

Materials for SPFCs to be or not to be protonic.

Nikolaos Bonanos

Fuel Cells & Solid State Chemistry Dept.
Risø, Technical University of Denmark,
P.O. Box 49, 4000 Roskilde, Denmark.

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nikolaos.bonanos@risoe.dk

Outline of presentation

- Historical background, terminology
- Incentives for high temperature PCFC
- The thermodynamic argument
- Materials, defects, properties
- Case studies and achievements
- Which way to go now

HTPC

OBPC

SOFC

p-SOFC ≡ SPFC

Historical background

Solid state protonic conductors I: Danish-French workshop on solid state materials for low to medium temperature fuel cells and monitors, with emphasis on proton conductors, Paris (FR), 8–11 Dec. 1981. Eds. J. Jensen, and M. Kleitz, Odense (DK), 1982.

H. Iwahara, T. Esaka, H. Uchida & N. Maeda, Proton conduction in sintered oxides and its application to steam electrolysis for hydrogen production. *Solid State Ionics* 3/4 359 (1981).

This morning's speakers entered in the early 1980s.

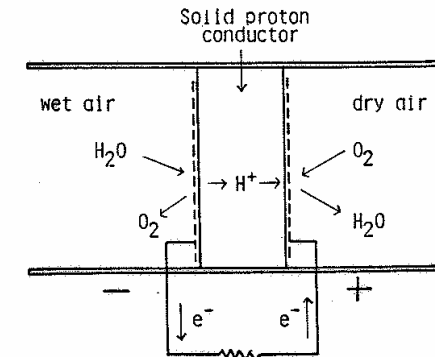


Fig. 1. Concept of steam concentration cell.

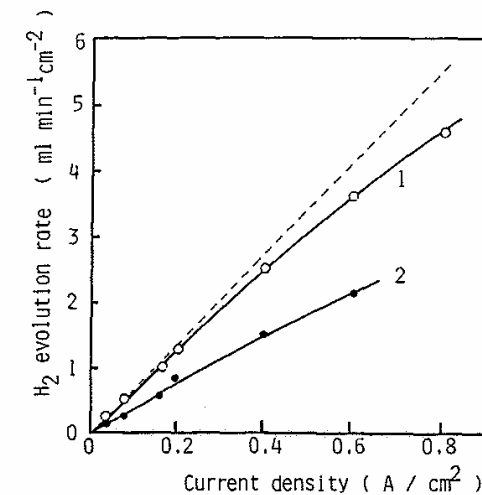
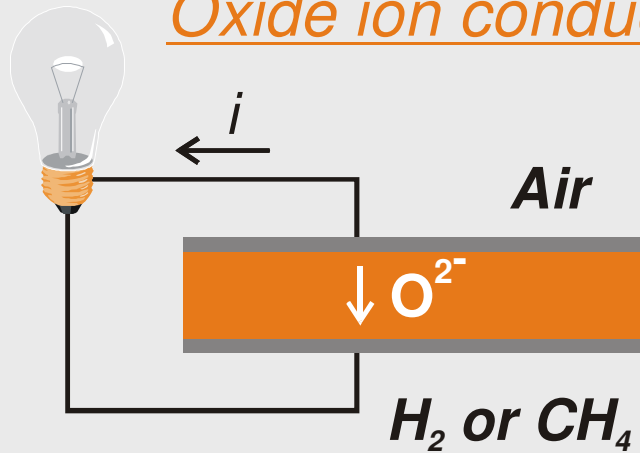


Fig. 4. Hydrogen evolution rate versus current density at 900°C. Electrolyte: (1) $\text{SrCe}_{0.90}\text{Sc}_{0.10}\text{O}_{3-\alpha}$, (2) $\text{SrCe}_{0.95}\text{Sc}_{0.05}\text{O}_{3-\alpha}$ (broken line shows theoretical rate).

Oxide ion conductor



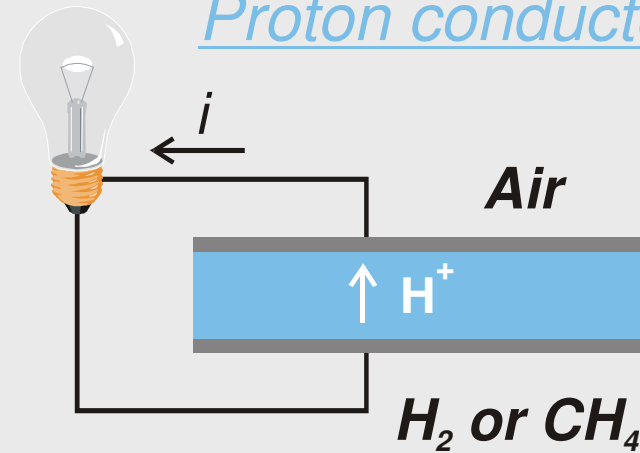
At air electrode:



At fuel electrode:



Proton conductor



At air electrode:



At fuel electrode:



Efficiency incentive when running on hydrogen

H₂ / O₂ cell, irrespective of conduction mechanism, will generate an emf:



$$E = E^0 - \frac{RT}{4F} \ln \left(\frac{P_{\text{H}_2\text{O}}^2}{P_{\text{H}_2}^2 P_{\text{O}_2}} \right)$$

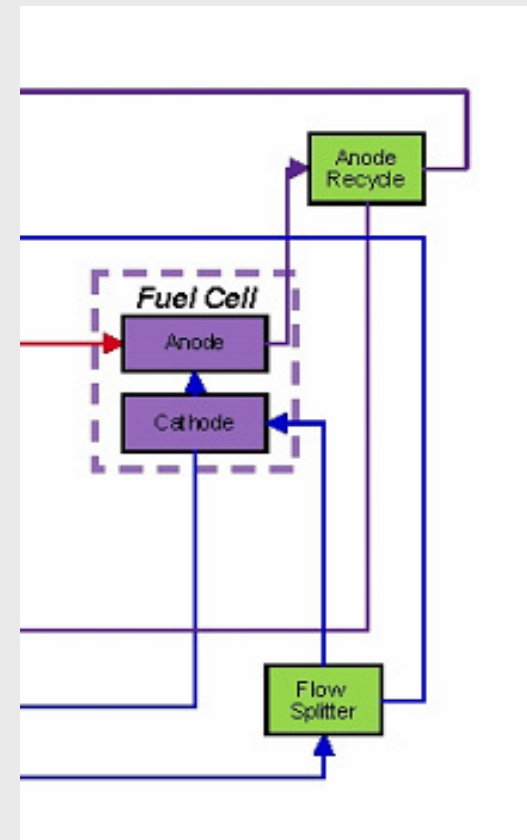
53 mV/decade

106 mV/decade

Ox: steam in H₂ counts

Pr: steam in O₂ counts

Most SOFC systems are envisaged to run with air, supplying oxygen in excess of the reaction stoichiometry, typically by 6 times.



2 (Nernst) × 5 (O₂ in air) × 6 (stoic): it is **60 times** better to evolve the steam in the air compt.

Running on hydrocarbons: reforming reaction

Fuel conditioning (reforming) carried out in reactor, thermally coupled to the fuel cell.



Table 8-2 Typical Steam Reformed Natural Gas Reformate

| Mole Percent | Reformer Effluent | Shifted Reformate |
|------------------|-------------------|-------------------|
| H ₂ | 46.3 | 52.9 |
| CO | 7.1 | 0.5 |
| CO ₂ | 6.4 | 13.1 |
| CH ₄ | 2.4 | 2.4 |
| N ₂ | 0.8 | 0.8 |
| H ₂ O | 37.0 | 30.4 |
| Total | 100.0 | 100.0 |

Source: the Fuel Cell Handbook, 7th edition (2004)

pre-reformer

Schematic SOFC with pre-reformer

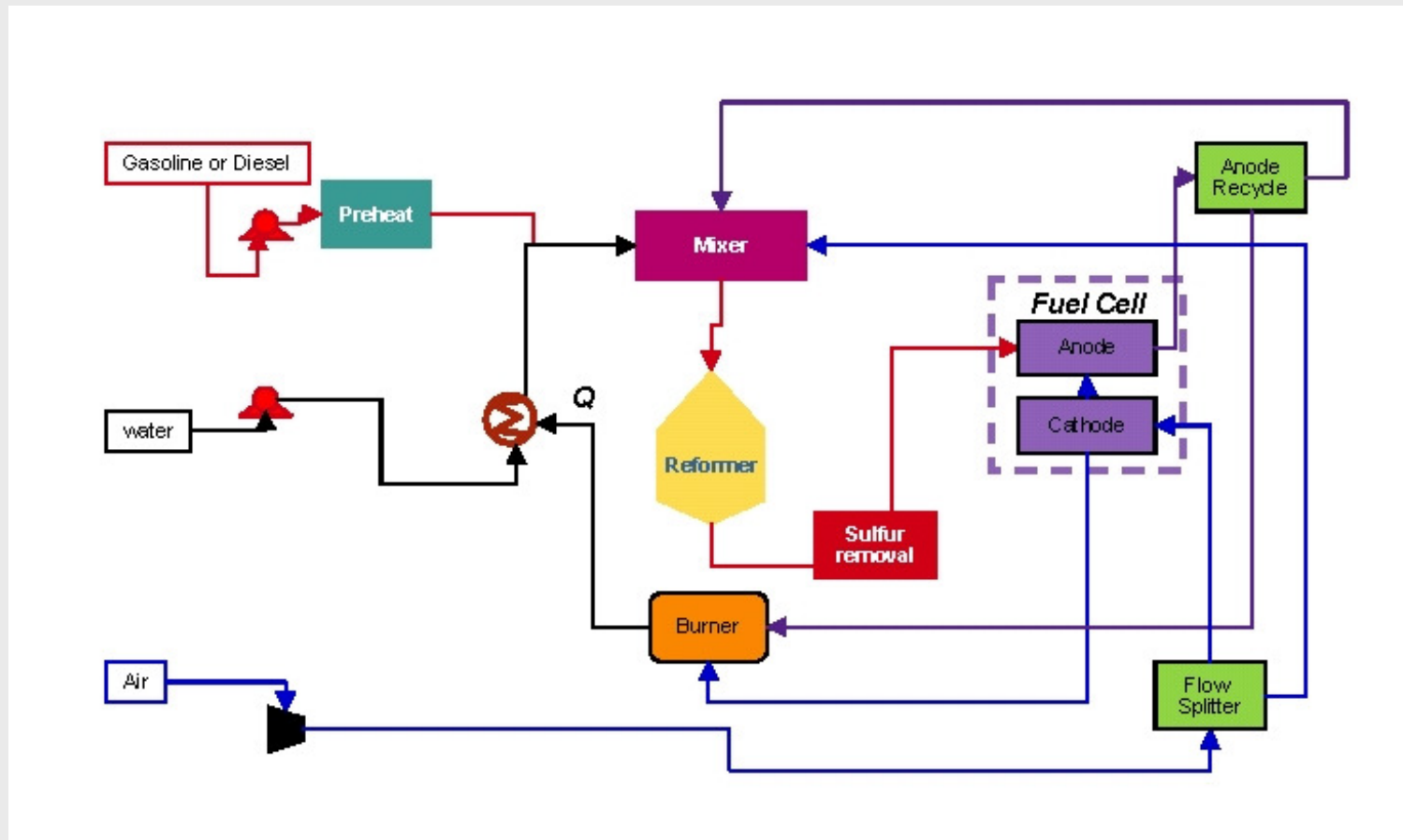
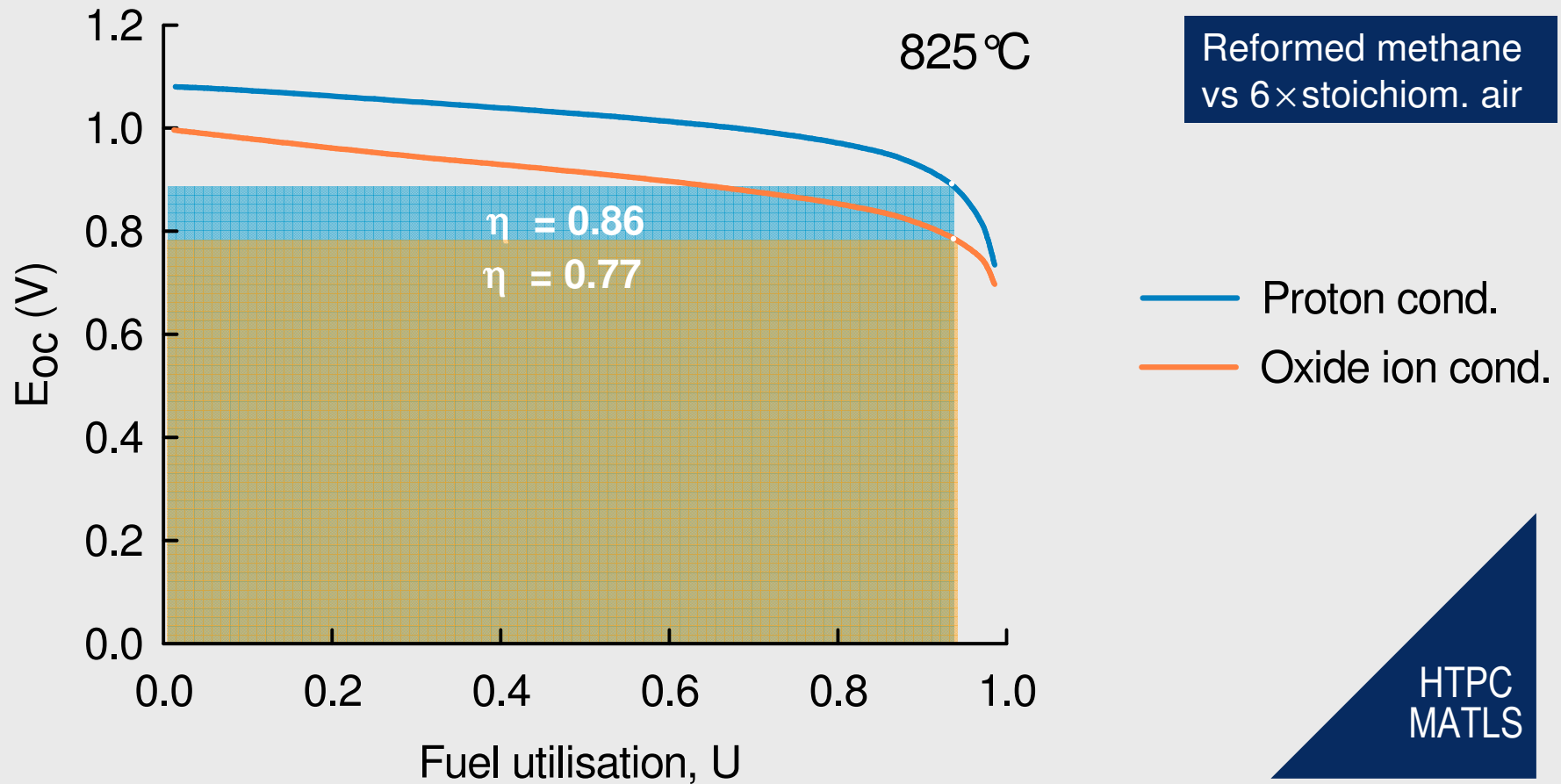


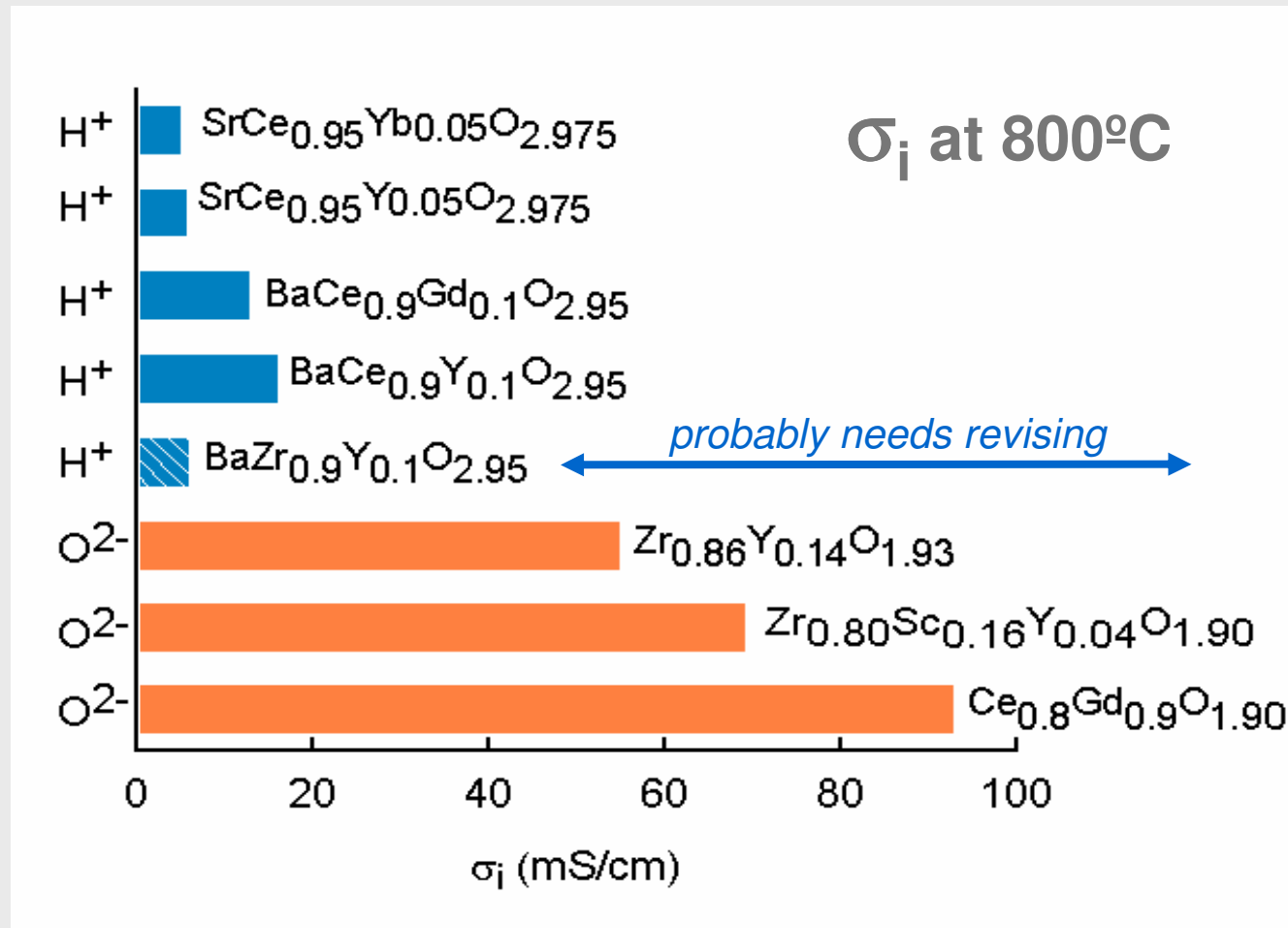
Image obtained from the Fuel Cell Handbook, 7th ed. (2004)

Electrical efficiency: cell run on pre-reformed methane

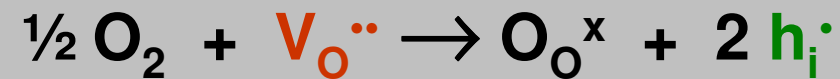


J. Hartvigsen, S. Elangovan & A. Khandkar, AIChE Meeting, St Louis, USA, Aug. 1993.

Typical SEs that have been used for SOFCs & SPFCs



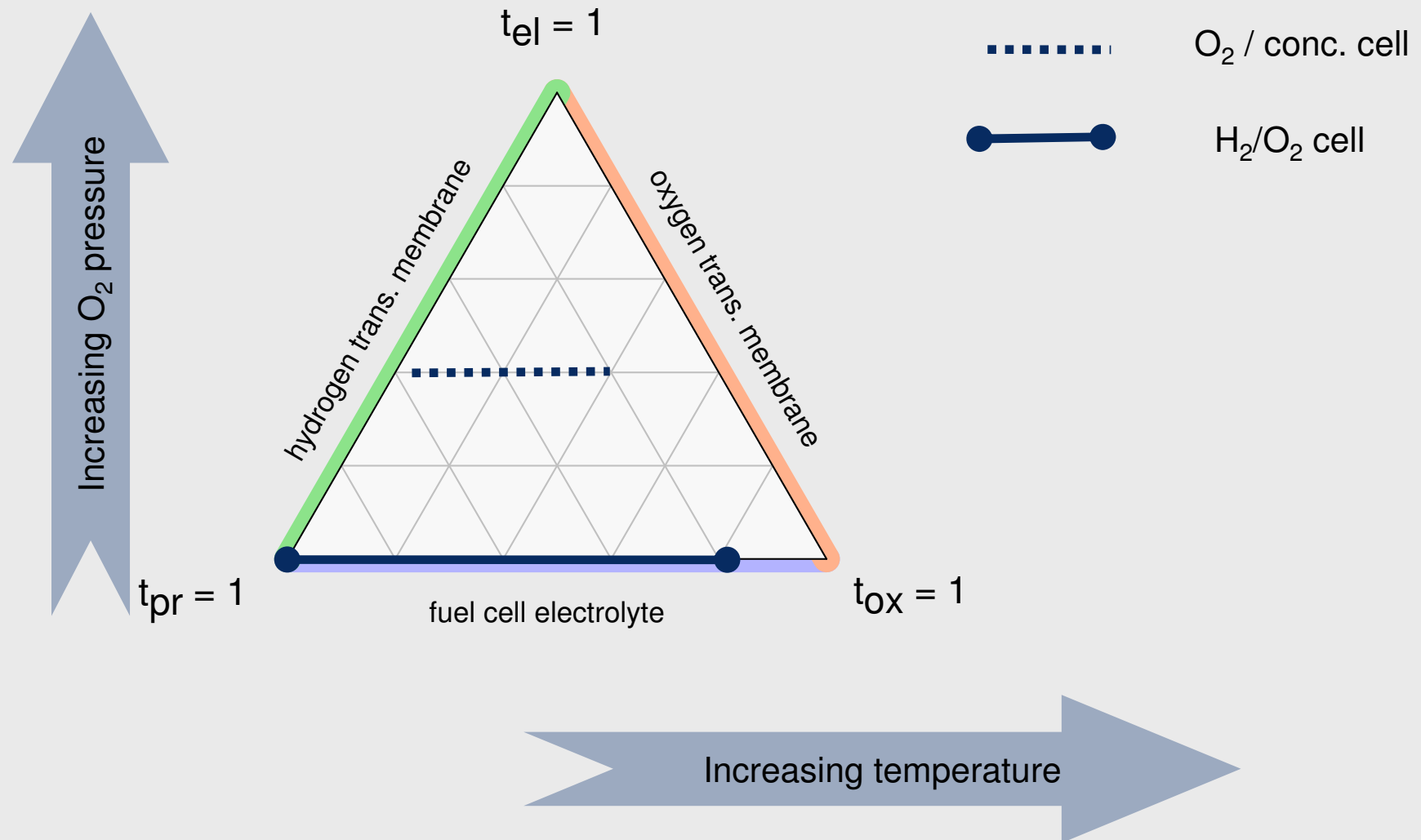
Point defects in high temperature proton conductors



$$2 [V_O^{\bullet\bullet}] + [OH_O^\bullet] + [h_i^\bullet] - [e'] - [M_B'] = 0$$

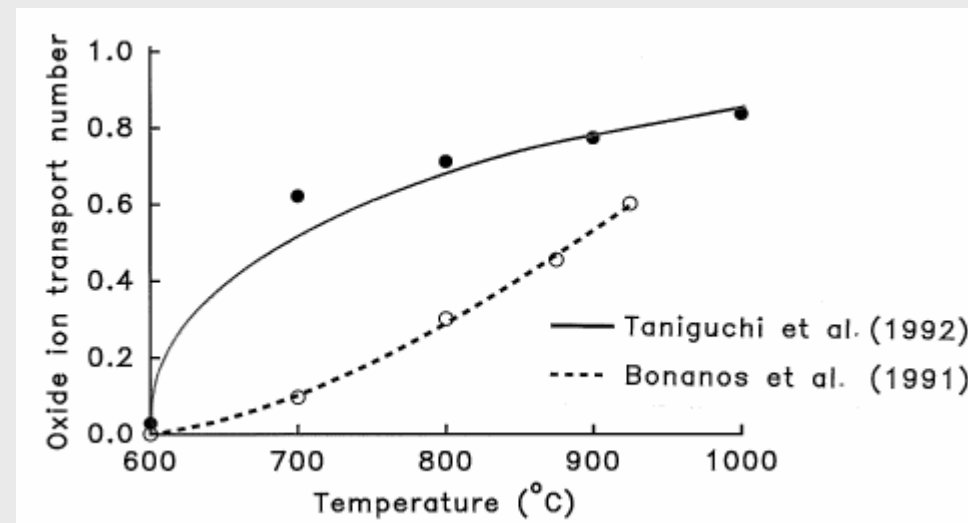
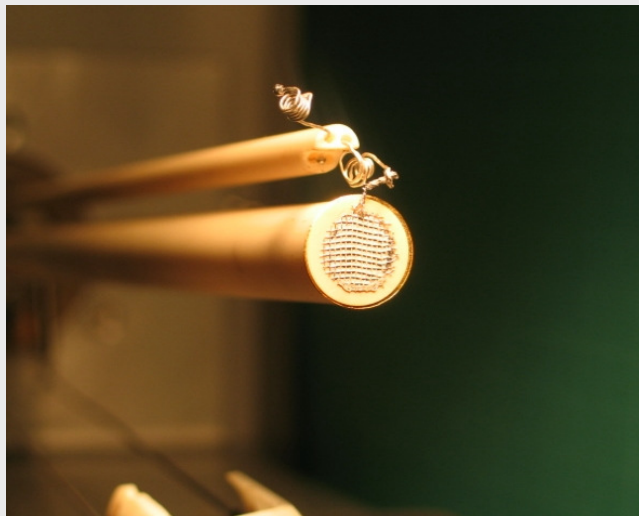
$$[V_O^{\bullet\bullet}] + [O_O^\times] = 3$$

Trends in the transport numbers of some typical HTPCs



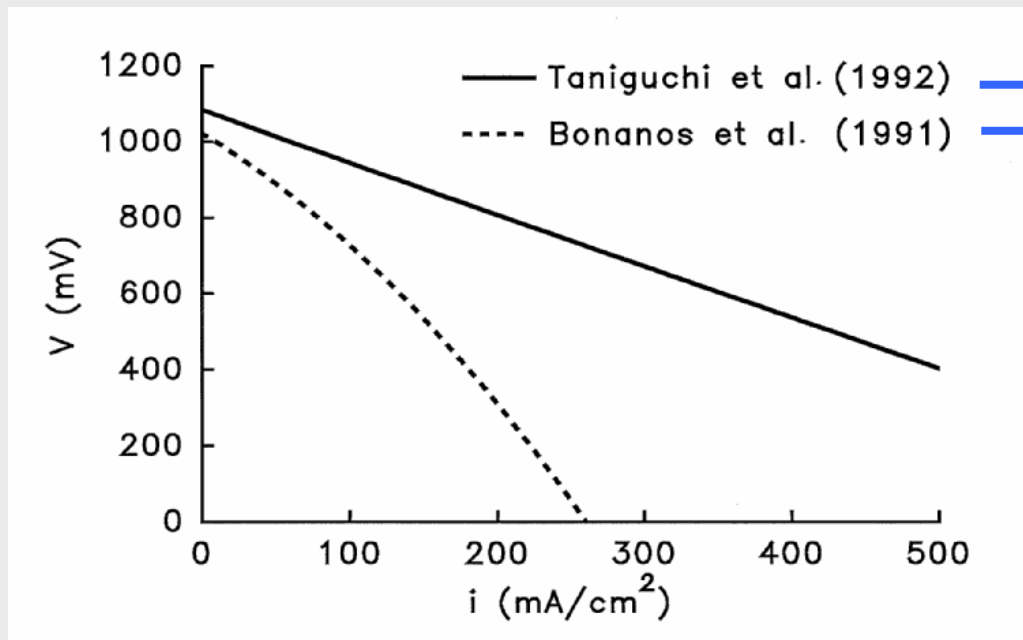
Button cell assembly

Can be used for fuel cells and to determine transport numbers



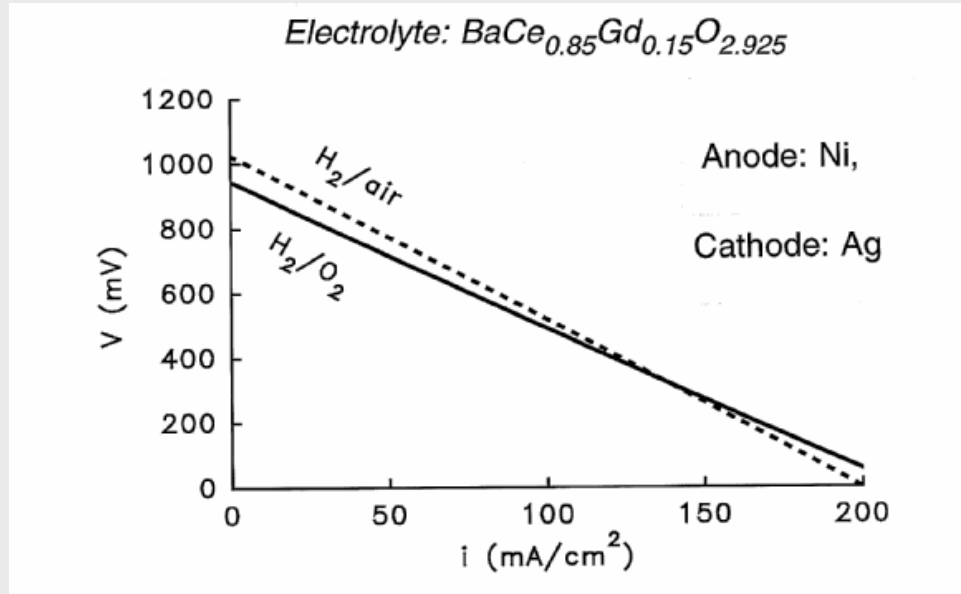
A flow-through humidity meter is essential for these experiments.

Results of button cells with BCG electrolyte



Bonanos, Knight and Ellis, Perovskite solid electrolytes: structure, transport properties & fuel cell applications, SSI 79, 161 (1995).

Results of button cells with BCG electrolyte



we need thinner electrolytes

Comparison of $BaCeO_3$ -based fuel cells

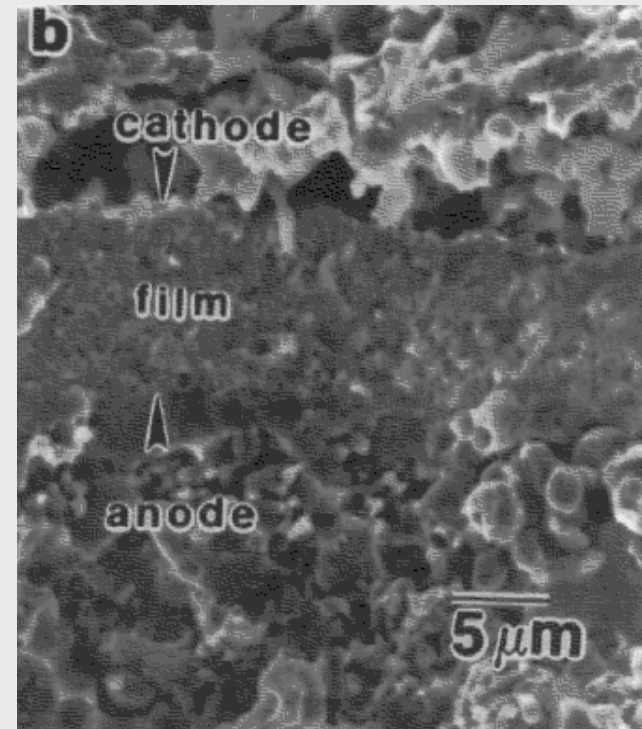
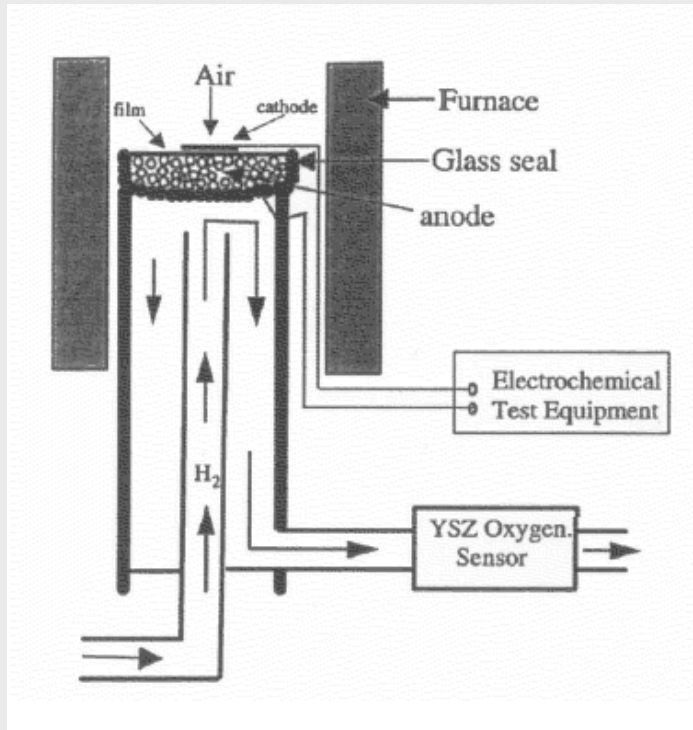
Current density at 700 mV, at 800°C

With electrolyte thickness ~0.5mm

| Electrolyte | Anode, Cathode | Fuel, Oxidant | i (mA cm ⁻²) | Reference |
|------------------------------|----------------|---------------------------------|----------------------------|------------------------|
| $BaCe_{0.9}Nd_{0.1}O_{2.95}$ | Pt, Pt | H ₂ , air | 70 | Iwahara et al (1988) |
| $BaCe_{0.9}Nd_{0.1}O_{2.95}$ | Pt, Pt | H ₂ , air | 105 | Iwahara et al (1990) |
| $BaCe_{0.9}Gd_{0.1}O_{2.95}$ | Pt, Ag | H ₂ , O ₂ | 105 | Bonanos et al (1989) |
| $BaCe_{0.8}Gd_{0.2}O_{2.9}$ | Pt, Pt | H ₂ , air | 285 | Taniguchi et al (1992) |

Bonanos, Knight and Ellis, *Perovskite solid electrolytes: structure, transport properties & fuel cell applications*, SSI 79, 161 (1995).

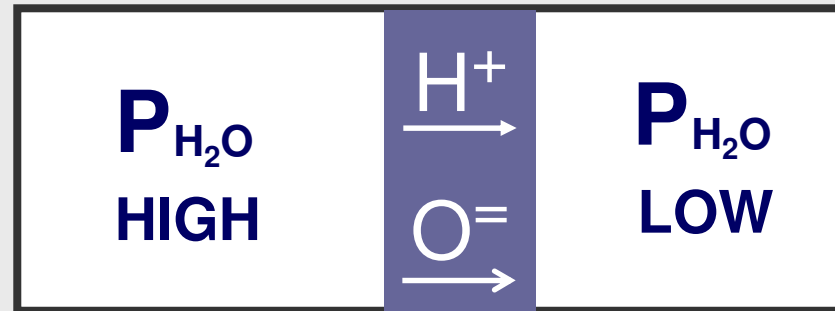
Fabrication of anode supported cell



Respectable thick supported films of BCG could be formed on BCG/Ni cermets, but the ionic transport number of the electrolyte was reduced due to dissolution of NiO.

V. Agarwal & M. L. Liu. Electrochemical properties of $BaCe_{0.8}Gd_{0.2}O_3$ electrolyte films deposited on Ni- $BaCe_{0.8}Gd_{0.2}O_3$ substrates. J. Electrochem. Soc. 144(3) 103, 1997.

Electrochemical steam permeation



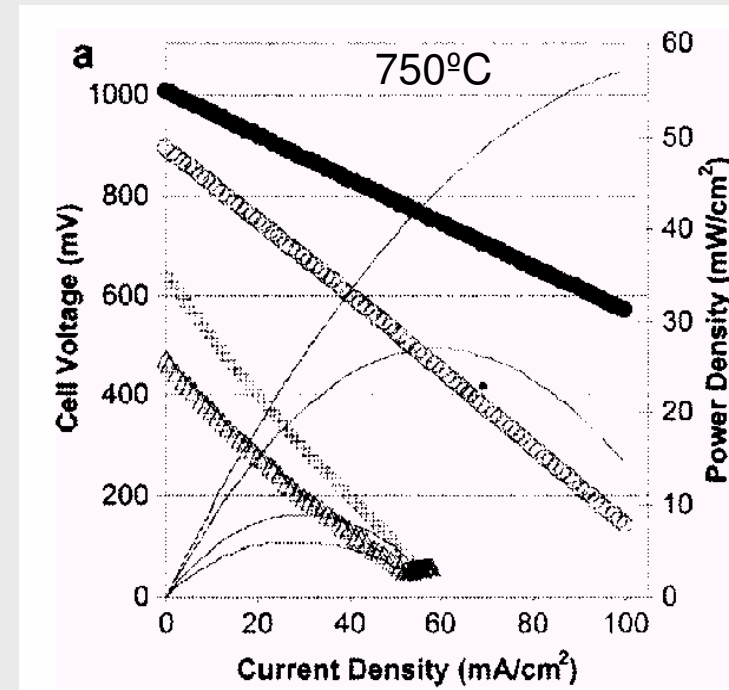
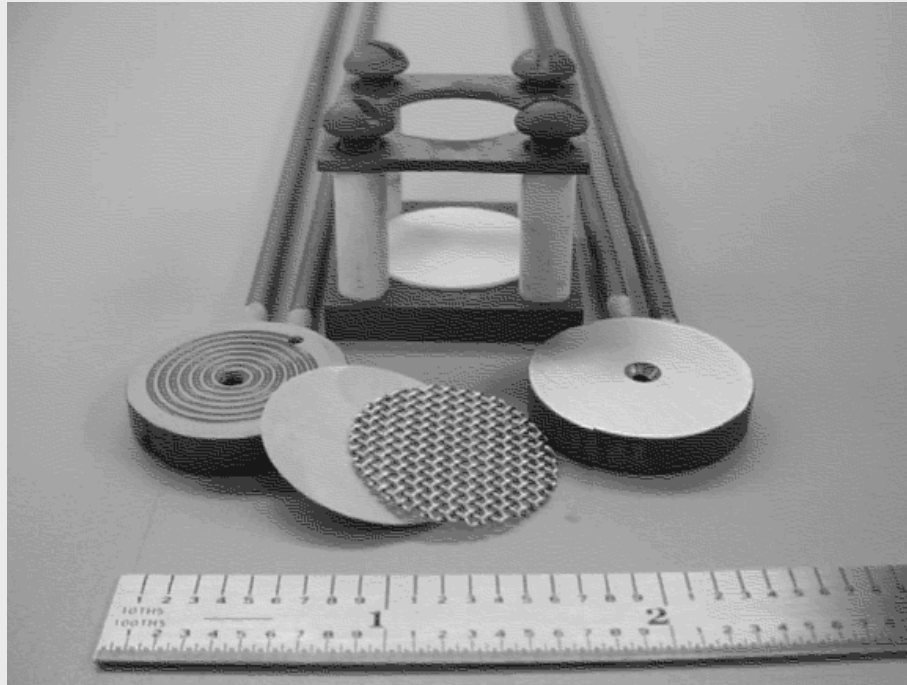
Net transport of H_2O \rightarrow

No net charge transport

Rate expression for ambipolar transport of water: Kreuer SSI 125, 285 (1999)

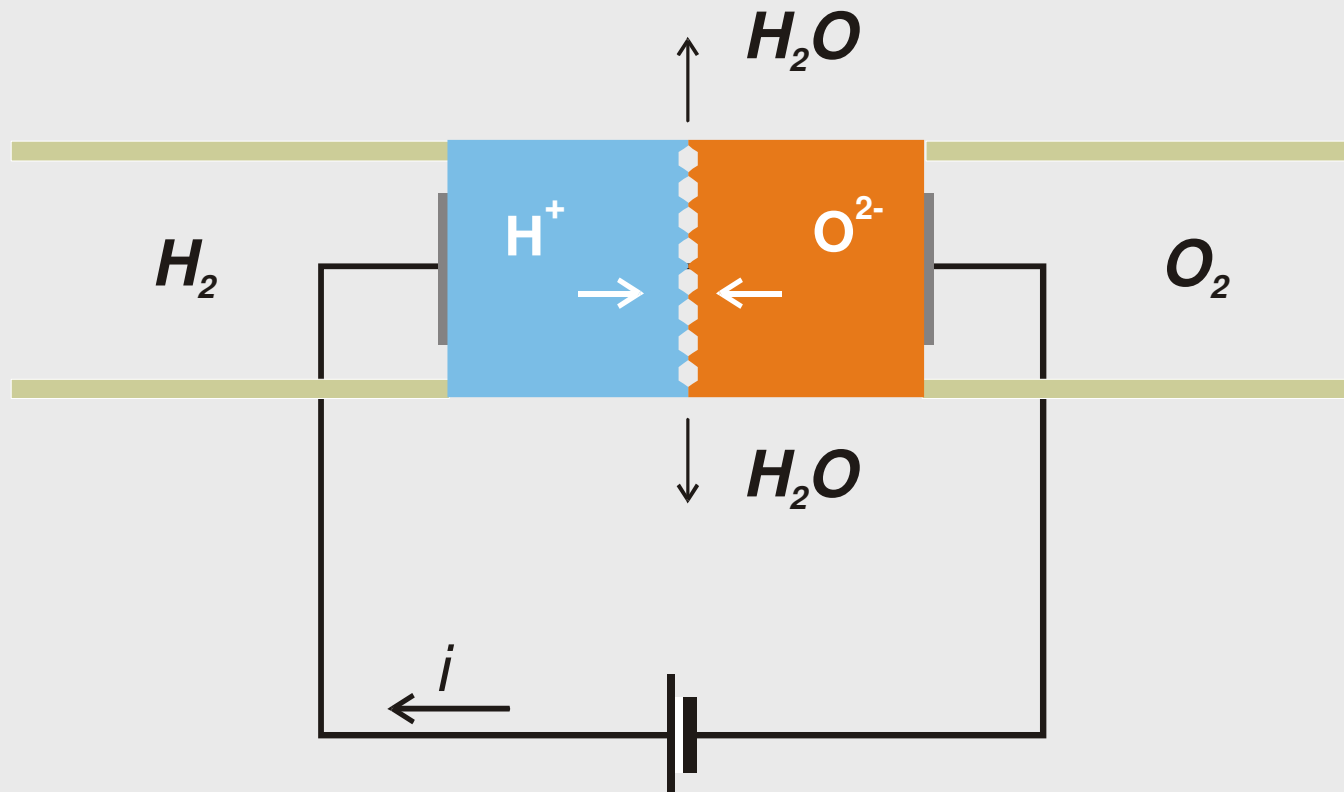
Relevance to operation of PCFC on HCs: Coors JPS 118, 150 (2003)

PCFC run on dry methane: Protonetics and CoorsTek



W.G. Coors, Steam reforming & Water-Gas Shift by Steam Permeation in a Protonic Ceramic Fuel Cell, J. Electrochem. Soc. 51(7), A994 2004.

Concept of proton conductor / oxide ion conductor junction



Steam emitting diode (1993)

IDEAL-SOFC (2007)

Future directions

Materials

- Those discussed herein
- Barium zirconate [!]
- Lanthanum niobate [?]

Architectures

- Electrolyte supported: maybe
- Cermet anode support: most probably not due to reactions
- Metal supported: best option ✓
- Junction (IDEAL-SOFC) ✓

Acknowledgements & quotation

- **Co-authors: past (BP research) & present (Risø)**
- **NEDO (Japan) & INTAS (EU) for past research funding**
- **The hosts of this workshop and ESF for kind invitation**
- **Providers of material for talk, esp. those I forgot to ask**

"It doesn't matter whether the cat is black or white, as long as it catches mice" Deng Xiaoping (1904-1997).