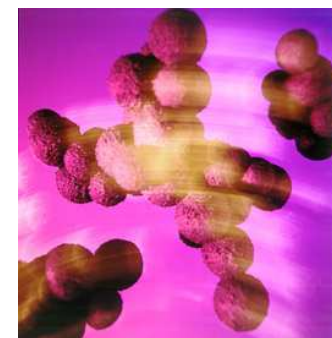




Berislav Blizanac, Gordon Rice, Jian-Ping Shen, Yipeng Sun,
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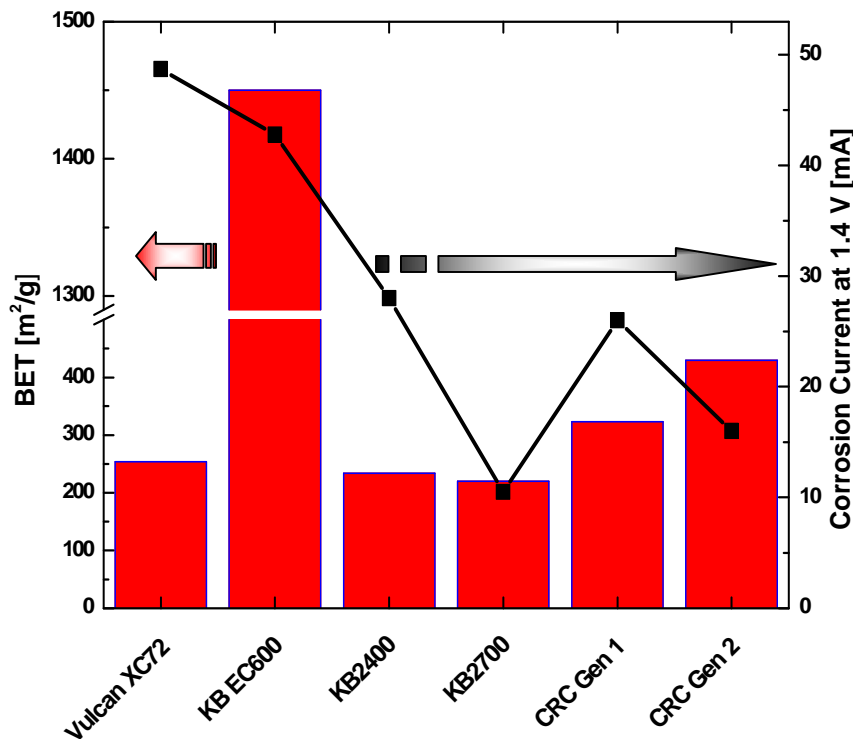
High Performance and Superior Durability of Cabot Advanced Electrocatalysts for PEM Fuel Cell Applications

212th Meeting of The Electrochemical Society
Washington DC, October 7-12, 2007

Requirements for a “Good Catalyst”

- **High mass activity (Pt normalized)**
 - Optimization of the metallic phase (Pt-alloys).
 - Optimization of the support (BET, surface properties, etc..).
- **Durability**
 - Durability of the Carbon phase.
 - Durability of the catalytically active (metallic) phase.
- **Beneficial surface properties**
 - Adjusted hydrophilicity to improve ink formulation and improve operation under low RH.

Support Optimization: The Trade-off



TRADITIONAL PARTIALLY GRAPHITIZED CARBON BLACK



FLOATS ON WATER

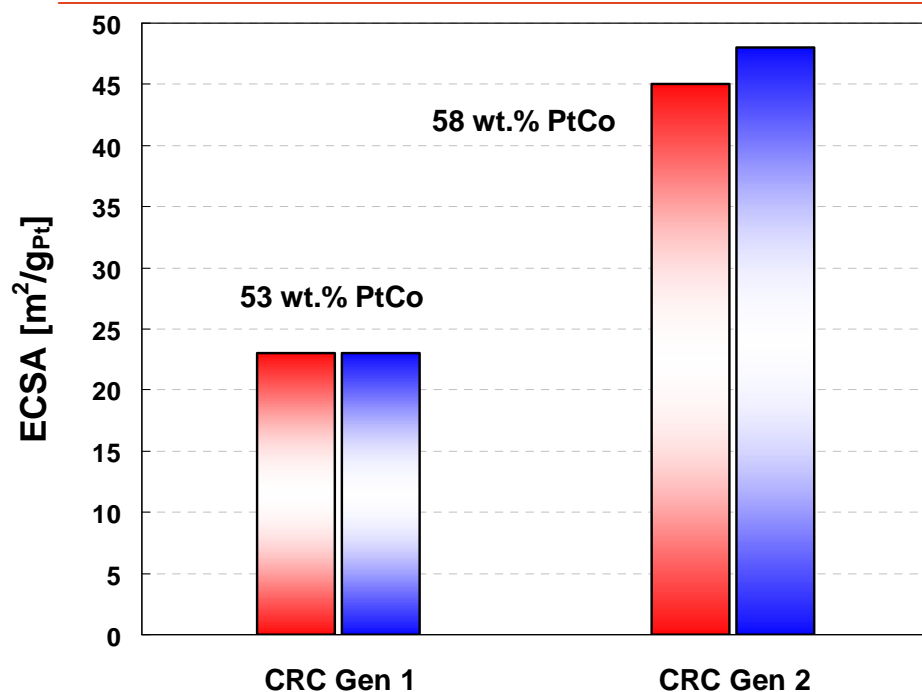
CABOT CRC Gen. 2



WETTED BY WATER

- CABOT Gen 2 CRC supports exhibit corrosion currents as low as or lower than traditionally graphitized carbons and commercial high surface area graphite, while providing the advantage of 2x in BET surface area.
- Along with the increased durability towards electrochemical oxidation, the CABOT “treatment” also alleviates the problem of high hydrophobic character of traditionally graphitized carbons. CABOT carbons demonstrate high durability along with the advantage of being wetted by water.

Metallic Phase Dispersion: ECSA



Liquid cell measurements in TFRDE configuration:
0.1 M HClO₄, 293 K, 20 mV/s

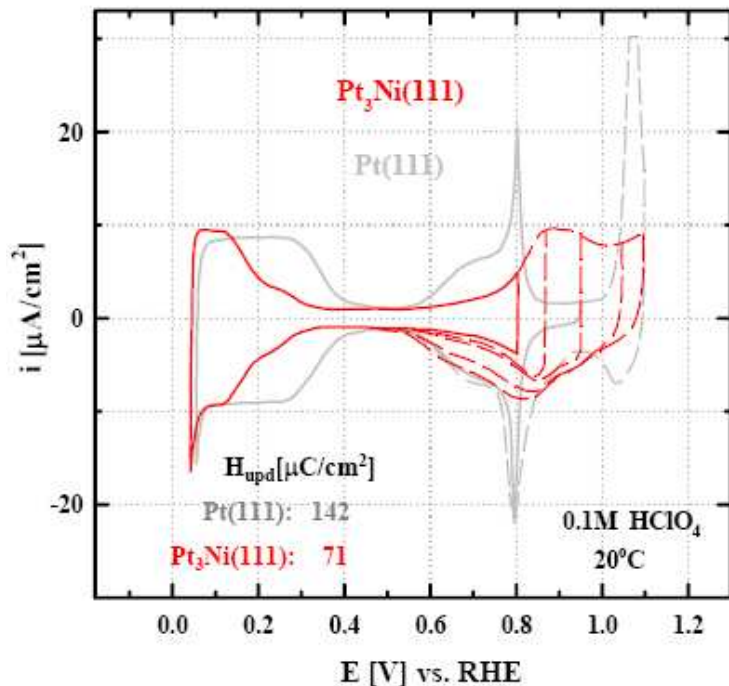
■ From HAD, based on 210 μC/cm²_{Pt}

■ From CO stripping, based on 420 μC/cm²_{Pt}

The difference in metallic phase dispersion, indirectly also confirmed from physical characterization data (i.e. XRD, HRTEM).

- Cabot's new version of CRC carbons with increased BET and hydrophilic nature results in considerably better dispersion of metallic phase (up to 40% increase in ECSA compared to CRC Gen 1 supports).
- The significant difference between ECSA-based and XRD-based (estimated) crystallite size is indication of a degree of alloying.

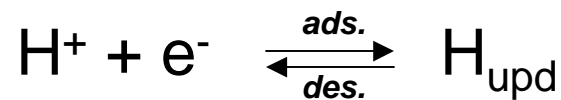
Ambiguity in ECSA measurements by utilizing the electroadsorption phenomena



ORR activity improved >10 times

(V. Stamenkovic, N.M. Markovic et al., LBL&ANL)

| | $H_{\text{upd}} [\mu\text{C}/\text{cm}^2]$ |
|---------------------------------|--|
| Pt(100) | 270 |
| Pt(110) | 208 |
| Pt(111) | 142 |
| Pt(hkl) average | 210 |
| Pt ₃ Ni(hkl) average | 150 |



$$\left(\frac{\Theta}{1-\Theta}\right) \exp\left(\frac{r\Theta}{RT}\right) = \exp\left(\frac{-E_{\text{RHE}}F}{RT}\right) \exp\left(\frac{-\Delta G_{\text{H}_{\text{upd}}}}{RT}\right)$$

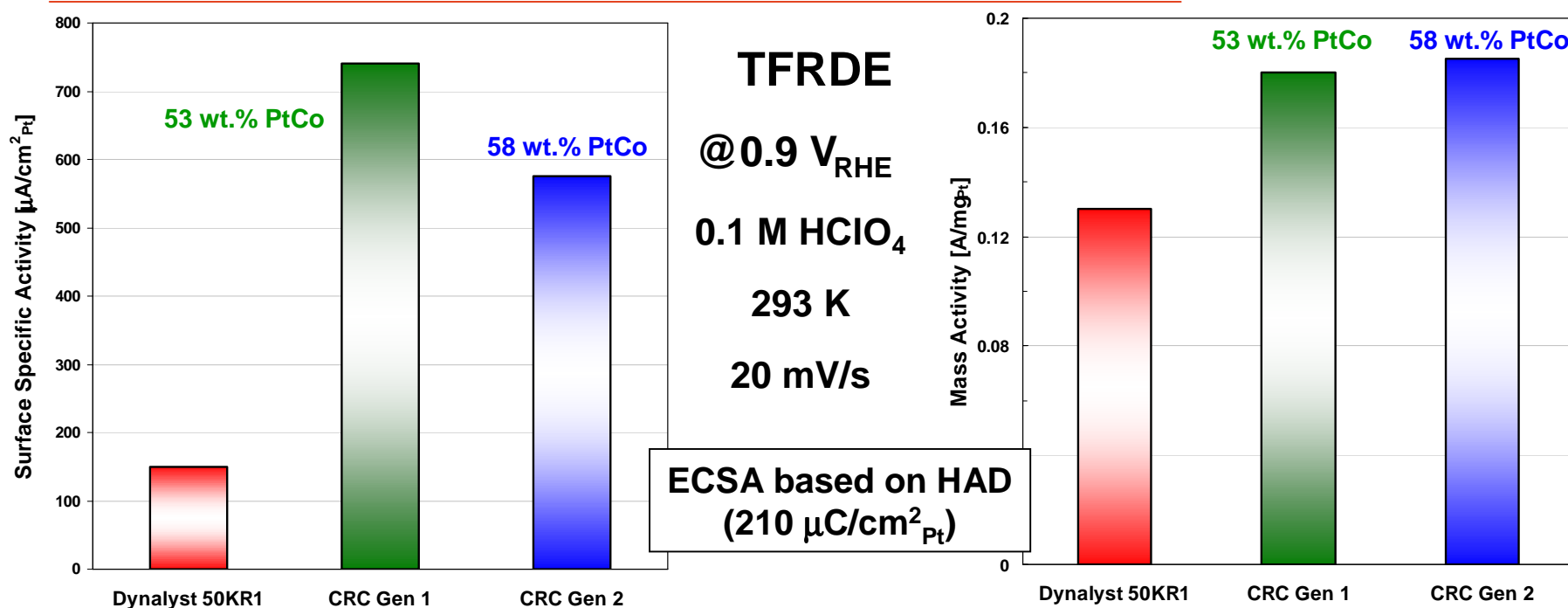
Non-Langmuir electroadsorption isotherm



Uniquely dependent upon electronic properties of the surface.

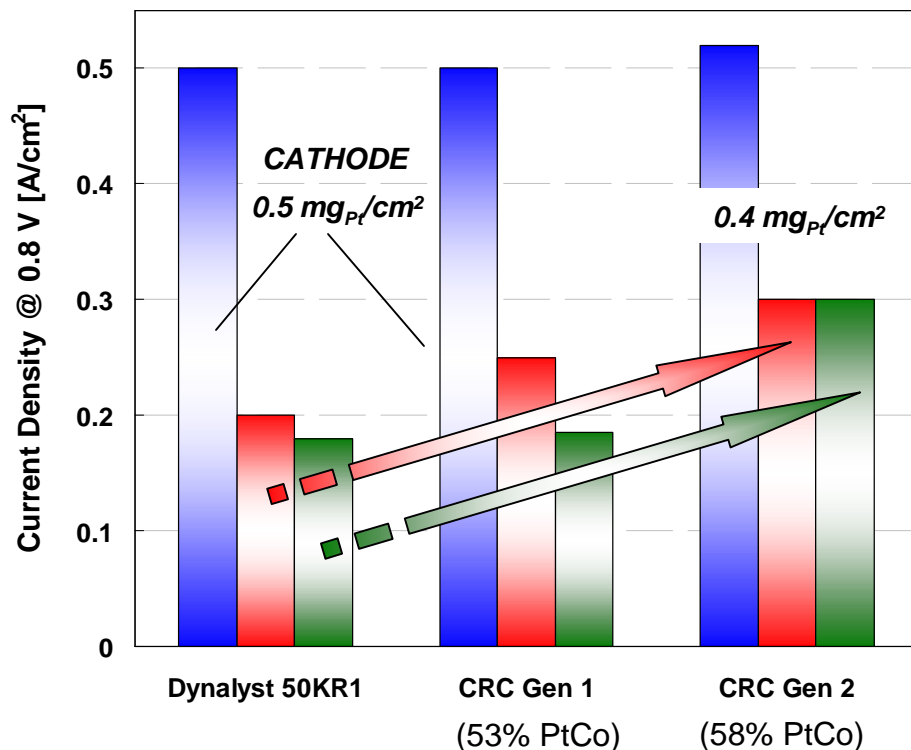
Since adsorption properties are changed on alloys as a result of electronic modifications, ECSA determination based on these adsorption phenomena becomes ambiguous.

Ex-Situ Catalytic Activity Characterization



- The mass activity of Cabot's (un-optimized) higher wt.% alloy materials are 1.5X that of Pt.
- Optimization of metallic/alloy phase should result in further mass activity improvement.

MEA: Beginning of Life Performance



CABOT HIGH PRESSURE

80°C, Nafion®:Carbon=0.84
ANODE: 0.52 L/min H₂, 200 kPa, 100% RH
CATHODE: 2.04 L/min Air, 200 kPa, 100% RH

CABOT STANDARD HIGH RH

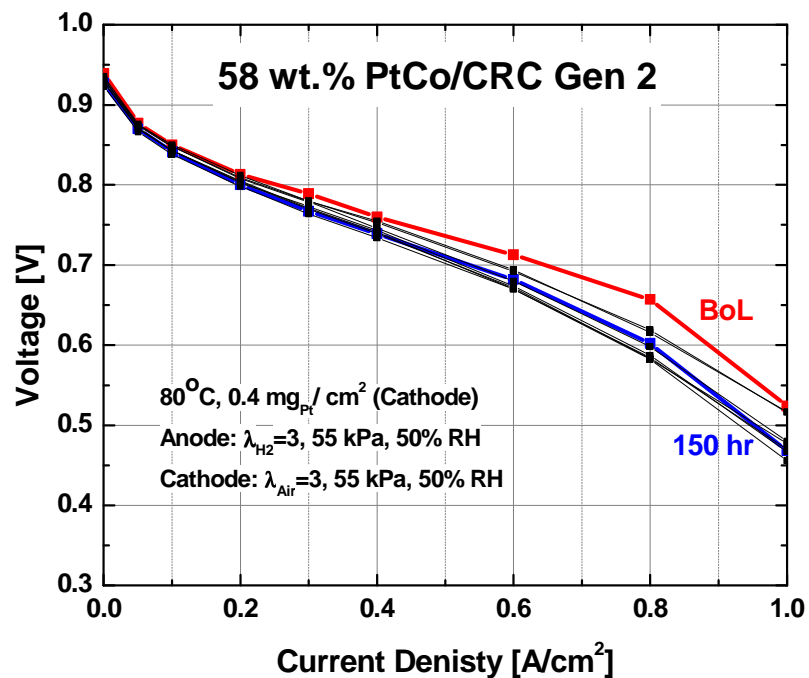
80°C, Nafion®:Carbon=0.84
ANODE: $\lambda_{H_2}=2$, 55 kPa, 100% RH
CATHODE: $\lambda_{Air}=2$, 55 kPa, 100% RH

CABOT LOW RH

80°C, Nafion®:Carbon=0.84
ANODE: $\lambda_{H_2}=2$, 55 kPa, 100% RH
CATHODE: $\lambda_{Air}=2$, 55 kPa, 50% RH

Compared to CRC- Generation 1, Cabot's new version of CRC catalysts have considerably higher performance, especially under lower RH condition (up to 50% higher performance).

Catalyst Durability: Carbon (Support) Phase



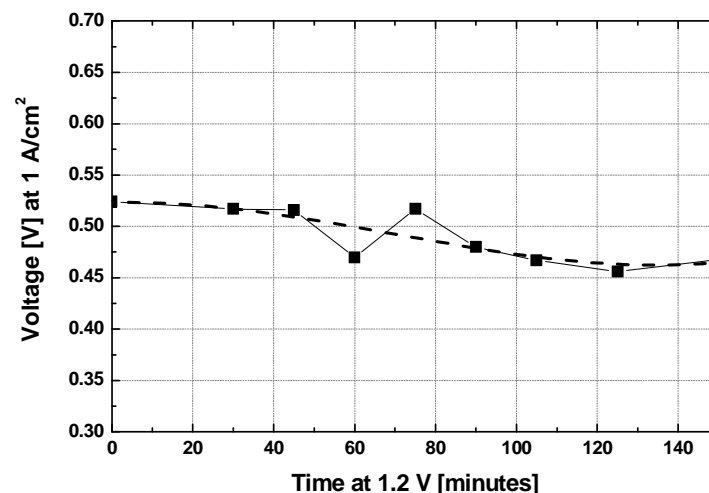
CABOT High Voltage Protocol

80°C, 0.4 mg_{Pt}/cm² (Cathode)

ANODE: 0.5 L/min H₂, ambient, 100% RH

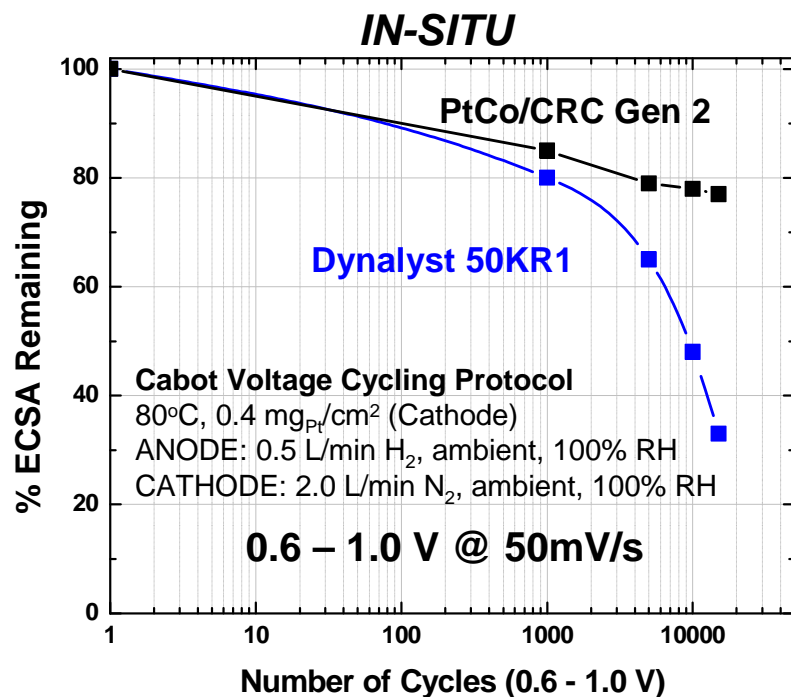
CATHODE: 2.0 L/min N₂, ambient, 100% RH

1.2 V applied to cathode



- Approximately 50 mV loss in performance at 1 A/cm² after 150 hours of standard high voltage protocol.

Catalyst Durability: Metallic Phase



EX-SITU (Pristine vs. Post-mortem)

| Catalyst | Particle Size P _f (nm) in Fresh Powder (XRD FWHM) | Particle Size P _{vc} (nm) in Fresh Powder (XRD FWHM) | % Loss in Theoretical Surface Area |
|--------------------------------|--|---|------------------------------------|
| Dynalyst 50KR1 (50 wt.% Pt/KB) | 3.03 | 9.05 | 67 |
| 53 wt.% PtCo/CRC Gen 2 | 4.93 | 6.42 | 23 |

Theoretical Surface Area = 270/(Particle Diameter in nm)

$$\% \text{ Loss in Theoretical Surface Area} = [1 - (P_f / P_{vc})] * 100$$

In-situ and Ex-situ catalyst durability measurements in excellent agreement.

- Although particles on new CRC start larger than in standard carbon supported catalyst, the rate of surface area loss is significantly slower.
- The smaller final crystallite size for Pt-alloy indicate higher stability as a result of alloying (loss in surface area is not only driven by initial dispersion).

Summary

- CABOT has developed a new fuel cell carbon support with corrosion durability equivalent to highly graphitized carbons, but with BET surface area 2x that of graphitized carbons.
- The unique surface chemistry of the new carbons result in much lower hydrophobic character.
- The unique surface chemistry of carbon support allows for the manufacture of electrocatalyst materials characterized by:
 - Performance greater than Cabot's standard EC materials.
 - High resistance to electrochemical oxidation.
 - High durability to voltage cycling (high stability of both Carbon support and metallic phase).
- Now that the support phase has been optimized, further optimization of metallic/alloy phase is under way to further improve the mass activity.