnace with independent gas flow

Multi-cell MCFC test stand

OLGA A MARINA

Pacific Northwest National Laboratory

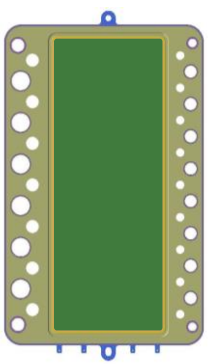
Workshop on Gas Clean-Up for Fuel Cell Applications
March 6-7, 2014

High Temperature Fuel Cell R&D at PNNL; Impurities Overview

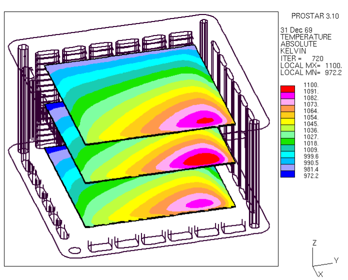
Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle *Since 1965*

- Cell/stack/system design, fabrication, and testing
- Identification and mitigation of performance degradation mechanisms in cells and stacks
- Development and application of modeling and simulation tools for improved cell/stack/system design
- Partnered with industrial developers to accelerate commercialization of fuel cell systems



Gen 4
403 cm^2 Active Area



Continuum Electrochemistry modeling

SOFC Component Lamination

- Selected Impurities in Biogas/Landfill Gas:

Impurity	Volatility Class
*AsH_3	II
*HCl	III
*H_2S	II
*Hg	II
K	I
Na	I
*PH_3	II
*Sb	II
*Se	II

- **Class I**: least volatile and will remain in the ash
- **Class II:** more volatile and will partition between solid and gaseous species
- **Class III:** highly volatile and show little tendency to condense from the vapor phase

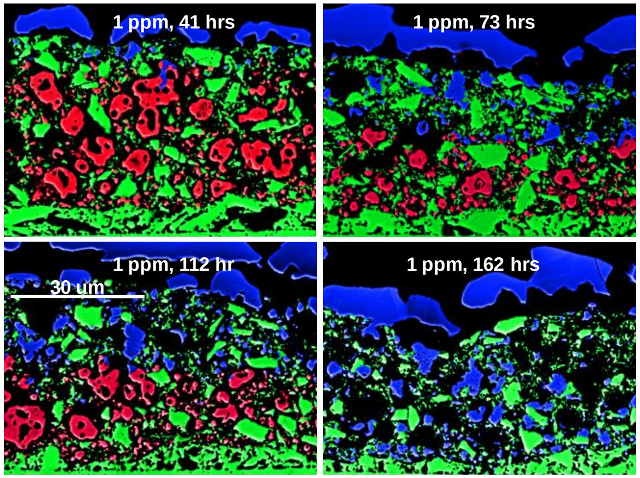
Pigeaud, Maru, Wilemski, Helbe, Trace Element Emissions, DOE, 1995, pp 7-13.

* SOFC and/or MCFC assessments conducted at PNNL (*Marina, Pederson et al, ECS Transactions 26 (2010) 363-370*)

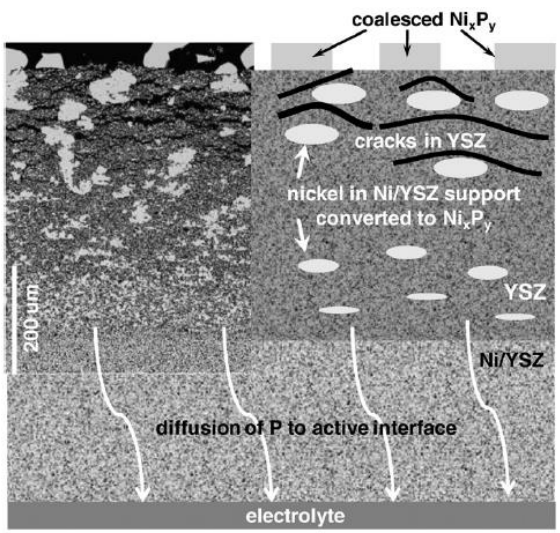
Phosphorus in Fuel Gas: Very Low Threshold for Reaction with Ni; Excellent Cleanup Options

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

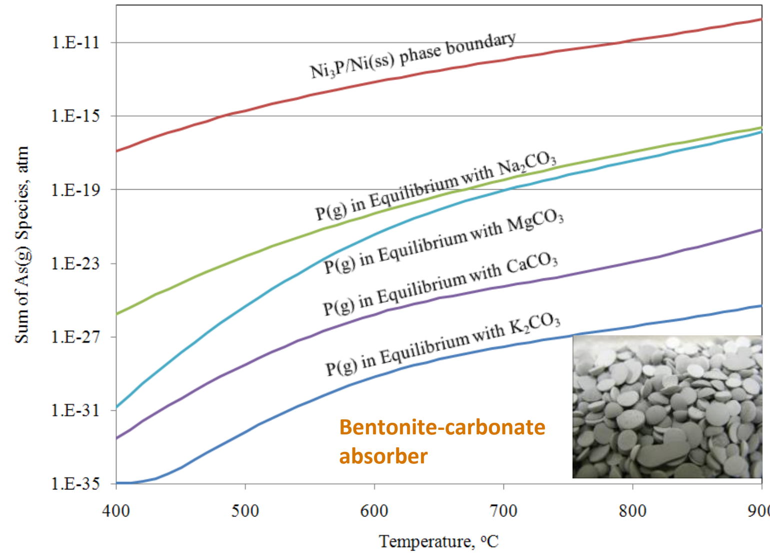
- EBSD/SEM micrographs of electrolyte-supported SOFC cells following exposure to synthesis gas containing phosphorus

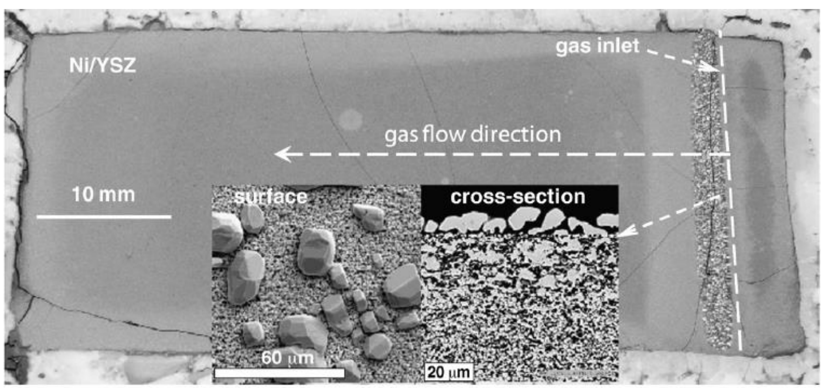


Red: Ni; Green: YSZ; Blue: Ni_3P



- First nickel phosphide forms at exceptionally low P(g) fugacities. Alkali carbonates can capture P to below the thermodynamic threshold for $Ni_3P(s)$



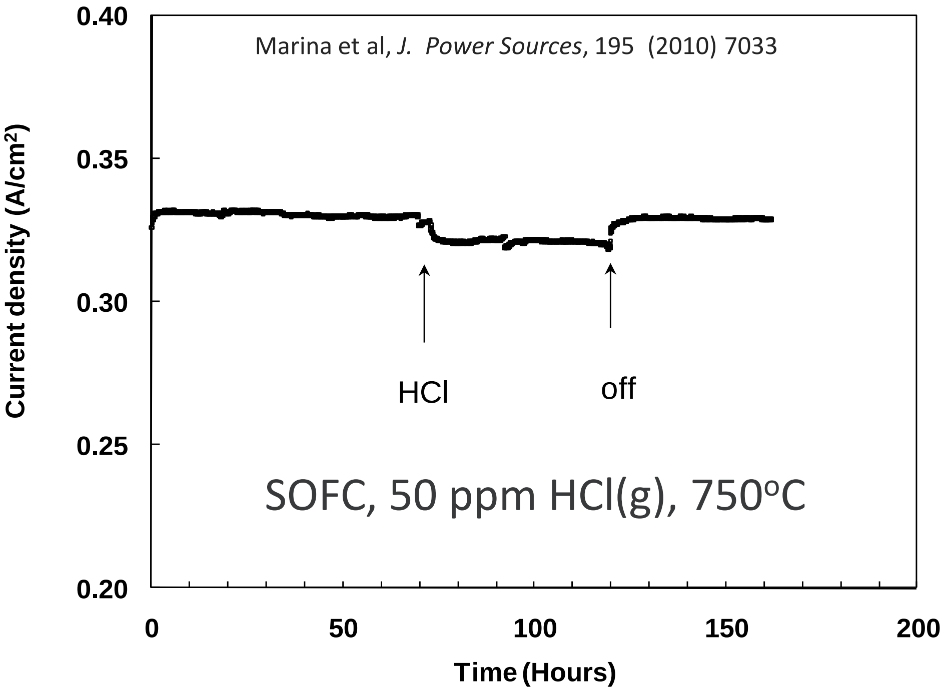


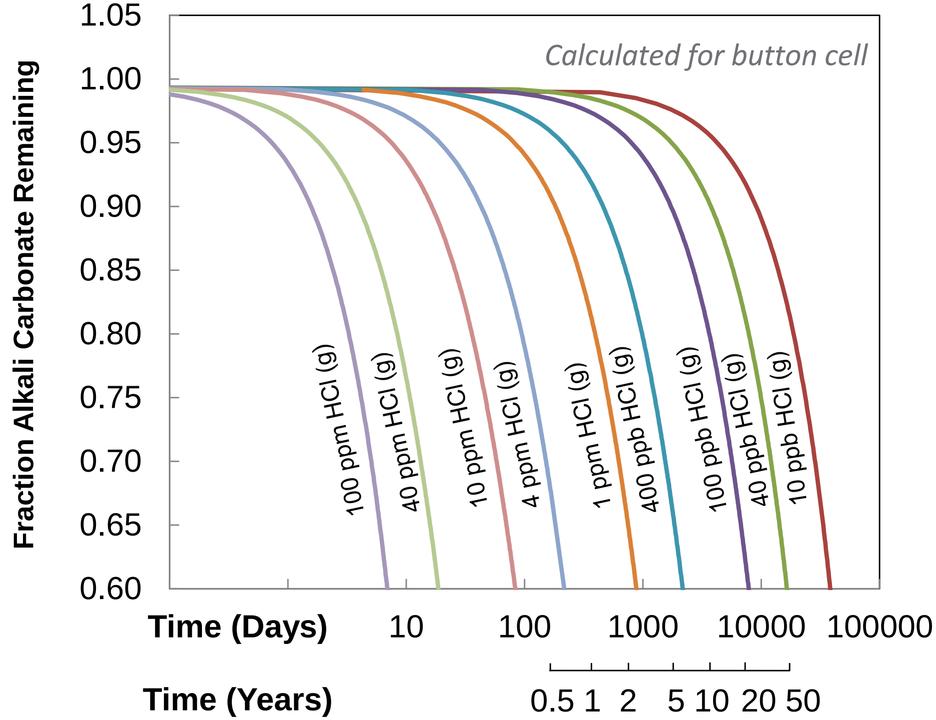
- Phosphorus captured at inlet of fuel cell stack;
- Similar behavior for arsenic and antimony in fuel gas

OA Marina Marina et al. ***SSI*** **181 (2010) 430;** ***J. Power Sources*****, 196 (2011) 636;** ***J. Power Sources*****, 195 (2010) 7140; 193 (2009) 730;** ***J.*** **196 (2011) 4911.**

Anode Poisoning by HCl(g) Low and Reversible for Both SOFC and MCFC; Clean-Up to <1ppm by Solid Sorbents

- Chlorides as high as 1 wt% in biomass
- Concentrations to 500 ppm in syngas reported



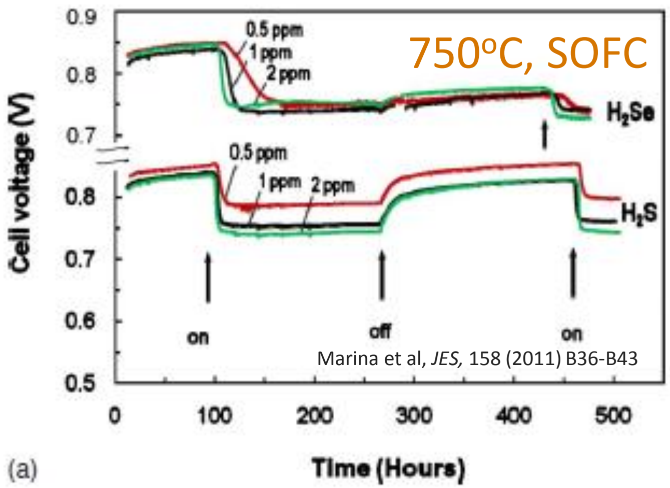


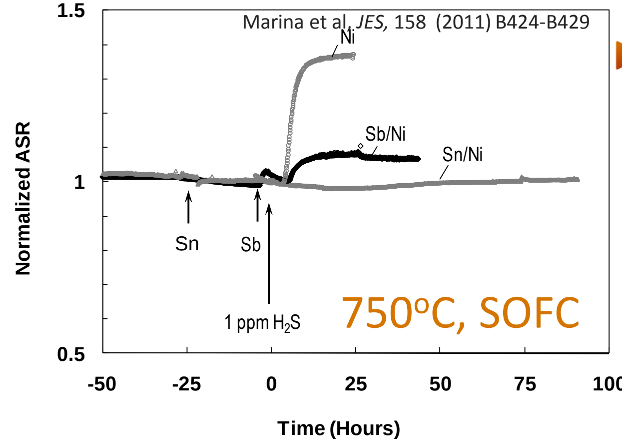
- SOFC anode poisoning consistent with reversible surface adsorption
- Ni chloride solid phases not expected
- $NiCl_x(g)$ activities negligibly low

- Chlorides will displace carbonates in MCFCs
- Electrolyte loss by chloride volatilization is the principal degradation mechanism

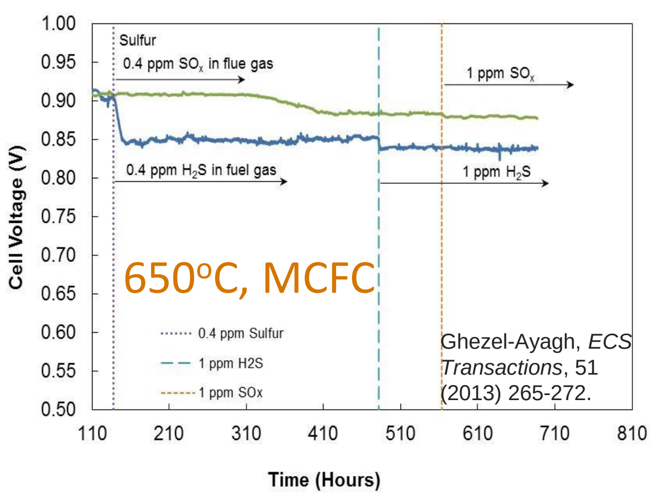
Ni Anodes for Both SOFC and MCFC Reversibly Poisoned by $H_2S(g)$ in Fuel Gases; Modified Anodes Provide Higher Sulfur Tolerance

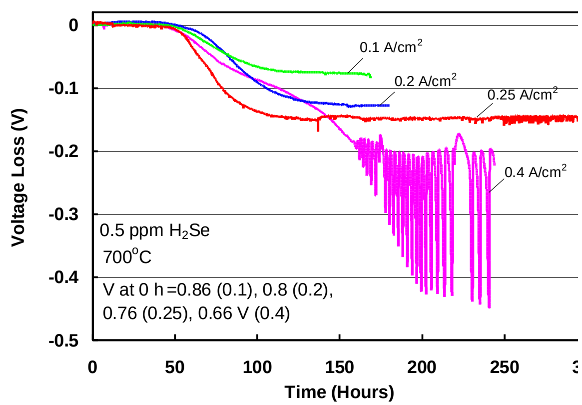
Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

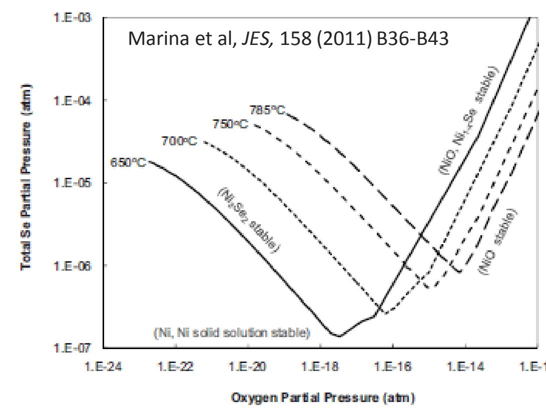




- Options for improving sulfur tolerance exist: e.g. special alloys, addition of ceria







- High fuel utilization, high anodic polarization can dramatically lower the concentration of S or Se needed to form solid reaction products at the anode/electrolyte interface

- Modest decrease in fuel cell performance due to <10 ppm $H_2S(g)$ exposure.

Research Needs, High Temperature Fuel Cells

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle *Since 1965*

- More thorough understanding of mechanisms of degradation resulting from interactions with impurities in biogas, landfill gas, shale gas, and other fuels
- Long-term testing of cells and stacks under realistic conditions of current density and fuel utilization
  - Expected impurity concentrations following cleanup
  - Expected impurity concentrations with cleanup system upset
  - Testing with emerging cleanup options
- Thermochemical modeling of impurity interactions – significant gaps in data exist relevant to fuel cell systems.

Phosphorus, Chlorine and Sulfur in Biomass

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by **Battelle** *Since 1965*

	Phosphorus, wt %	Chlorine, wt %	Sulfur, wt %
Concentrations in biomass	0.14 (loblolly pine) 0.29 (ND weeds) 2-4 (grass ash) 11.5 (willow ash)	0.5 (corn straw) 0.1 (woody) 0.42-0.96 (eucalyptus on saline sites)	0.13 (corn straw) 0.03 (woody) 0.42 (dairy) 0.52 (feedlot) 1.45 (sewage)
Interactions with SOFC	Forms Ni_xP_y solid phases even below 1 ppb	<100 ppm – minor reversible losses Solid phases unlikely	<0.1 ppm – no effect 1-10 ppm –minor reversible losses >1000 ppm – solid phases formed
Interactions with MCFC	No direct study, but expect formation of Ni_xP_y solid phases even below 1 ppb	Loss of electrolyte through alkali chloride volatilization	<0.1 ppm – no effect 1-10 ppm –minor reversible losses Dissolution in molten carbonate electrolyte

- Lack of complete agreement in literature regarding tolerance for both MCFCs and SOFCs to Cl and S