Mixed Protonic/ Electronic Conductors: SSAS and DAFC Applications

Jason Ganley, Ted Olszanski, and Neal Sullivan
24 September 2013
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

• 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

How GFCs Work

EXCESS GAS
$ $
OIL OUT 
GAS OUT
GAS CLEAN-UP
FUEL PRE-FORMER
FUEL & AIR IN
ELECTRICITY OUT
$ $

GAS FLOW
OIL FLOW

Independent Energy Partners

Colorado Fuel Cell Center
H₂ Pumps vs. H₂ Membranes

- **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

- Phase 1 SBIR: ARPA-E
  - “One-step” natural gas to chemicals process
  - Hydrogen produced as side product, need to shift equilibrium
- CFCC testing MPEC membranes for H₂ flux from “model gas”
  - Composite ceramic – combined MPEC
    - BaCe₀.₈Y₀.₂O₃-δ (a.k.a. BCY, is a PCC)
    - Ce₀.₈Y₀.₂O₂-δ (a.k.a. YDC, is an EC)
  - Goal: 0.3 µmol cm⁻² s⁻¹ H₂ flux
  - Coking issues, high mech. failure rate, thermal cycling problems
CFCC Electrode Modification

- $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (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
• 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?

• Improvement: a porous MPEC interlayer
• Electrons and protons get where they need to go!
  – Gas (O₂ or steam) can get in/out of porous layer
  – LaCoO₃ may be layered, or impregnated throughout MPEC layer
• YDC demonstrates electronic conduction in reducing environments
• What about oxidizing environments? Hmmmm…
Regenerative Fuel Cells (RFCs)

A fuel cell that may be run in electrolytic mode – generating fuel when power is provided.
PCC membrane operating in (a) fuel cell and (b) fuel synthesis modes.
Oxidizing or Reducing?

Chemically oxidizing + positive polarization = STRONGLY OXIDIZING ENVIRONMENT.

Chemically reducing + negative polarization = STRONGLY REDUCING ENVIRONMENT.

Chemically oxidizing + spent electrons = OXIDIZING ENVIRONMENT.

Chemically reducing + electrons from fuel = REDUCING ENVIRONMENT.

This all changes if you switch to an oxide ion conductor!
Reducing Environments

• 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$_2$O) 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?
This study observes hole (p-type) conduction at high oxygen partial pressure... and holes are part of the protons fuel cell process.

Oxygen Vacancy Competition

- Two oxygen vacancy reactions for oxidizing env.
- Electrolytic and fuel cell modes each have \( \text{O}_2 / \text{H}_2\text{O} \) at same electrode in a protonic cell
  - Water makes protonic defects
  - Oxygen creates holes

\[
\text{H}_2\text{O} + \text{V}_\text{O}^{\bullet\bullet} + \text{O}_\text{O}^\times = 2\text{OH}_\text{O}^\bullet
\]

\[
\frac{1}{2}\text{O}_2 + \text{V}_\text{O}^{\bullet\bullet} = \text{O}_\text{O}^\times + 2\text{h}^\bullet
\]

- Incorporated oxygen atoms are opposed in these reactions...
- Can tailor MPEC for environment, temperature, and cell function
The Bottom Line

• 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

\[ \text{BaCe}_{0.9}\text{Yb}_{0.1}\text{O}_{3-\delta} \quad \text{BaCe}_{0.9}\text{Co}_{0.1}\text{O}_{3-\delta} \]
\[ \text{BaCe}_{0.9}\text{Eu}_{0.1}\text{O}_{3-\delta} \quad \text{BaCe}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta} \]
\[ \text{BaCe}_{0.9}\text{Sm}_{0.1}\text{O}_{3-\delta} \quad \text{BaCe}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta} \]

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

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

• Move on after Ceramatec project
• Electrode-supported button cell tests
  – Thin electrolytes
  – Special focus on fuel cell cathodes
  – Steam electrolysis tests
  – Catalyst screening (La$_2$NiO$_4$, LaCoO$_3$, etc.)
• Demonstrate cell reversibility (H$_2$, O$_2$ / H$_2$O)
• Ammonia as fuel, SSAS with addition of N$_2$ in electrolytic mode
• Cell temperatures of 500 – 700°C, atmospheric pressure tests
Questions?

Jason C. Ganley
Colorado School of Mines
Dept. of Chemical & Biological Engineering
1613 Illinois Street, AH 155
Golden, CO 80401
(303) 384-2163
jganley@mines.edu