Fuel Cells and Electrolyzers: Challenges and Opportunities

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Fuel Cell Parameters

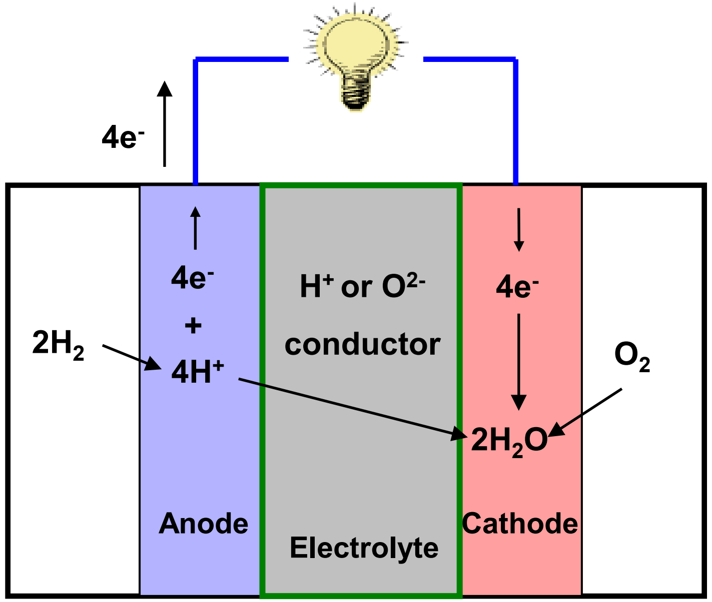
Fuel cell voltage

Anode: $2H_2 \rightarrow 4H^+ + 4e^-$

Cathode: $O_2 + 4e^- \rightarrow 2O^{2-}$

Overall: $2H_2 + O_2 \rightarrow 2H_2O$

$$\Delta G^o = -nFE^o$$



$E^o = \Delta G^0 / nF = (-471{,}000\ \text{J/mol}) / (4)(96{,}487\ \text{C/mol}) = 1.23\ \text{J/C or V}$

Fuel cell efficiency

$\text{Efficiency} = \Delta G^0 / \Delta H^0 = (471{,}000\ \text{J/mol}) / (572{,}000\ \text{J/mol}) = 0.83 = 83\%$

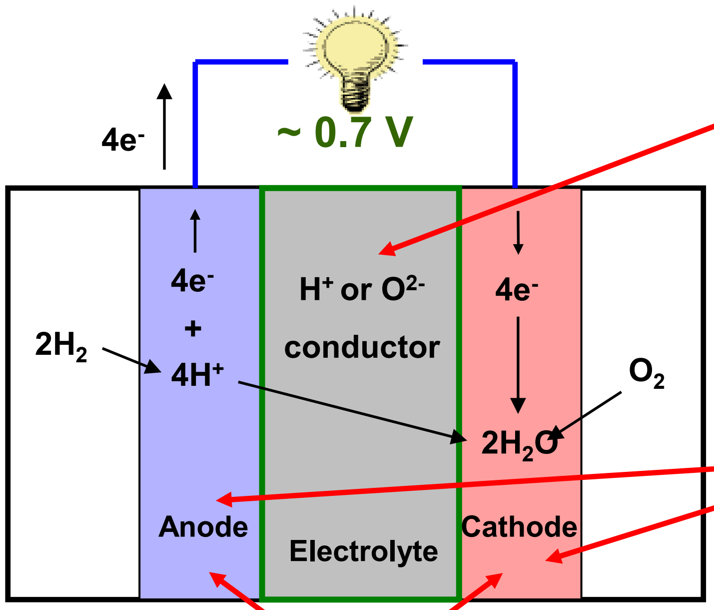
Types of Fuel Cells

Fuel cell type	Anode reaction	Cathode reaction	Temp. (°C)
Phosphoric acid fuel cell (PAFC)	$H_2 \rightarrow 2H^+ + 2e^-$	$0.5O_2 + 2H^+ + 2e^- \rightarrow H_2O$	200
Proton exchange membrane fuel cell (PEMFC)	$H_2 \rightarrow 2H^+ + 2e^-$	$0.5O_2 + 2H^+ + 2e^- \rightarrow H_2O$	~ 90
Direct methanol fuel cell (DMFC)	$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$	$1.5O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$	~ 60
Direct ethanol fuel cells (DEFC)	$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$	$3O_2 + 12H^+ + 12e^- \rightarrow 6H_2O$	~ 60
Alkaline fuel cells (AFC)	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$	$0.5O_2 + H_2O + 2e^- \rightarrow 2OH^-$	~ 90
Molten carbonate fuel cells (MCFC)	$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$	$0.5O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$	~ 600
Solid oxide fuel cell (SOFC)	$H_2 + O^{2-} \rightarrow H_2O + 2e^-$	$0.5O_2 + 2e^- \rightarrow O^{2-}$	> 500

Challenges of Fuel Cell Technologies

- Commercialization is hampered by high cost, durability, and operability challenges
- Linked to severe materials challenges and system issues

$\Delta G = - n F E$
$E = 1.23$ V



PEMFC & DMFC – Membrane

- High cost of Nafion membrane
- Limited $T_{op} < 100\ ^{o}C$ in order to be wet
- Complex external humidification system
- Methanol crossover from anode to cathode
- Degradation (peroxide attack, F^- release)

PEMFC & DMFC – Catalyst

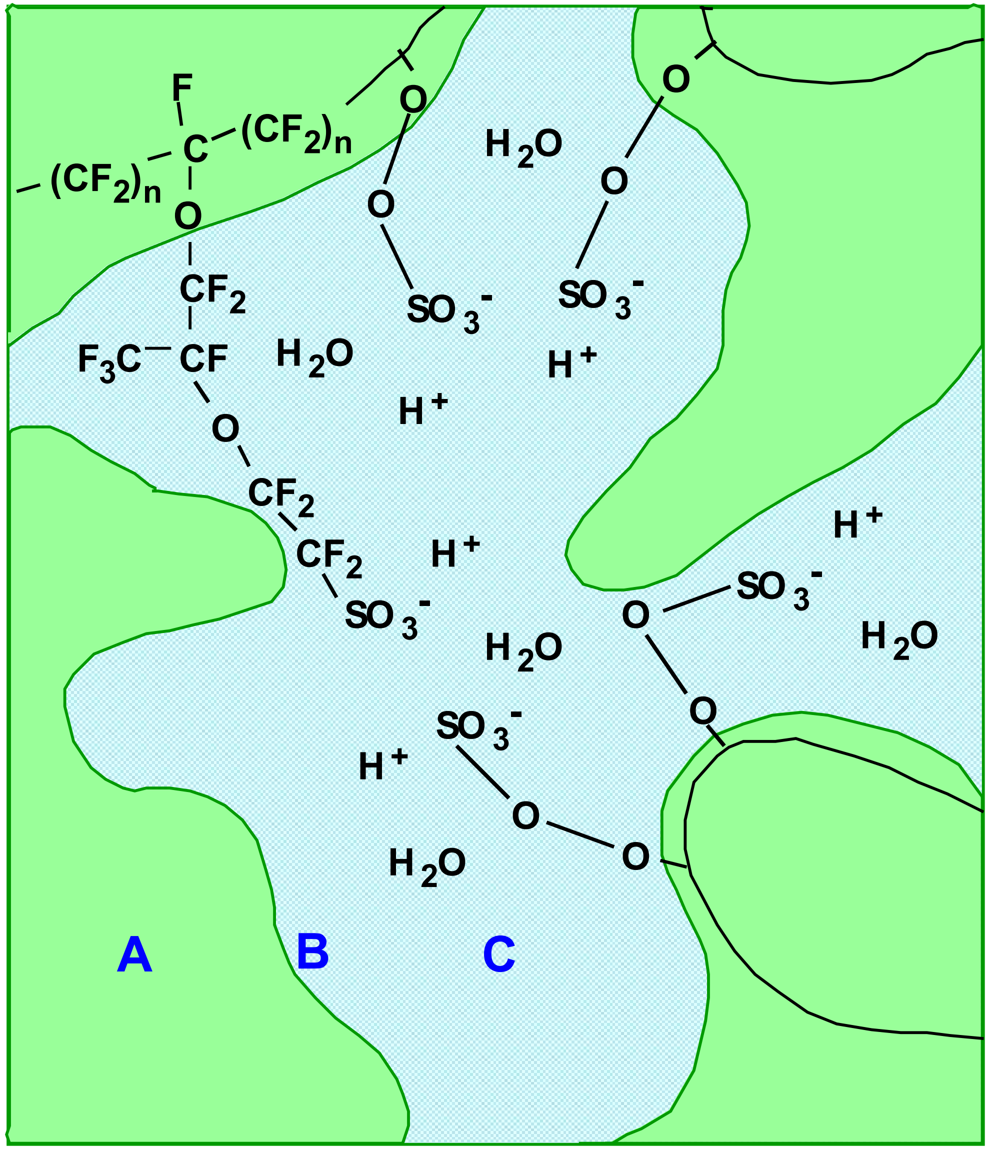
- Expensive, less abundant Pt catalyst
- Poisoning of Pt by CO at $T_{op} < 100\ ^{o}C$
- Poor utilization of Pt (80 % waste)
- Catalyst/support instability/degradation

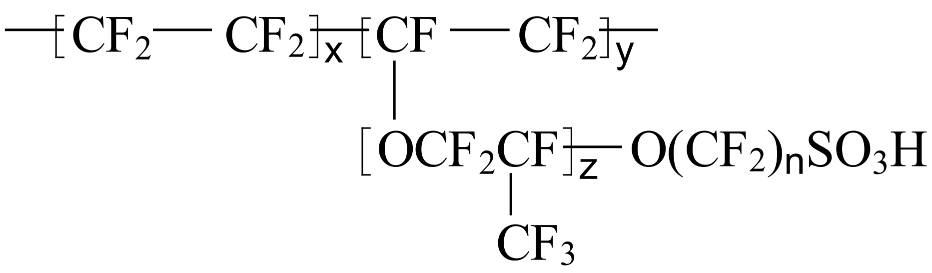
SOFC – Catalyst (500 – 800 ^{o}C)

- Poor oxygen reduction kinetics
- Poor H/C fuel oxidation efficiency
- Coking, poor tolerance to sulfur in fuel
- Thermal expansion mismatch

- PEMFC: Hydrogen production, storage, and transportation – infrastructure issues
- SOFC: Sealing issues, thermal degradation
- All: Heat and water management issues

Nafion Membrane



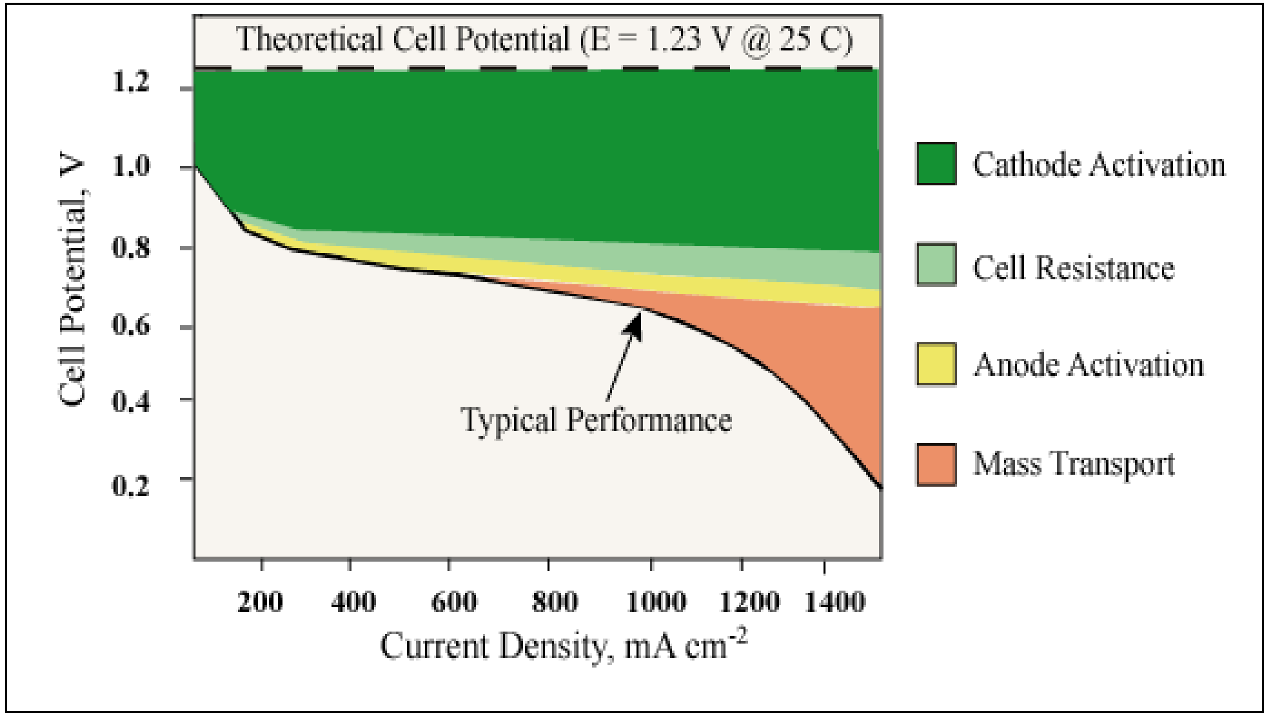


$$-[CF_2-CF_2]_x-[CF(-[OCF_2CF(CF_3)]_z-O(CF_2)_nSO_3H)-CF_2]_y-$$

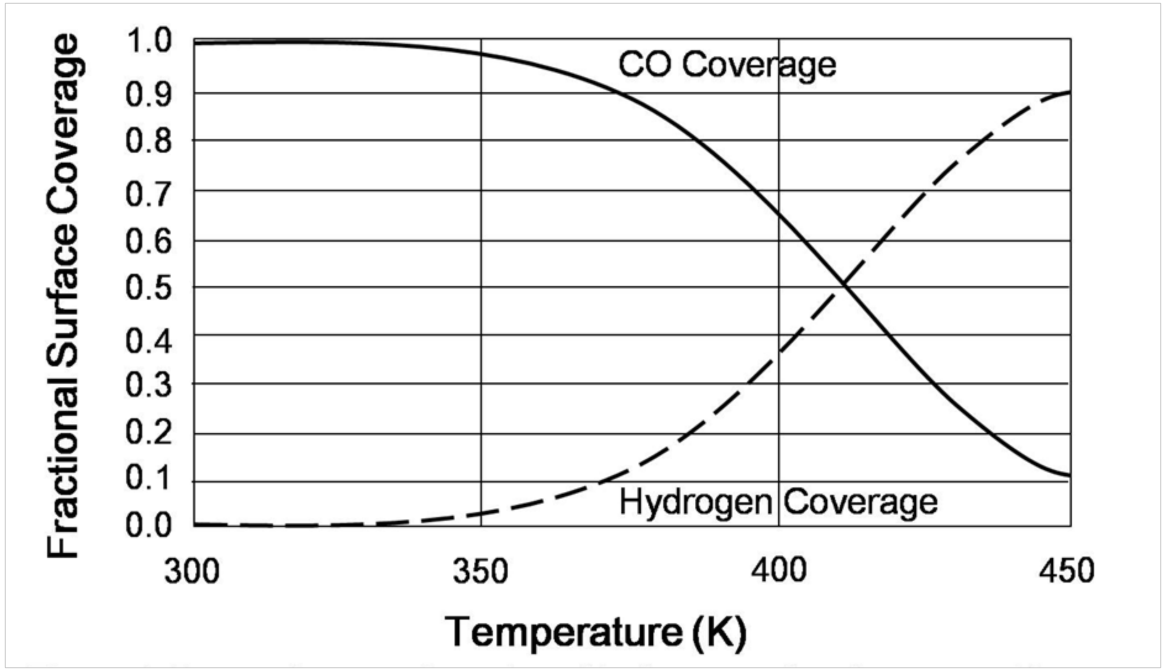
Polarization Losses and CO Coverage on ON Pt

$\Delta G = - n F E$

$E = 1.23$ V



T. R. Ralph and M. P. Hogarth, *Platinum Metals Reviews* **46**, 3 (2002)



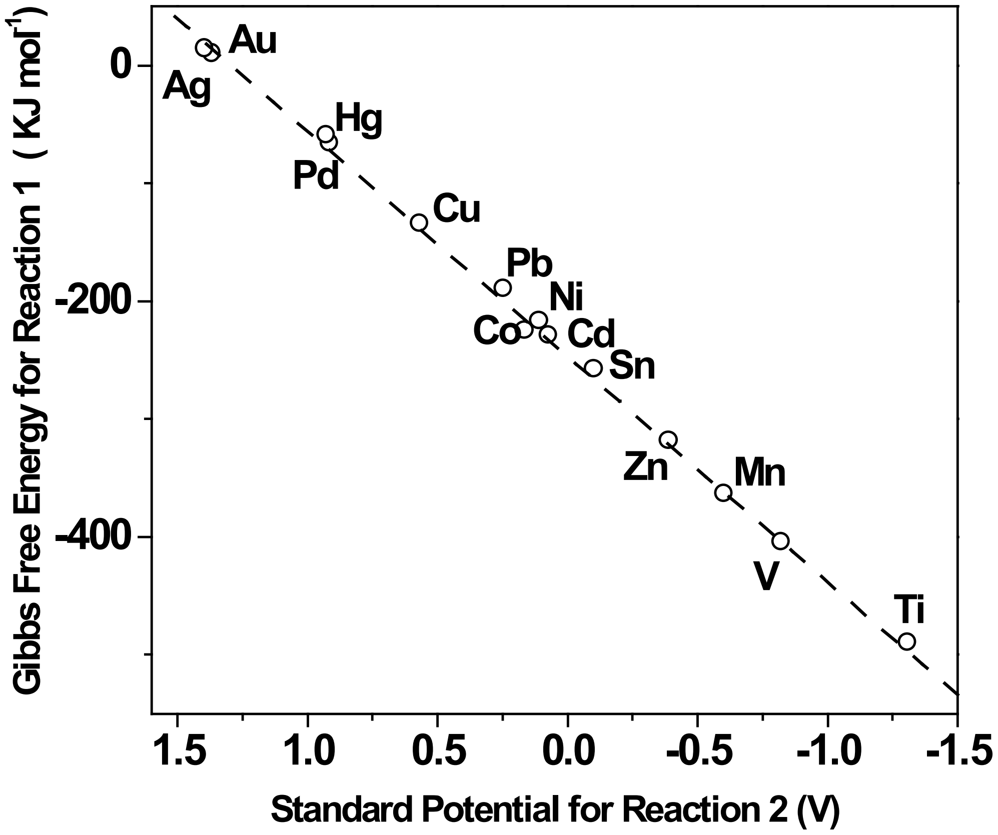
Langmuir-type adsorption of hydrogen and carbon monoxide on a smooth platinum surface as a function of temperature.

Low-cost Non-platinum Catalysts

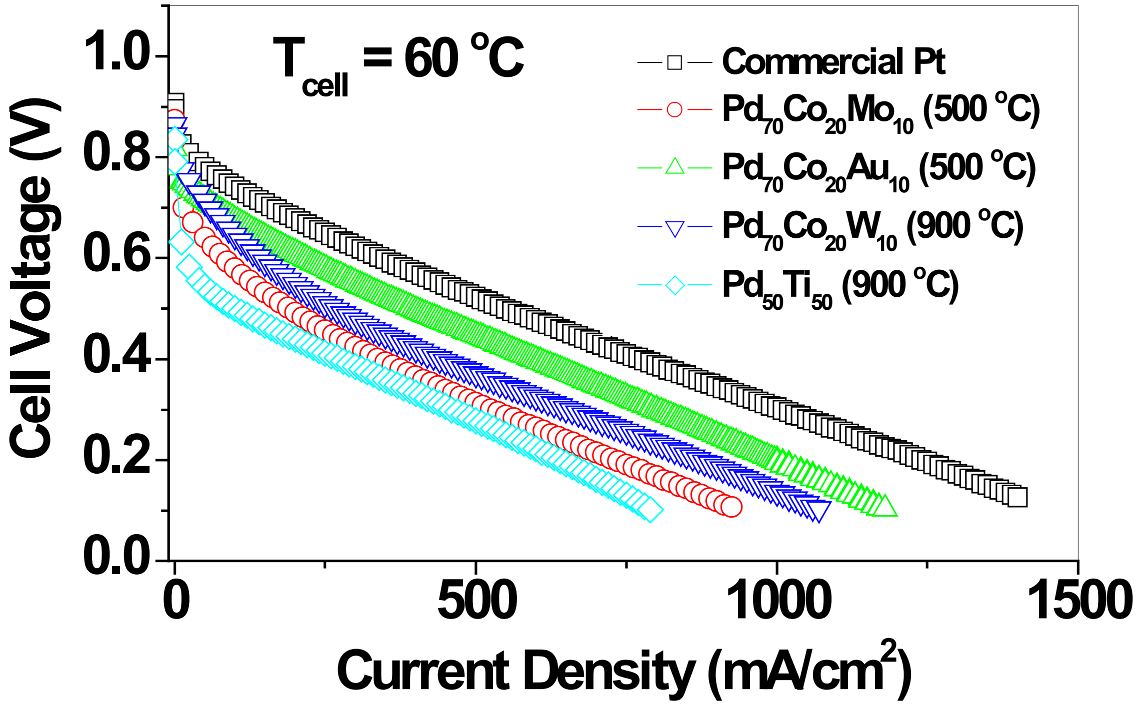
$2\,M + O_2 \rightarrow 2\,MO$ ΔG^o (first step) (1)

$2\,[MO + 2\,H^+ + 2\,e^- \rightarrow M + H_2O]$ E^o_{MO} (following step) (2)

$O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O$ $E^o = 1.23$ V (overall reaction) (3)

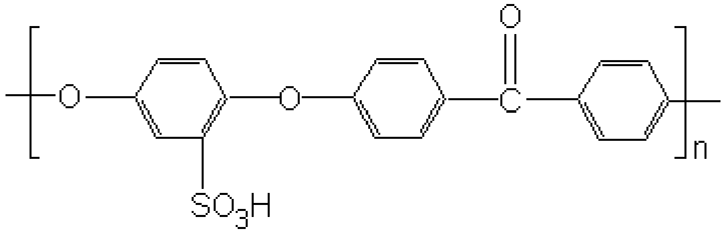


J. L. Fernández, D. A. Walsh, and A. J. Bard, *J. Am. Chem. Soc.* **127**, 357 (2005)

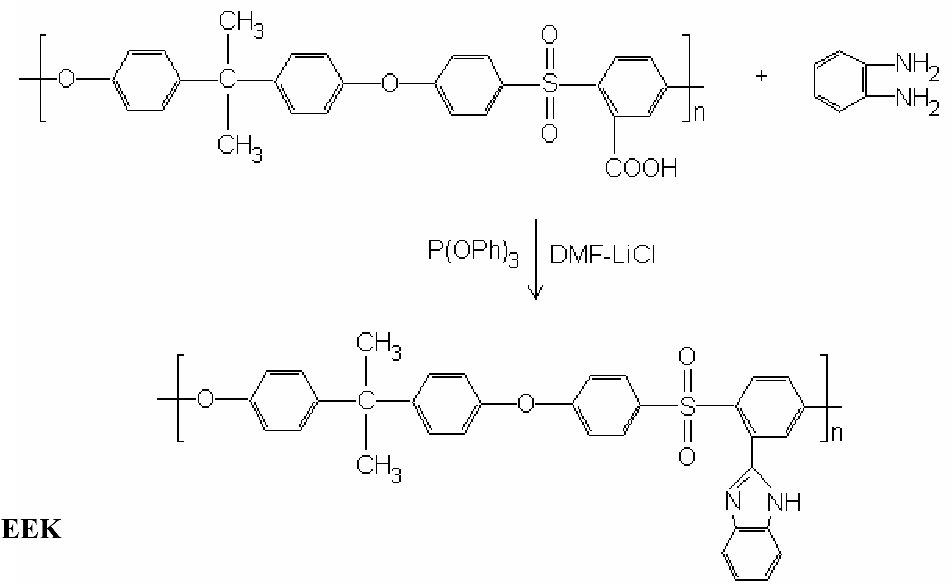


J. L. Fernández, V. Raghuveer, A. Manthiram, and A. J. Bard, *J. Am. Chem. Soc.* **127**, 13100 (2005)
V. Raghuveer, A. Manthiram, and A. J. Bard, *J. Phys. Chem. B* **109**, 22909 (2005)

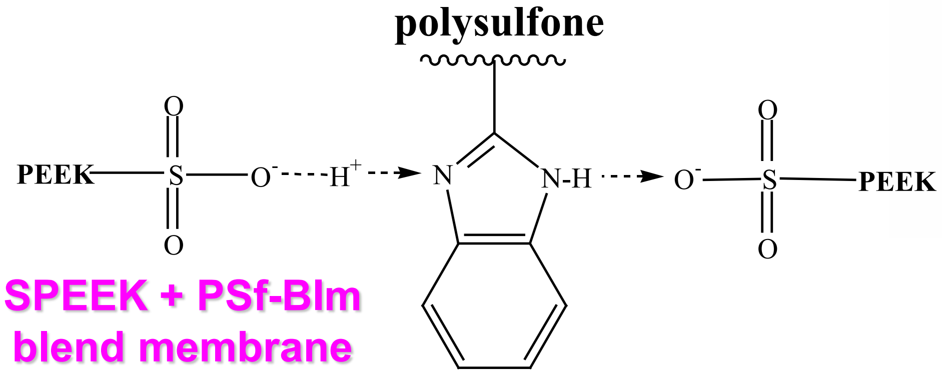
Membranes Based on Acid-base Interactions



Sulfonated poy(ether ether ketone)
SPEEK (acidic polymer)



Poly(sulfone) bearing benzimidazole
PSf-BIm (basic polymer)

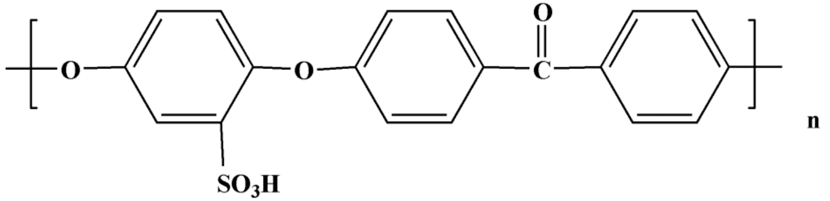


SPEEK + PSf-BIm blend membrane

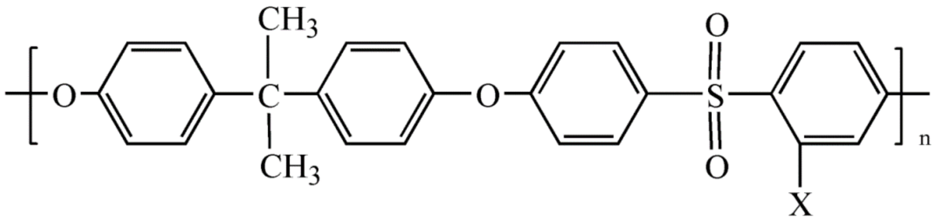
Y.-Z. Fu, A. Manthiram, and M. Guiver, *Electrochemistry Communications* **8**, 1386 (2006)

- Benzimidazole: Can act as a bridge to transport proton under anhydrous conditions (Grotthuss-type hopping & vehicle-type mechanisms)
- > 100 °C operation: Can eliminate humidification systems & suppress CO poisoning
- N-heterocycles: Insertion into SPEEK channels suppresses methanol crossover
- PEEK and PSf: Low cost industrial polymers, compatible aromatic polymers, excellent mechanical properties and thermal stability

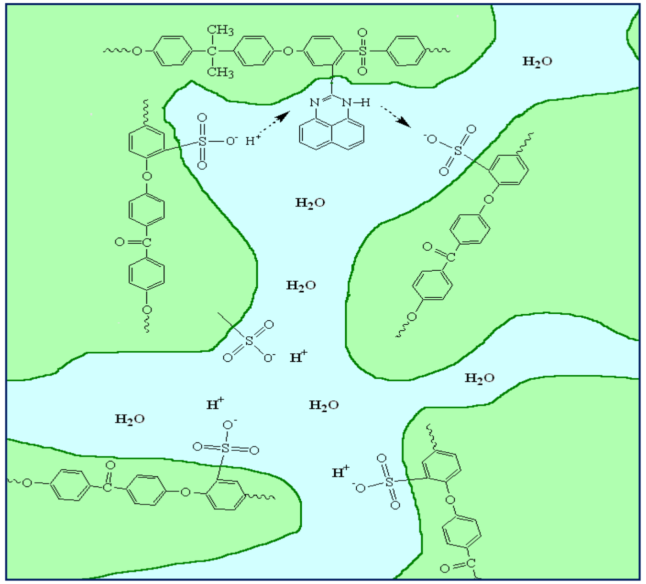
Blend Membranes Based on Different Polymers



Sulfonated poly(ether ether ketone) (SPEEK), acidic

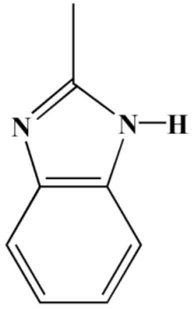


Poly(sulfone) tethered with heterocycles, basic

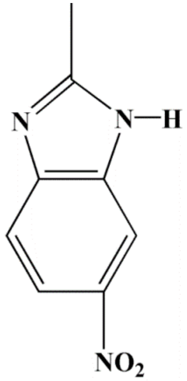


Basic science

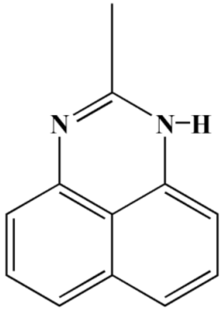
- pKa influence
- Size influence
- Site influence



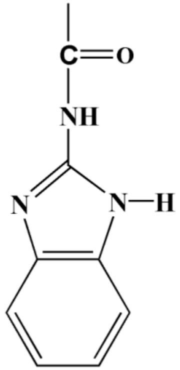
BIm



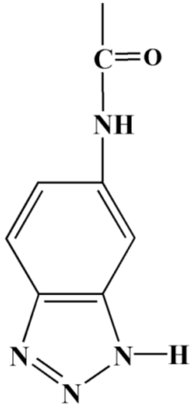
NBIm



PImd



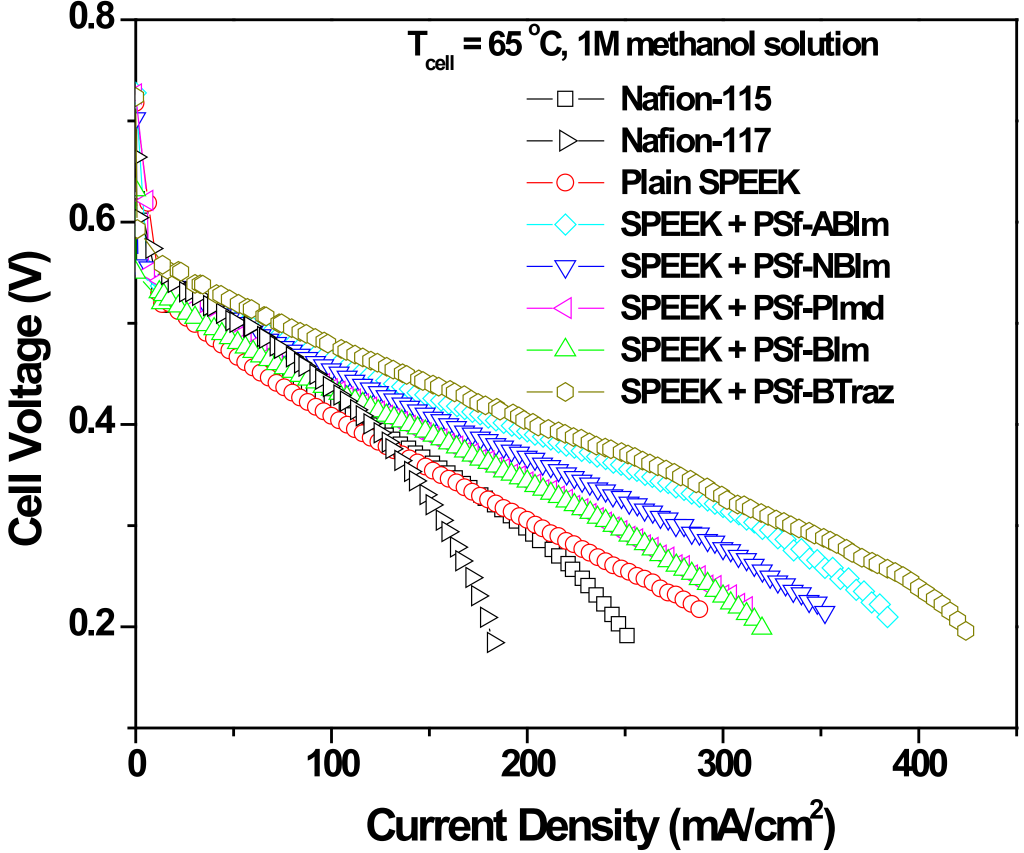
ABIm



BTraz

W. Li, A. Manthiram, and M. Guiver, *Journal of Membrane Science* **362**, 289 (2010)

Performance of Blend Membranes in DMFC



W. Li, A. Manthiram, and M. Guiver, *Journal of Membrane Science* **362**, 289 (2010)
W. Li, Y.-Z. Fu, A. Manthiram, and M. Guiver, *Journal of Electrochemical Society* **156**, B258 (2009)

- All blend membranes show better performance than plain SPEEK due to suppressed methanol crossover and increased proton conductivity
- Blend membrane consisting of PSf-BTraz shows the best performance

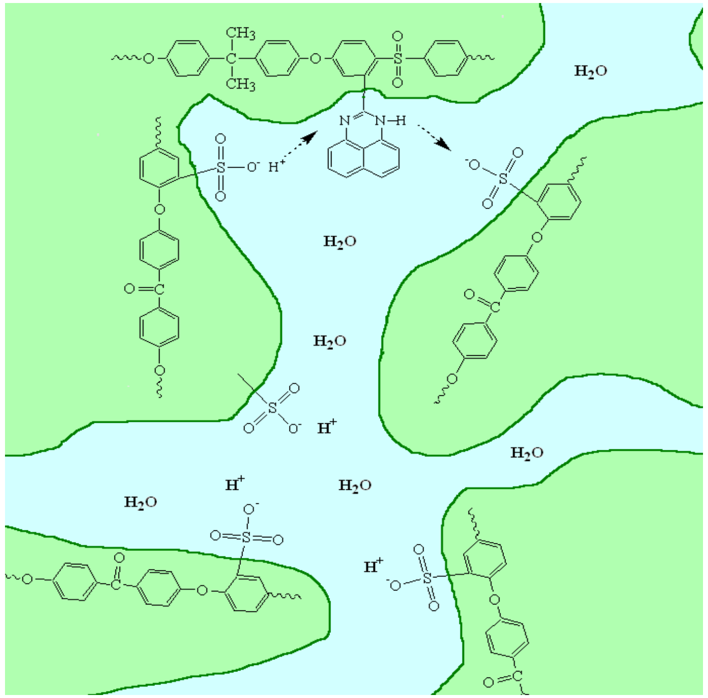
Performance of Blend Membranes in DMFC

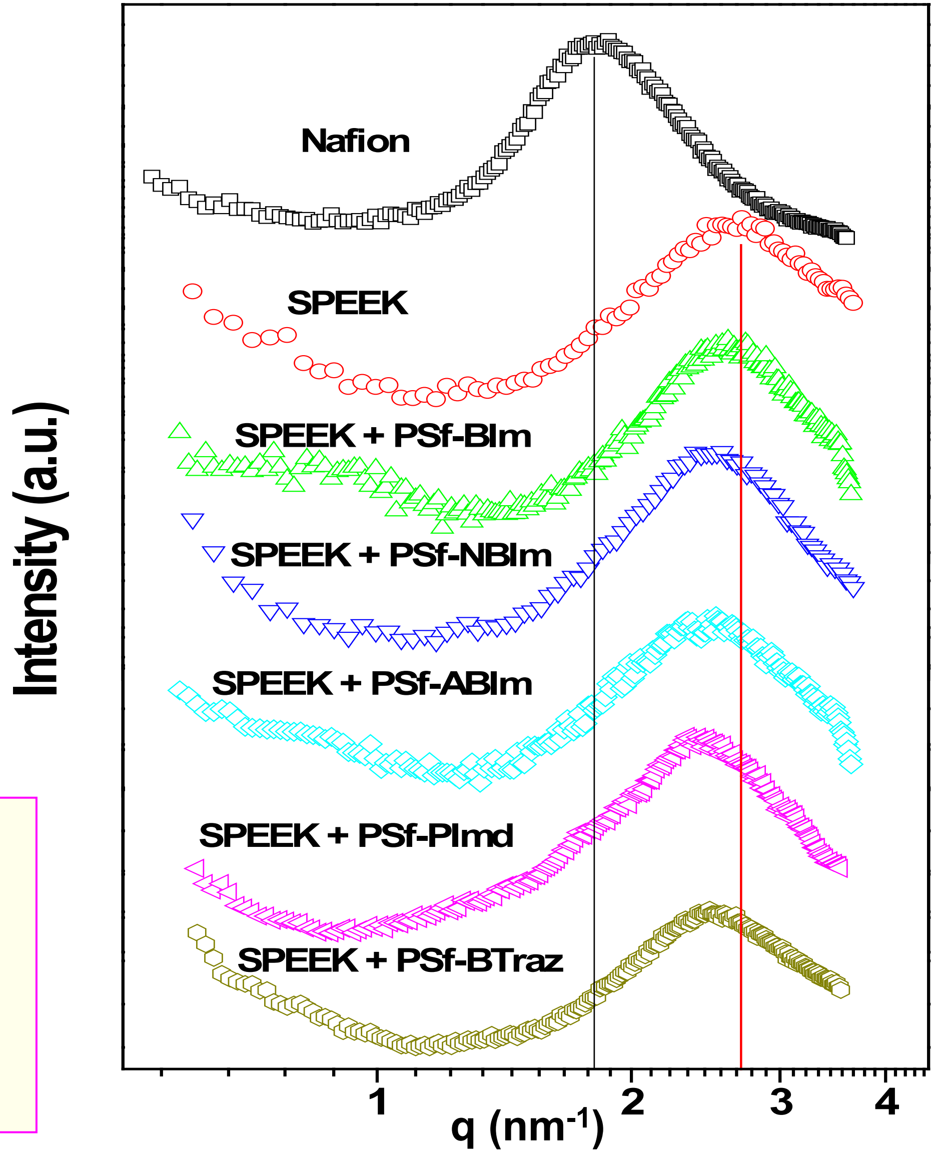
Membranes	OCV (V)	Maximum power density (mW/cm^2)	Methanol crossover current density (mA/cm^2)	Proton Conductivity at 65 ^{o}C, 100% R.H. (mS/cm)
Nafion-115	**0.63**	**59**	**122**	**144**
Nafion-117	**0.71**	**49**	**86**	**143**
SPEEK	**0.69**	**64**	**115**	**69**
SPEEK / PSf-ABIm	**0.71**	**95**	**95**	**93**
SPEEK / PSf-NBIm	**0.73**	**84**	**87**	**87**
SPEEK / PSf-BIm	**0.72**	**73**	**91**	**79**
SPEEK / PSf-PImd	**0.74**	**73**	**77**	**73**
SPEEK / PSf-BTraz	**0.72**	**101**	**87**	**96**

W. Li, A. Manthiram, and M. Guiver, *Journal of Membrane Science* **362**, 289 (2010)

- Blend membranes offer better performance than Nafion at a much reduced cost (~ 20 %) due to low methanol crossover – two times higher power density than Nafion
- Potential to operate with high concentration of methanol – increase in energy density

Ionic Cluster Size in Various Blend membranes





- SPEEK and blend membranes show smaller cluster size than Nafion
- Blend membranes show larger cluster size compared to plain SPEEK, suggesting the insertion of heterocycle groups into the channels formed by the sulfonic *acid groups*

W. Li, A. Manthiram, and M. Guiver, *Journal of Membrane Science* **362**, 289 (2010)

University of Texas at Austin

Solid Oxide Fuel Cell Materials

Electrolytes

Fluorite $Zr_{1-x}Y_xO_{2-0.5x}$ (YSZ): operates > 800 °C
Fluorite $Ce_{1-x}Gd_xO_{2-0.5x}$ (GDC): operates at ~ 500 °C, electronic cond. at > 600 °C
Perovskite $La_{1-x}Sr_xGa_{1-x}Mg_xO_{3-x}$ (LSGM): operates at 600 – 800 °C

Anodes

$Zr_{1-x}Y_xO_{2-0.5x}$ + Ni metal (cermet)
YSZ provides oxide-ion conduction and Ni provides electronic conduction
Ni is poisoned by carbon deposition from hydrocarbon fuel and sulfur impurities
$La_{1-x}Sr_xVO_{3-\delta}$, $Sr_2MoMO_{6-\delta}$ (M = Mg or Mn)

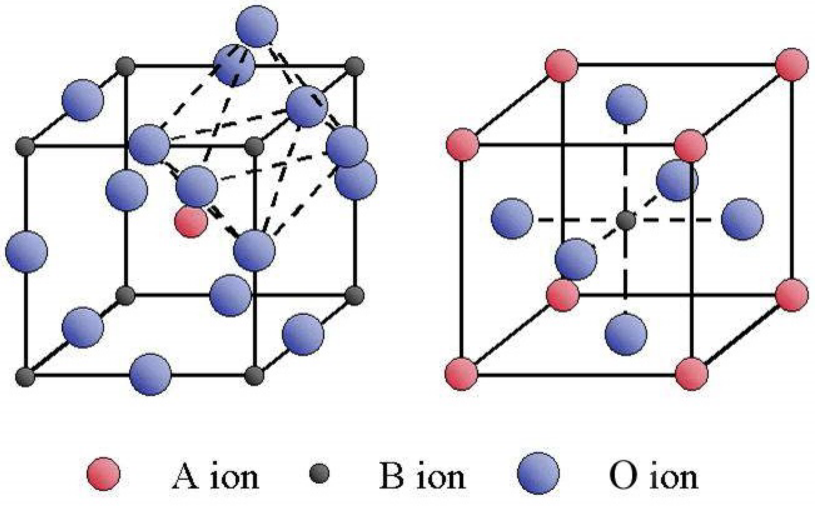
Cathodes

Perovskite $La_{1-x}Sr_xMnO_3$ (LSM): operates at > 800 °C
Perovskite $La_{1-x}Sr_xCoO_{3-\delta}$ (LSM): operates at 600 - 800 °C, but large TEC

Interconnects

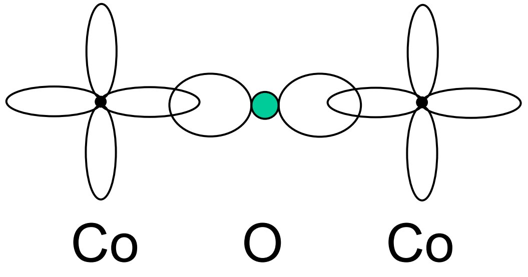
Perovskite $La_{1-x}Sr_xCrO_3$

Mixed Conducting $ABO_{3-\delta}$ Perovskite Oxides

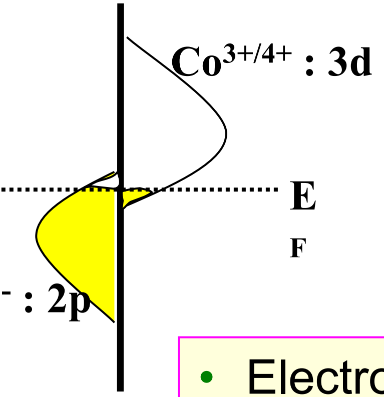


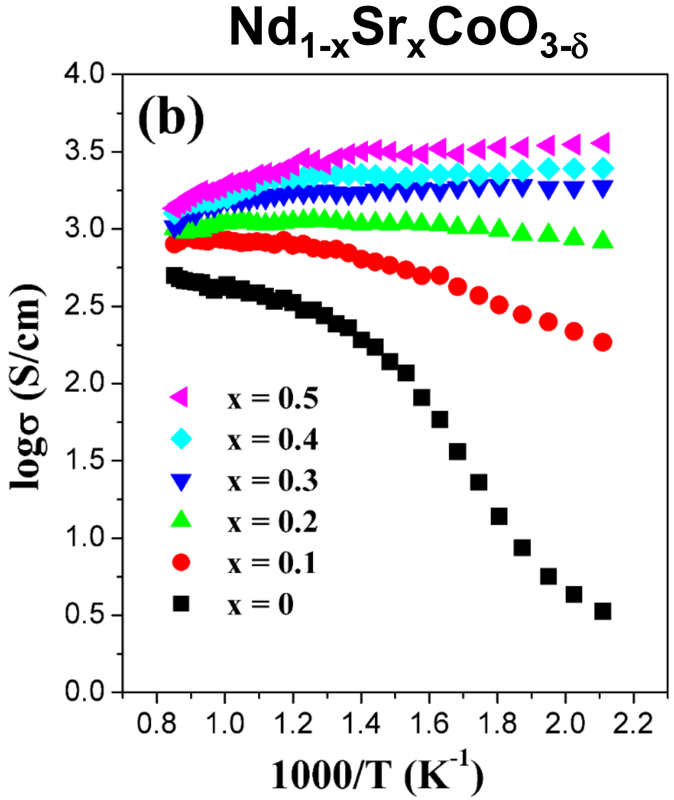
$$a = 2(r_B + r_O) \qquad \sqrt{2}\, a = 2(r_A + r_O)$$
$$1 = 2(r_A + r_O) / 2(\sqrt{2}\,(r_B + r_O))$$

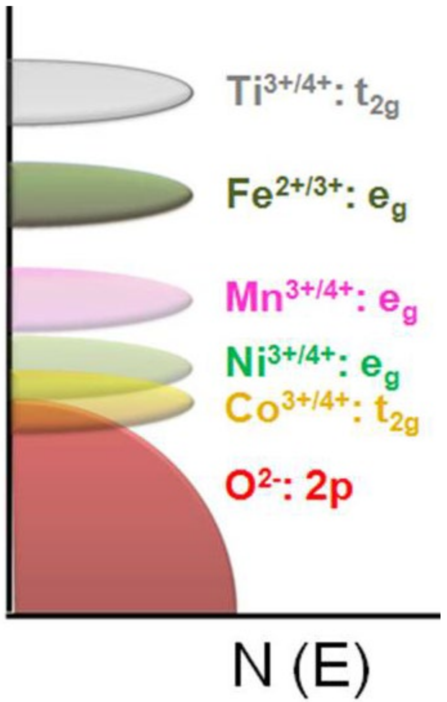
$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$



$La_{1-x}Sr_xCoO_{3-\delta}$



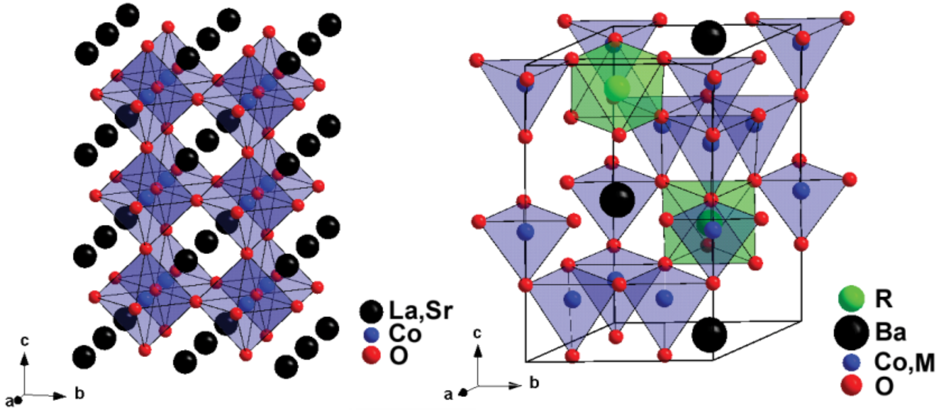


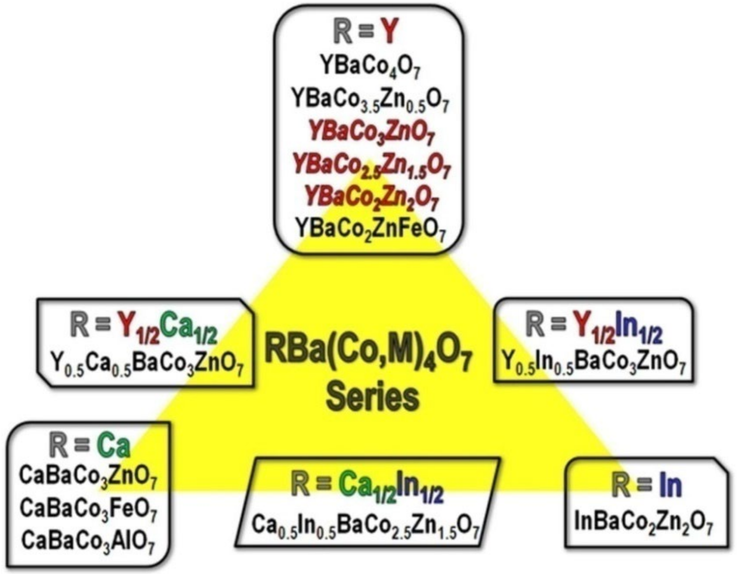


- Tolerance factor is temperature and pressure dependent, so O-Co-O bond bending decreases with temperature or Sr doping, resulting in semiconductor to metal transition at a critical temperature or critical x

- Electrocatalysts in SOFC and water electrolysis, oxygen separation membranes, partial oxidation of methane to syn gas (H_2 + CO)

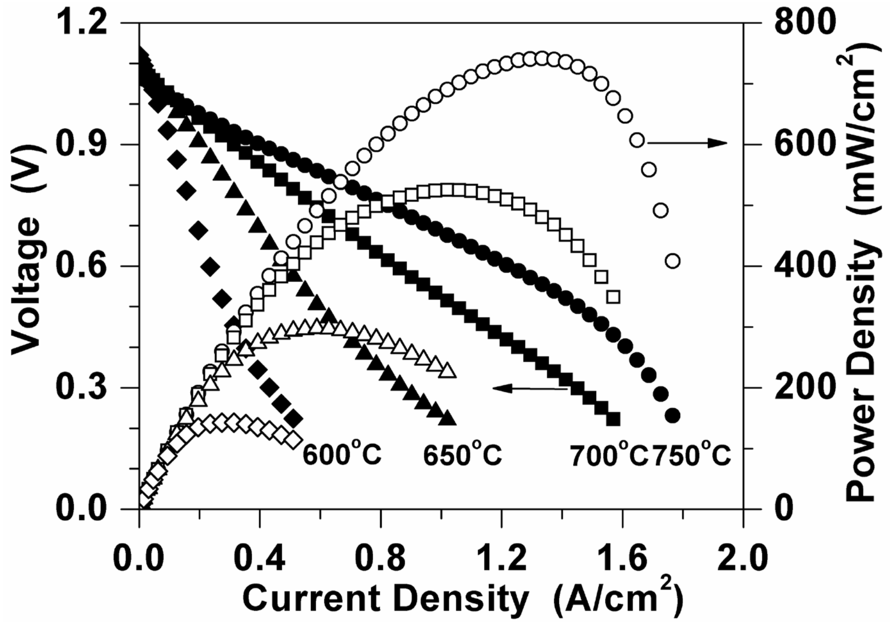
Low-TEC Cobalt Oxides without Spin-state Transition

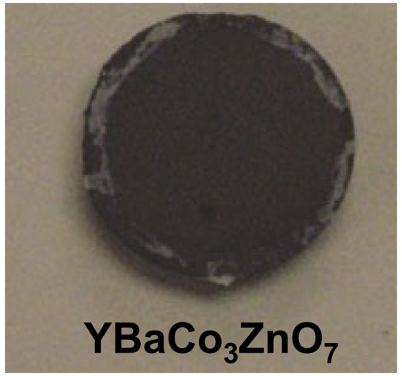




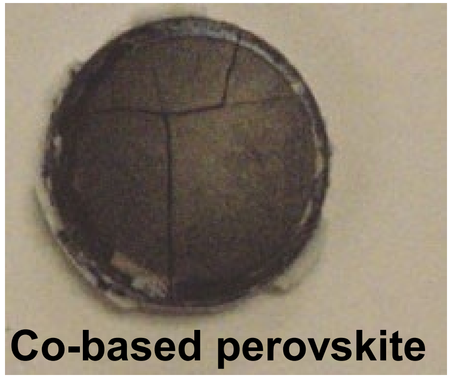
J. -H. Kim and A. Manthiram, *Chemistry of Materials* **22**, 822 (2010)

Octahedral Co^{3+}: $t_{2g}^6e_g^0$
Low spin: 0.545 nm
High spin: 0.06 nm
Tetrahedral Co^{3+}: $(e^3t_2^3)$





$YBaCo_3ZnO_7$

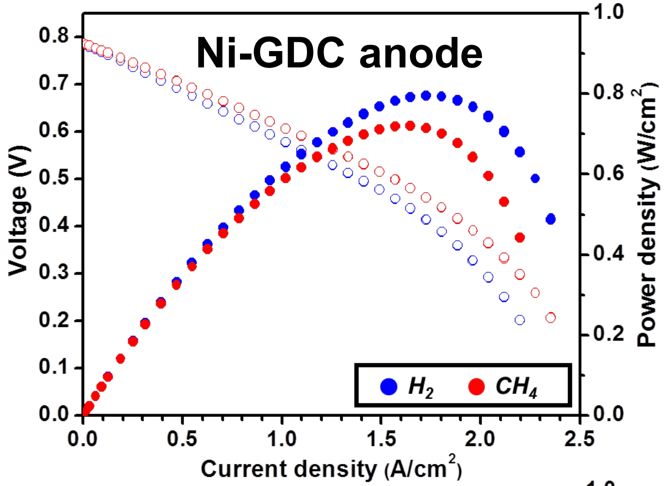


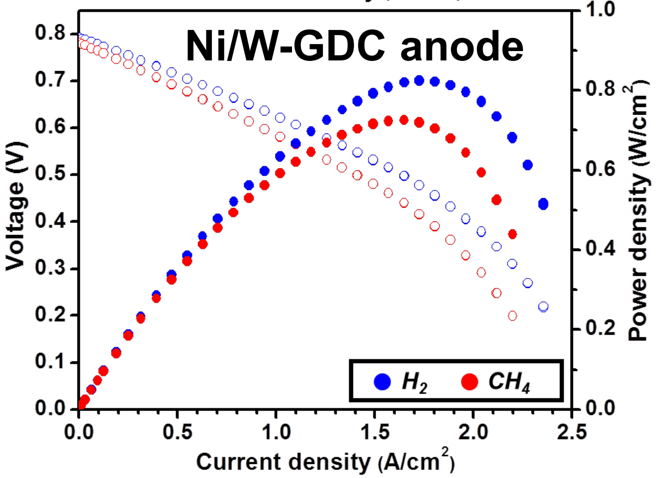
Co-based perovskite

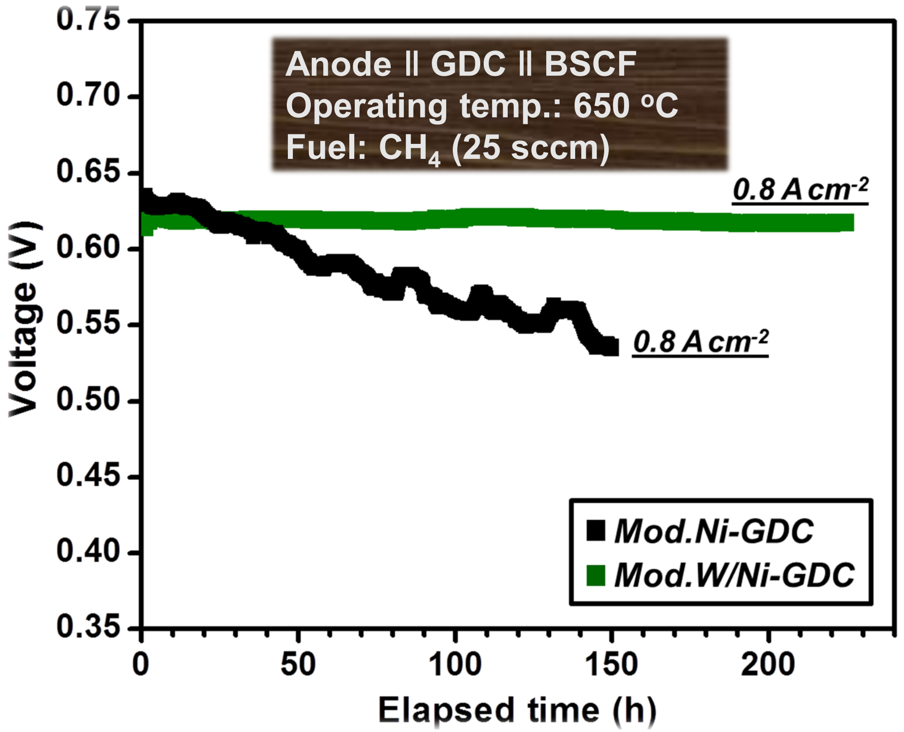
- $YBaCo_3ZnO_7$ has TEC values of 10 – 12 x 10^{-6} K^{-1}, ideally matching with electrolyte

Suppression of Carbon Deposition on Ni Anode

$$\begin{tikzcd}
WO_{3-\delta-x}\ (0 < \delta \leq 3) + H_2O\ (g) \arrow[r] & H_xWO_{3-\delta}\ (\equiv WO_{3-\delta-x}(OH)_x) \arrow[d] \\
2\ WO_{3-\delta-x} + x\ CO_2 + x\ H_2 \arrow[u] & 2\ WO_{3-\delta-x}(OH)_x + x\ C \text{ deposited over Ni} \arrow[l]
\end{tikzcd}$$







D. Yoon and A. Manthiram, *Energy & Environmental Science* **7**, 3069 (2014)

- OH groups on W assist the removal of C as CO_2

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