Mixed Protonic/ Electronic Conductors: SSAS and DAFC Applications

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Presentation Outline

- Review of ongoing work at the CFCC
- Mixed Protonic / Electronic Conductors (MPECs)
- Applications for MPECs / Ceramatec SBIR
- Regenerative Fuel Cells (RFCs)
  - General Characteristics
  - Application to ammonia systems
- Characteristics of MPEC or composite electrodes
  - Protonic mobility
  - Electronic conductivity
  - Catalytic activity

Work at the CFCC

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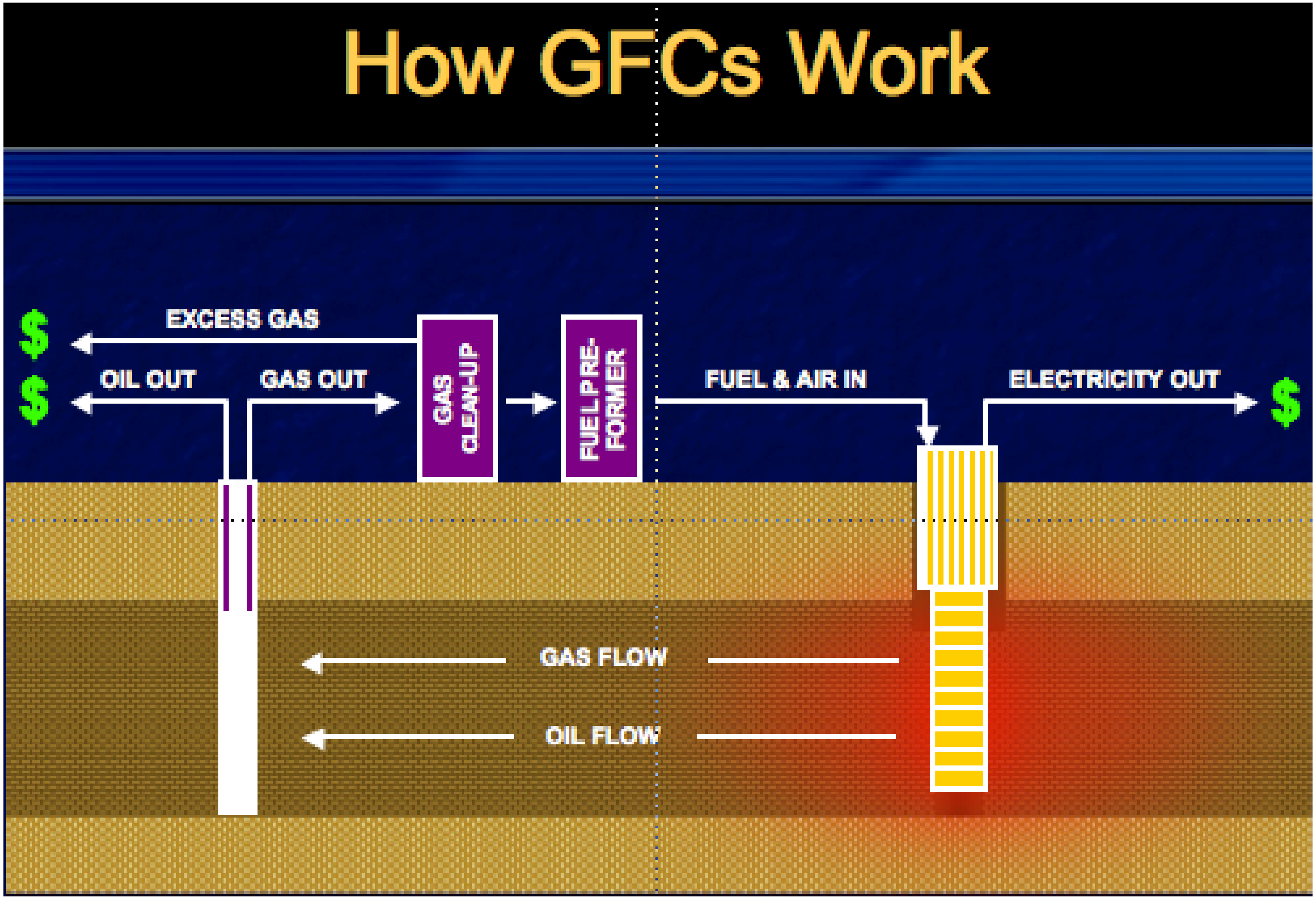
- **Ceramic fuel cell development**
  - Focus on intermediate temperature (500 – 700°C)
  - Proton-conducting ceramics (perovskites)
  - Electrode development (fuel cell cathodes: air electrodes)
  - Rapid prototyping of fuel cells: cold, uniaxial pressing of electrode-supported button cells, dip-coating of electrolytes
  - Geothermal fuel cell!
- **High temperature ceramic membranes**
  - Hydrogen pumping
  - Hydrogen permeation

Geothermal Fuel Cell



Independent Energy Partners

H_2 Pumps vs. H_2 Membranes

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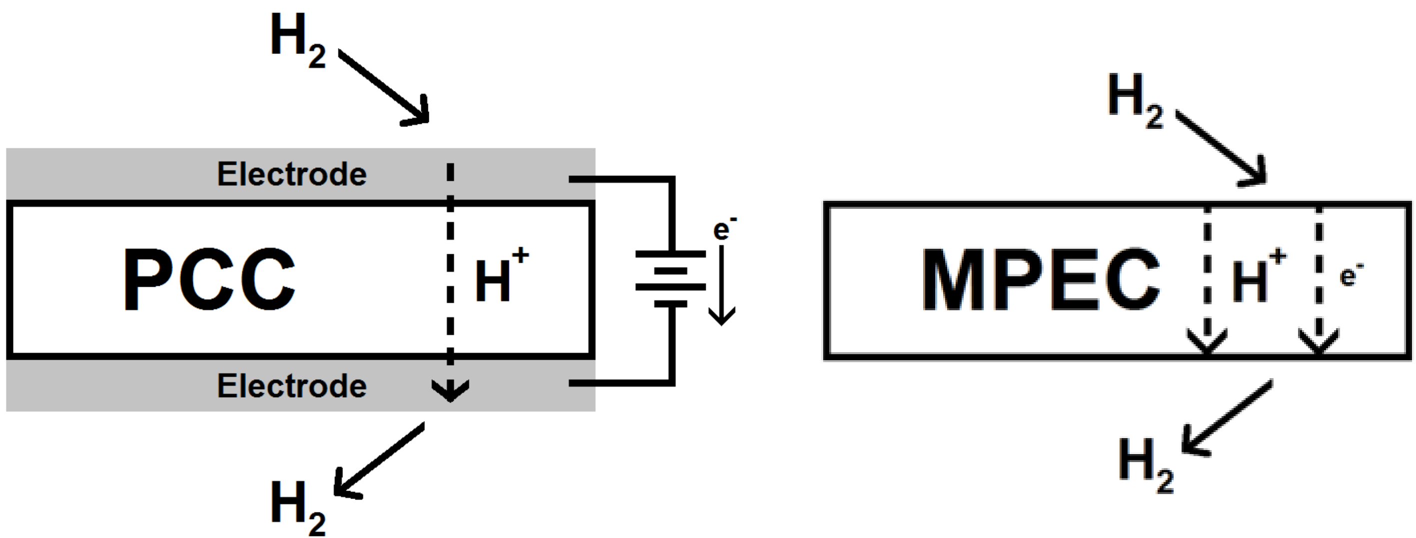
- Pumps: proton-conducting ceramics (PCCs), electrical insulators
- Membranes: use ceramics that conduct both H^+ and e^-
  - Mixed protonic / electronic conductors (MPECs)
  - No external power req'd; pressure/conc. driving force
  - No electrodes



A Bit More About MPECs

- Subset of mixed ionic/electronic conductors (MIECs)
- If used alone, restricted to membrane apps
  - Where the ions go, the electrons go
  - Can't produce or consume electrical work
  - Rely on pressure and concentration potentials to operate
- Very useful for integrated electrochemical systems!
  - Fuel cell or electrolytic cell electrode components
  - Protective layers for protonic electrolytes
- Functionality depends on application environment
  - Reducing or oxidizing? Temperature?
  - Surroundings can change nature of ion/elec. conduction

CFCC Pitches In: Ceramatec

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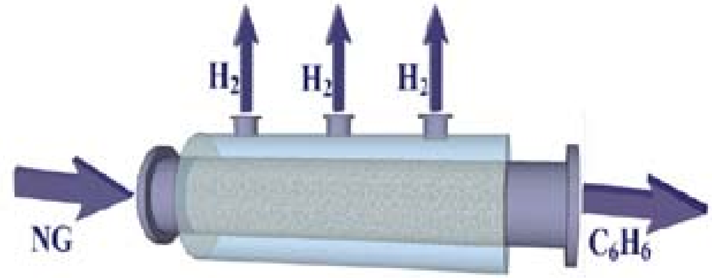
- Phase 1 SBIR: ARPA-E
  - "One-step" natural gas to chemicals process
  - Hydrogen produced as side product, need to shift equilibrium



$$2CH_4 \rightarrow C_2H_4 + 2H_2$$

$$6CH_4 \rightarrow C_6H_6 + 9H_2$$

- CFCC testing MPEC membranes for H_2 flux from "model gas"
  - Composite ceramic – combined MPEC
    - $BaCe_{0.8}Y_{0.2}O_{3-\delta}$ (a.k.a. BCY, is a PCC)
    - $Ce_{0.8}Y_{0.2}O_{2-\delta}$ (a.k.a. YDC, is an EC)
  - Goal: 0.3 μmol cm^{-2} s^{-1} H_2 flux
  - Coking issues, high mech. failure rate, thermal cycling problems

CERAMATEC® TOMORROW'S CERAMIC SYSTEMS

CFCC Electrode Modification

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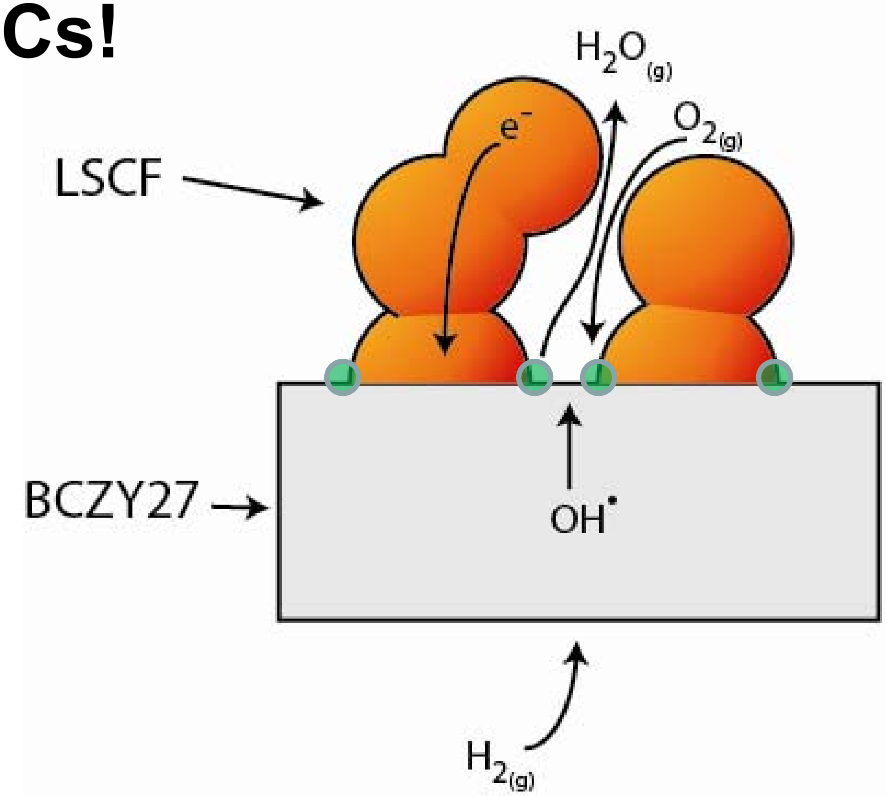
- $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF):common cathode for SOFCs. Also a MIEC (oxide ion / electron)
- Great for SOFCs
- Not good for PCC-based FCs!
- Water may form only at TPBs



Proton-conducting Backbone

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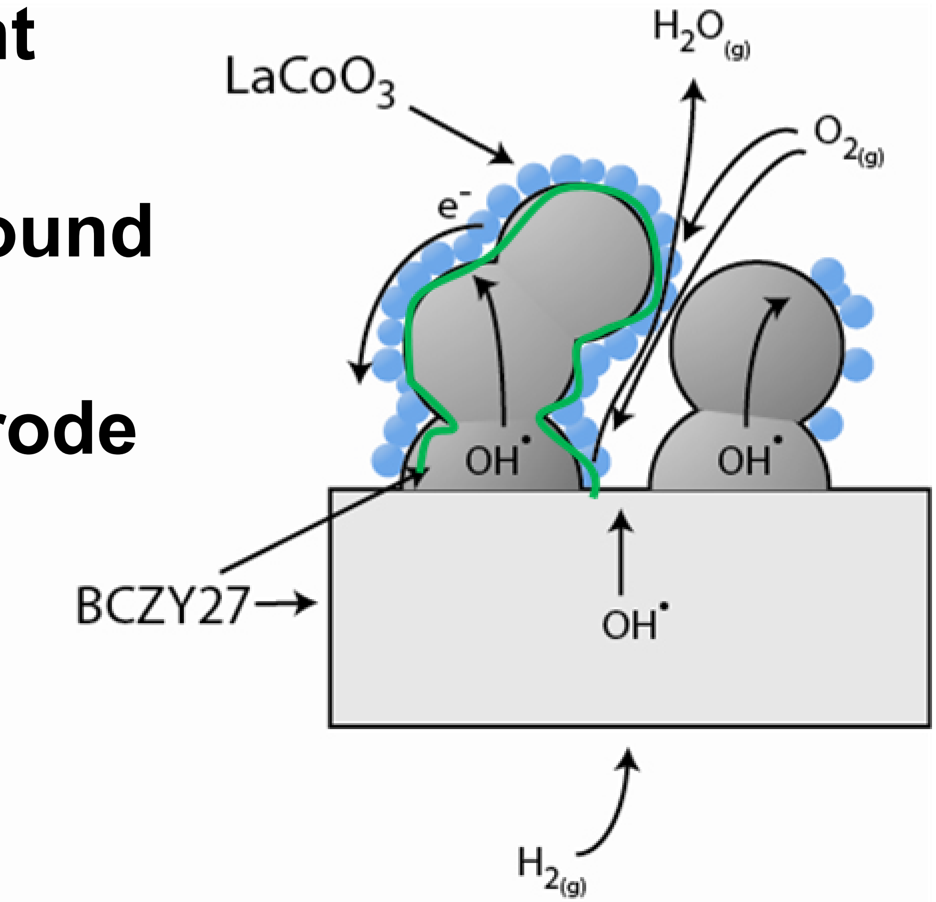
- Improvement: now protons get to more surfaces
- Comparable to finned heat exchanger enhancement
- Electrons still require a continuous pathway around the outside…
- Another problem: electrode structure is fragile



MPEC to the Rescue?

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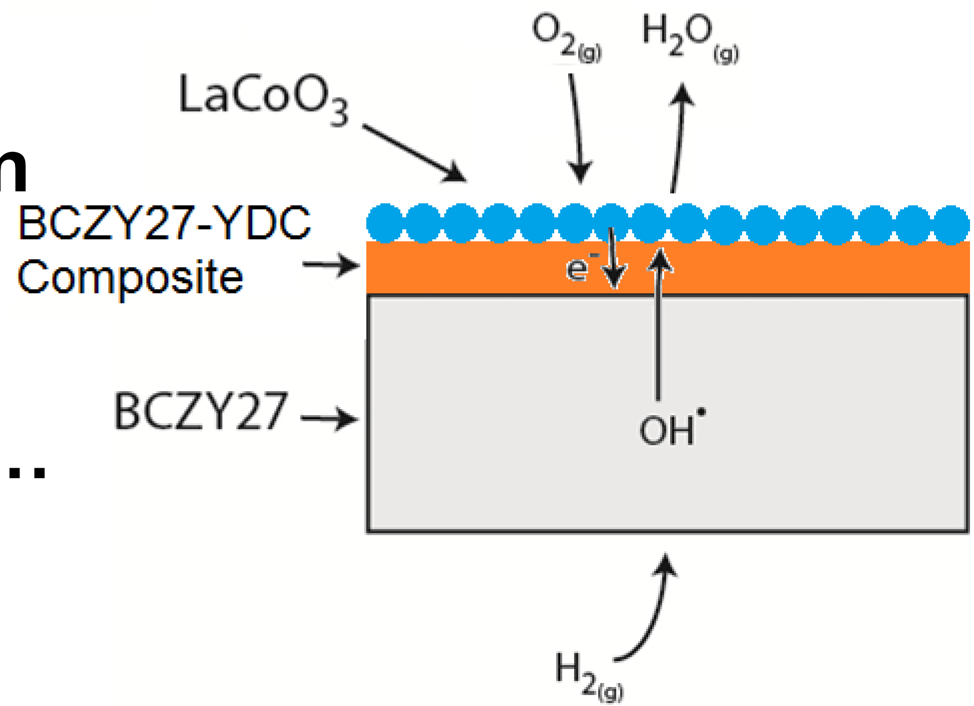
- Improvement: a porous MPEC interlayer
- Electrons and protons get where they need to go!
  - Gas (O_2 or steam) can get in/out of porous layer
  - $LaCoO_3$ may be layered, or impregnated throughout MPEC layer
- YDC demonstrates electronic conduction in reducing environments
- What about oxidizing environments? Hmmm…



Regenerative Fuel Cells (RFCs)

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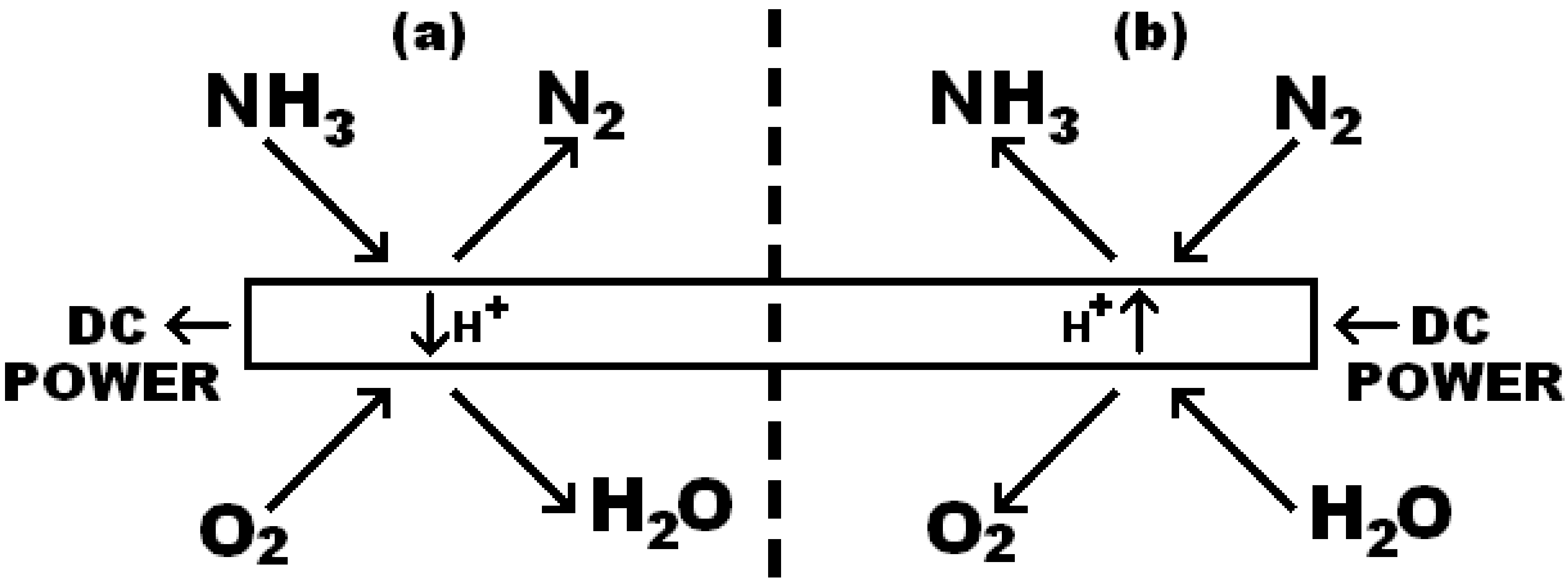
A fuel cell that may be run in electrolytic mode – generating fuel when power is provided.

Ammonia RFC



PCC membrane operating in (a) fuel cell and (b) fuel synthesis modes.

Oxidizing or Reducing?

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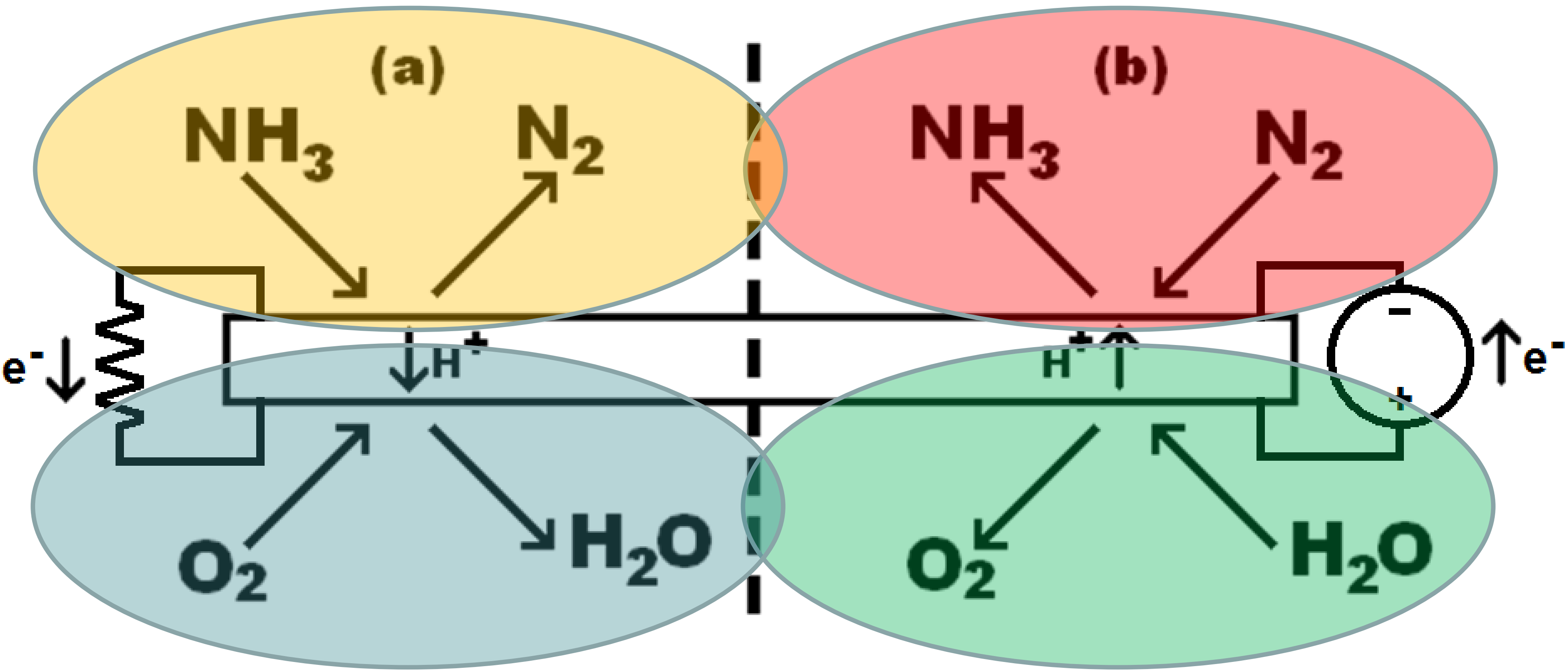

Chemically oxidizing + negative polarization =

Chemically reducing + positive polarization =

STRONGLY OXIDIZING ENVIRONMENT.

STRONGLY REDUCING ENVIRONMENT.

This all changes by changing the conductor!

Reducing Environments

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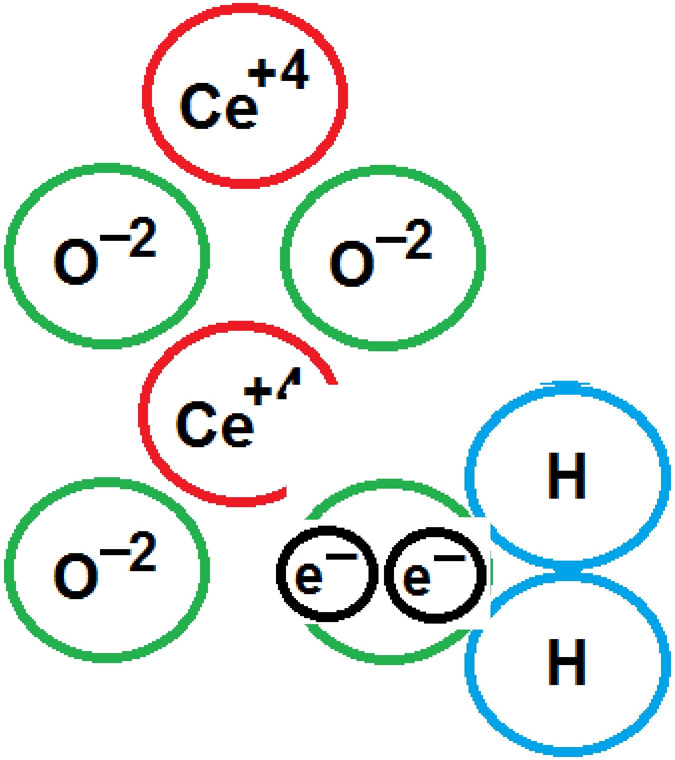
- Why do they allow MPEC behavior?
  - Ce^{+4} (dominates YDC20) reduced to Ce^{+3}
  - Oxygen vacancy and stranded lattice electron created
  - Acts as n-type conductor



New oxygen vacancy (w/H_2O) assists with proton conduction, lattice electron assists with electronic conduction.

Oxidizing Environments

- These are a little different
  - Oxygen vacancies already exist: Y^{+3} in place of Ce^{+4}
  - Oxide ions are therefore free to hop through the lattice
- Porous layer of PCC/YDC? H^{+}, O^{-2} make water at point of contact, water escapes.
- But this doesn’t help with electronic conductivity. Or does it?

Electronic Conduction in YDC

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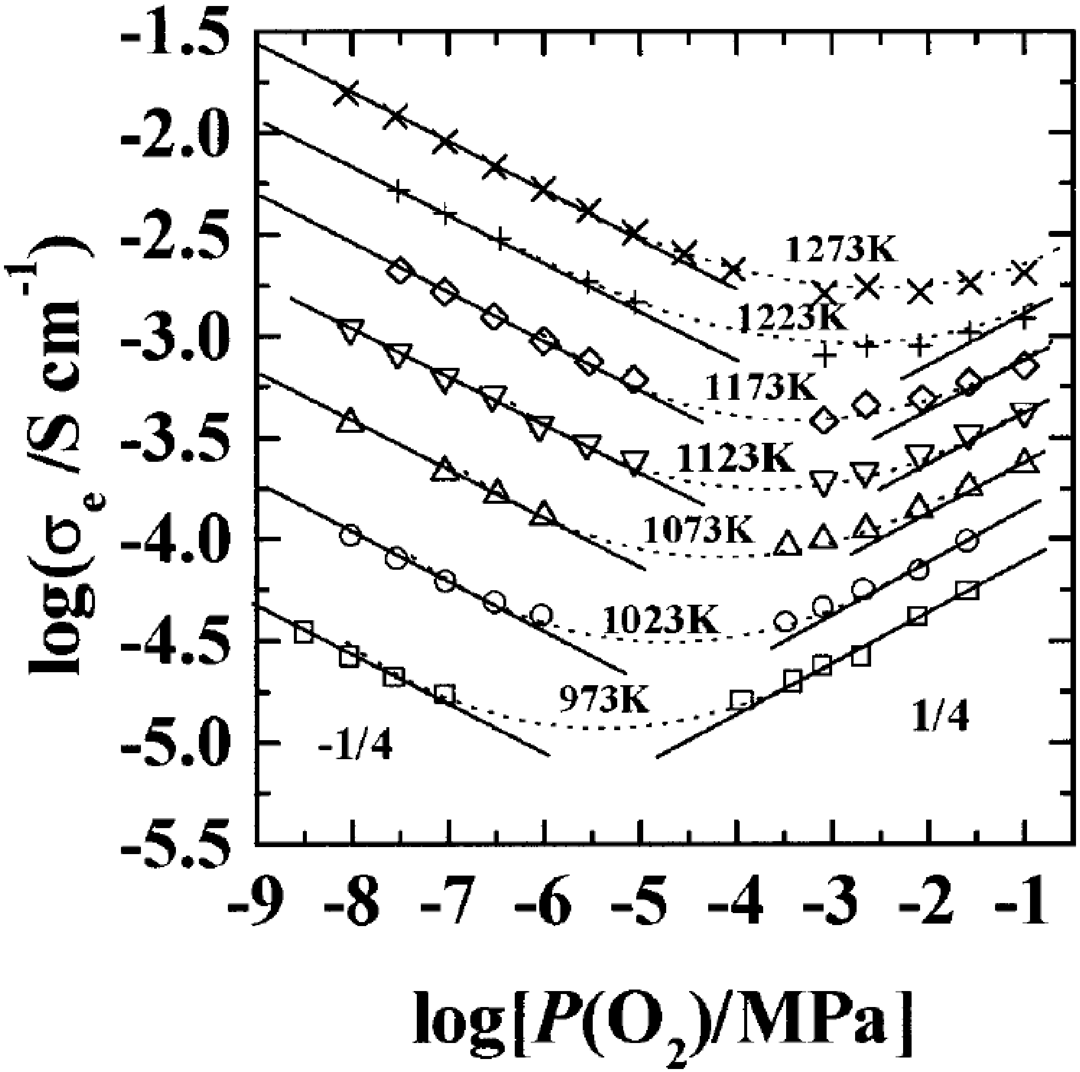

This study observes hole (p-type) conduction at high oxygen partial pressure… and holes are part of the protonic fuel cell process.

Xiong, et al. *J. Electrochem. Soc.*, **149** (11) E450-E454 (2002).

Oxygen Vacancy Competition

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- Two oxygen vacancy reactions for oxidizing env.
- Electrolytic and fuel cell modes each have O_2 / H_2O at same electrode in a protonic cell
  - Water makes protonic defects
  - Oxygen creates holes

$$H_2O + V_O^{\bullet\bullet} + O_O^{\times} = 2OH_O^{\bullet}$$

$$\frac{1}{2}O_2 + V_O^{\bullet\bullet} = O_O^{\times} + 2h^{\bullet}$$

- Incorporated oxygen atoms are opposed in these reactions…
- Can tailor MPEC for environment, temperature, and cell function

The Bottom Line

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- **In oxidizing environments, YDC isn't a great idea**
  - **P-type electrical conduction, but…**
  - **Ionic conduction dominated by hole conduction**
- **A better idea: dope proton conductors with multivalent (+2/+3) cations**

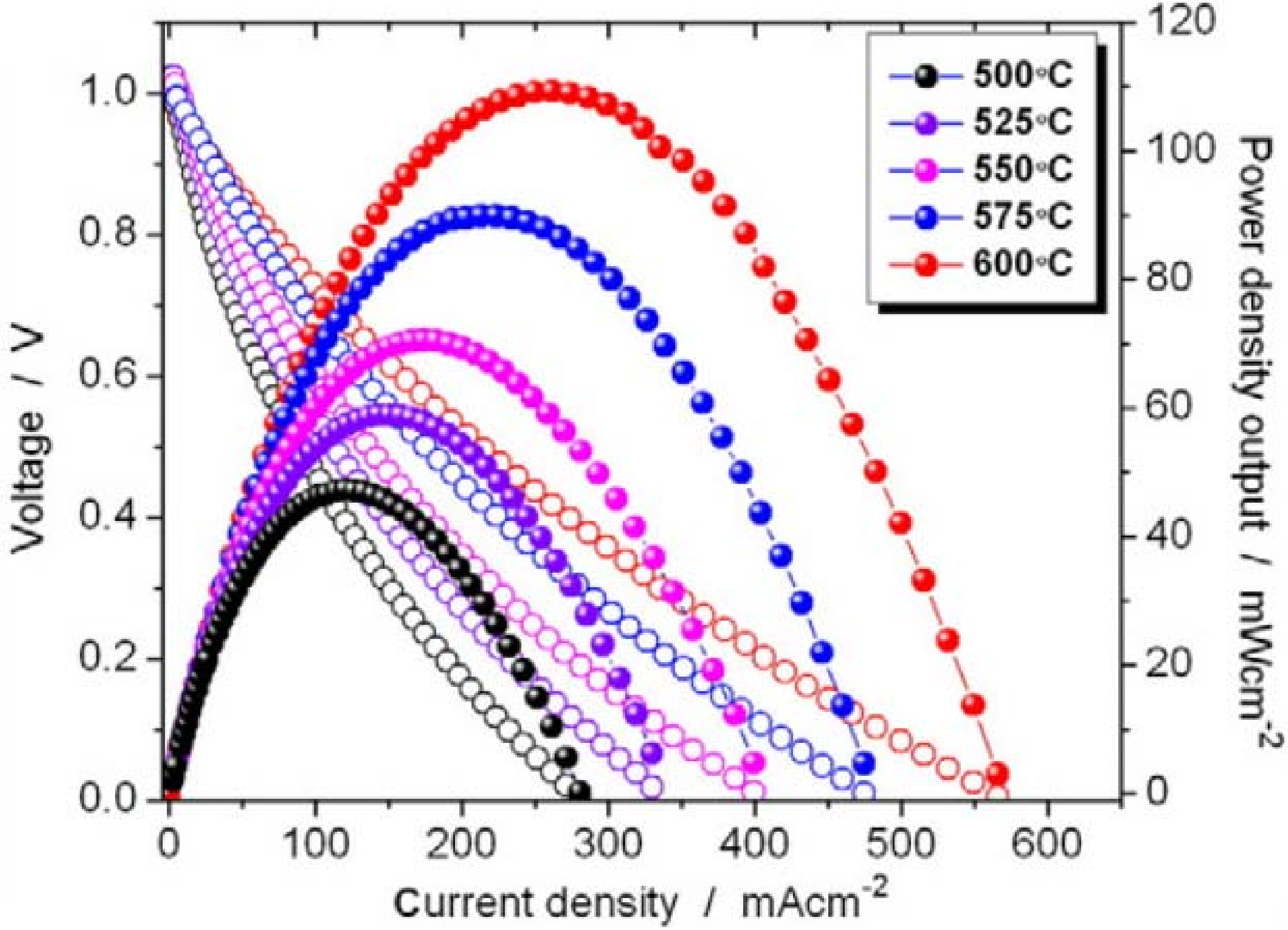
$BaCe_{0.9}Yb_{0.1}O_{3-\delta}$ $BaCe_{0.9}Co_{0.1}O_{3-\delta}$

$BaCe_{0.9}Eu_{0.1}O_{3-\delta}$ $BaCe_{0.9}Ni_{0.1}O_{3-\delta}$

$BaCe_{0.9}Sm_{0.1}O_{3-\delta}$ $BaCe_{0.9}Fe_{0.1}O_{3-\delta}$

Or, mix +3 cations with different ionization energies (In, Pr, Bi, Gd).

Some Promise: BCYb



Pergolesi, et al. *EChem. Comm.*, **12** (7) 977-980 (2010).

Composite Electrode, or MPEC?

- Composite: separate ionic and electronic phases
  - Pathways can be tortuous, or dead-ends!
  - Will there be interphase chemical interaction?
  - Differences in thermal expansion?
- Unified MPEC drawbacks exist
  - Better at either ion or electron/hole conduction
  - Electron or hole conduction is never “great”
  - Almost zero electrocatalytic activity
- If MPECs are used, must:
  - Be in thin layers
  - Be capable of catalyst support

CFCC Plans

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- Move on after Ceramatec project
- Electrode-supported button cell tests
  - Thin electrolytes
  - Special focus on fuel cell cathodes
  - Steam electrolysis tests
  - Catalyst screening (La_2NiO_4, $LaCoO_3$, etc.)
- Demonstrate cell reversibility (H_2, O_2 / H_2O)
- Ammonia as fuel, SSAS with addition of N_2 in electrolytic mode
- Cell temperatures of 500 – 700°C, atmospheric pressure tests

Questions?

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