

# PBI-Phosphoric Acid Based Membrane Electrode Assemblies: Status update

PAFC Workshop

16 November 2009

Emory De Castro

# BASF Fuel Cell –

Formed from legacy companies with history of catalyst, gas diffusion electrodes, and membrane innovation



2008

Customer application lab in Japan opens April 2008

2007

BASF merges fuel cell activities and forms BASF Fuel Cell

2006

BASF acquires PEMEAS and Engelhard

2005

E-TEK becomes division of PEMEAS

2004

Celanese and investors form PEMEAS

2003

Celanese Ventures introduces Celtec-P MEA to market

2001

Celanese Ventures MEA production plant goes on stream

2000

BASF identifies fuel cell as growth area and launches fuel cell project

1999

Celanese takes over fuel cell project after demerger from Hoechst

BASF develops and manufactures reformer catalysts

1998

Engelhard develops and markets catalysts for fuel cell and reformer

1994

Hoechst develops first high temperature MEA

1990

E-TEK formed to commercialize catalysts and gas diffusion technology

# Celtec®-P: MEAs for High Temperature\* PEMFC

## **Membrane:**

Based on polybenzimidazole (PBI) and phosphoric acid

## **Electrodes:**

Catalysts and layer structure tailored for high temperature conditions (typically 160 – 180°C) and PBI-PA membrane

## **Applications:**

- Stationary power supply, CHP
- Backup power
- Auxiliary power units
- micro-portable



\* 120 – 180 °C

# Celtec®-MEAs

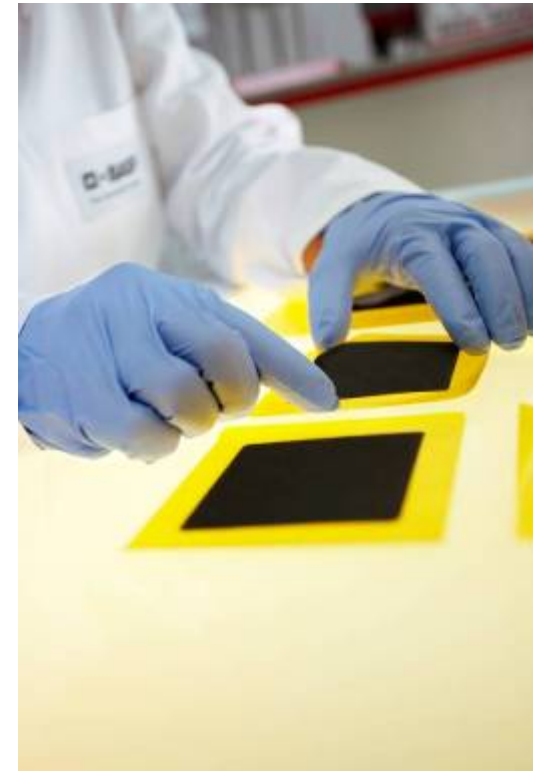
## Enabling Competitive Fuel Cells

### **Celtec-P MEA for high temperature PEMFC**

- In the market since 2004

### **Advantages for customers**

- Better robustness
- Simplified system
- Higher overall efficiency
- A hybrid of the best advantages of a phosphoric acid system with the manufacturing simplicity of a MEA



# Customer Partnerships to Develop Markets from 10W to 10kW

## *Portable Electronics:*



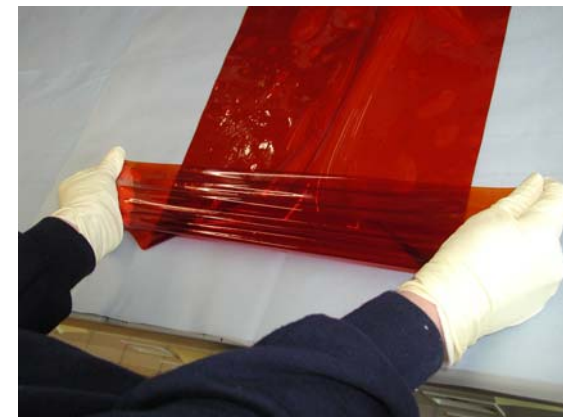
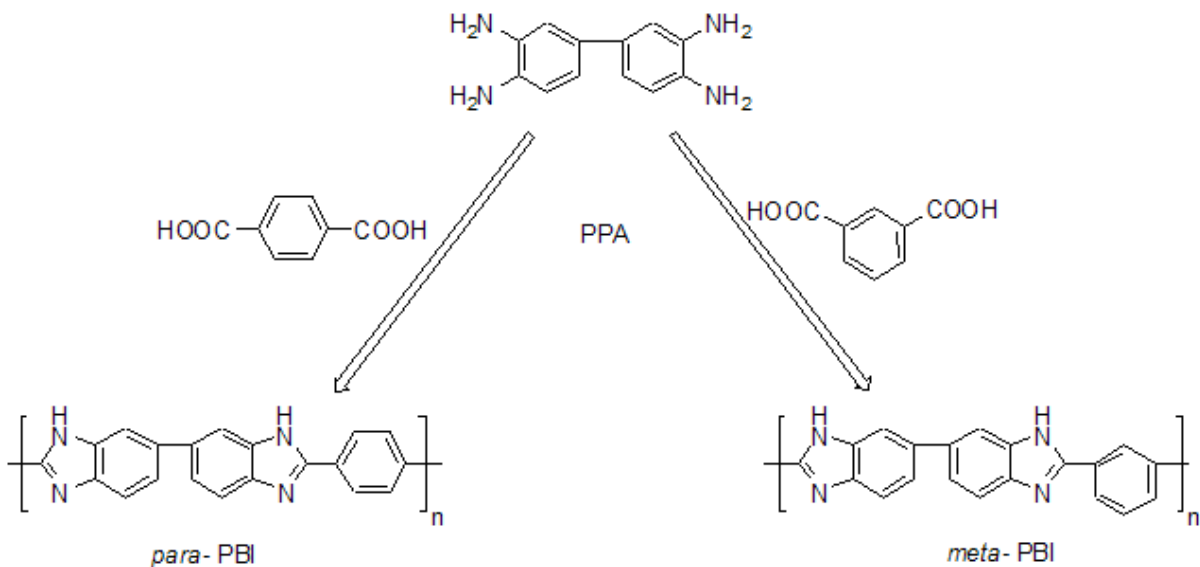
## *Residential:*



## *Back-up and Premium Power:*

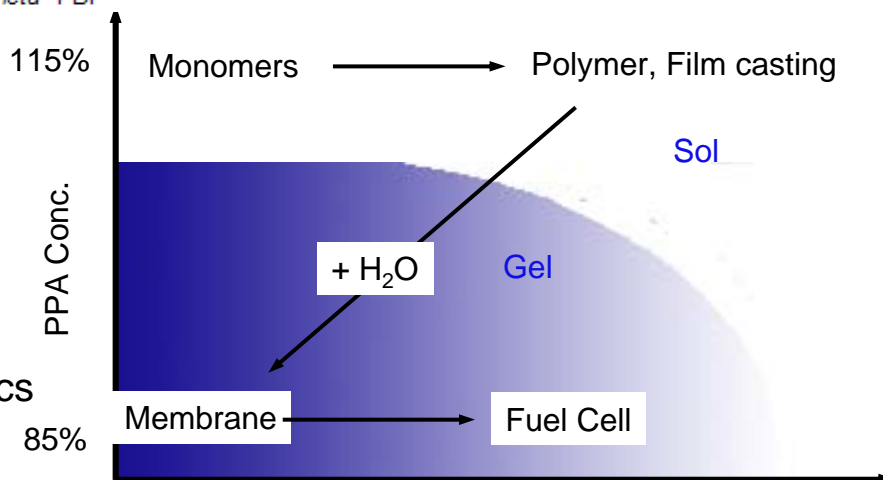


# Celtec®-P MEAs – BASF Fuel Cell Core MEA Technology



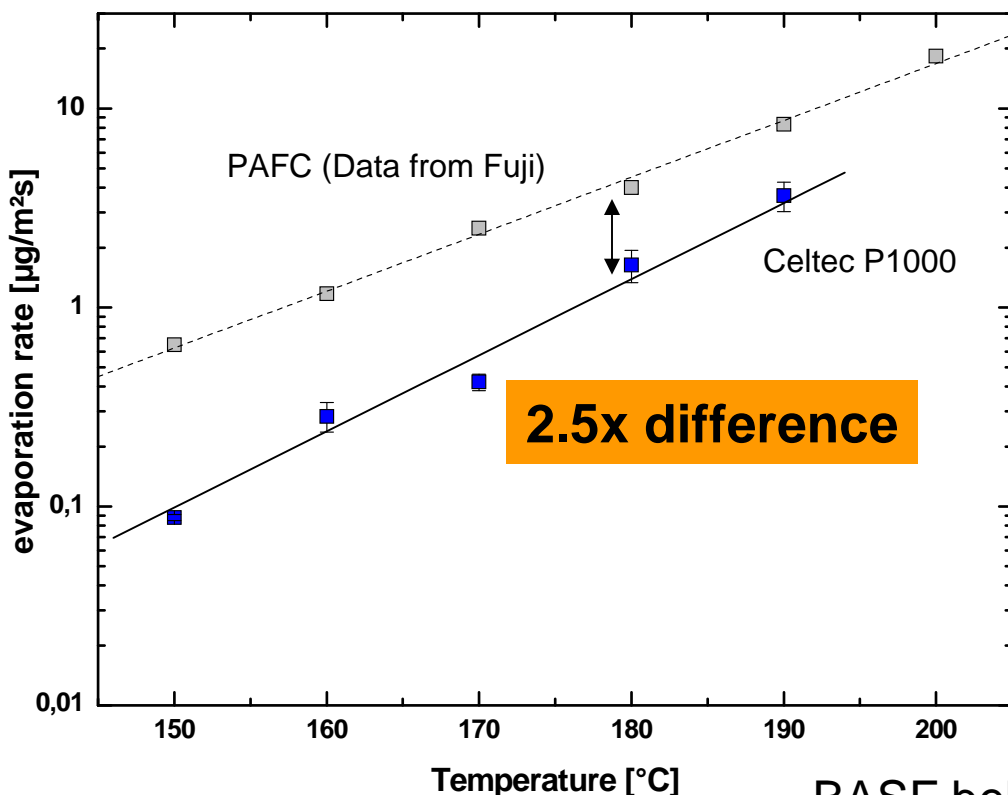
## MEA Operation

- T=120°C to 180°C
- High Tolerance to impurities
- Especially suitable for small stationary systems, APUs, small mobile systems for power electronics



# Acid evaporation from Celtec MEAs

## Hydrogen bonding with PBI may help retain acid



Celtec P 1000:  $50\text{cm}^2$ ,  
 $i=0.35\text{A}/\text{cm}^2$   $100\text{kPa}_a$ ,  $\text{H}_2$ -Air 1.5-2

PAFC data:  $100\text{cm}^2$ ,  $100\text{kPa}_a$   
 $i=0.3\text{ A}/\text{cm}^2$ ,  $\text{H}_2$ -Air 1.25-2

Fuji Electric PAFC data  
I. Okae, S. Kato, A. Seya, and  
T. Kamoshita, 'Study of the Phosphoric  
Acid Management in PAFCs',  
The Chemical Society of Japan  
67th Spring Meeting, 148 (1990).

BASF believes this basis may allow either simpler  
system or longer lifetimes based on acid retention

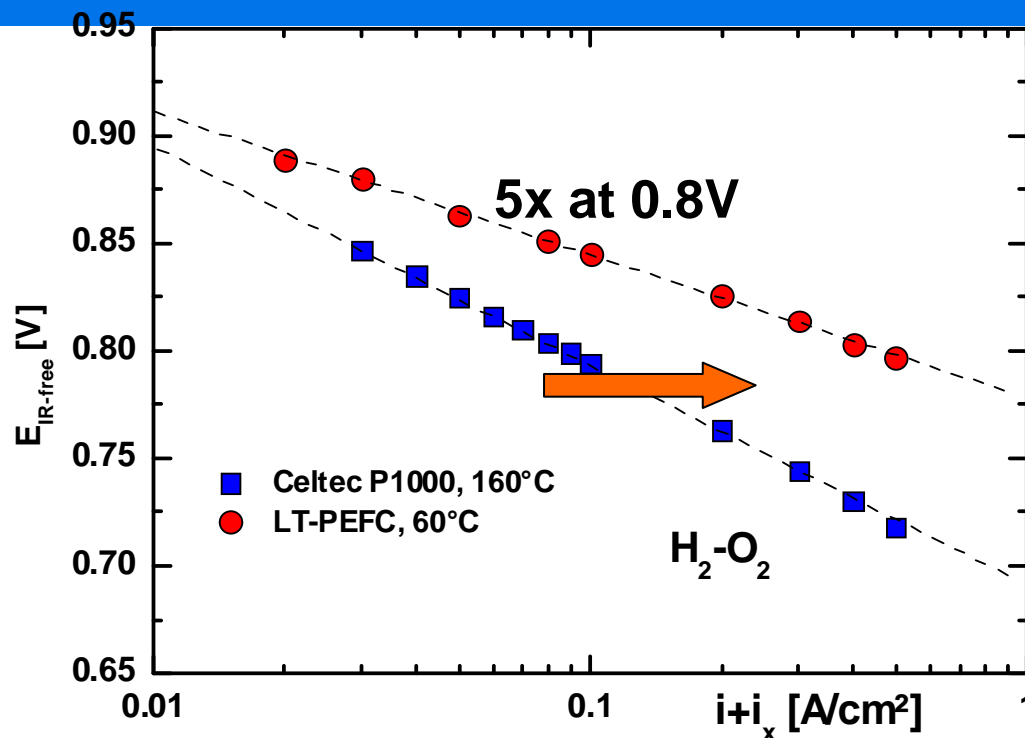
D.C. Steel. B. Benicewicz. L. Xiao. T.J. Schmidt in

*Handbook of Fuel Cells – Fundamentals, Technology and Applications*. Edited by Wolf Vielstich, Harumi Yokokawa, Hubert A. Gasteiger.  
Volume 5: *Advances in Electrocatalysis, Materials, Diagnostics and Durability*. © 2009 John Wiley & Sons, Ltd. ISBN: 978-0-470-72311-1.

- Celtec-P is a gel type membrane with low solid content
  - We continue to seek out approaches to improve the mechanical properties, e.g. creep or pressure sensitivity
- Benefits of improved mechanical strength
  - Low creep resistance of membrane tightens tolerances for stack manufacturing, i.e., dimensional tolerances of BBP and gaskets become very tight, forcing greater compliance from manufacturers
  - Broadening of these tolerances gives a more robust MEA
  - *Opens up new approaches for higher speed roll-to-product processing for MEA fabrication*



# Cathode kinetics in HT-MEAs



Celtec P cathode  
(1mg/cm<sup>2</sup>, 160°C, 100kPa<sub>a</sub>,  
dry H<sub>2</sub>/O<sub>2</sub> at s=1.2/9.5)

Low temperature  
Nafion type cathode  
(0.2mg/cm<sup>2</sup>, 60°C, 101kPa<sub>a</sub>  
H<sub>2</sub>-O<sub>2</sub>, 100%RH)

\* LT data: Neyerlin et al.,  
JECS 153(10) A1955 (2006)

- Overall comparison at 0.8V: 5x better kinetics in Nafion type LT PEFC compared to HT PEF
- What is the reason of the difference?

D.C. Steel. B. Benicewicz. L. Xiao. T.J. Schmidt in  
*Handbook of Fuel Cells – Fundamentals, Technology and Applications*. Edited by Wolf Vielstich, Harumi Yokokawa, Hubert A. Gasteiger.  
Volume 5: *Advances in Electrocatalysis, Materials, Diagnostics and Durability*. © 2009 John Wiley & Sons, Ltd. ISBN: 978-0-470-72311-1.

# Challenges for electrocatalysis at the PBI/H<sub>3</sub>PO<sub>4</sub> interface

- Activation energy and reaction orders at the PBI/H<sub>3</sub>PO<sub>4</sub> interface in high temperature PEFCs are identical than those at the Nafion interface in low temperature PEFCs
  - Identical reaction mechanism
- Major difference is observed in the exchange current density: Roughly 2.5 orders of magnitude lower values at the PBI/H<sub>3</sub>PO<sub>4</sub> interface in high temperature PEFCs compared to Nafion interface in low temperature PEFCs (Normalized to 101.325 kPa and 80°C)
  - Strong adsorption of phosphate ions on Pt leads to reduction of surface sites for O<sub>2</sub> adsorption
  - Oxygen solubility in phosphoric acid

# Approaches to improve kinetics in HT-cathodes

Modified Cathode Overpotential – current relationship

$$\eta_{ORR} = \frac{2.3RT}{a_c F} \log \left[ \frac{i}{10L_c A_{Pt,ec} i_{0,s}^* (1 - \Theta_{anion})^x (c_{O_2}^0)^\gamma} \right]$$

① Increase Pt Loading

② Increase Pt surface area

③ Increase  $i_{0,s}^*$

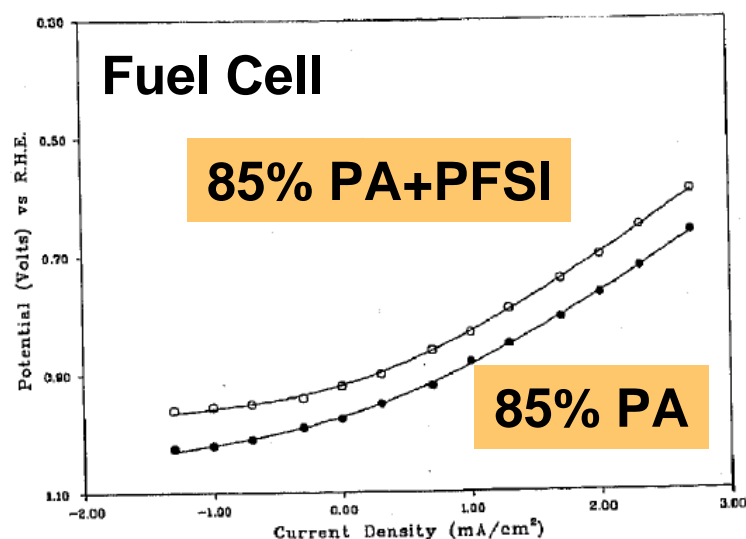
④ Decrease surface coverage of spectator species (anions)

⑤ Increase Solubility of  $O_2$

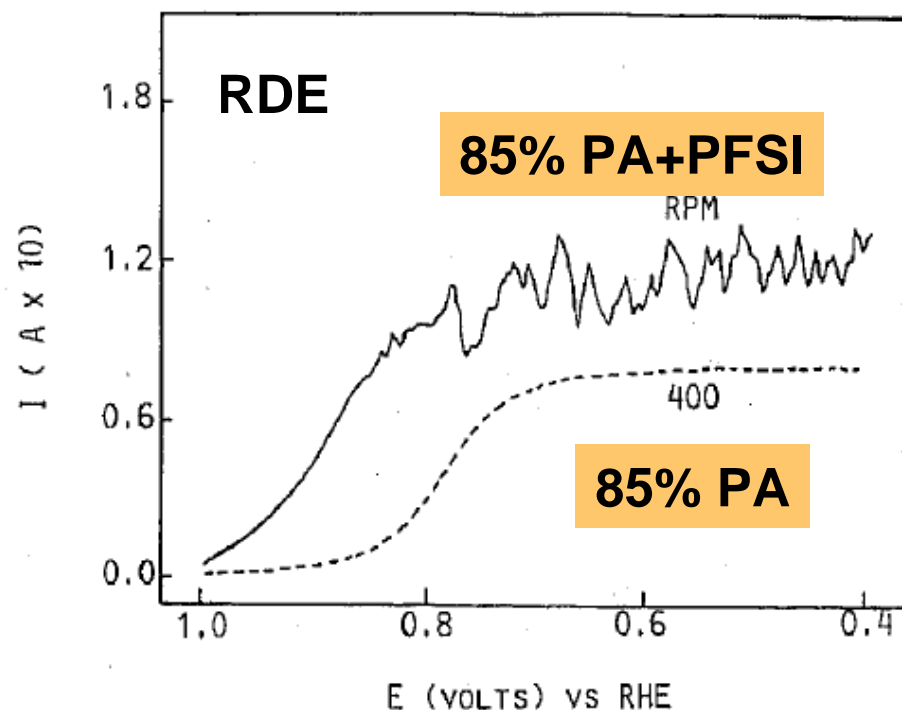
# Approaches to improve kinetics in HT-cathodes

Table I. The solubility and the diffusion coefficient of oxygen in phosphoric acid and PFSI

Electrolyte	Solubility $M l^{-1}$	Diffusion coefficient $cm^2 s^{-1}$
85% $H_3PO_4$	$3.3 \times 10^{-4}$	$1.21 \times 10^{-6}$
84% PFSI	$4.7 \times 10^{-3}$	$6.53 \times 10^{-6}$



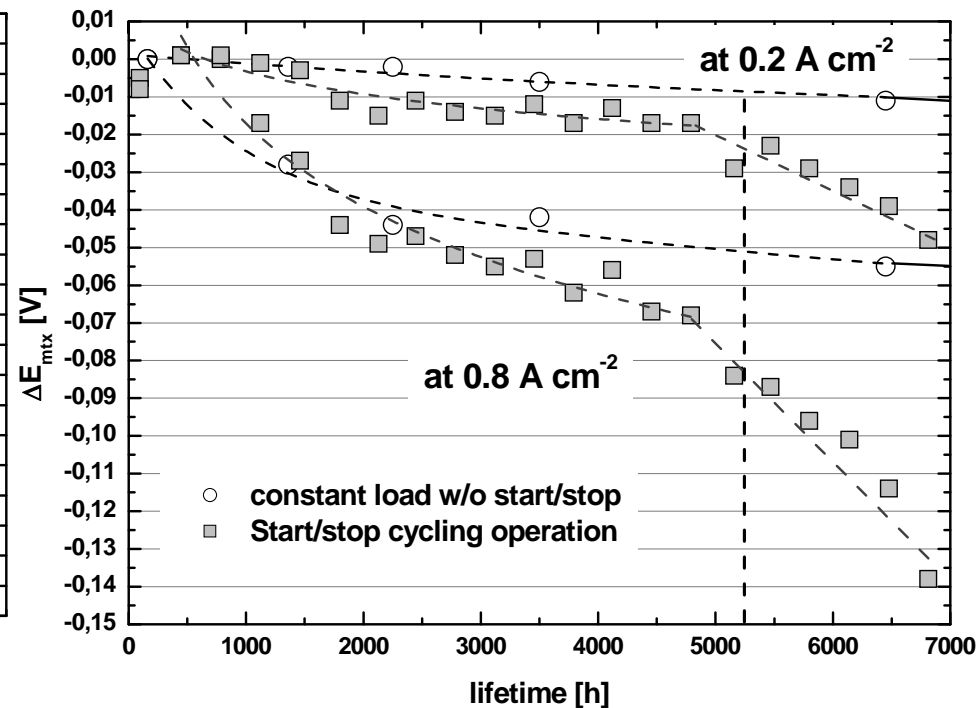
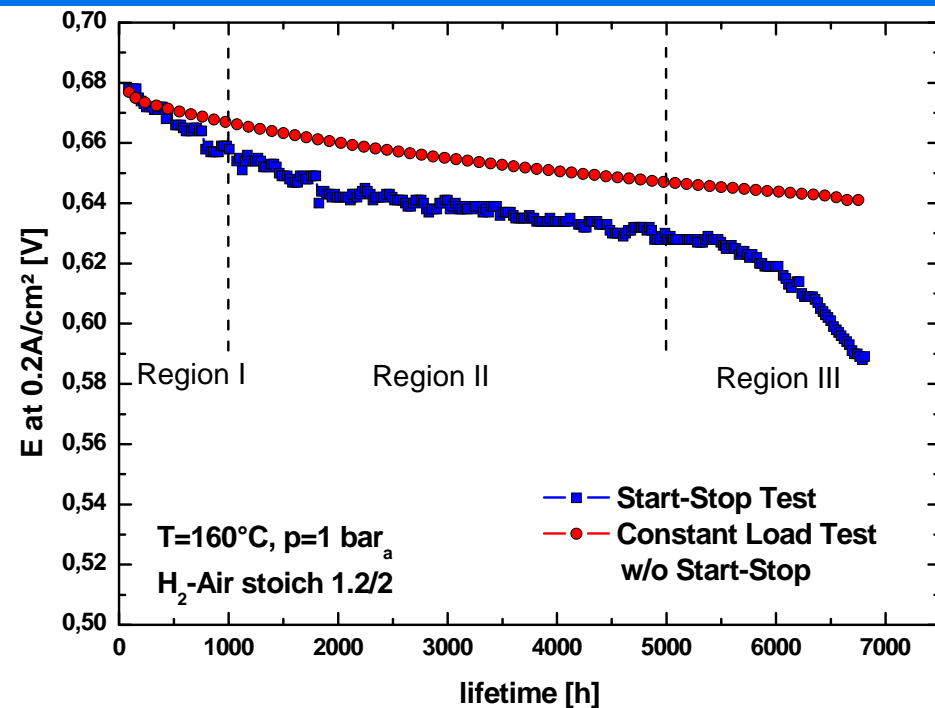
PFSI = perfluorosulfonimide



Razaq et al., JECS 136, 385 (1989)

- Development of alloys more resistant to phosphate anion absorption
  - Tools and techniques for alloy development far more advanced than what existed 20 years ago (for example XAFS, XANES, etc)
  - Synthetic techniques to create more sophisticated alloys have also progressed
- Pursuit of routes to increasing oxygen solubility
  - Significant wealth of new materials relevant to oxygen solubility have been developed

# Cathode Stability: Why are improvements necessary?



- Start-Stop operation triggers degradation due to cathode potential excursions to 1.3V or above
- Main effects: increase of mass transport overpotentials  
→ carbon corrosion

# Comparison HT and LT PEFC

**LT PEFC: Pt/Ketjen Black, 80°C,  
66%RH inlet, 0.4mg Pt, 150kPa, 1.3s**

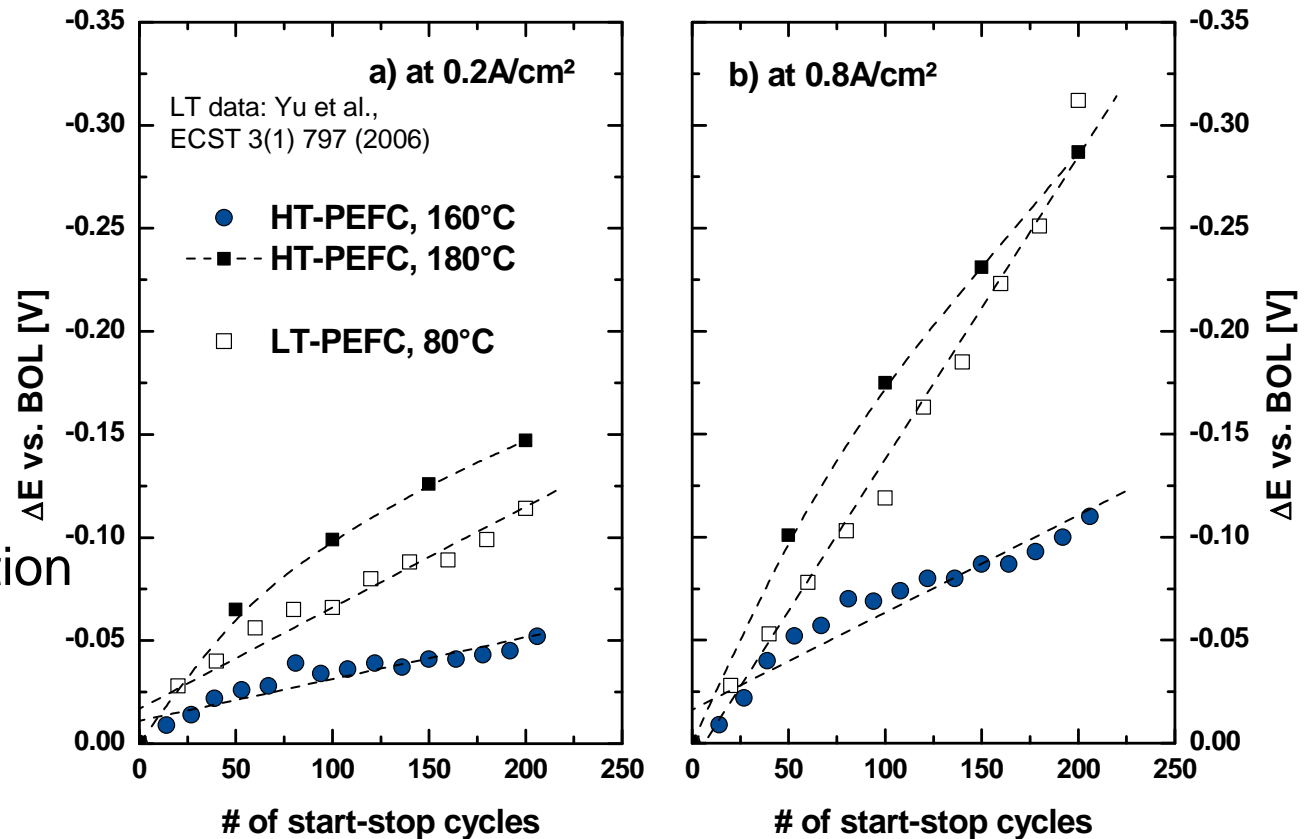
**HT PEFC: Pt-Alloy/Vulcan, 160°C  
dry, 0.7mg Pt, 100kPa, 2.5s**

$$i_{\text{corr}} = f(A_c, t_{\text{res}})$$

$$A_c (\text{LT}) \sim 0.45 A_c (\text{HT})$$

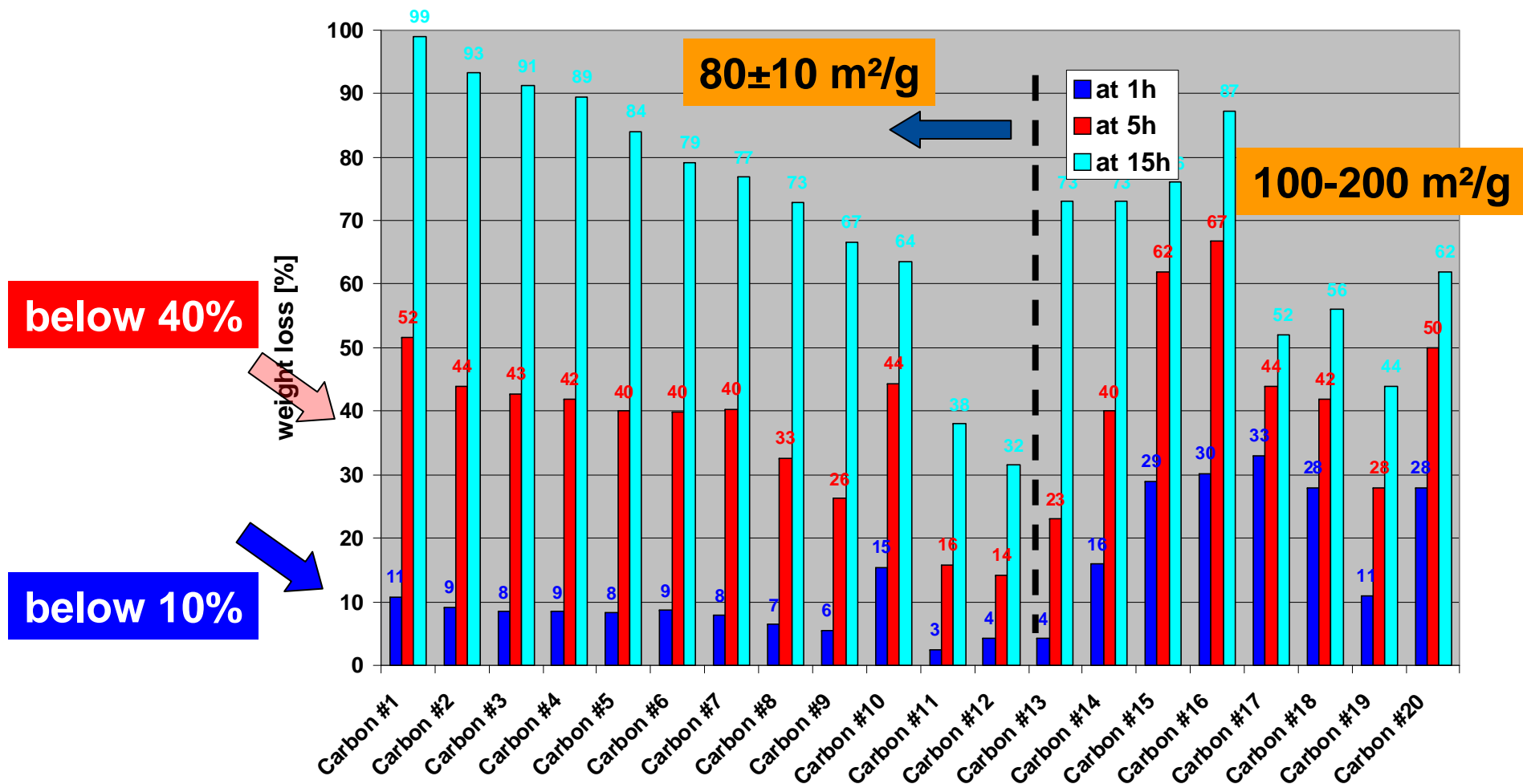
$$t_{\text{res}} (\text{LT}) \sim 0.5 t_{\text{res}} (\text{HT})$$

➡  $p_{\text{H}_2\text{O}}$  drives reaction



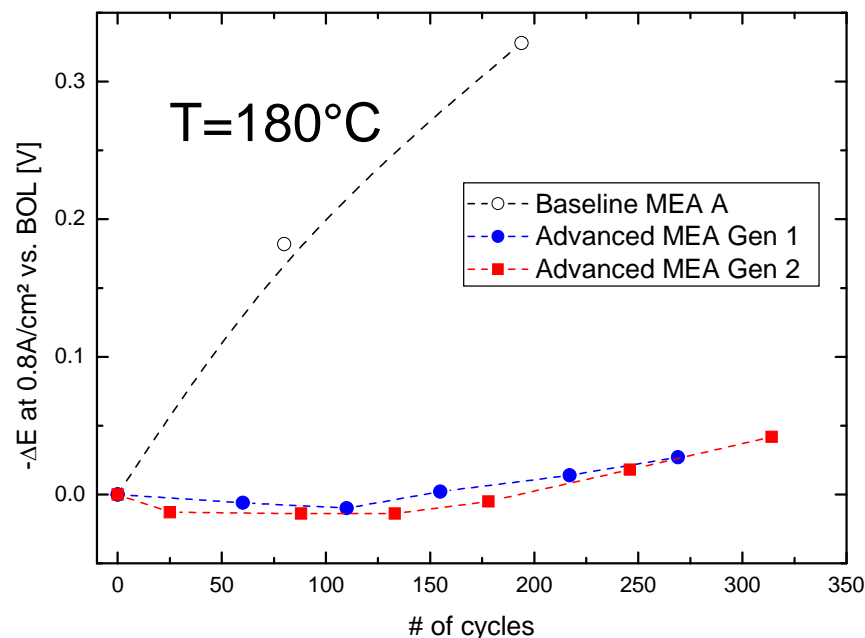
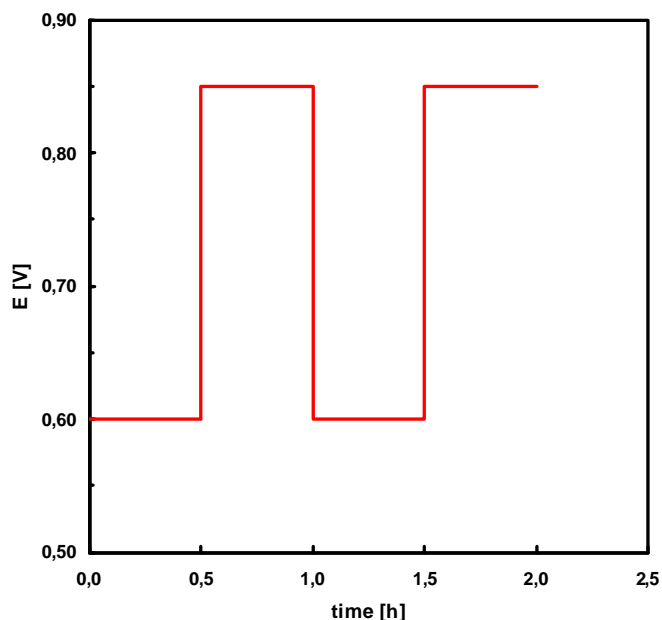
T.J. Schmidt, in *Polymer Electrolyte Fuel Cell Durability*,  
F. Büchi, M. Inaba, T.J.Schmidt (Eds.) Springer, 199-222 (2009)

# Stabilized carbons: Carbon Corrosion Results at 1.2V and 180°C





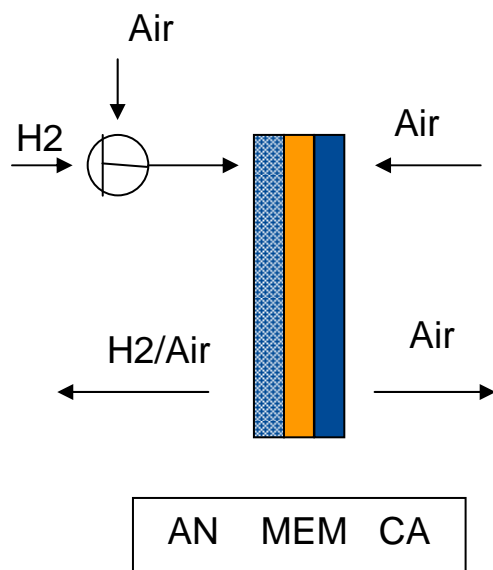
# Voltage Cycles/Operation at high cathodic potentials under accelerated conditions



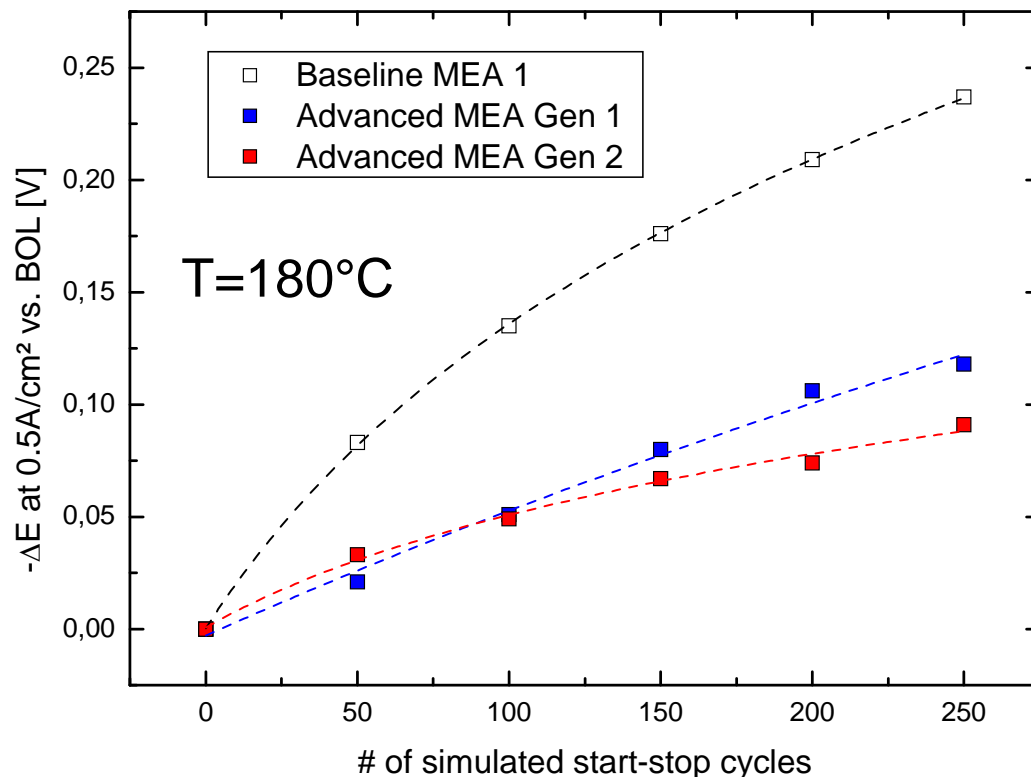
Test: 30 minutes cycles between 0.6V and 0.85V probes catalyst stability

Cycle stability significantly improved with new cathode materials

# Start-Stop under accelerated conditions



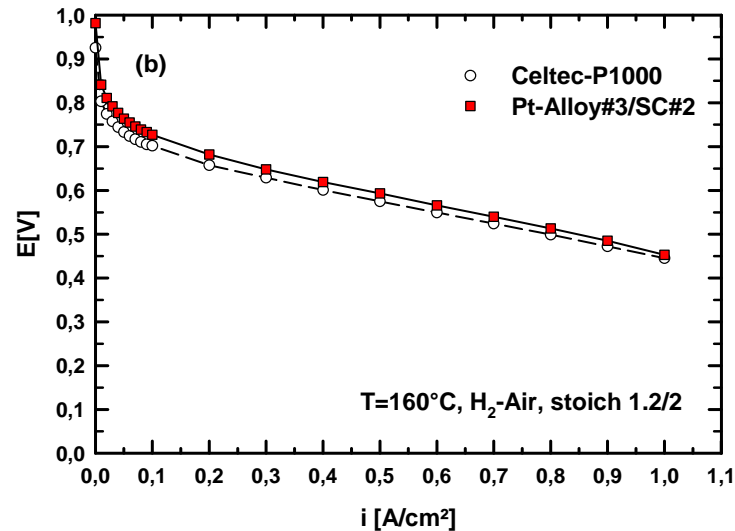
Simulated Start-Stop: Every 30s passing a H2/Air (Air/H2) front through anode



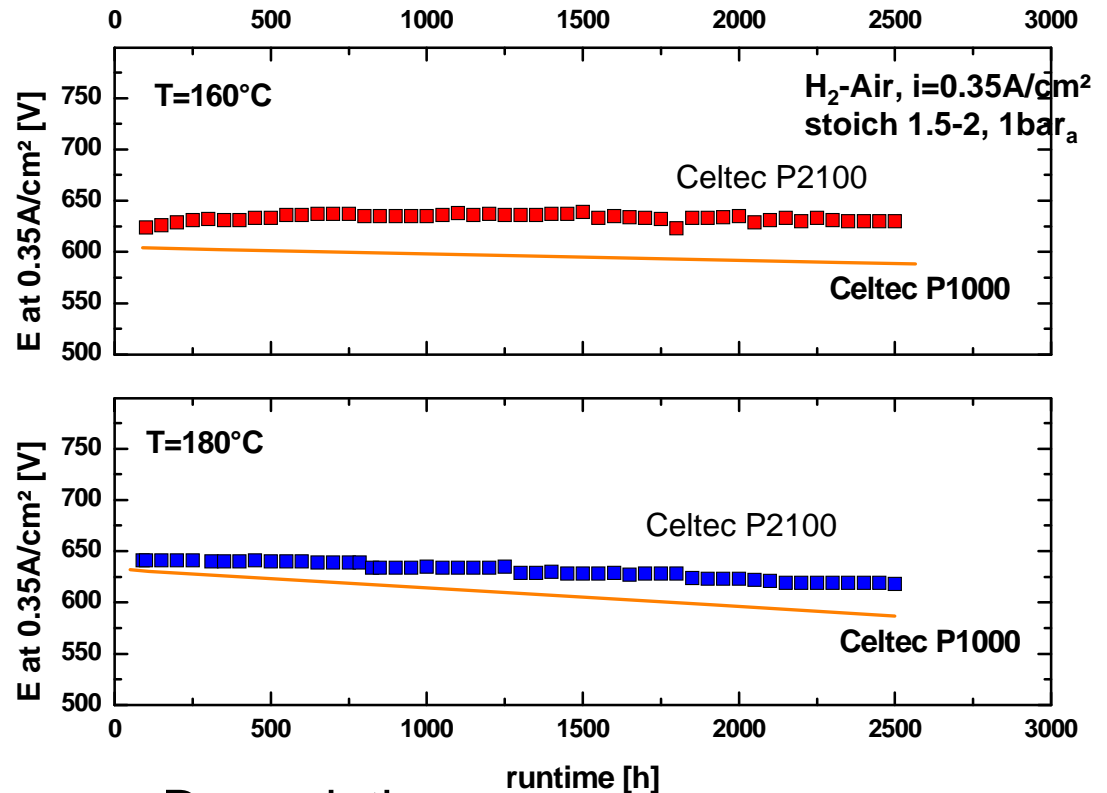
D.C. Steel, B. Benicewicz, L. Xiao, T.J. Schmidt in

*Handbook of Fuel Cells – Fundamentals, Technology and Applications*. Edited by Wolf Vielstich, Harumi Yokokawa, Hubert A. Gasteiger. Volume 5: *Advances in Electrocatalysis, Materials, Diagnostics and Durability*. © 2009 John Wiley & Sons, Ltd. ISBN: 978-0-470-72311-1.

# Lifetime tests



New Cathode Generation:  
Performance is unaffected



Degradation

$160^{\circ}\text{C}$ : virtually no degradation

$180^{\circ}\text{C}$ : degradation rate in continuous operation improved by factor of 2.4

# Summary

## R&D Directions in HT-MEA Development

- Increase Membrane Mechanical Strength
  - Simplifies stack building
  - Reduces tolerance requirements
  - Path for next generation manufacturing
- Cathode Alloys
  - Use 21<sup>st</sup> century tools to design for reduced phosphate anion absorption and realize kinetic potential
  - Exploit new materials with high(er) oxygen solubility
- cathode corrosion
  - stability improvements have be achieved
  - cathode corrosion stability remains focus of development to enter more widespread markets