Performance Measurement of MEAs

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214th Meeting of the Electrochemical Society-HTM Working Group
Honolulu, HI, Thursday, October 16th, 2008

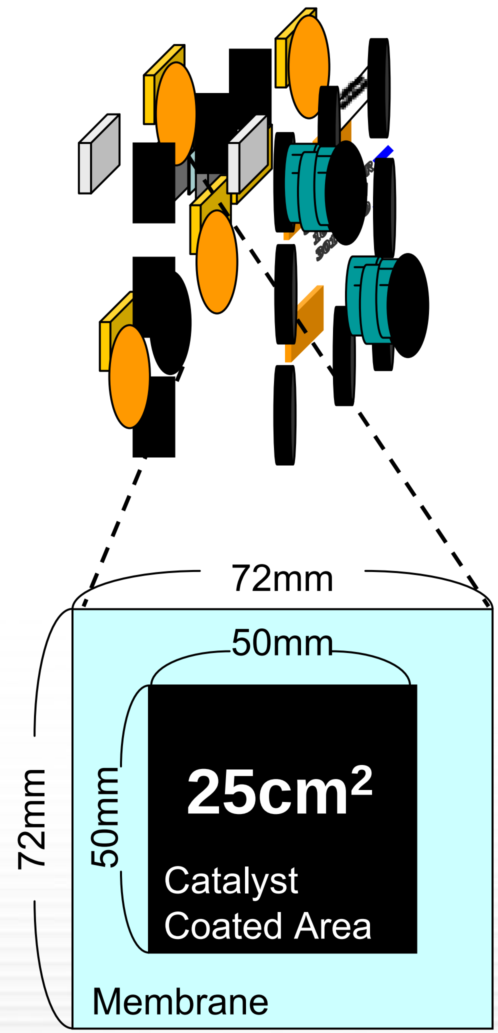
Outline

1. **Measurement of MEA Performance**
   i. Measurement of ECA
   ii. Measurement of ORR activity
   iii. Effect of RH and T on
      a) Performance/Activity
      b) Membrane resistance
      c) Catalyst Layer resistance
2. **Current Status - PEMFC**
3. **Overview of Requirements &Testing**
   i. Expected MEA operating environment
   ii. Electrolyte membrane target performance
   iii. Electrolyte membrane durability
   iv. Target cost of membrane
   v. Automotive fuel cell MEA degradation map

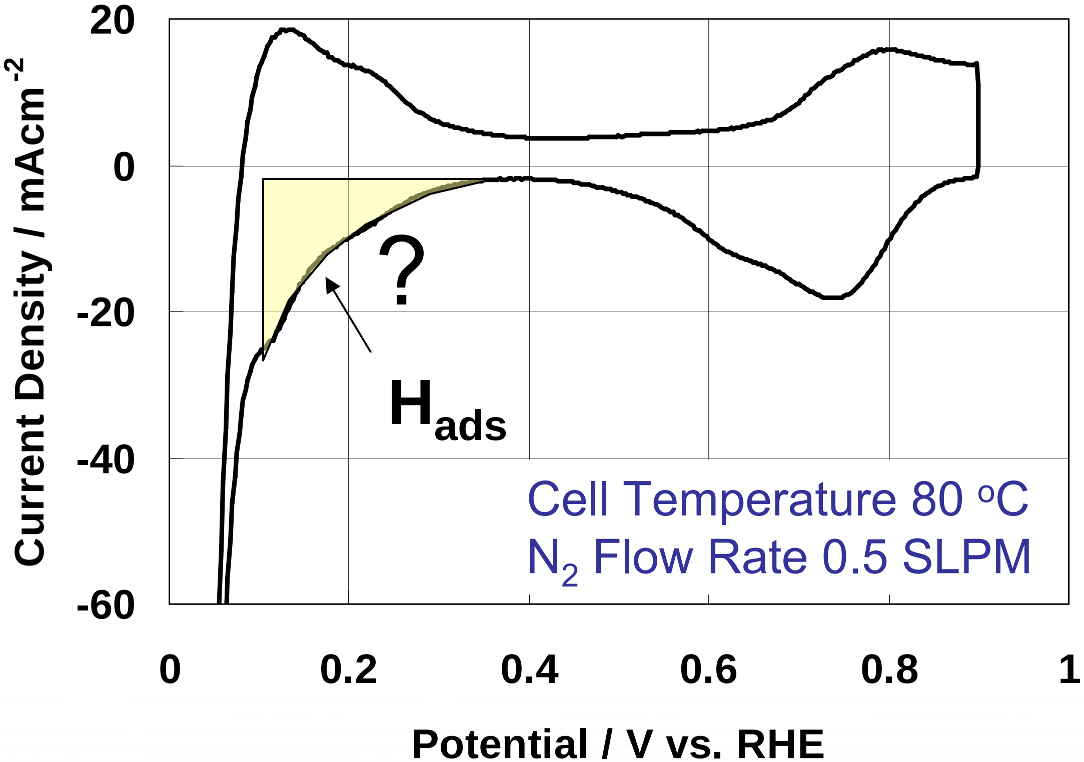
Measurement of MEA Performance

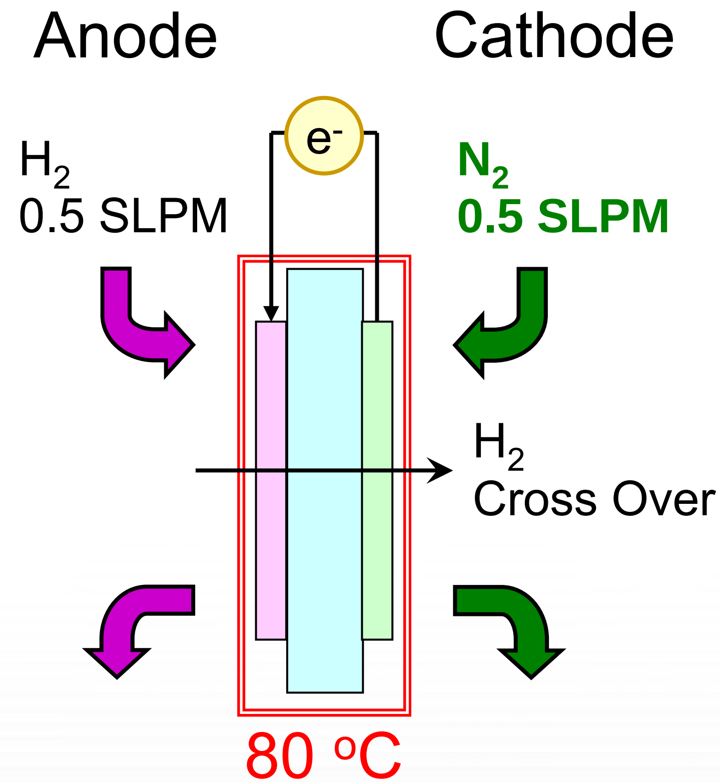
Fuel Cell Specification

Typical subscale cell used in testing of MEA performance and durablity.



Cyclic Voltammograms- Issues



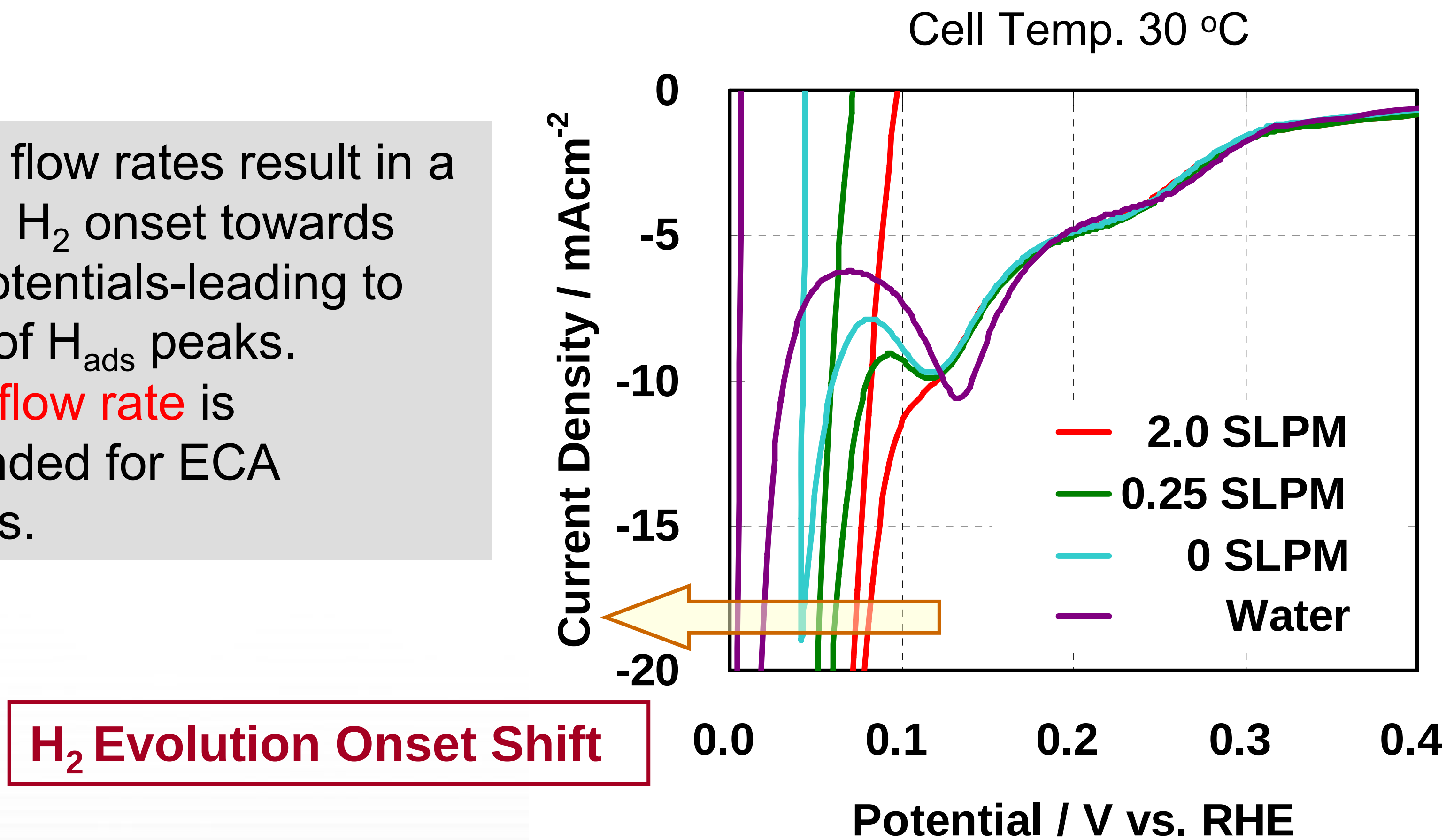


- **N_2 Flow Rate at Cathode***
- **Cell Temperature**
- **Cell RH**

*M. Uchimura and S. S. Kocha, *AIChE Abstracts Fall* 2007.

Effect of N_2 Flow Rates on CV

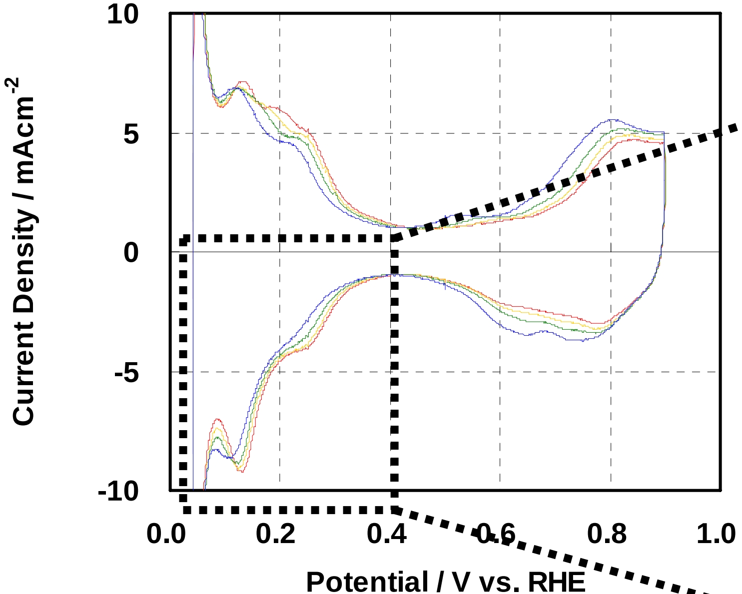
- High N_2 flow rates result in a shift of the H_2 onset towards positive potentials-leading to smearing of H_{ads} peaks.
- Zero N_2 flow rate is recommended for ECA diagnostics.

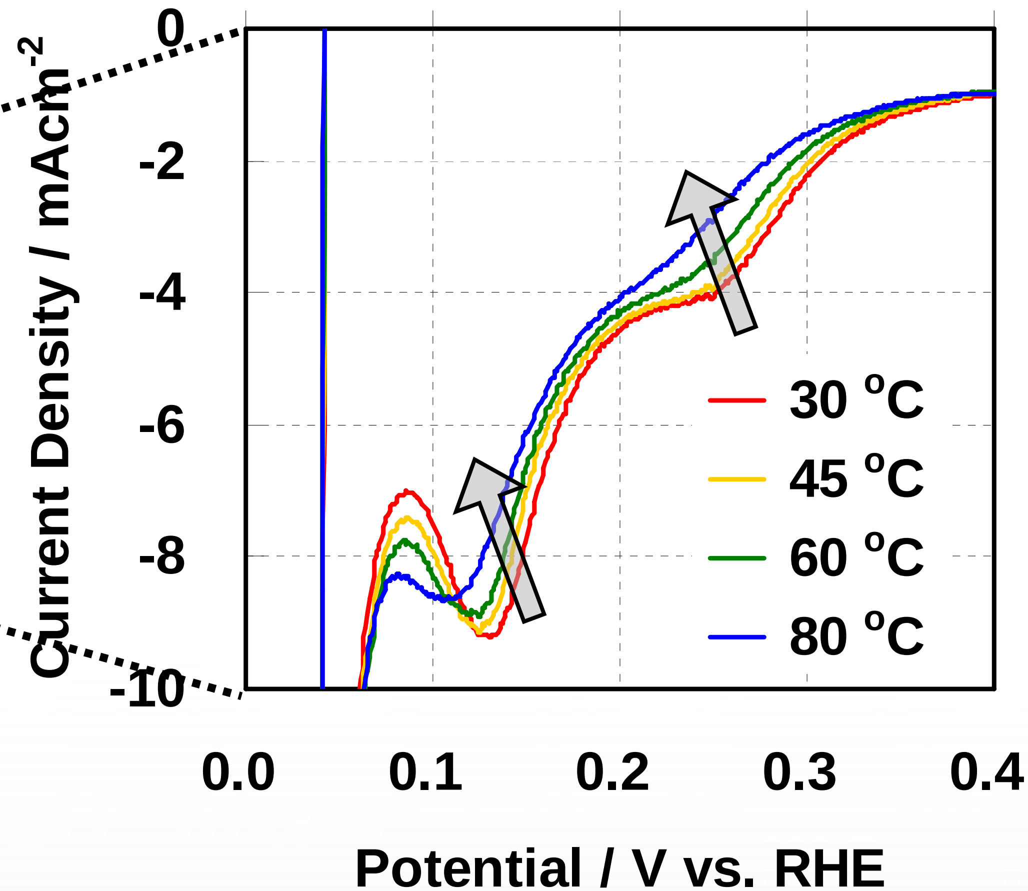


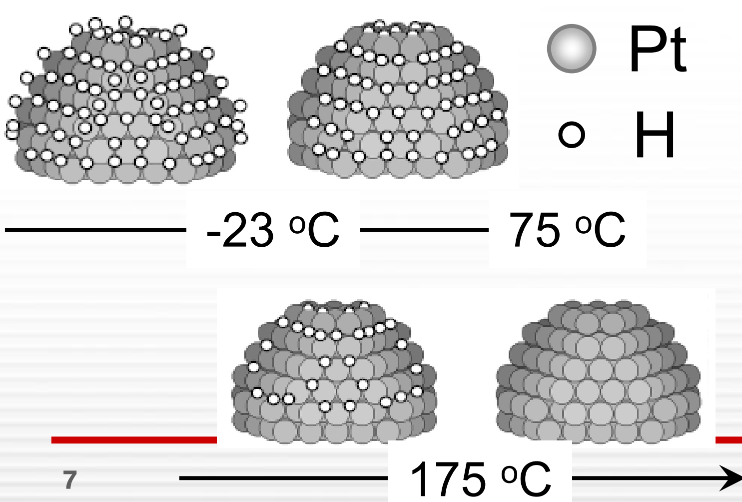
1) R. Woods, *J. Electroanal. Chem.*, 49, 217-226 (1974).
2) D. A. J. Rand and R. Woods, *J. Electroanal. Chem.*, 35, 209 (1972).

M. Uchimura and S. S. Kocha, *ECS Transactions* 11, 1215 (2007).

Effect of Cell Temperature on CV



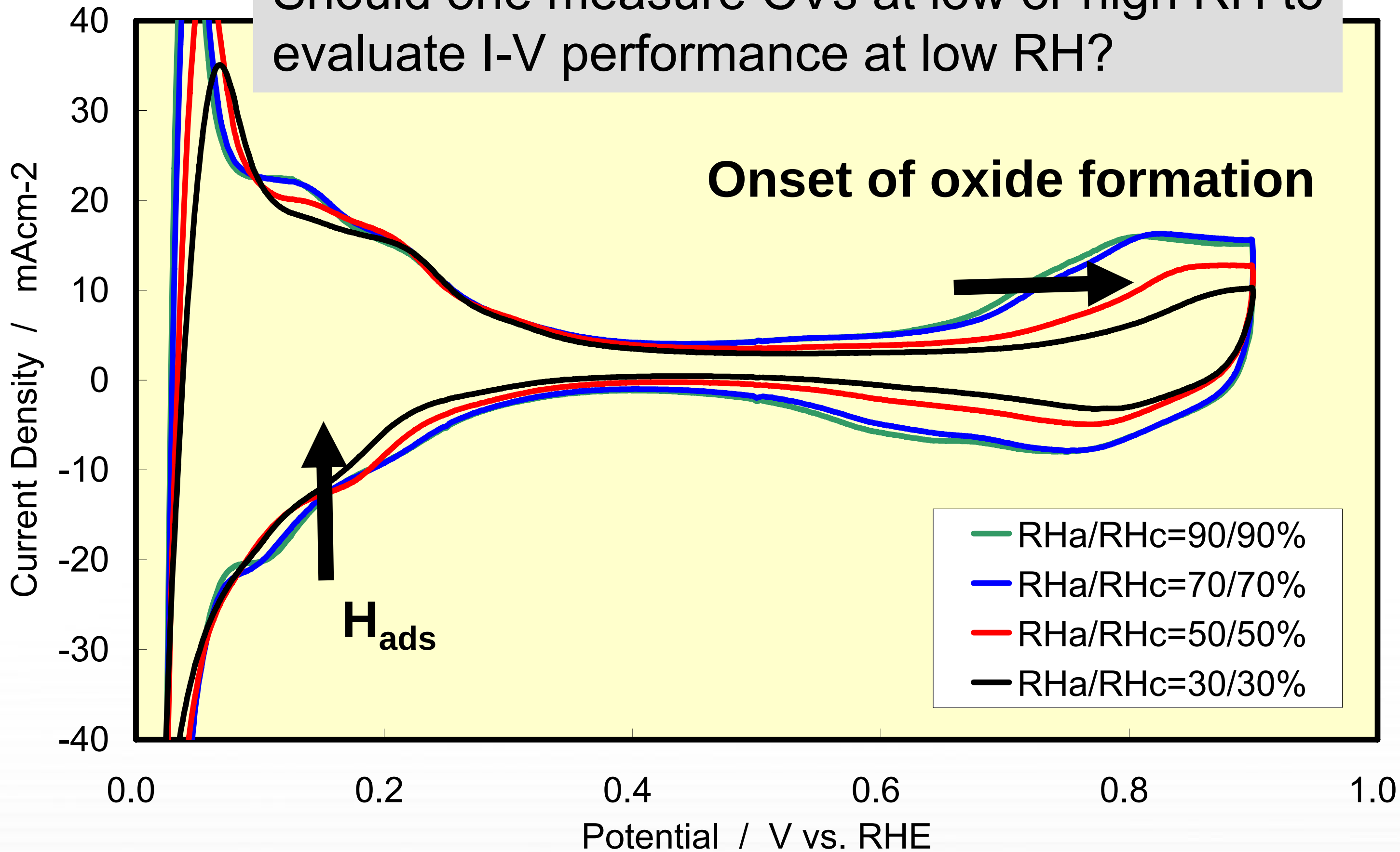




Ph.D. Disseration of M. Oudenhuijzen
“Support Effects in Heterogeneous Catalysis”,
Chapter 6, p.104 (2002).

Effect of RH - CV

Should one measure CVs at low or high RH to evaluate I-V performance at low RH?



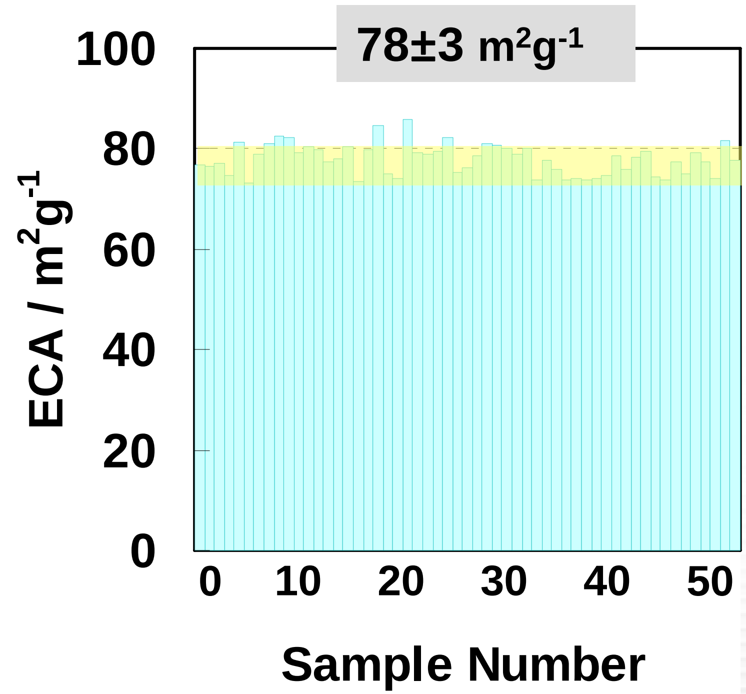
Onset of oxide formation shifts positively as RH decreases.

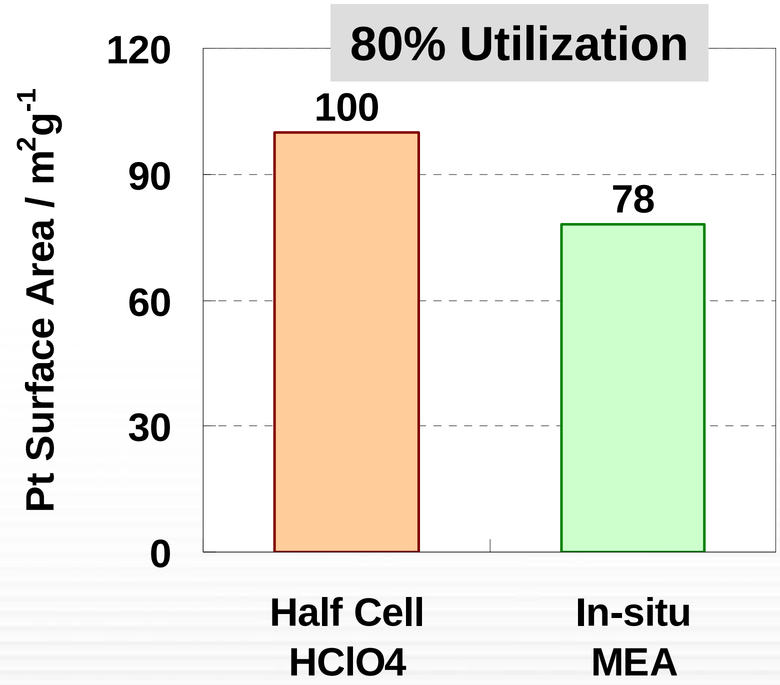
Nissan, unpublished data.

Reproducibility and Utilization

ECA Measurement Conditions

N_2 Flow Rate / SLPM	0
Cell Temperature / °C	30
Voltage Scan Range / V	0.04 - 0.9





M. Uchimura and S. S. Kocha, *ECS Transactions* 11, 1215 (2007).

ORR Activity

Scatter in values of ORR activity reported in the literature.

Reasons for Scatter

- Catalyst Loading
- Surface Area
- Operating Conditions
- Protocol Used
  - Pre-conditioning
  - Intermediate-conditioning
  - Direction of Sweep

Oxide Coverage

Nissan Abstracts on Pt - Oxides : This meeting

214th Meeting of the Electrochemical Society
Honolulu, HI, 2008

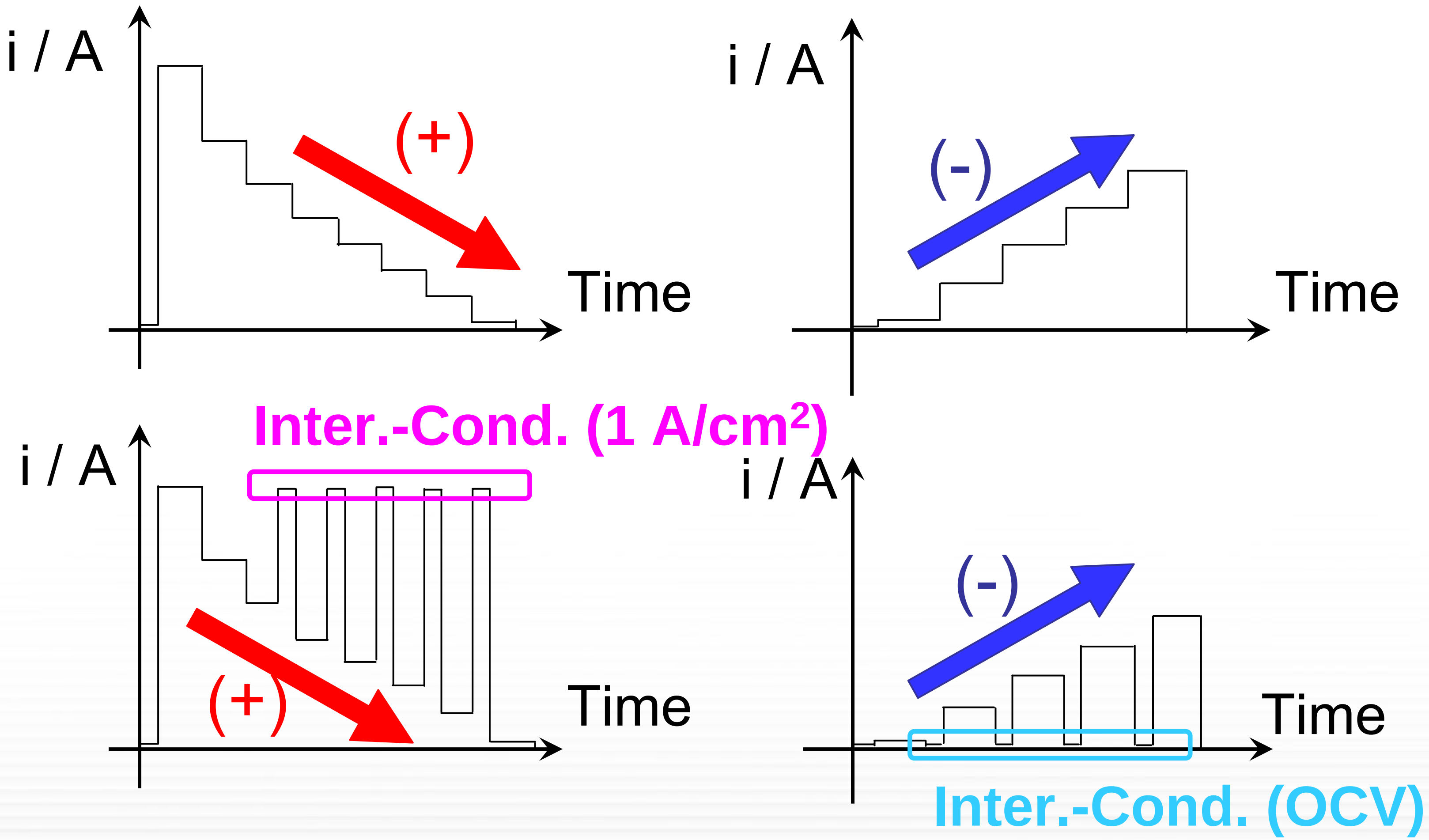
Abstract 914
The Influence of Pt-oxide Coverage on the ORR Reaction Order in PEMFCs
M.Uchimura and S. Kocha

Abstract 919
MEA Performance Modeling for Breakdown of Catalyst Layer Polarization Components.
Y. Suzuki, S. Sugawara, N. Horibe, S. Kocha and K. Shinohara

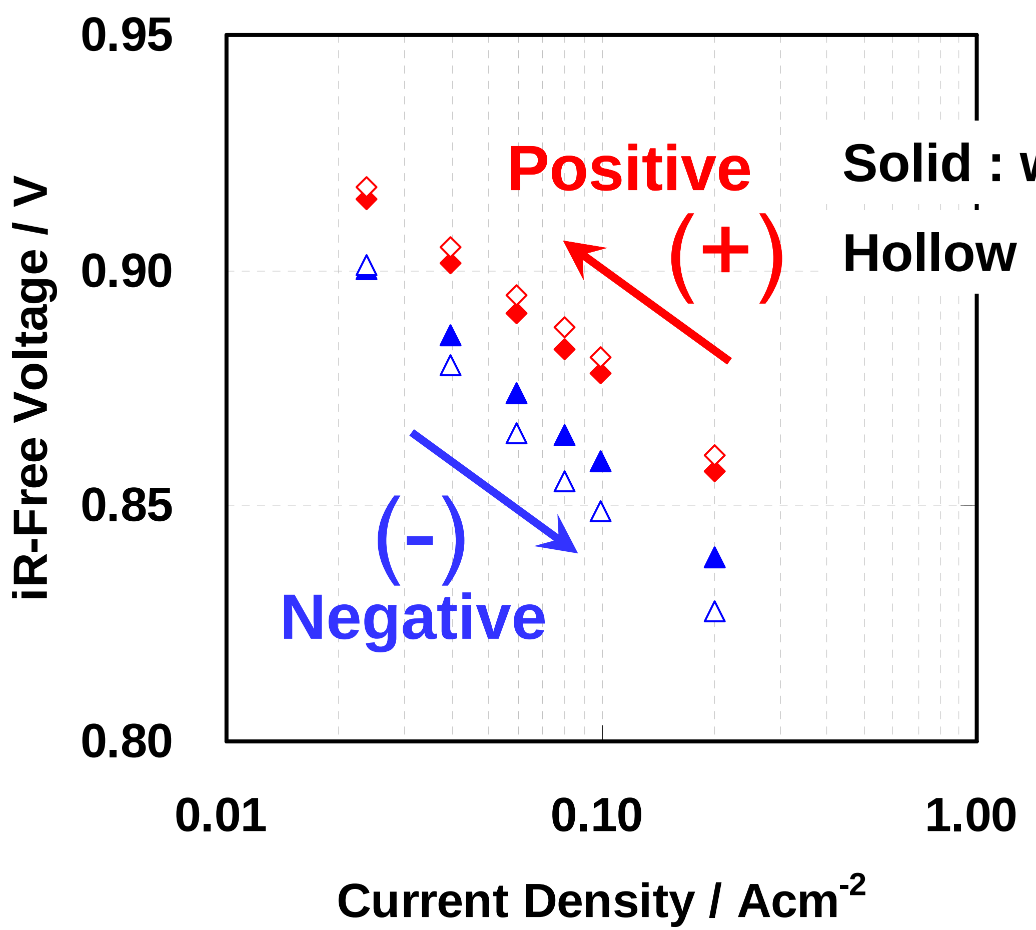
Abstract 1036
Simultaneous Electrochemical Measurement of ORR Kinetics and Pt Oxide Formation/Reduction
S. Sugawara, K. Tsujita, S. S. Kocha , K. Shinohara, S. Mitsushima and K. Ota,

Schematic of Measurement Protocols

Cell Temp. 80 °C, RH 100 %, P_{O2} : ~ 70 kPa



ORR Activity - Tafel Plots



Solid : w/o Inter.-conditioning

Hollow : w/ Inter.-conditioning

	$i_{0.9}$ / $mAcm^{-2}$	
Positive	**42**	×1.75
Negative	**24**	

Benchmarking data from different laboratories is difficult

ORR Activity – Modeling

Importance of Pt Oxide Film on ORR Kinetics

N.M. Markovic, et al., J. Electroanal. Chem., 467, 157 (1999).

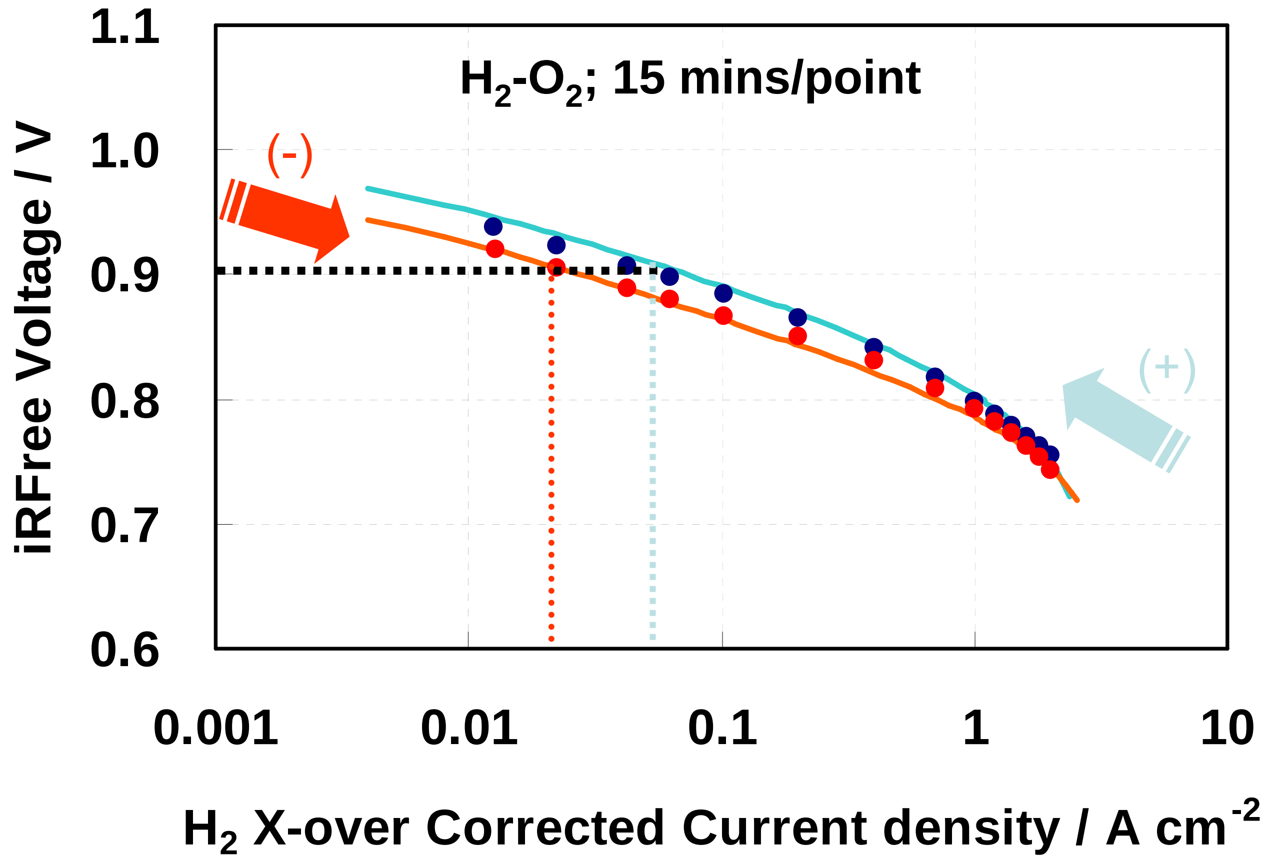
$$i = nFKC_{O_2}(1-\theta)\exp\left(-\frac{\beta F\eta}{RT}\right)\exp\left(-\frac{\gamma r\theta}{RT}\right)$$

Adsorbed oxygen species can
(1) block the adsorption of O_2 on active Pt sites.
(2) alter the adsorption energy of reaction intermediates.

Abstract 919
(214th Meeting of the Electrochemical Society, Honolulu, HI, 2008)
MEA Performance Modeling for Breakdown of Catalyst Layer Polarization Components.
Y. Suzuki, S. Sugawara, N. Horibe, S. Kocha and K. Shinohara

Effect of oxide on activity was included and fitted to MEA ORR results.

ORR Activity – Modeling



Model

- Extended Butler-Volmer Eq.
- Resistance-EIS + Finite trans. model
- Oxide Coverage (θ)
- Single i_0

Abstract 919

MEA Performance Modeling for Breakdown of Catalyst Layer Polarization Components, *Y. Suzuki, S. Sugawara, N. Horibe, S. Kocha and K. Shinohara*

Effect of RH

The key parameters that need to be measured to characterize high temperature/low RH membranes using MEAs in subscale fuel cells are the following:

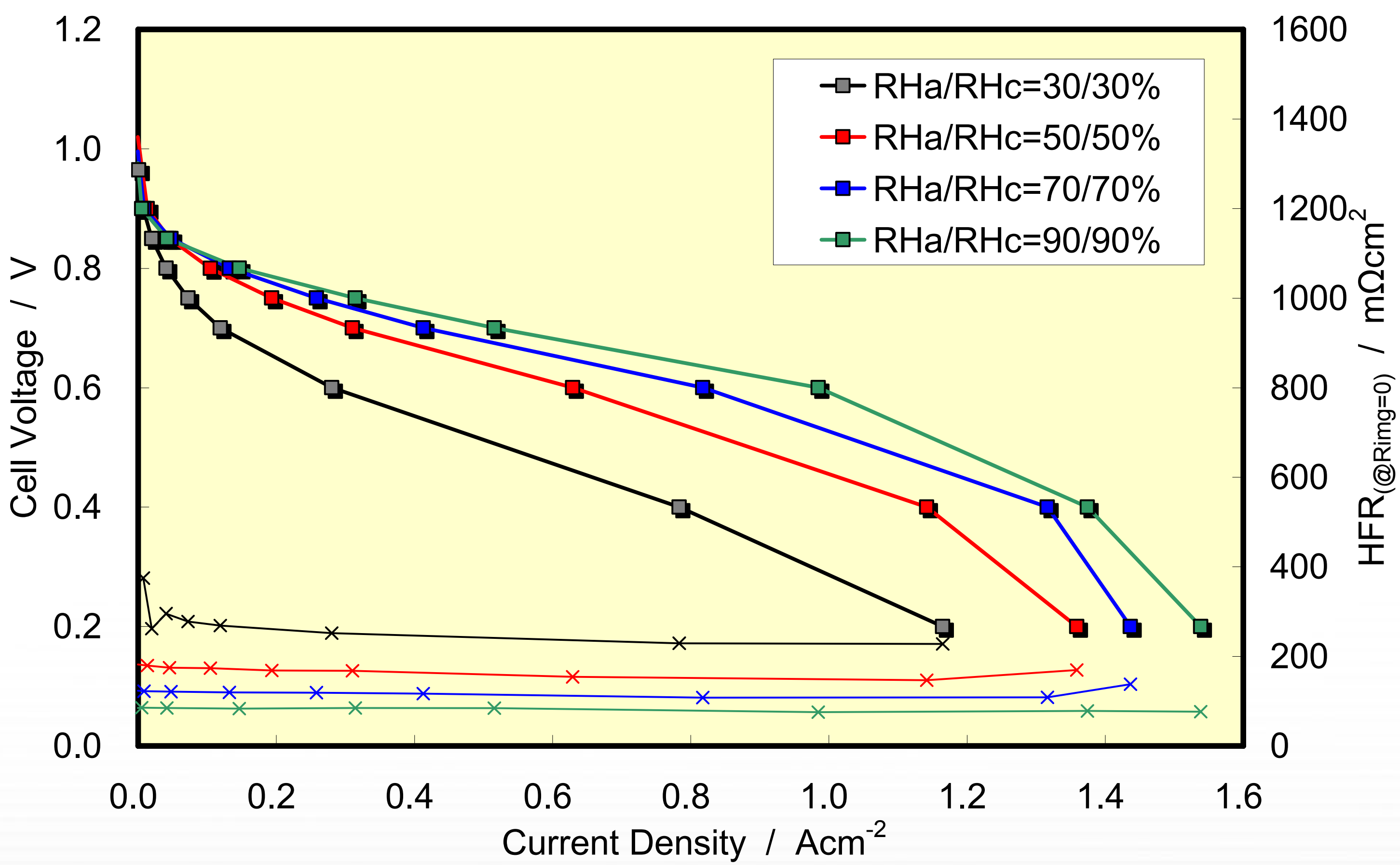
- Catalyst Activity
- Membrane Resistance
- Catalyst Layer Resistance

Effect of RH: Activity

Kinetic reaction order: < 1
ECA : Small effect
Tafel : Higher at lower RH
Activity: decreases at low RH below 50%

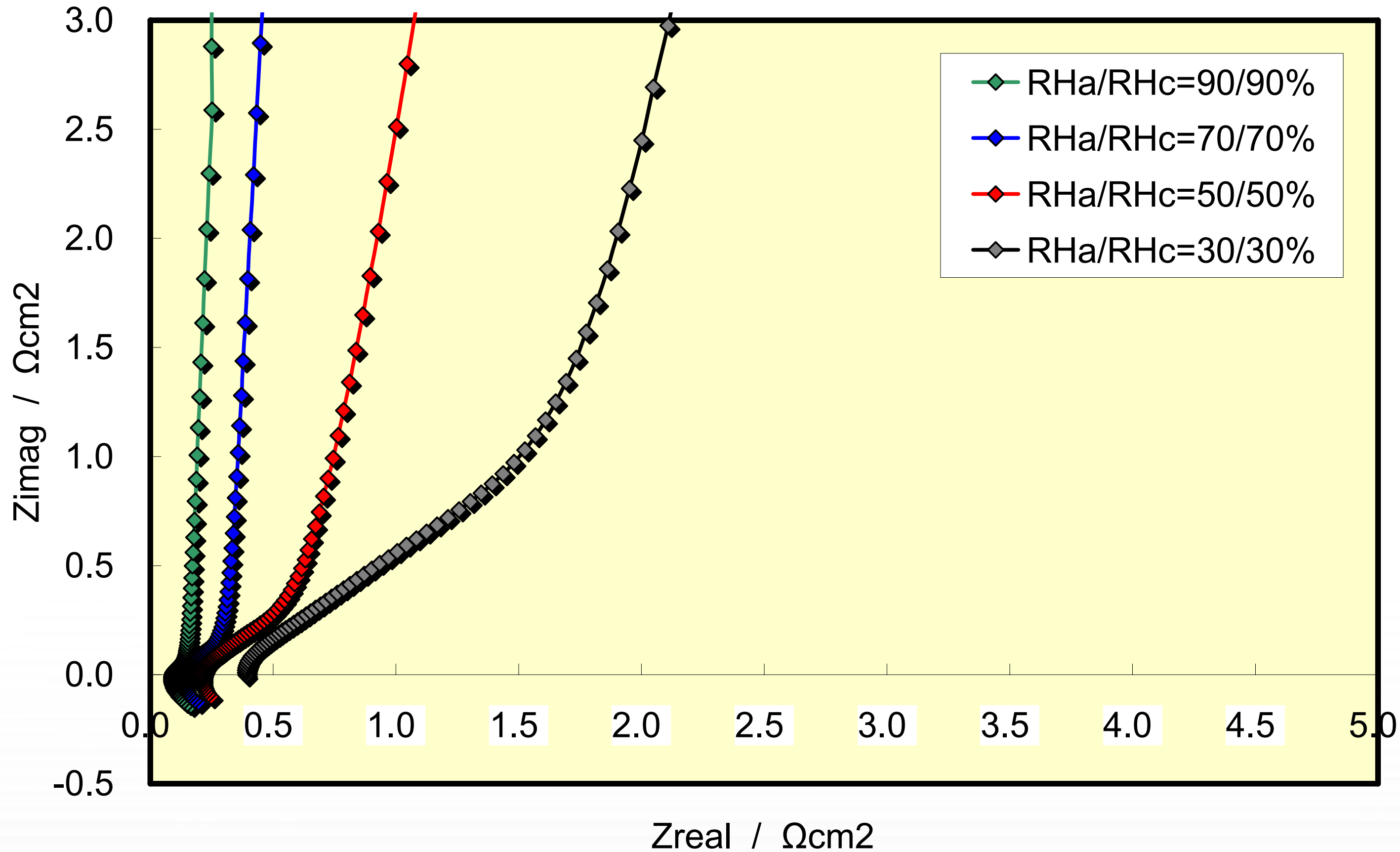
"*Effect of Elevated Temperature and Reduced RH on ORR Kinetics for PEM Fuel Cells*"
Hui, Xu, Ying Song, H. Russell Kunz, and James M. Fenton, J. Electrochem. Soc., 152 (9), (2005)

Effect of RH – IV Peformance, HFR



HFR increases and performance decreases as RH decreases.

Effect of RH – Catalyst Layer R



Ionomer resistance in the catalyst layer increases at lower RH.

Current Status - PEMFC

Current Status – Improved Stacks

Not Enough!

MEA (Membrane Electrode Assembly): Double the power density is achieved through improved conductivity of the electrolyte layer within the MEA, where the main chemical reaction occurs, coupled with a more densely-packed cell structure.

Cell Structure: A more densely-packed cell structure is achieved through the replacement of the carbon separator with a new thin metal separator. The separator functions to break down the hydrogen, oxygen and cooling water necessary for the chemical reaction. A specific coating applied to the separator helps improve conductivity and prevents chemical corrosion, leading to increased efficiency and durability throughout the fuel cell stack's life-cycle.

Electrode: Higher durability electrode material results in a 50% reduction of the platinum required compared to the previous generation. This in turn, provides a significant breakthrough in the cost of these components.

Stack size and cost: The combined improvements in the cell result in double the power density, which enables a downsizing of the fuel cell stack size by one-third and significant cost reduction, without sacrificing performance. Compared to the previous generation, the new generation stack's power output is increased 1.4 times from 90kW to 130kW, which can power larger vehicles. Stack size is reduced by 25% to 68L from 90L, which allows for improved packaging flexibility.

Need further improvements in terms of a HTM-MEA that operates at high T and low RH to achieve PEMFC system cost targets.

Overview of Requirements & Testing

PEMFC: Targets and Protocols in Japan

Membrane and catalyst performance targets for automotive fuel cells

A. Iiyama[1], K. Shinohara[1], S. Iguchi[2] and A. Daimaru[3]

[1] *Fuel Cell Laboratory, Nissan Motor Co., Ltd., Yokosuka, Japan*
[2] *Automobile R&D Center, Honda R&D Co., Ltd., Utsunomiya, Japan*
[3] *Fuel Cell System Development Div., Toyota Motor Corp., Susono, Shizuoka, Japan*

FCCJ

The Fuel Cell Commercialization Conference of Japan (FCCJ) has worked with three automobile manufacturers in Japan to define the target performance, durability, and cost of fuel cells for transportation application, and in January 2007 produced a booklet describing them.[1] This article provides an overview of these target values and highlights the durability parameters specifically required in the automotive application in relation to the current knowledge of degradation mechanisms of fuel cells. On the basis of this information, FCCJ has proposed a methodology for testing membrane-electrode assemblies (MEAs) as an approach to the evaluation of materials for the two most important components: electrolyte membranes and electrode catalysts.

Handbook of Fuel Cells – Advances in Electrocatalysis, Materials, Diagnostics and Durability, Edited by Wolf Vielstich, Hubert A. Gasteiger, Harumi Yokokawa. Volume 5: *Current Edition*. © 2009 John Wiley & Sons, Ltd. ISBN: 0-471-49926-9.

Operating Environment & Target Performance

Table 1. Expected MEA (membrane-electrode assembly) operating environment.[1]

Category	No.	Item		2010	2015–2020	2020–
Operation condition	1	Cell operating temperature (includes start-up) (coolant outlet temperature)		−30 to 90 °C	−30 to 100 °C	−40 to <120 °C
	2	Operation gas inlet: lower limit of RH		40%	30%	Nonhumidified
	3	Operating gas outlet pressure (atm_{abs})		1.4	1.2	~1.0
	4	Operation gas stoichiometry	Air	1.5	1.3	1.2
			H_2	1.3	1.1	~1.0 (no recirculation)

Table 2. Electrolytic membrane target performance.[1]

Category	No.	Item			2010	2015–2020	2020–
Operation function	1	Membrane resistance ($\Omega\,cm^2$)	Low temperature region[a] −20 °C		<0.15	<0.10	<0.05
			High temperature region		90 °C	100 °C	120 °C
				High humidity (95% RH)	<0.0125	<0.0125	–
				Low humidity (30% RH)	<0.08	<0.05	<0.0125
Structural function	2	Gas permeability at 80 °C, 95% RH ($cm^3/(cm^2\,s\,k\,Pa)$)	Oxygen		$(1–9) \times 10^{-8}$	$(1–9) \times 10^{-9}$	$(1–9) \times 10^{-9}$
			Hydrogen		$(1–9) \times 10^{-7}$	$(1–9) \times 10^{-8}$	$(1–9) \times 10^{-8}$
	3	Glass transition temperature (softening point)			>130 °C	>140 °C	>160 °C
	4	Volumetric swelling rate at 100 °C boiling of pure water			Measure		

[a] The samples should be prepared as follows; first, well humidified in the room temperature, then lowering the temperature to −20 °C while keeping the samples in sealed condition.

Membrane Durability

Table 4. Target cost of electrolytic membrane

No.	Production level	Cost
1	10 000 000 m^2/year	\$10/m^2

Table 3. Electrolytic membrane durability.[1]

Category	No.	Test item		Evaluation item	2010	2015–2020	2020–
Material stability	1	Hot water tolerance	Hot water immersion test 95 °C, distilled water; 6, 24, 100 h	Remaining IEC	>90%	>95%	>95%
				Remaining ion conductivity	>90%	>95%	>95%
				Remaining tensile strength and strain	>90%	>95%	>95%
				Ion dissolution (F^-, SO_4^{2-})		Measure	
				(Assumed remaining rates after 1000 h)			
	2	Chemical tolerance	H_2O_2 gas exposure test		Need to establish method in future. Currently, OCV durability is used to represent MEA durability.		
Structural stability	3	Freeze tolerance	Freeze/thaw cyclic test −30 to 80 °C, dry	Number of cycles until gas cross-leak (breakage) occurs (fixed by frame)	Need to establish method in future		
					(>2000)	(>5000)	(>5000)
	4	Moisture tolerance	Humidity cycle test 0 (dry) to 100% RH, at 80 °C	Gas leak (breakage)	Need to establish method in future		
					(10 000 cycles)		
	5	Creep tolerance	Compressive creep test 95 °C in distilled water/95% RH		Measure		
			Tensile creep test		Need to establish method in future		

Membrane Durability - Map

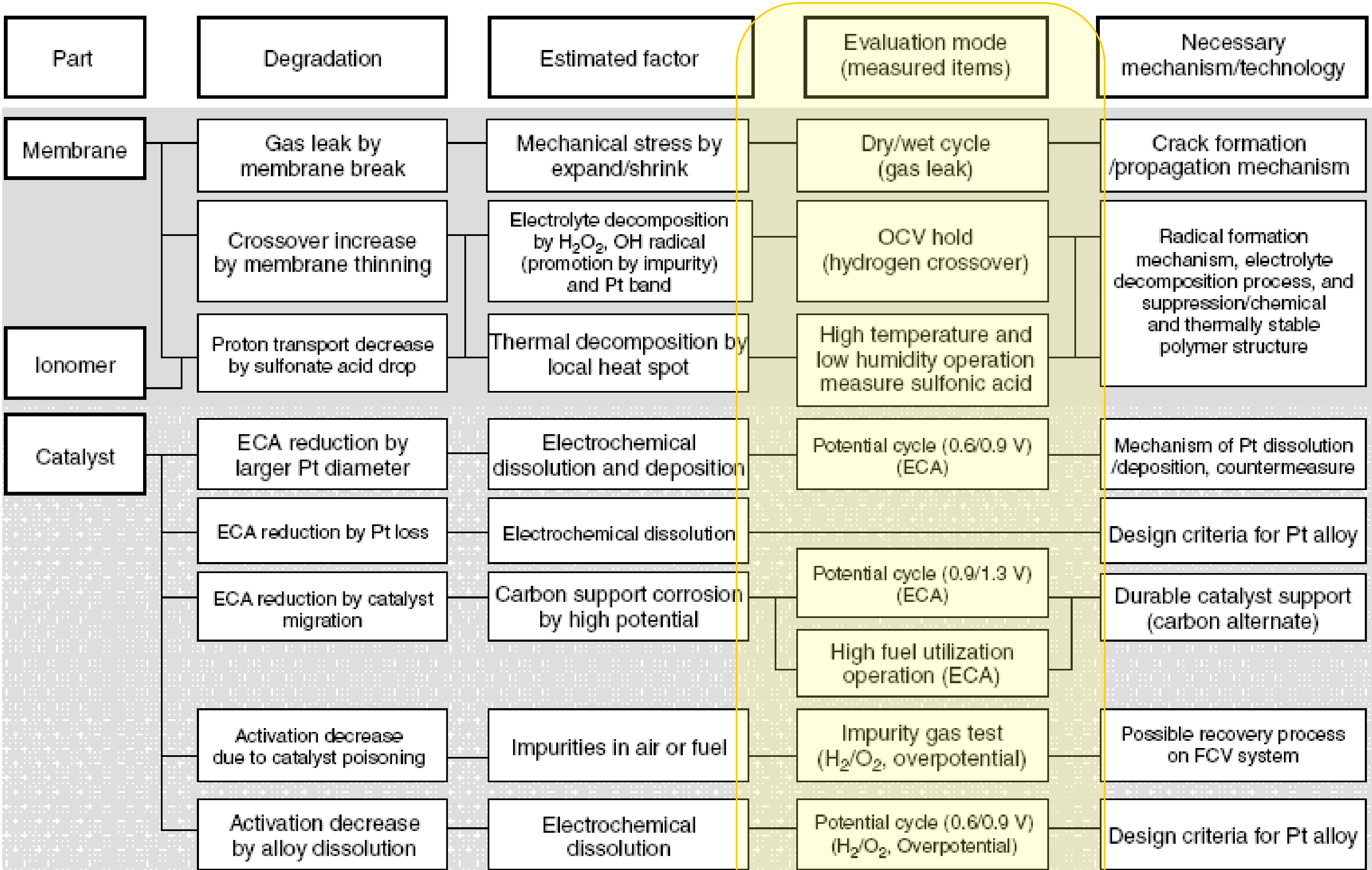


Figure 2. Automotive fuel cell MEA degradation map.[1]

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