Hydrogen Production with Mixed Protonic-Electronic Conducting Perovskite Membranes

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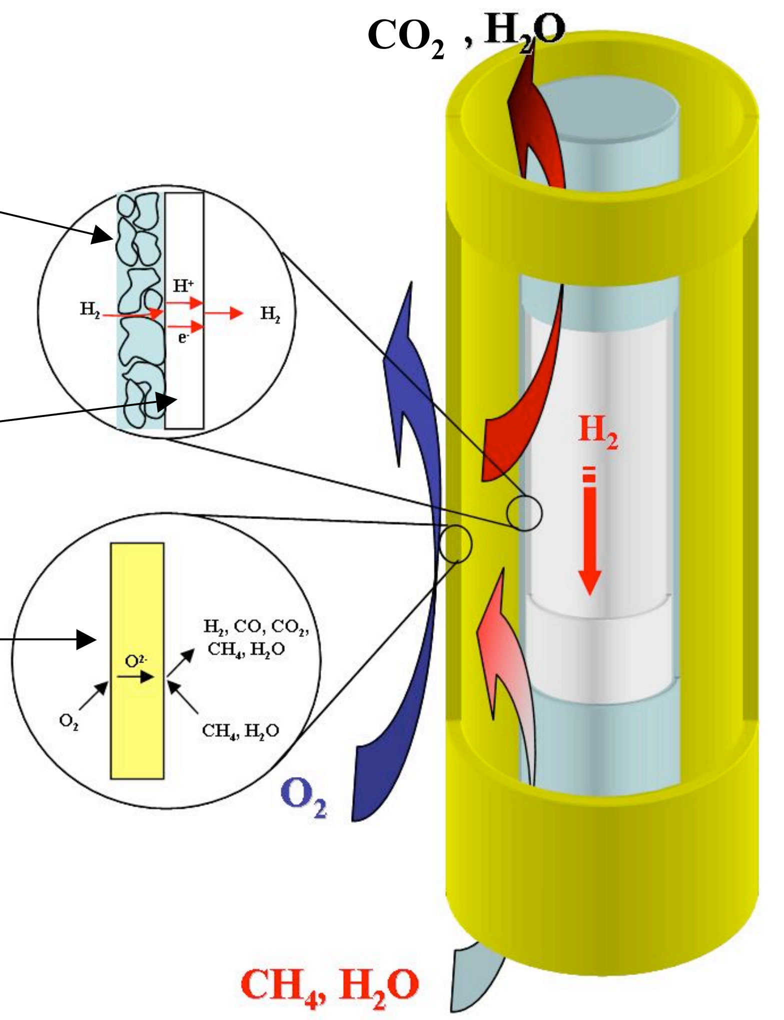
Outline

- Introduction
- Fundamentals and Materials Development
- Membrane Reactor Fabrication and Results
- Recent Membrane Materials Advances
- Conclusions

Concept - Autothermal Catalytic Membrane Reactor for Production of Pure H_2



Ni-$SrCeO_3$ porous tubular support
- Support for hydrogen membrane
- Ni catalyzes endothermic steam reforming or water gas-shift reaction

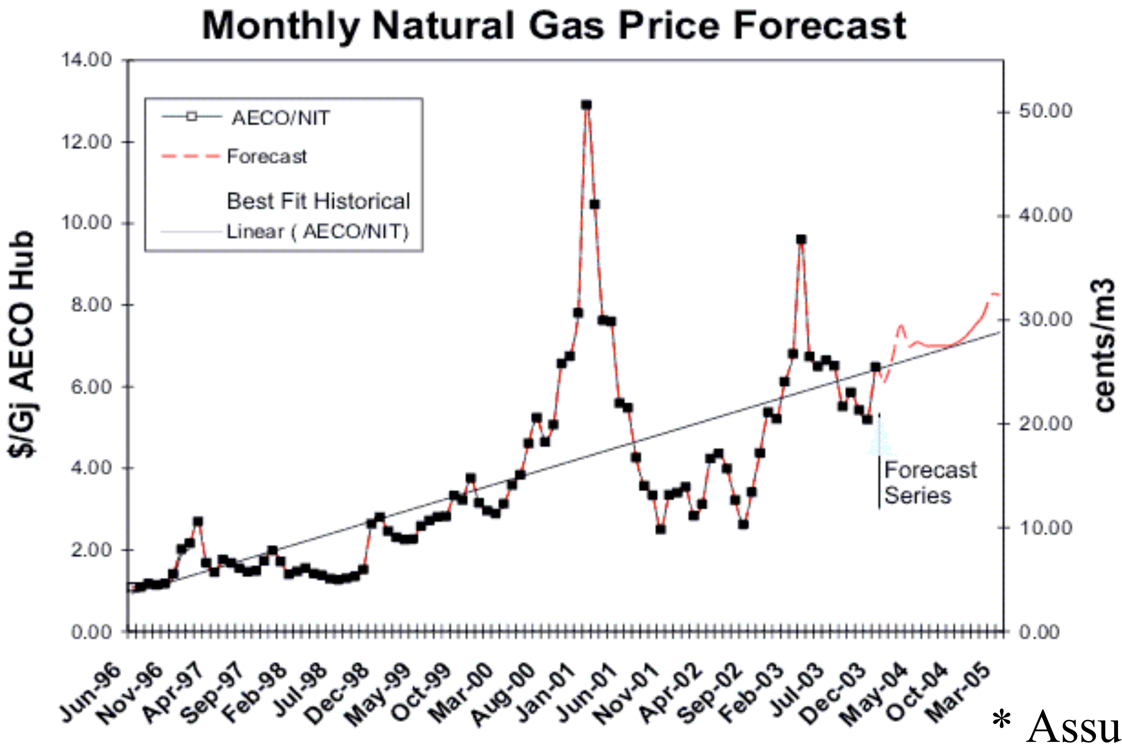
$SrCe_{1-x}Eu_xO_{3-\delta}$ dense hydrogen membrane
- Mixed proton-electron conductor
- ~10 μm dense layer

Oxygen transport membrane
- Exothermic oxidation of hydrocarbon feed gas

Ultimately can produce pure H_2 from any hydrocarbon feed stock:
- *Natural gas*
- *Coal based syn gas*
- *Biomass*

Cost of Hydrogen Production from Natural Gas*

$$CH_4 + 0.375\ O_2 + 1.25\ H_2O = CO_2 + 3.25\ H_2$$



Monthly Natural Gas Price Forecast

Feb. 2004, Copyright, http://www.energyshop.com

$3.25\ H_2/CH_4$

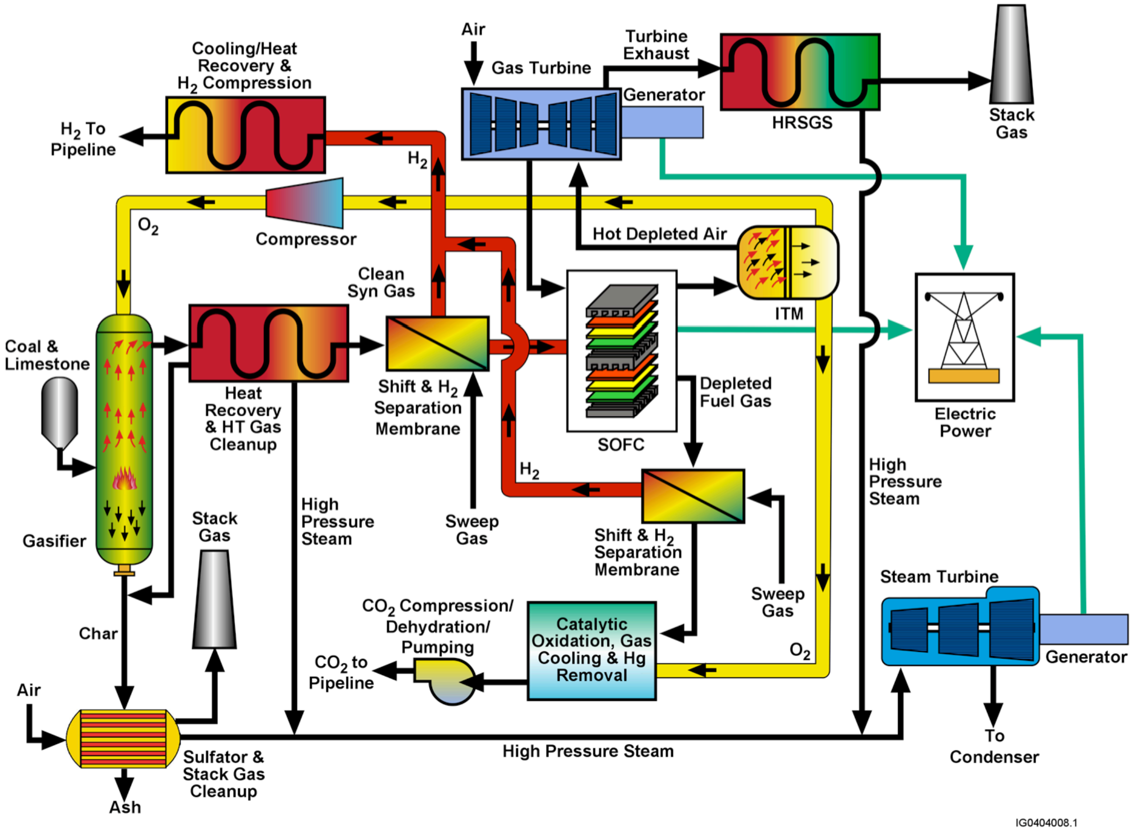
$CH_4 \sim 0.20C\$/m^3$

$\sim\$0.15/m^3\ H_2$

~ 0.015 ¢/liter H_2

* Assumes 100% conversion and selectivity, air and water are free, and ignores capital cost

DOE’s Future Gen



- Hydrogen and electricity co-generation from coal
- Zero emissions and CO_2 capture

“Hydrogen Production from Fossil Fuels with Proton and Oxygen-Ion Transport Membranes,” E. D. Wachsman and M. C. Williams, *Interface*, Volume 13, No.3, Fall 2004

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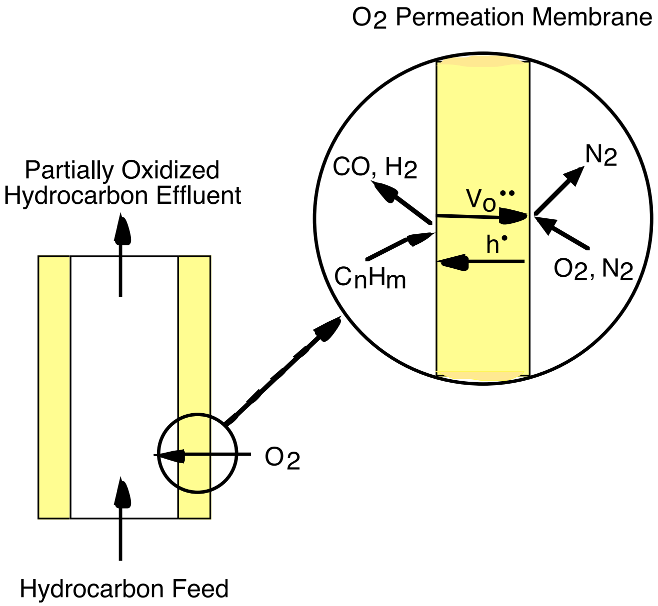
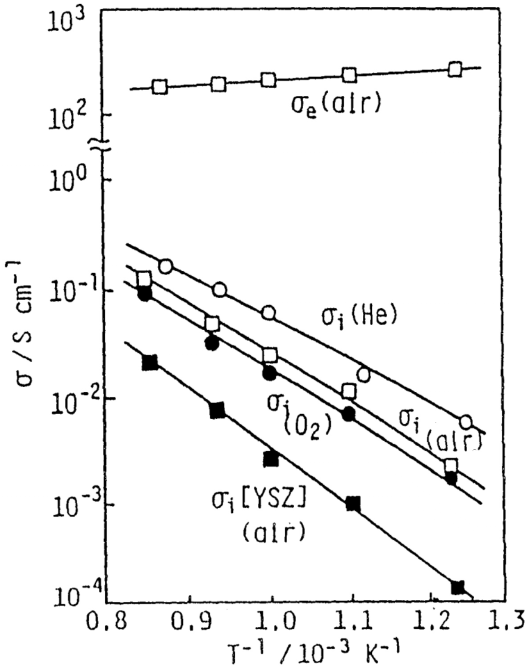
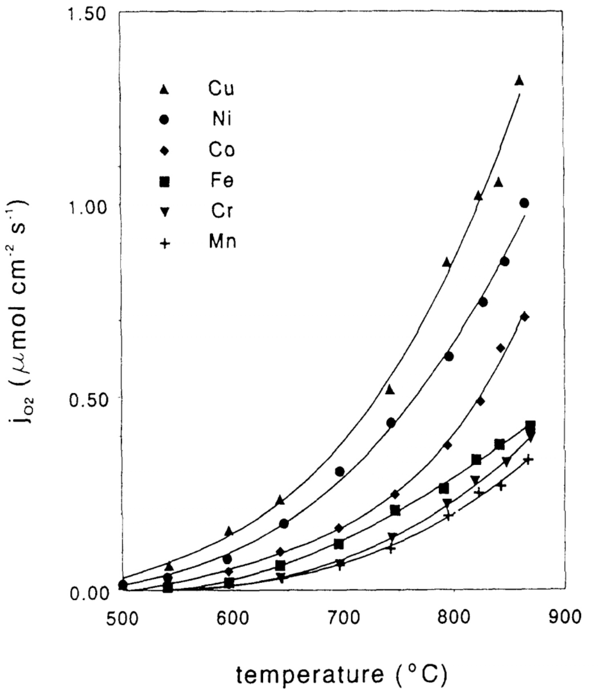
OXIDE-ION CONDUCTING MIEC's





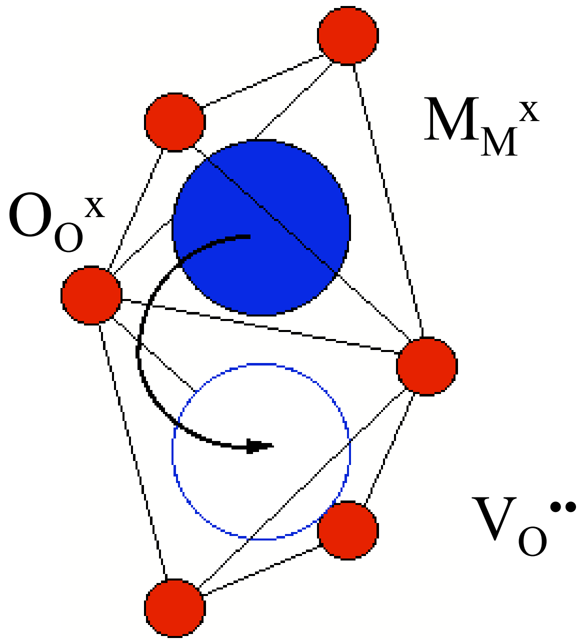
σ_i and σ_e of $La_{0.8}Sr_{0.2}Co_{0.8}Fe_{0.2}O_{3-d}$
Teraoka, et al (1998)

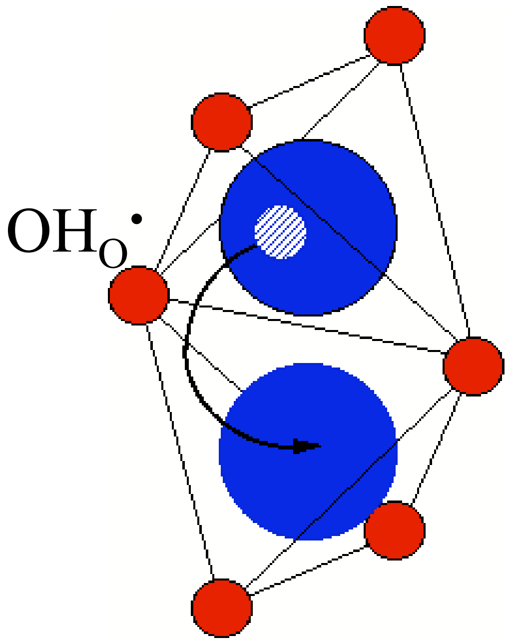


J_{O2} of $La_{0.6}Sr_{0.4}Co_{0.8}B_{0.2}O_{3-d}$
Teraoka, et al (1998)

- Ionic and electronic conductivity results in O_2 permeation limited by oxide-ion conductivity $\sigma_{V_O^{\bullet\bullet}}$

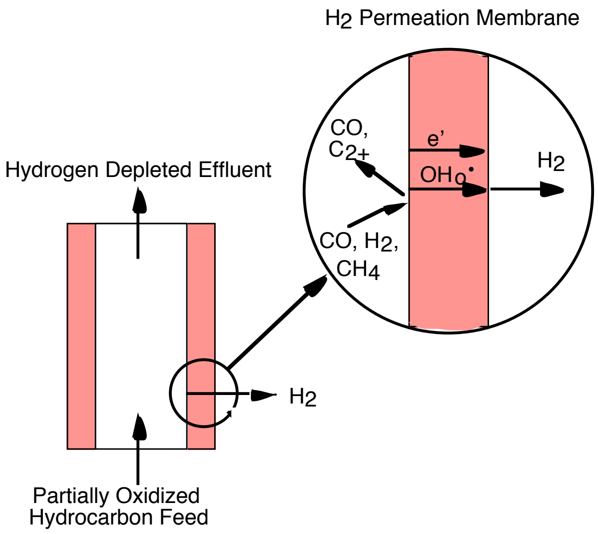
OXIDE-ION vs. PROTONIC CONDUCTION





- Oxygen ions jump from a filled (O_O^x) to a vacant ($V_O^{\bullet\bullet}$) site
- H-bonded protons form an OH group ($OH_O^{\bullet}$)
- Protons move around O_O^x and jump to neighboring O_O^x

PROTONIC vs. OXIDE-ION CONDUCTORS



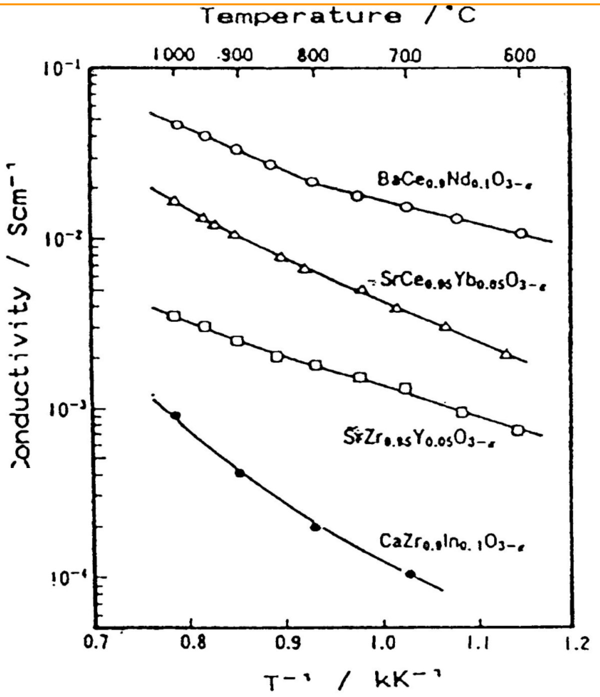
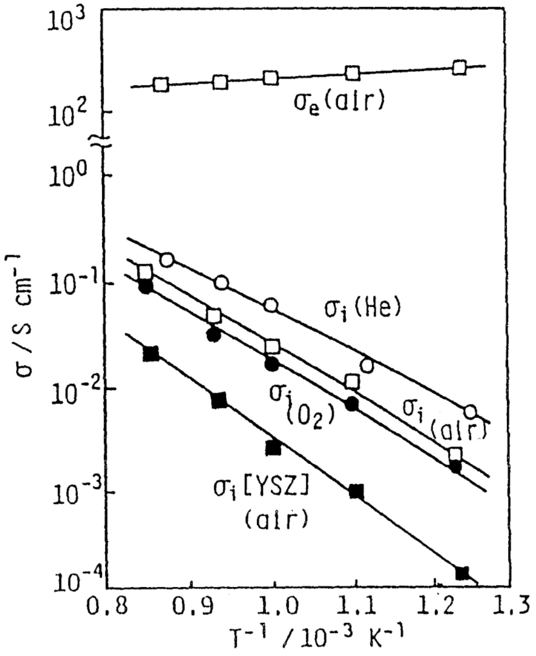


Figure 2
Conductivities of typical protonic conductor based on perovskite-type oxides. Iwahara, et al.



σ_i and σ_e of $La_{0.8}Sr_{0.2}Co_{0.8}Fe_{0.2}O_{3-d}$
Teraoka, et al (1998)

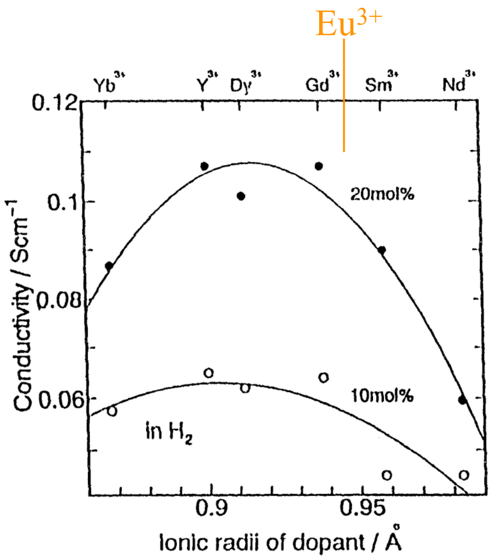
- Protonic conductors have comparable ionic conductivity but negligible electronic conductivity
- H_2 flux limited by electronic conductivity ($\sigma_{e'}$)

Adding Electronic Conductivity to a Proton Conductor

- Add electronic conductivity by doping Ce site with multivalent cation ($M^{3+/2+}$) that can be reduced to 2+
  - $M_{Ce}'' = M_{Ce}' + e'$ (n-type conduction)

E. D. Wachsman and N. Jiang, October 2, 2001, U.S. Patent No. 6,296,687.

- Match ionic radii for
  - Phase stability
  - Proton conductivity
  - > $Eu^{3+/2+}$



Conductivity of $BaCe_{1-x}M_xO_{3-d}$ as a function r_M ,
Iwahara et al (1993)

H_2 Flux Relationship

$$J_{OH_O^{\bullet}} = -\frac{1}{L}[\frac{RT}{4F^2}\int_{P'_{O_2}}^{P''_{O_2}} \sigma_t t_{OH_O^{\bullet}} t_{V_O^{\bullet\bullet}} \, d\ln P_{O_2} + \frac{RT}{2F^2}\int_{P'_{H_2}}^{P''_{H_2}} \sigma_t t_{OH_O^{\bullet}} (t_{V_O^{\bullet\bullet}} + t_{e'}) d\ln P_{H_2}$$

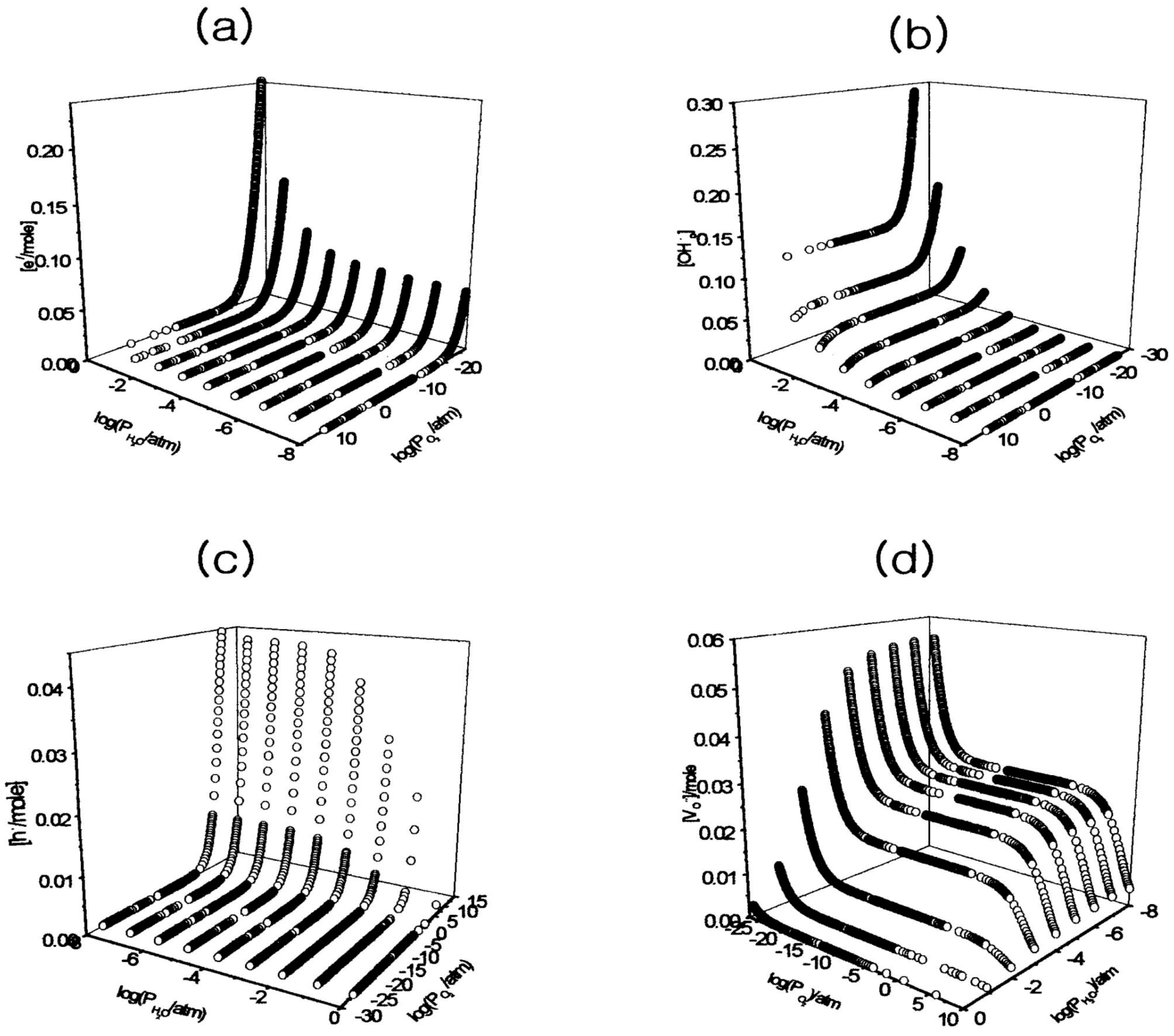
Proton flux across calculated using Wagner equation:

- Assumes that bulk diffusion is rate limiting step
- σ_t is the total conductivity
  - $\sigma_i = z_i \, q \, u_i \, [i]$, ($i = OH_O^{\bullet}, V_O^{\bullet\bullet}, e'$)
- Transference number, $t_i = \sigma_i / \sigma_t$
  - High flux requires both high protonic and high electronic conductivity
- F is Faraday’s constant
- L is the membrane thickness
- Integrate both O_2 and H_2 potential gradients

Complex Defect Equilibria

Charge Neutrality	n	p	$[V_O^{\cdot\cdot}]$	$[OH_O^{\cdot}]$	$[Eu^{/}_{Ce}]$	$[Eu^{//}_{Ce}]$
$n = 2[V_O^{\bullet\bullet}]$	$\{2K_R\}^{\frac{1}{3}} P_{O_2}^{-\frac{1}{6}}$	$\frac{K_i}{\{2K_R\}^{\frac{1}{3}}} P_{O_2}^{\frac{1}{6}}$	$(\frac{K_R}{4})^{\frac{1}{3}} P_{O_2}^{-\frac{1}{6}}$	$\{\frac{K_R K_W^3}{4}\}^{\frac{1}{6}} P_{O_2}^{-\frac{1}{12}} P_{H_2O}^{\frac{1}{2}}$	$\frac{K_i [Eu]_t}{K_A \{2K_R\}^{\frac{1}{3}}} P_{O_2}^{\frac{1}{6}}$	$[Eu^{//}_{Ce}] = [Eu]_t$
$[Eu^{//}_{Ce}] = [V_O^{\bullet\bullet}]$ $p << K_A$	$\{\frac{K_R}{[Eu]_t}\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{4}}$	$\{\frac{K_i^2 [Eu]_t}{K_R}\}^{\frac{1}{2}} P_{O_2}^{\frac{1}{4}}$	$[Eu]_t$	$\{K_W Eu_t\}^{\frac{1}{2}} P_{H_2O}^{\frac{1}{2}}$	$\{\frac{K_i^2 [Eu]_t^3}{K_A^2 K_R}\}^{\frac{1}{2}} P_{O_2}^{\frac{1}{4}}$	$[Eu^{//}_{Ce}] = [Eu]_t$
$[Eu^{//}_{Ce}] = [V_O^{\bullet\bullet}]$ $p >> K_A$	$\{\frac{K_i K_R}{K_A [Eu]_t}\}^{\frac{1}{3}} P_{O_2}^{-\frac{1}{6}}$	$\{\frac{K_i^2 K_A [Eu]_t}{K_R}\}^{\frac{1}{3}} P_{O_2}^{\frac{1}{6}}$	$K_R \{\frac{K_A [Eu]_t}{K_i K_R}\}^{\frac{2}{3}} P_{O_2}^{-\frac{1}{6}}$	$\{K_W K_R\}^{\frac{1}{2}} \{\frac{K_A [Eu]_t}{K_i K_R}\}^{\frac{1}{3}} P_{O_2}^{-\frac{1}{12}} P_{H_2O}^{\frac{1}{2}}$	$[Eu^{/}_{Ce}] = [Eu]_t - [Eu^{//}_{Ce}]$	$K_R \{\frac{K_A [Eu]_t}{K_i K_R}\}^{\frac{2}{3}} P_{O_2}^{-\frac{1}{6}}$
$[Eu^{/}_{Ce}] = 2[V_O^{\bullet\bullet}]$	$\{\frac{2K_R}{[Eu]_t}\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{4}}$	$\{\frac{K_i^2 [Eu]_t}{2K_R}\}^{\frac{1}{2}} P_{O_2}^{\frac{1}{4}}$	$\frac{[Eu]_t}{2}$	$\{\frac{K_W Eu_t}{2}\}^{\frac{1}{2}} P_{H_2O}^{\frac{1}{2}}$	$[Eu^{/}_{Ce}] = [Eu]_t$	$\{\frac{2K_A^2 K_R [Eu]_t}{K_i^2}\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{4}}$
$n = [OH_O^{\bullet}]$	$\{K_W K_R\}^{\frac{1}{4}} P_{O_2}^{-\frac{1}{8}} P_{H_2O}^{\frac{1}{4}}$	$\{\frac{K_i^4}{K_W K_R}\}^{\frac{1}{4}} P_{O_2}^{\frac{1}{8}} P_{H_2O}^{-\frac{1}{4}}$	$\{\frac{K_R}{K_W}\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{4}} P_{H_2O}^{-\frac{1}{2}}$	$\{K_W K_R\}^{\frac{1}{4}} P_{O_2}^{-\frac{1}{8}} P_{H_2O}^{\frac{1}{4}}$	$\{\frac{K_W K_R [Eu]_t^4}{K_A^4 K_i^4}\}^{-\frac{1}{4}} P_{O_2}^{\frac{1}{8}} P_{H_2O}^{-\frac{1}{4}}$	$[Eu^{/}_{Ce}] = [Eu]_t$
$[Eu^{/}_{Ce}] = [OH_O^{\bullet}]$	$\{\frac{K_W K_R}{[Eu]_t^2}\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{4}} P_{H_2O}^{\frac{1}{2}}$	$\{\frac{[Eu]_t^2 K_i^2}{K_W K_R}\}^{\frac{1}{2}} P_{O_2}^{\frac{1}{4}} P_{H_2O}^{-\frac{1}{2}}$	$\frac{[Eu]_t^2}{K_W} P_{H_2O}^{-1}$	$[Eu]_t$	$[Eu]_t$	$\{\frac{K_A^2 K_W K_R}{K_i^2}\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{4}} P_{H_2O}^{\frac{1}{2}}$
$2[Eu^{//}_{Ce}] = [OH_O^{\bullet}]$ $p << K_A$	$\{\frac{K_W K_R}{4[Eu]_t^2}\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{4}} P_{H_2O}^{\frac{1}{2}}$	$\{\frac{4[Eu]_t^2 K_i^2}{K_W K_R}\}^{\frac{1}{2}} P_{O_2}^{\frac{1}{4}} P_{H_2O}^{-\frac{1}{2}}$	$\frac{[Eu]_t^2}{K_W} P_{H_2O}^{-1}$	$2[Eu]_t$	$\{\frac{4[Eu]_t^4 K_i^2}{K_W K_R K_A^2}\}^{\frac{1}{2}} P_{O_2}^{\frac{1}{4}} P_{H_2O}^{-\frac{1}{2}}$	$[Eu]_t$
$2[Eu^{//}_{Ce}] = [OH_O^{\bullet}]$ $p >> K_A$	$\{\frac{K_W K_R K_i^2}{4K_A^2 [Eu]_t^2}\}^{\frac{1}{4}} P_{O_2}^{-\frac{1}{8}} P_{H_2O}^{\frac{1}{4}}$	$\{\frac{4K_A^2 K_i^2 [Eu]_t^2}{K_W K_R}\}^{\frac{1}{4}} P_{O_2}^{\frac{1}{8}} P_{H_2O}^{-\frac{1}{4}}$	$\{\frac{4K_A^2 K_R [Eu]_t^2}{K_W}\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{4}} P_{H_2O}^{-\frac{1}{2}}$	$\{4K_A^2 K_W K_R [Eu]_t^2\}^{\frac{1}{4}} P_{O_2}^{-\frac{1}{8}} P_{H_2O}^{\frac{1}{4}}$	$[Eu]_t = [Eu_t] - [Eu^{//}_{Ce}]$	$\{\frac{K_A^2 K_R K_W [Eu]_t^2}{4K_i^2}\}^{\frac{1}{4}} P_{O_2}^{-\frac{1}{8}} P_{H_2O}^{\frac{1}{4}}$
$[Eu^{/}_{Ce}] = p$	$\frac{K_i}{[Eu]_t}$	$[Eu]_t$	$\{\frac{[Eu]_t^2 K_R}{K_i^2}\} P_{O_2}^{-\frac{1}{2}}$	$\{\frac{K_R K_W [Eu]_t^2}{K_i^2}\} P_{O_2}^{-\frac{1}{4}} P_{H_2O}^{\frac{1}{2}}$	$[Eu]_t$	K_A

Modeling Defect Equilibria and Transport -effect of P_{H2}, P_{O2}, P_{H2O}



Defect concentration for a logarithmical space for the case of x=0.05 (a) electrons (b) protons © hole (d) oxygen vacancy

S. J. Song, E. D. Wachsman, S. E. Dorris, and U. Balachandran, *Solid State Ionics*, **149**, 1-10 (2002).

Modeling Defect Equilibria and Transport

$$\sigma_i = z_i\, q\, u_i\, [i]$$

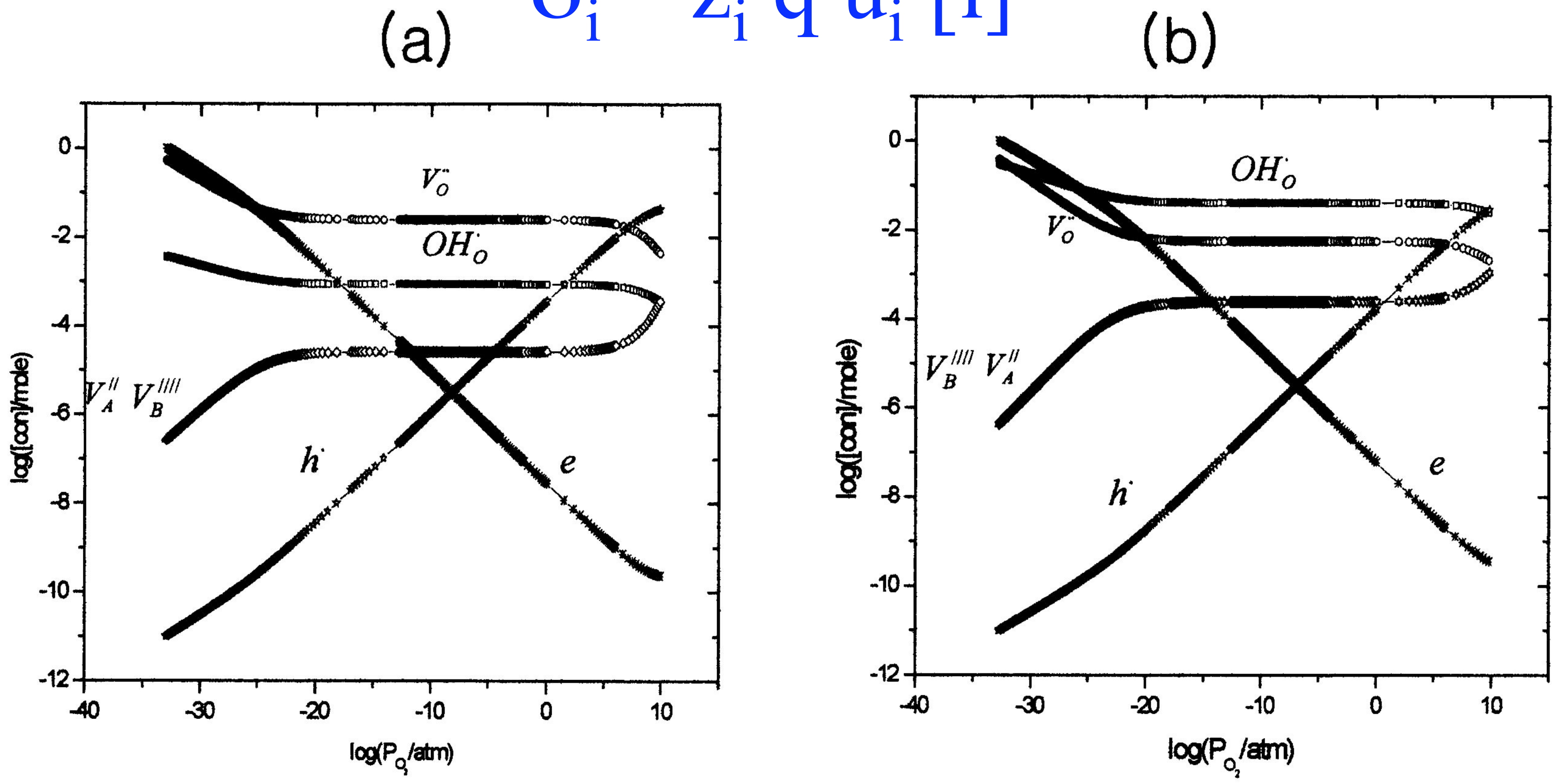
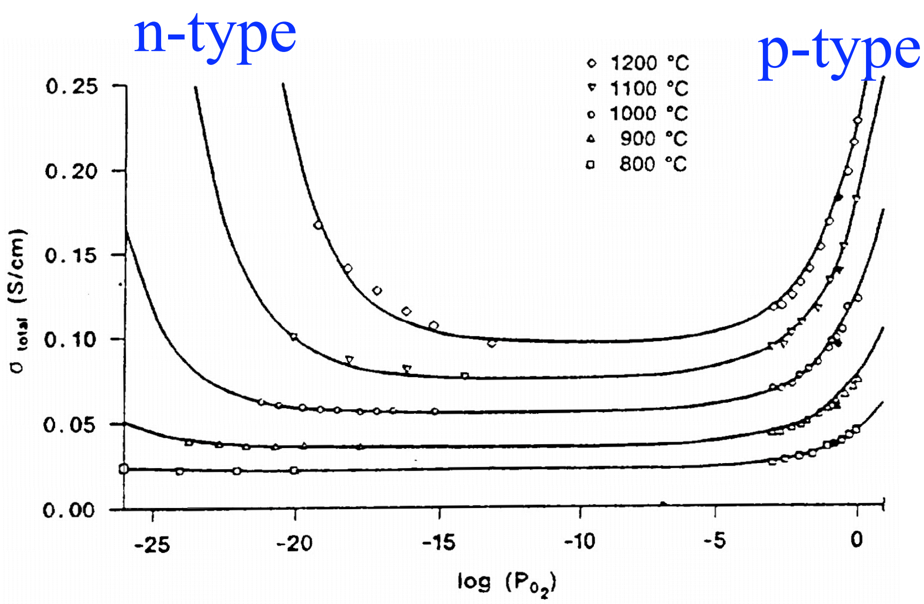


Fig 2. Proton and other defect concentrations as function of P_{O_2} , at 700°C.

$K_S = 10^{-14}$ $K_{OX} = 1.5*10^{-5}$ $K_I = 1*10^{-11}$ $K_W = 10$ A/B $ratio = 1$

Dopant level x=0.05. (a) $P_{H_2O} = 10^{-6} atm$ (b) $P_{H_2O} = 10^{-2} atm$

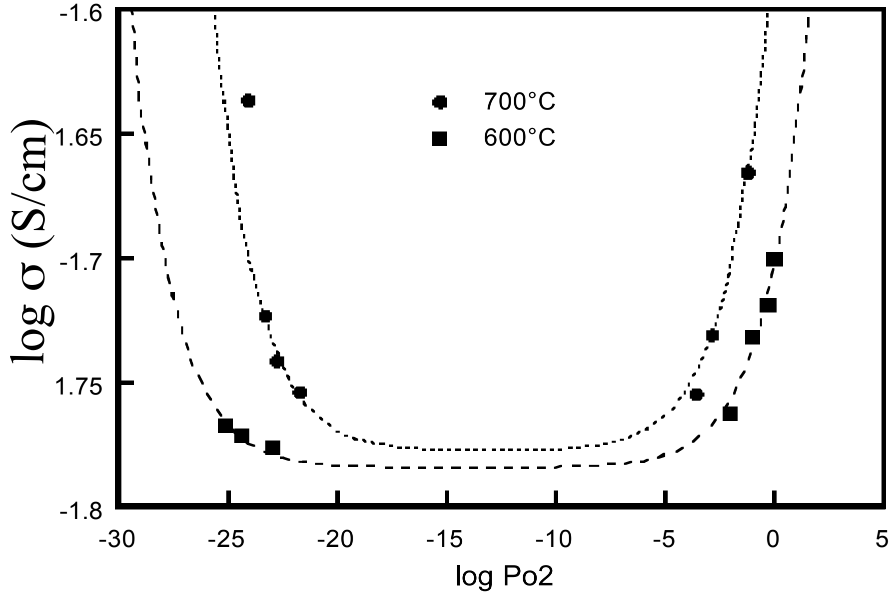
Selection of Dopant - Conductivity as a Function of P_{O_2}



$BaCe_{0.85}Gd_{0.15}O_{2.93}$

- Negligible n-type electronic conductivity except at very high temperature >1000°C

N. Bonanos (1992)



$BaCe_{0.85}Eu_{0.15}O_{2.93}$

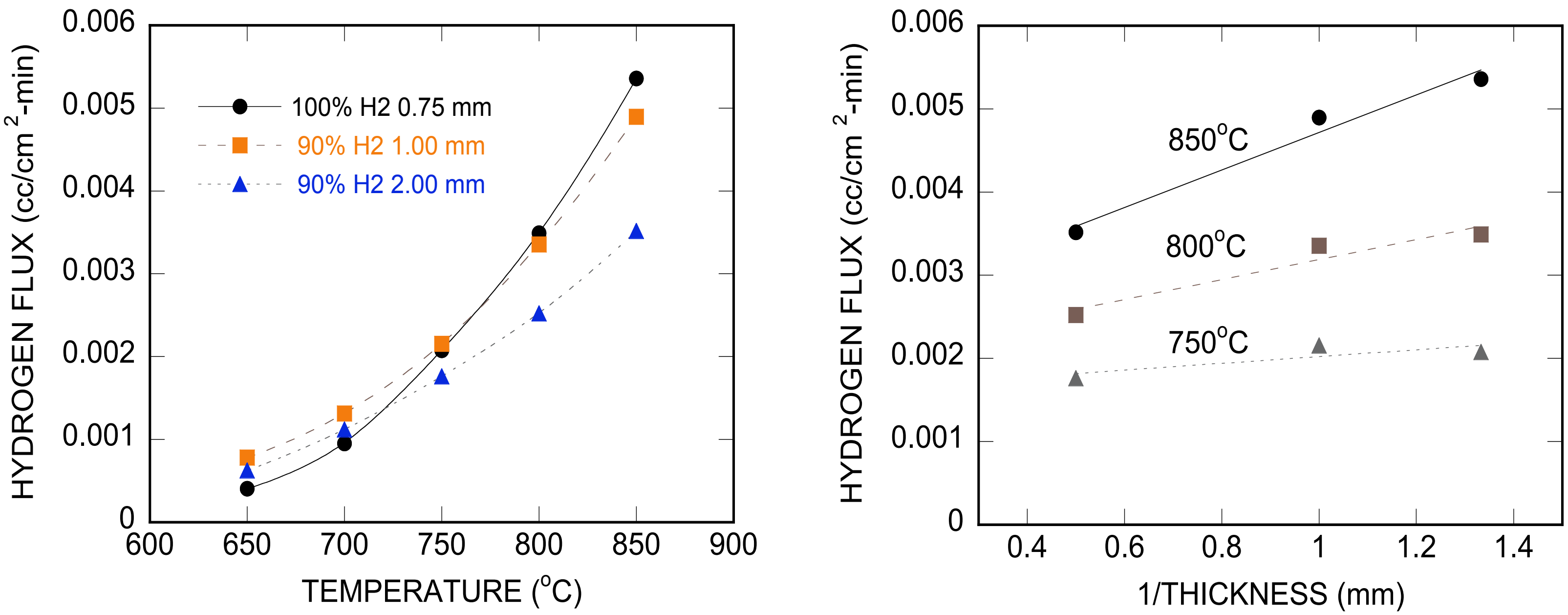
- Significant n-type electronic conductivity at much lower temperature and higher P_{O2}

J. Rhodes and E.D. Wachsman (2001).

H_2 Flux Relationship

$$J_{OH_O^{\bullet}} = -\frac{1}{L}[\frac{RT}{4F^2}\int_{P_{O_2}^{/}}^{P_{O_2}^{//}} \sigma_t t_{OH_O^{\bullet}} t_{V_O^{\bullet\bullet}} \, d\ln P_{O_2} + \frac{RT}{2F^2}\int_{P_{H_2}^{/}}^{P_{H_2}^{//}} \sigma_t t_{OH_O^{\bullet}} (t_{V_O^{\bullet\bullet}} + t_{e^{/}}) d\ln P_{H_2}$$

Flux ~ 1/membrane thickness (L)



- At high temperature (>750°C) permeation is bulk transport controlled
  - Flux is linear with 1/L
- At lower temperature permeation is surface kinetic controlled

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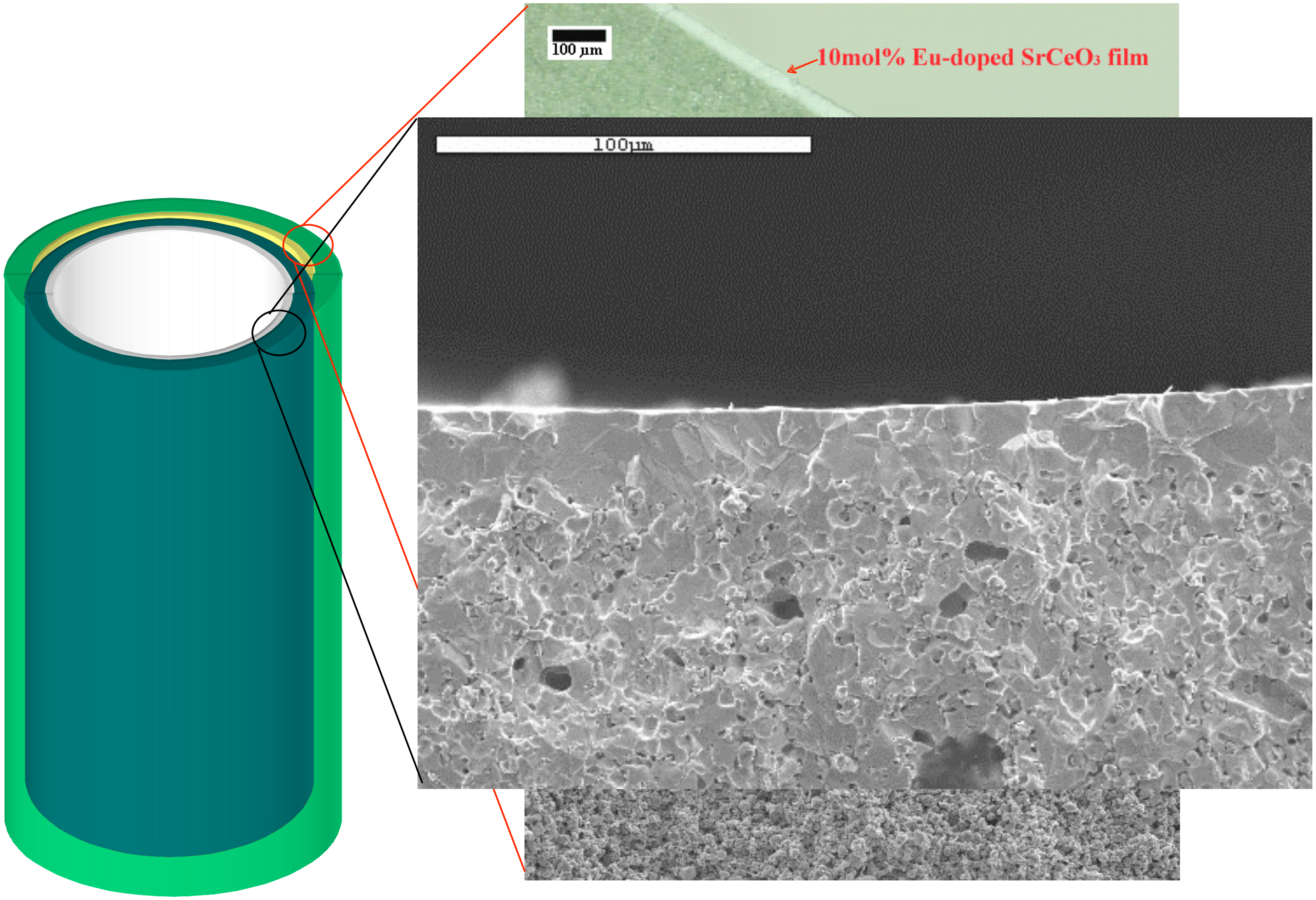
Hydrogen Membrane Cell Fabrication



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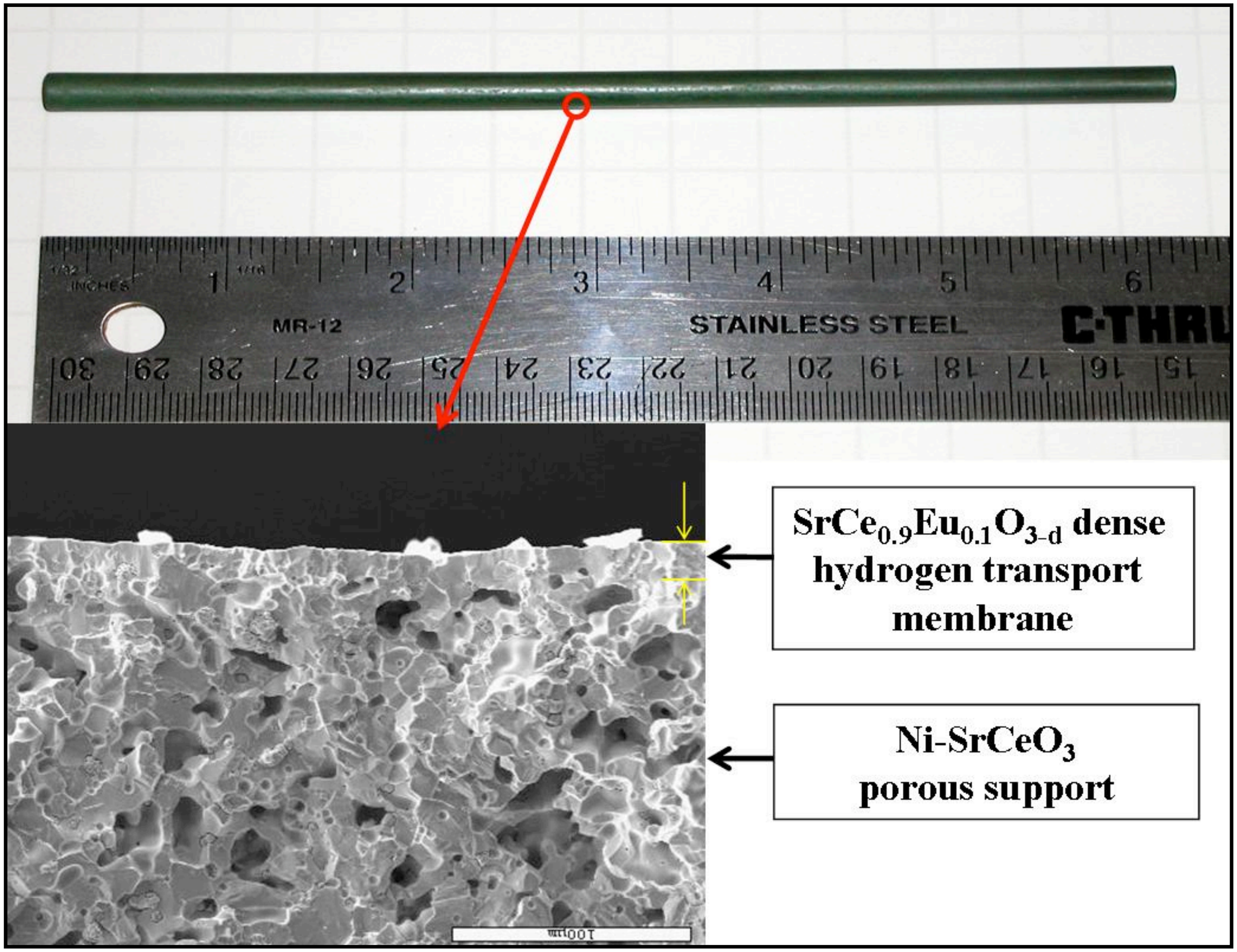
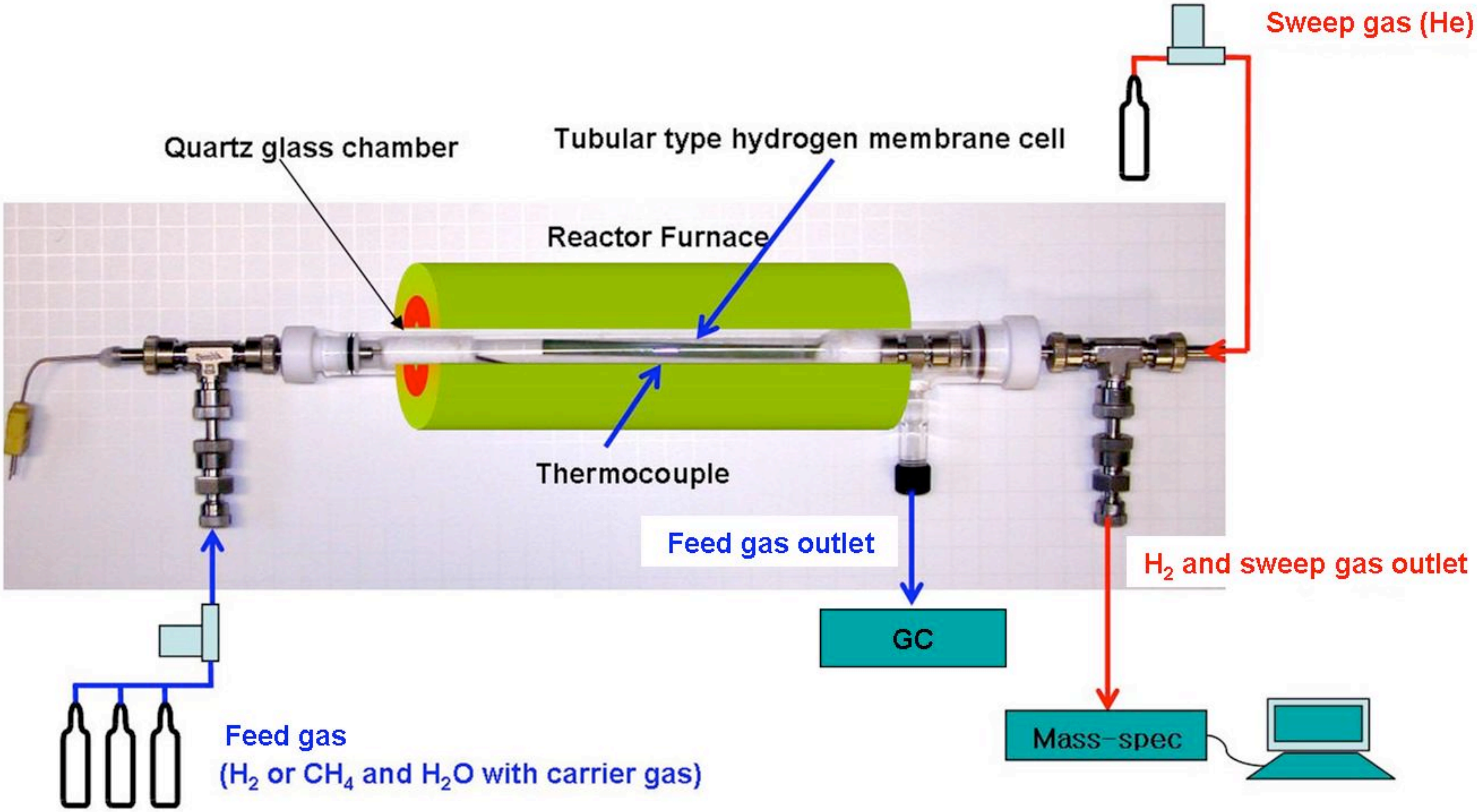
Fabrication of Membrane Reactor

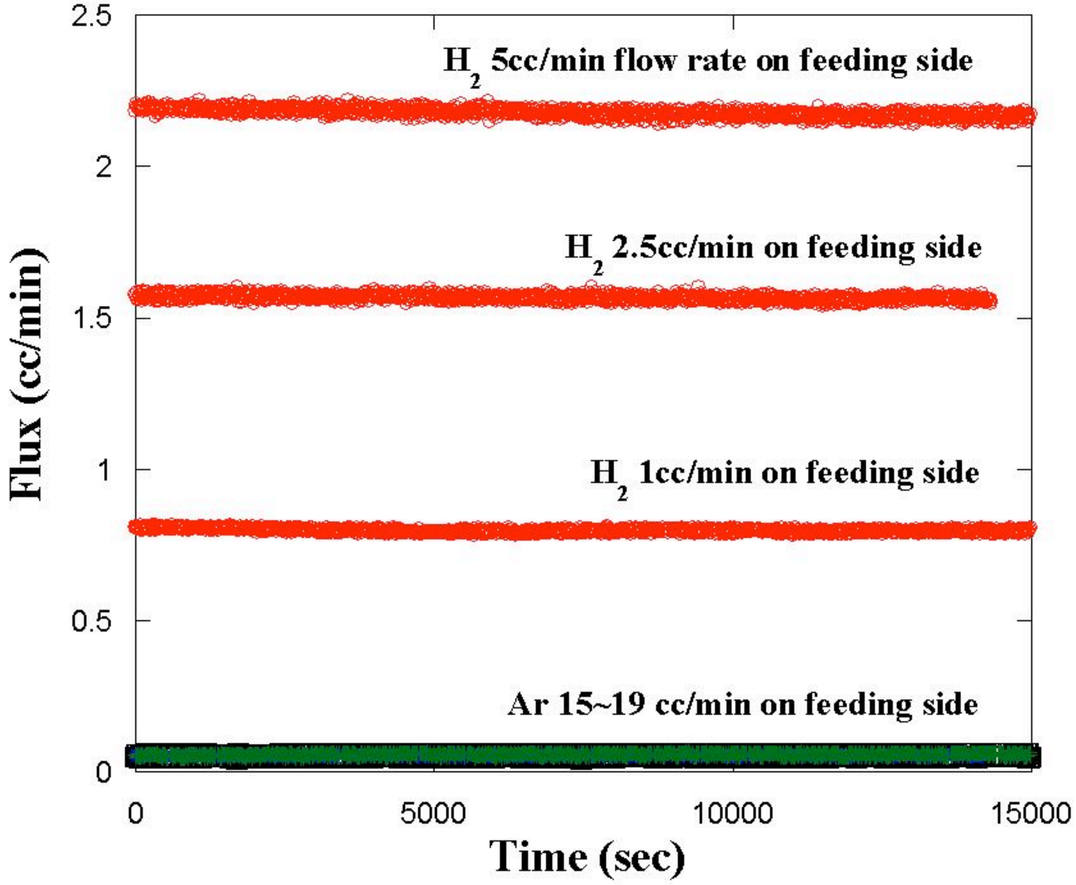


Hydrogen Membrane Evaluation



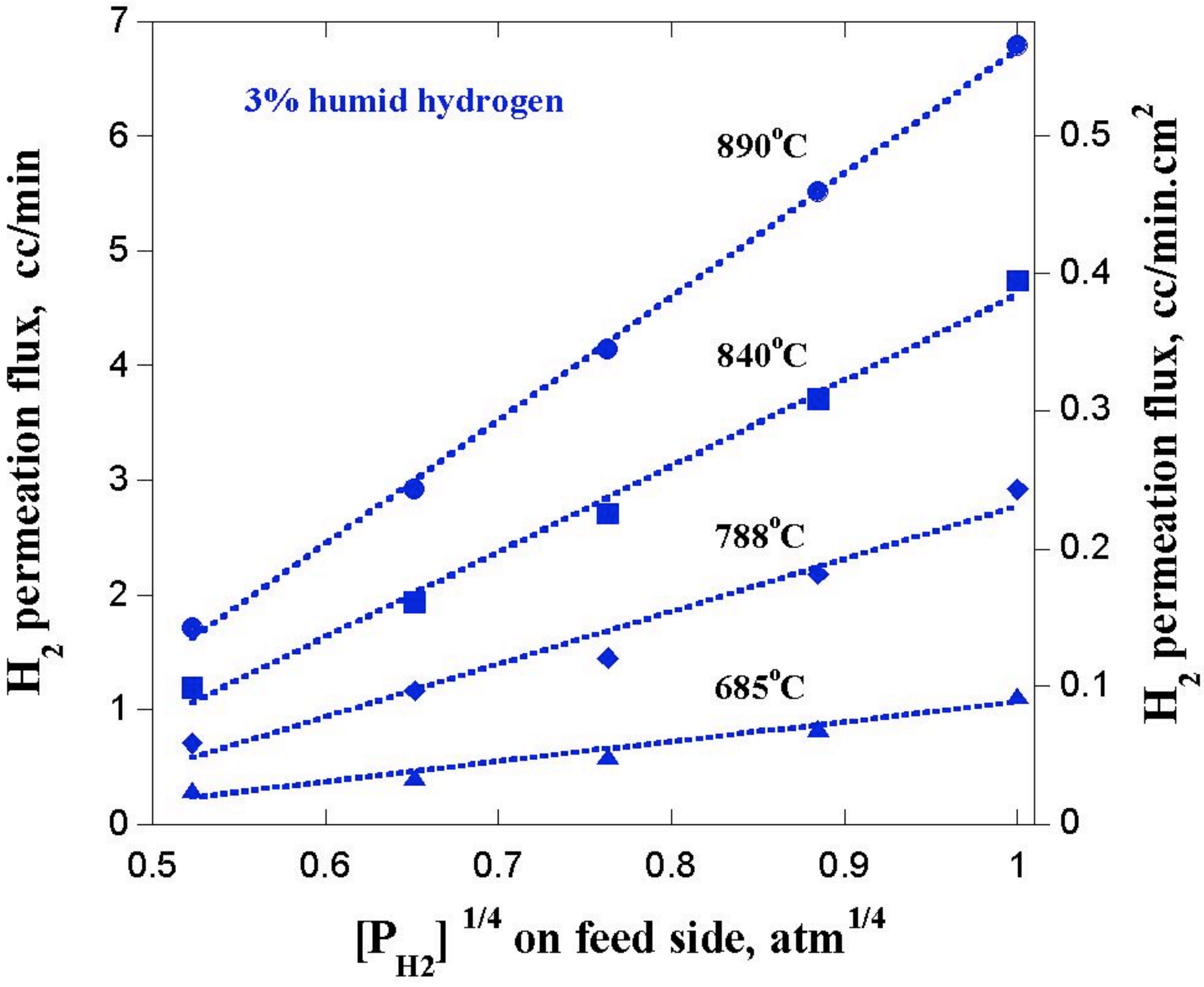
All tubes are continuously leak checked by Ar tracer in feed gas

Hydrogen Permeation and Leak Testing



- Confirms membranes are leak free
- Capable of producing 100% purity H_2

Hydrogen Permeation



Hydrogen flux ~ $P_{H2}{}^{1/4}$

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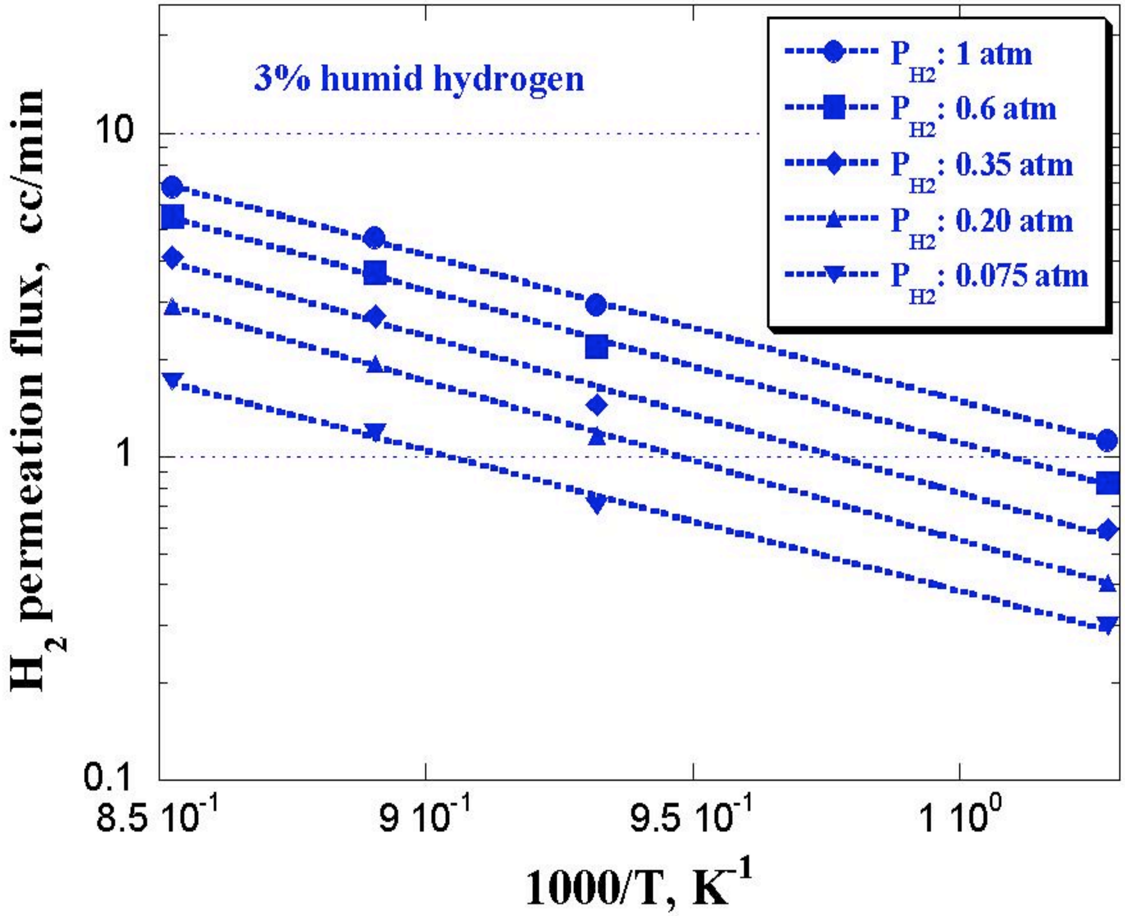
Hydrogen Permeation

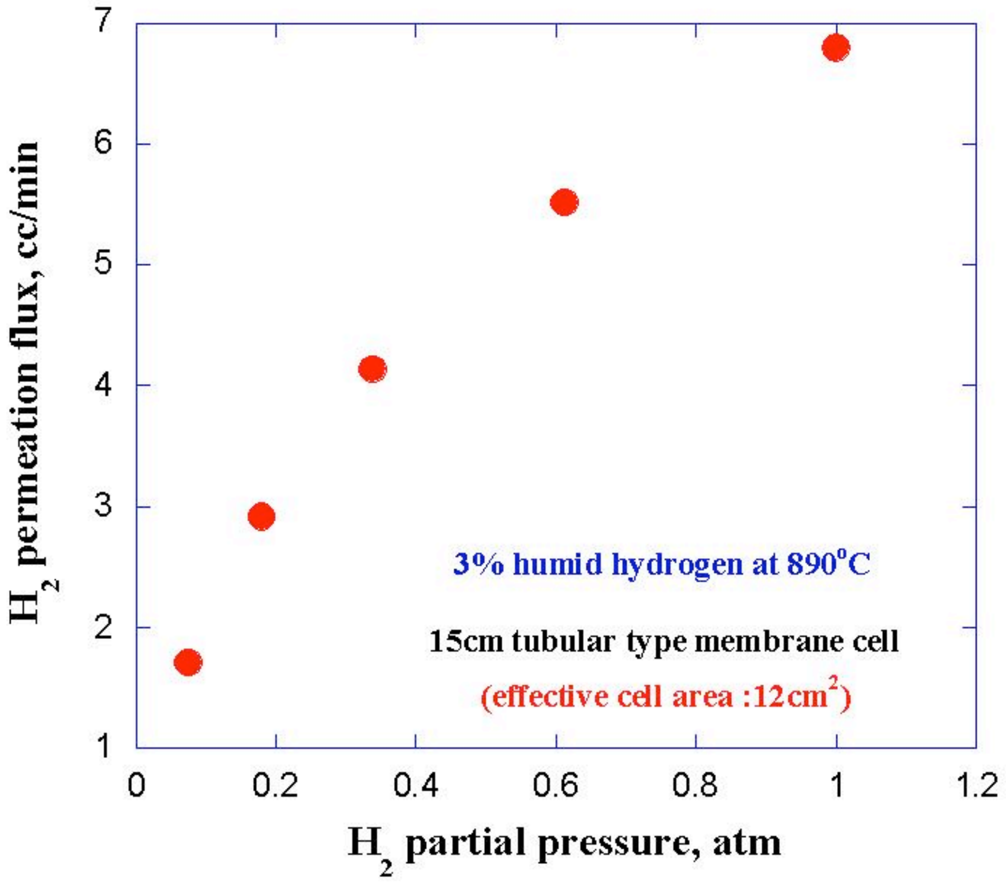


P_{H2} *(atm)*	0.075	0.20	0.35	0.60	1	average value
Activation energy, *E* (*eV*)	**0.86**	**0.97**	**0.96**	**0.93**	**0.89**	**0.924**

Activation energy of ~0.9 eV indicates flux limited by σ_e

– $\sigma_{OH\cdot}$ activation energy ~ 0.5 eV

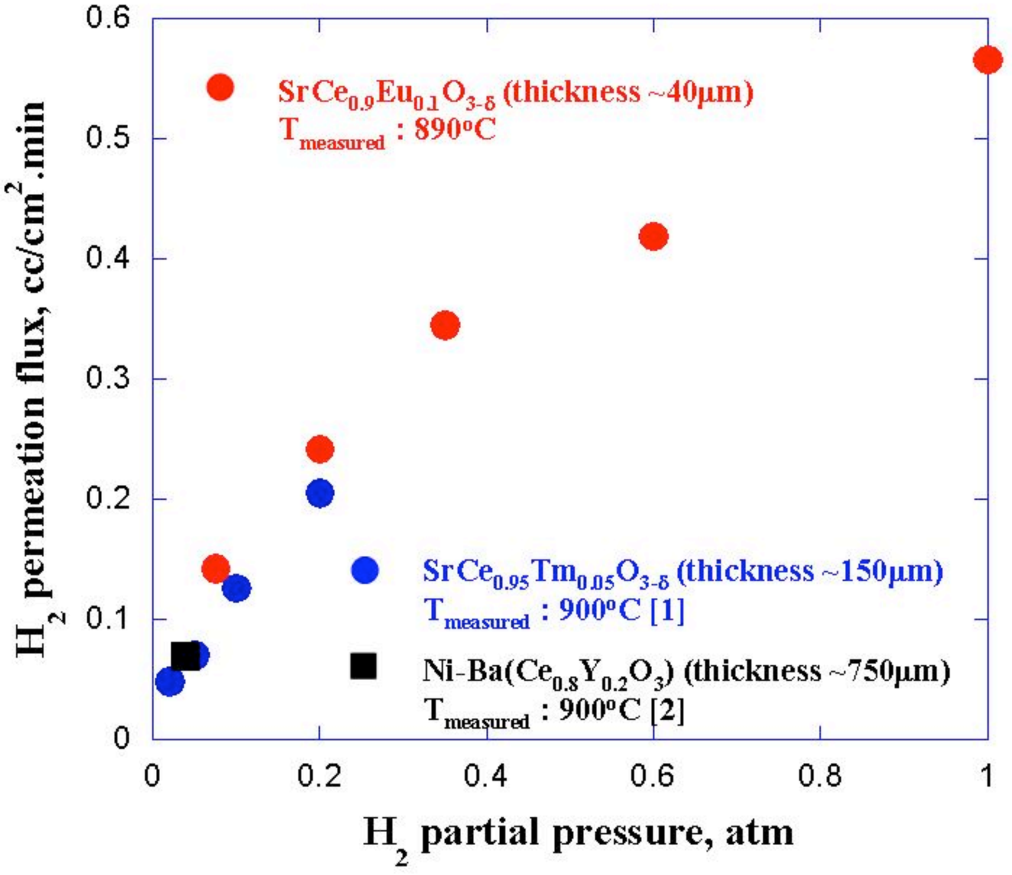
Hydrogen Permeation



● H_2 -3% H_2O balance Ar / $SrCe_{0.9}Eu_{0.1}O_3$ /He

Membrane tubes produce 7 cc/min of pure H_2

Hydrogen Permeation



Area normalized membrane flux comparable to best in literature.

However…

● H_2 -3% H_2O balance Ar / $SrCe_{0.9}Eu_{0.1}O_3$ /He

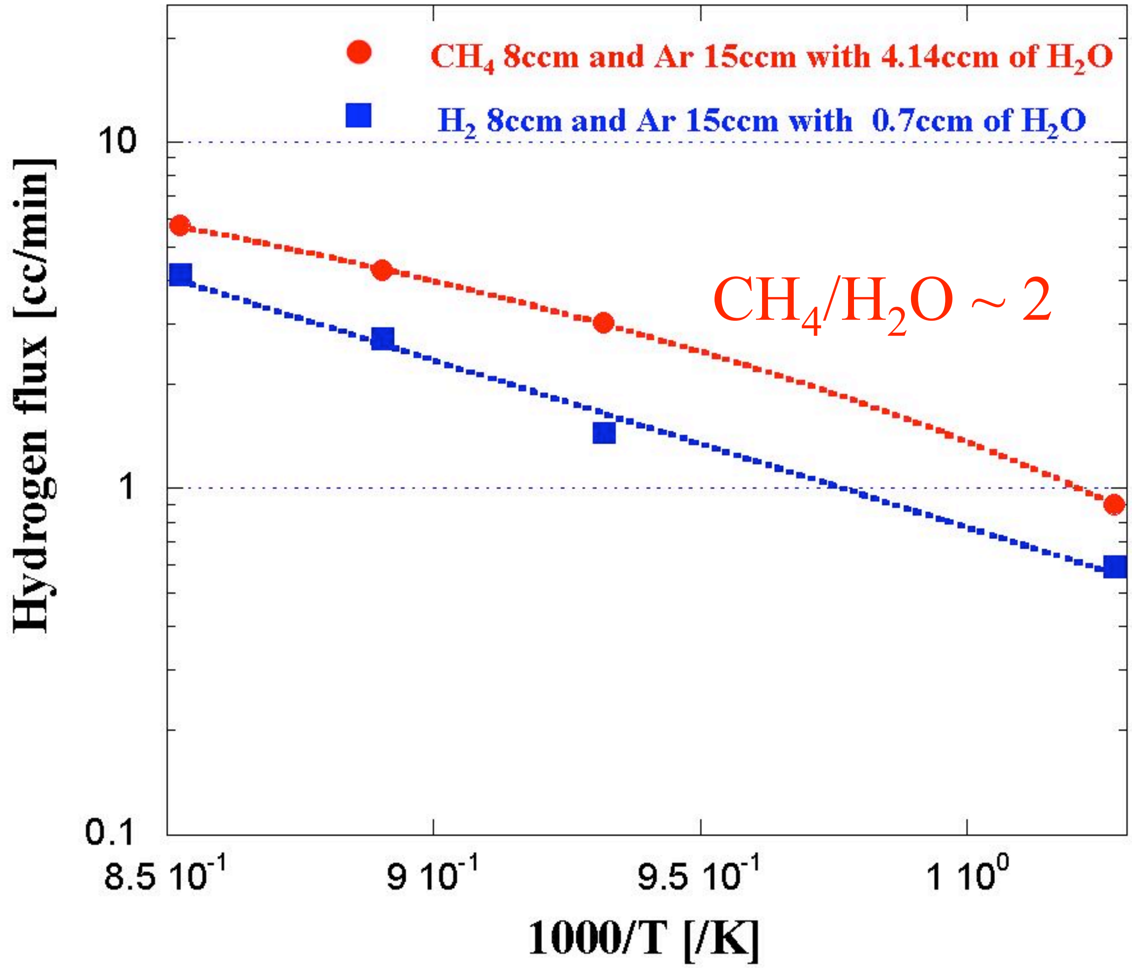
● H_2 balance He / $SrCe_{0.95}Tm_{0.05}O_3$ / 20% O_2 balance He

[1] S. Cheng, V. K. Gupta, and J. Y. S. Lin, Solid State Ionics **176** (2005) 2653.

■ 4% H_2 -3% H_2O balance He / Ni-$BaCe_{0.8}Y_{0.2}O_3$ / N_2 with 100ppm H_2

[2] C. Zuo, T. H. Lee, S.-J. Song, L. Chen, S. E. Dorris, U. Balachandran, and M. Liu, Electrochem. Solid-State Lett., **8** (2005) J35

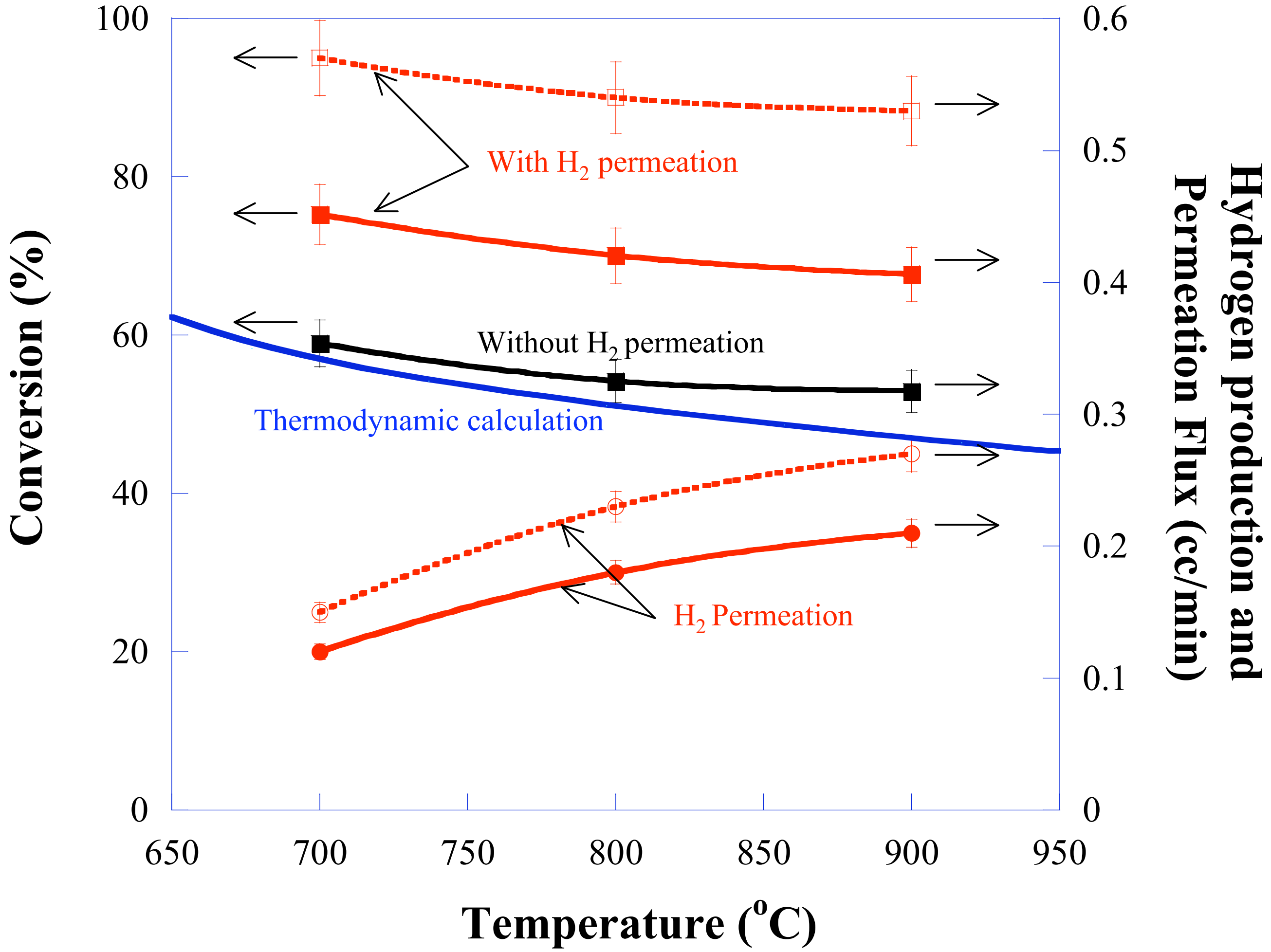
Hydrogen Production



Pure H_2 produced directly by internal steam reforming CH_4

- H_2 flux even higher than from comparable H_2 feed

Hydrogen Production



Water gas shift reaction: $CO + H_2O \rightarrow CO_2 + H_2$

- 3% CO and H_2O balance He
- Solid lines are $H_2O/CO=1$, dashed lines are $H_2O/CO\approx2$

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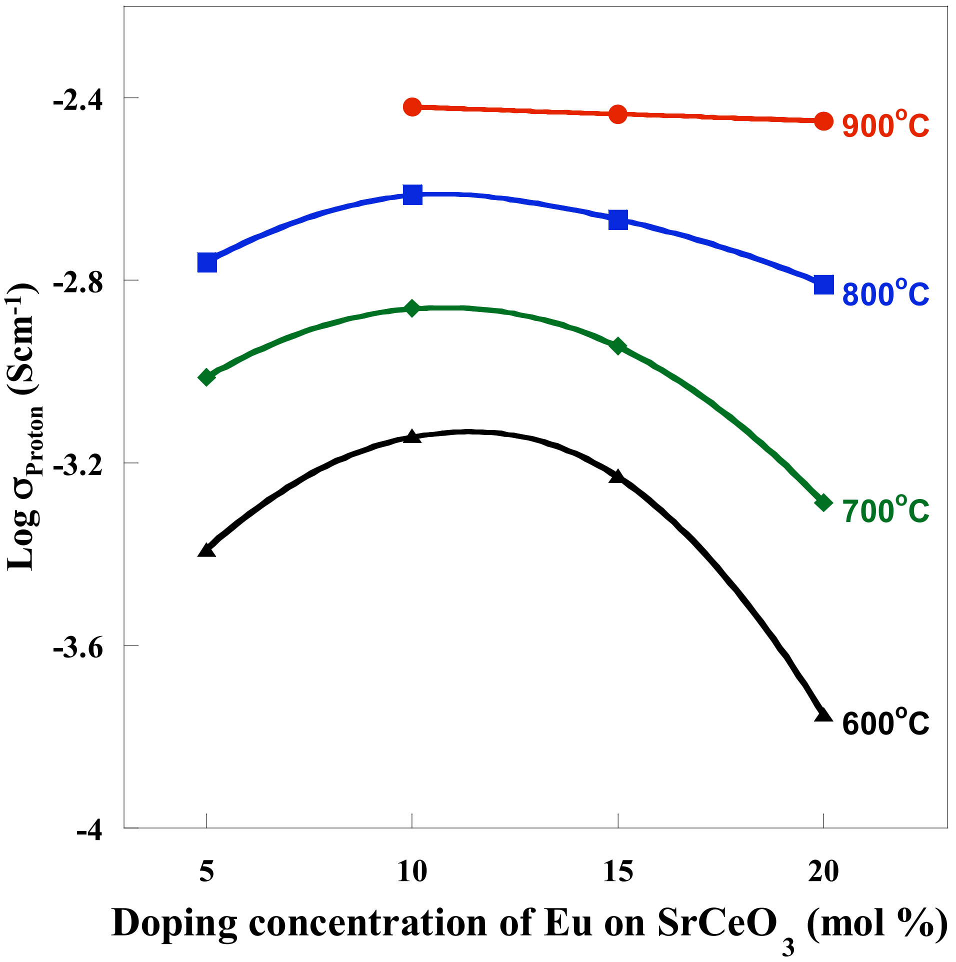
Conductivity of Eu-doped $SrCeO_3$



Activation Energy

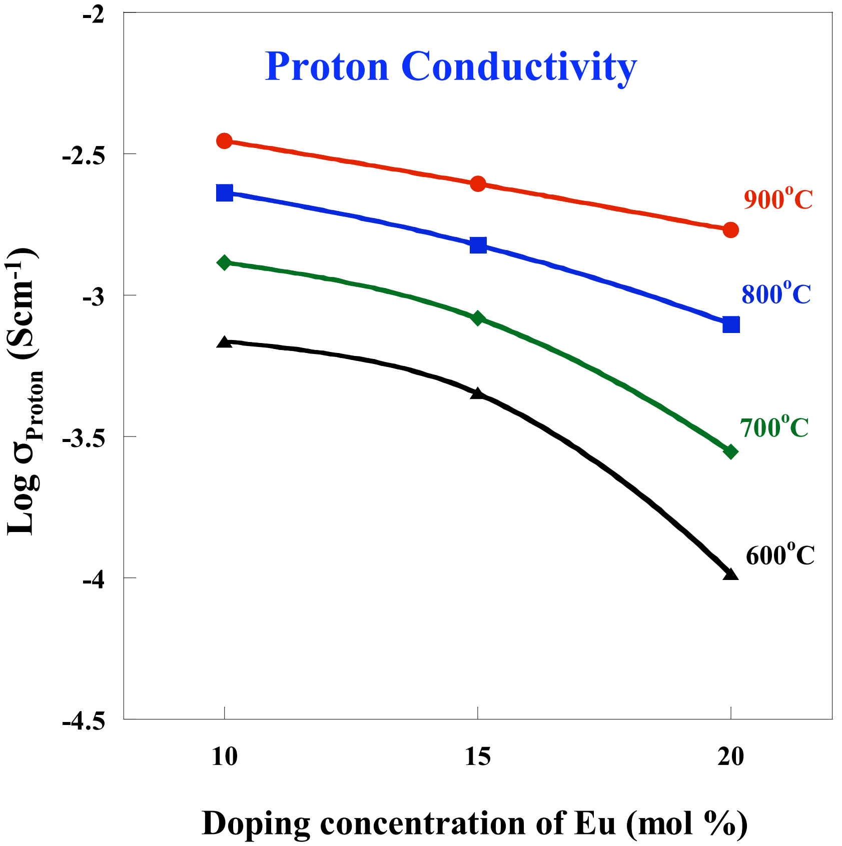
10 mol% 0.49 eV

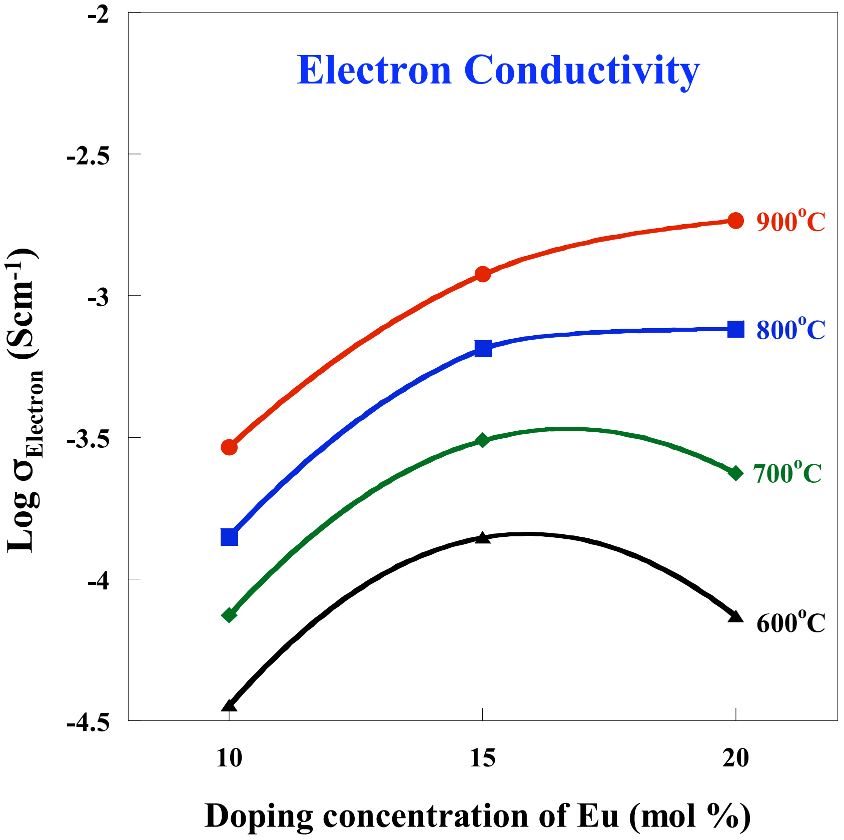
15 mol% 0.52 eV

20 mol% 0.87 eV

Total conductivity maximum at ~10% Eu

Proton vs. Electron Conductivity



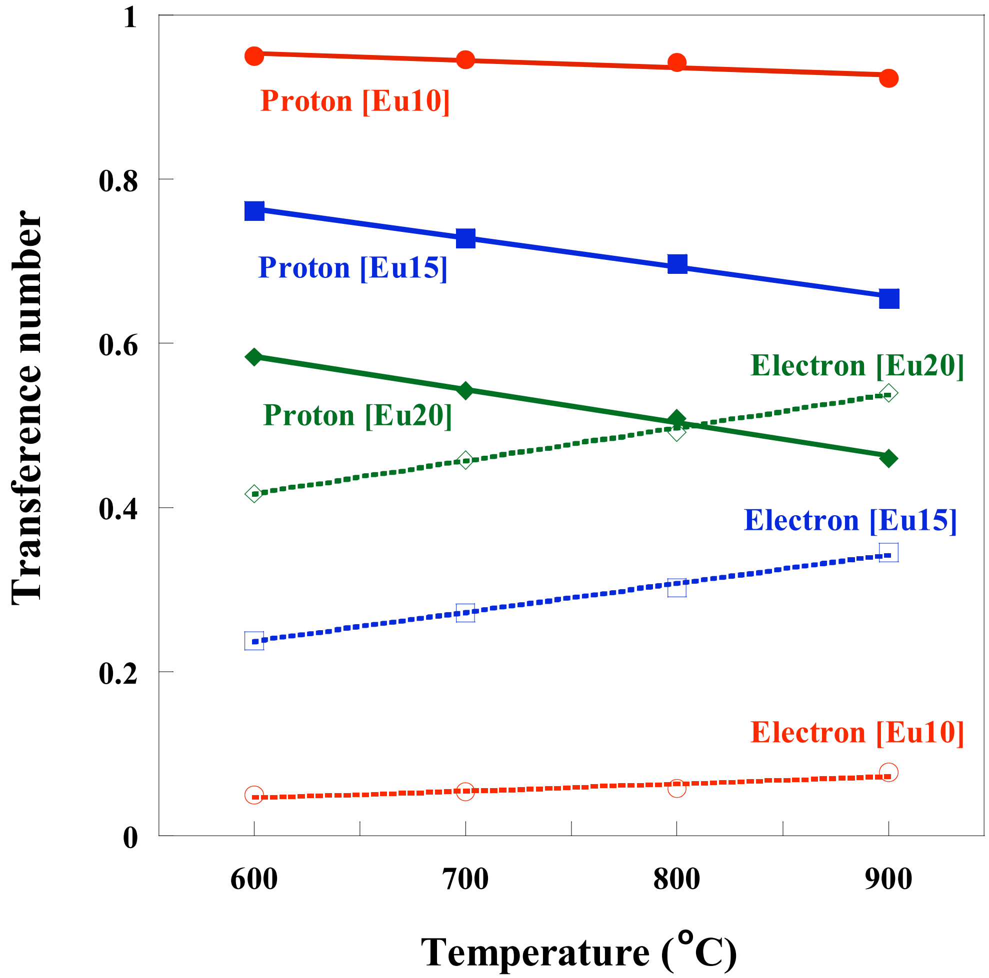


Increasing Eu concentration:

- Decreases $\sigma_{OH^{\bullet}}$
- Increases $\sigma_{e'}$

UF-DOE HiTEC

Increased Electronic Transference Number



$$t_{OH_O^\bullet} = \frac{\sigma_{OH_O^\bullet}}{\sigma_{OH_O^\bullet} + \sigma_{e'}}$$

$$t_{e'} = \frac{\sigma_{e'}}{\sigma_{OH_O^\bullet} + \sigma_{e'}}$$

H_2 flux limited by electronic conductivity

Conclusions

- High temperature protonic conductors offer tremendous potential for H_2 production
- Adding electronic conductivity significantly increases H_2 flux
- Demonstrated H_2 permeation flux of ~10 cc/min
  - H_2 flux is proportional to $[P_{H2}]^{1/4}$
  - H_2 flux is limited by electronic conduction
- Demonstrated *pure* H_2 production from internal steam reformed CH_4
- Demonstrated *pure* H_2 production from water-gas-shift reaction
  - Increased H_2 production of membrane reactor - *La Chatlier*
- Increasing Eu-dopant concentration will significantly increase H_2 permeation and production
  - Demonstrated >10X increase in t_e
  - Should result in 6 liter/hr H_2 production per tube

Acknowledgements

NASA Contract NAG3-2930
DOE HiTEC Contract DE-AC05-76RL01830

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Hydrogen Production, Transport, and Storage 2

Symposium B4

The Electrochemical Society

Chicago, May 6-11, 2007

Abstracts should be submitted via the ECS website by January 3, 2007.

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