Development of Durable, Low-Cost, High-Performance Pt Alloy Electrocatalysts for H_2/Air Fuel Cell Application

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Pt Alloy Catalyst for Automotive Fuel Cell Commercialization

- ✓ Activity: fourfold mass activity over SOA Pt/C; 0.44 A/mgPt@0.9V$_{iR\text{-}free}$ (Test at 80°C/80°C H_2/O_2 in MEA; fully humidified with total outlet pressure of 150 kPa; anode stoichiometry 2; cathode stoichiometry 9.5).
- ✓ Durability: less than 40% loss in Pt surface area in 300,000 voltage cycles (between 0.7V and 0.9V iR-free voltage in H_2/Air (30 sec hold at each potential))
- ✓ Carbon support durability: < 30mV performance loss after 100 hours @ 1.2 V.

Combinatorial Discovery

▪ Need for combinatorial discovery

✓ Empirical studies demonstrated 20-30 mV activity gains of binary systems, such as PtNi, PtCo and PtCr, over Pt/C.

✓ The optimum composition of these alloys remains unknown.

✓ As the number of elemental components increases, the number of possible compositions to be prepared and tested grows geometrically.

▪ Challenge of combinatorial approach

✓ Many combinatorial platforms rely on high throughput techniques for model systems (sputtering) followed by scale up in supported form

✓"Hits" cannot always be translated into real material systems.

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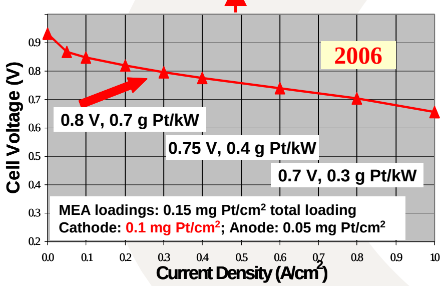
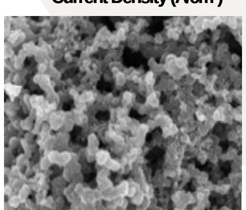
Cabot's Combinatorial Catalyst Discovery Platform

High throughput synthesis

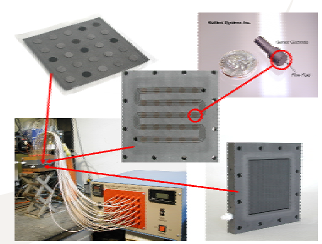
Rapid GDE fabrication

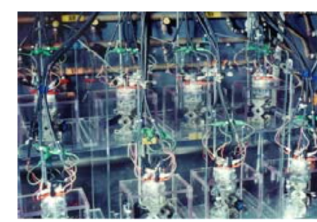




Electrochemical and physical characterization

High volume production



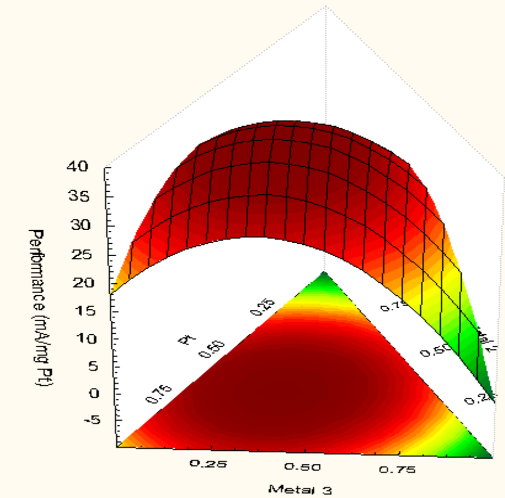


Rapid screening

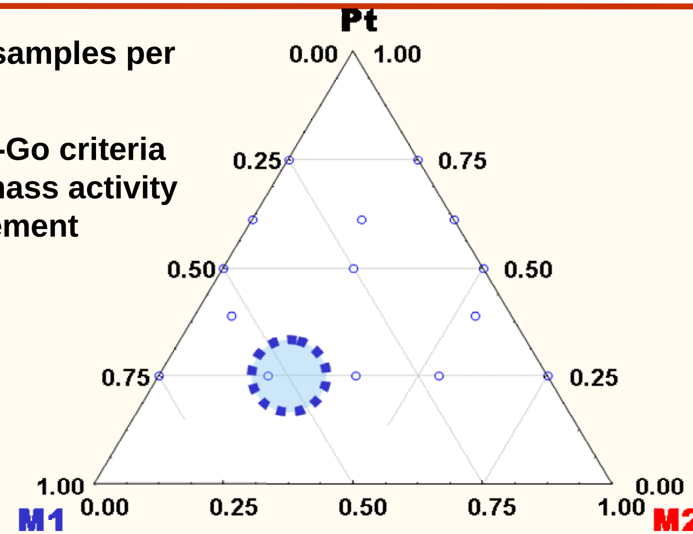
Ternary and Quaternary Alloy Libraries Completed

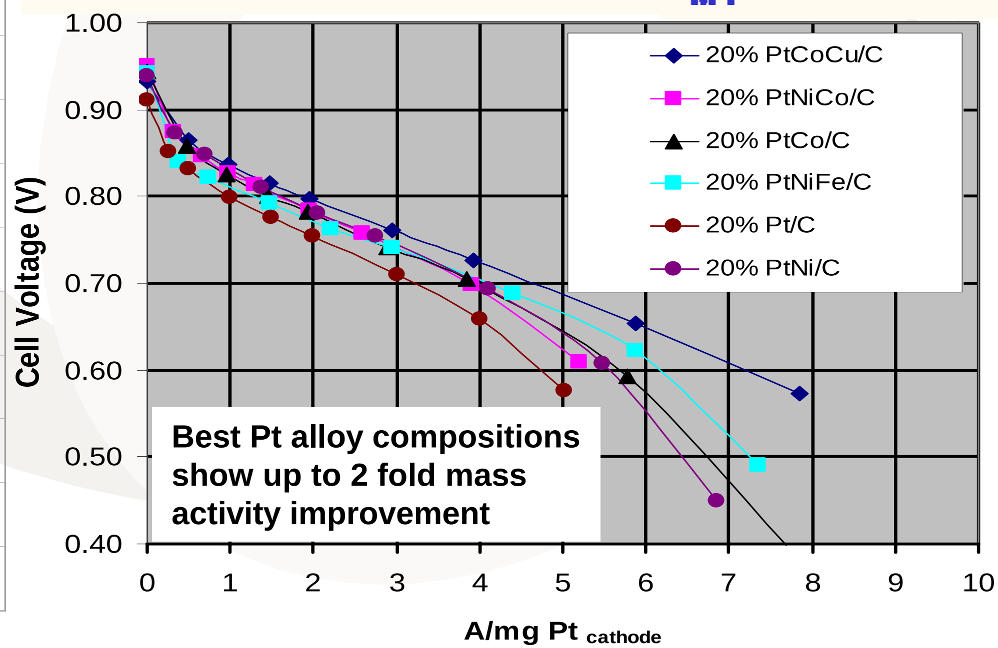
Pt Alloy Libraries

1	**PtCoCu**
2	**PtCoFe**
3	**PtFeCu**
4	**PtNiCu**
5	**PtNiFe**
6	**PtPdCu**
7	**PtPdCo**
8	PtPdFe
9	PtMnFe
10	PtPdMn
11	**PtNiCo**
12	PtCoAg
13	PtFeAg
14	PtNiAg
15	**PtPdNiCo**



- **25-75 samples per library**
- **Go/No-Go criteria >70 % mass activity improvement**

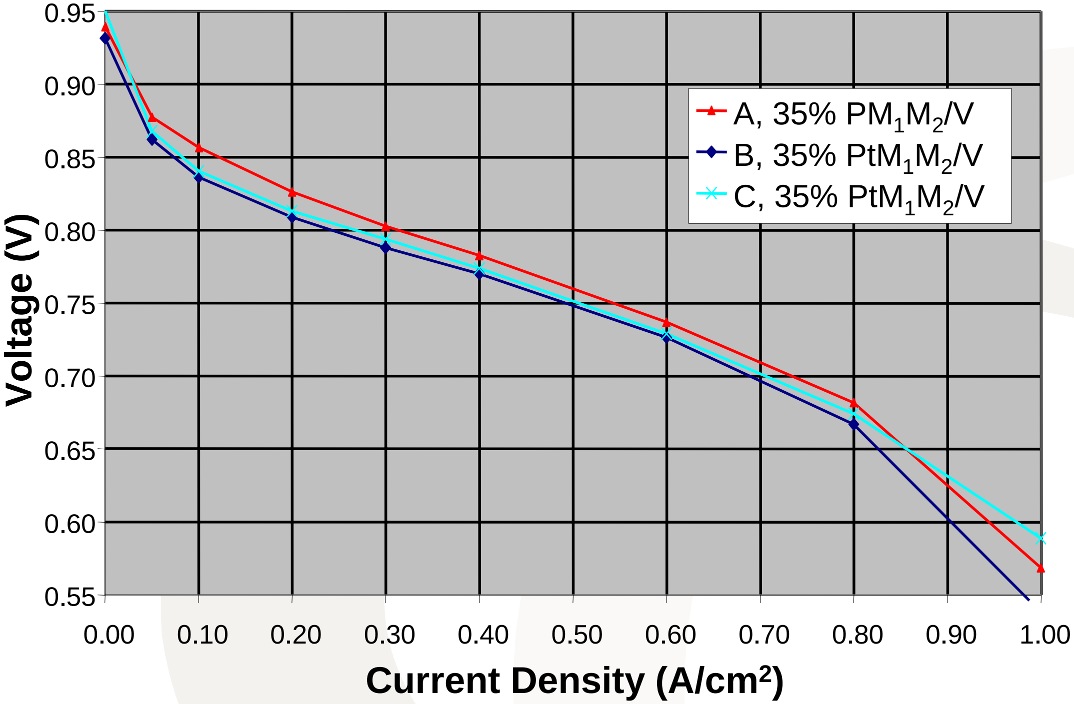




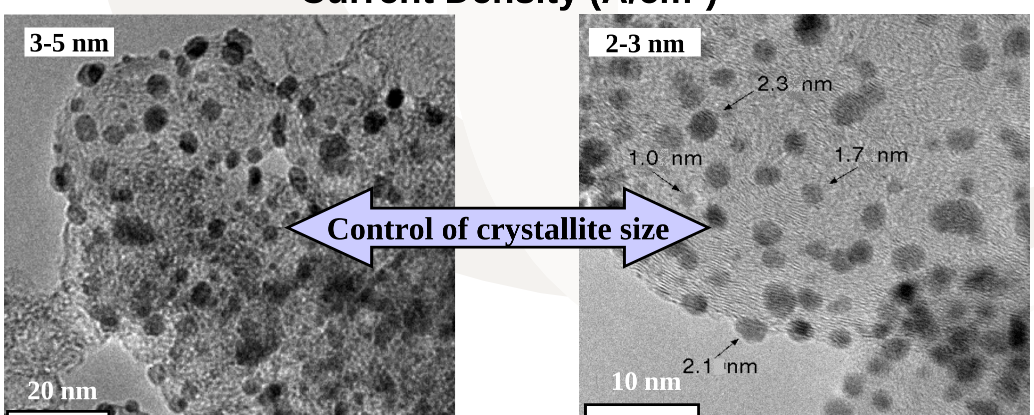
Test Conditions:

- **50 cm² MEA**
- **Nafion™ 112**
- **Cathode: 0.2 mgM/cm**
- **Anode: 0.05 mgPt/cm²**
- **80ºC, 1.5 H_2/2.5 air at 1A/cm²; 100% RH, 30 psig, 10min/point**
- **Non IR corrected**

Scale Up and Optimization of Best Alloy Compositions

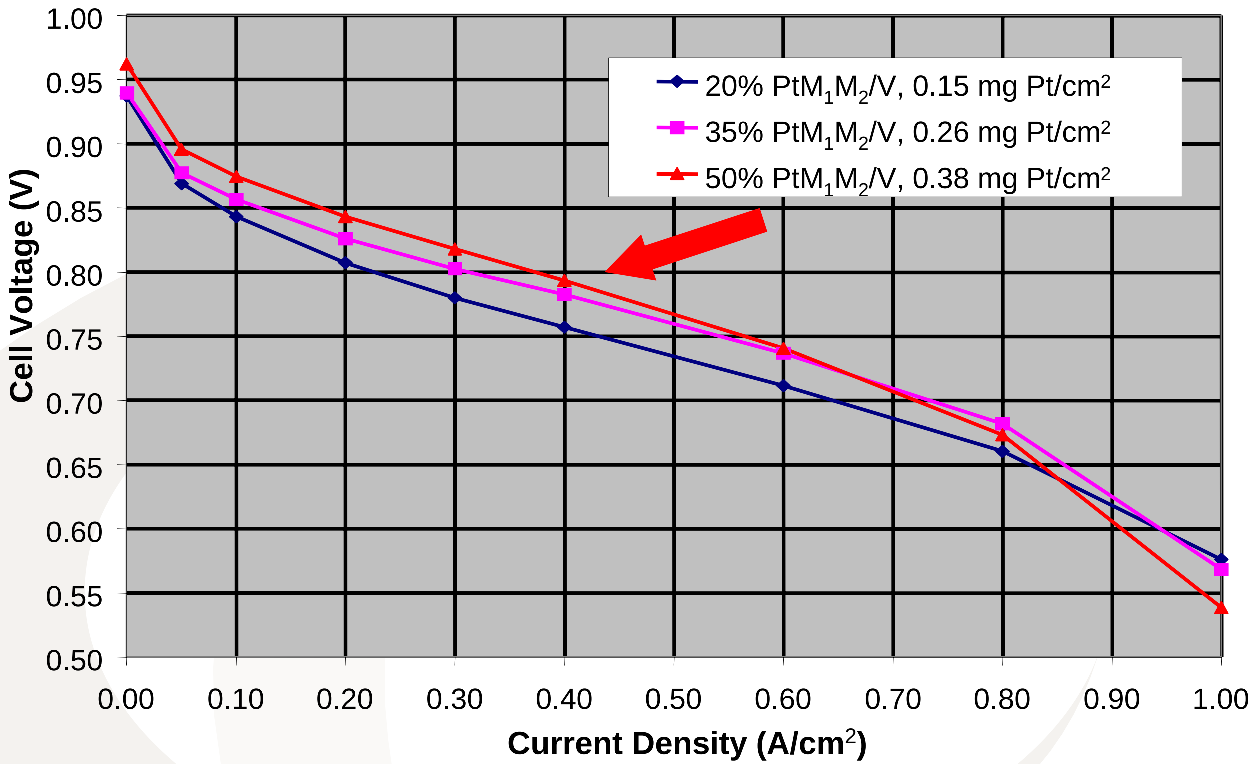


- Systematically investigated production conditions on physical and electrochemical properties of alloy.
- Characterization of catalyst powders by XRD, TEM, BET and EDS.
- Correlate physical properties to performance in MEA



	Average metal crystalline size (nm)	BET (m^2/g)
Sample A	3.7	108
Sample B	4.4	103
Sample C	4.3	98

Scale Up of Best Alloy Compositions



- Catalysts with 20-50 wt.% metal loading made on production unit.
- Same level of performance improvement compared to Pt/C was achieved.

Mass Activity for 20-50% Pt Alloy Catalysts

Catalyst Composition	Mass Activity at 0.9V (A/mg Pt)
CSMP 20% Pt/V	0.07
CSMP 50% Pt/KB	0.13
Commercial 20% Pt/V	0.07
CSMP 20% PtNiCo/V	0.13
CSMP 20% PtCoCu/V	0.25
CSMP 50% PtNiCo/V	0.09
CSMP 50% PtNiCo/KB	0.23
CSMP 50% PtCoCu/KB	0.22

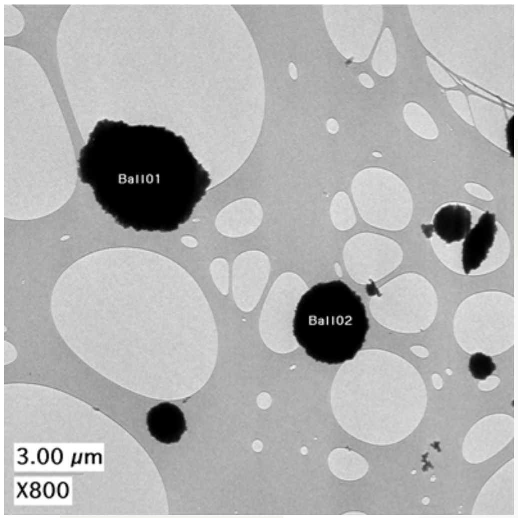
- Effect of metal loading, type of support and processing conditions on mass activity.
- Layer structure (loading, Nafion/C ratio) might have an effect on mass activity measurement.

Test Conditions:

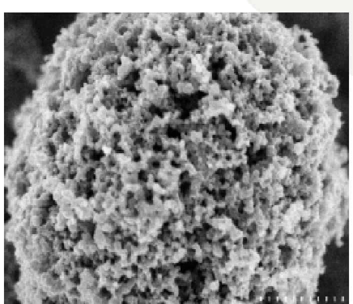
- **80°C cell, Nafion™ 112, 100% humidification, 9 psi backpressure, H_2/O_2 (2/9.5)**
- **20 wt.% M/C: Cathode: 0.2 mg Metal/cm^2, anode: 0.05 mgPt/cm^2**
- **50 wt.% M/C: Cathode: 0.5 mg Metalcm^2, anode: 0.05 mgPt/cm^2**

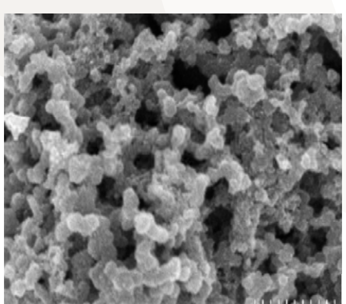
Electrocatalyst Powder Characterization – Composition and Uniformity by TEM/EDS and SEM

µm scale

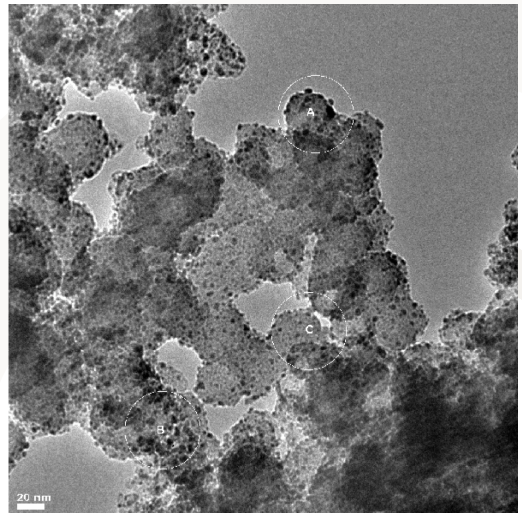


	A (%)	B (%)	Pt (%)
Ball02	29	28	43
Ball01	30	28	42
Expected	25	25	50



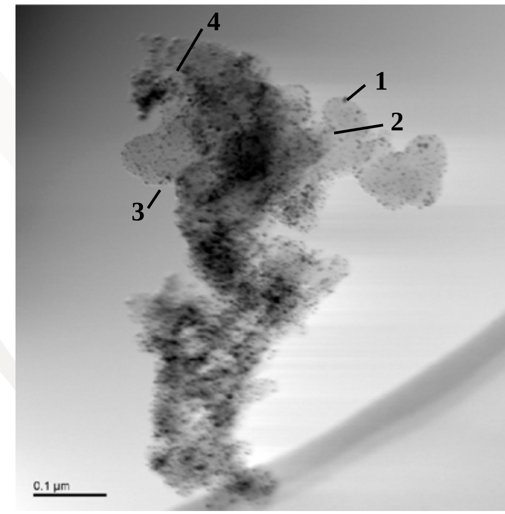


sub-µm scale



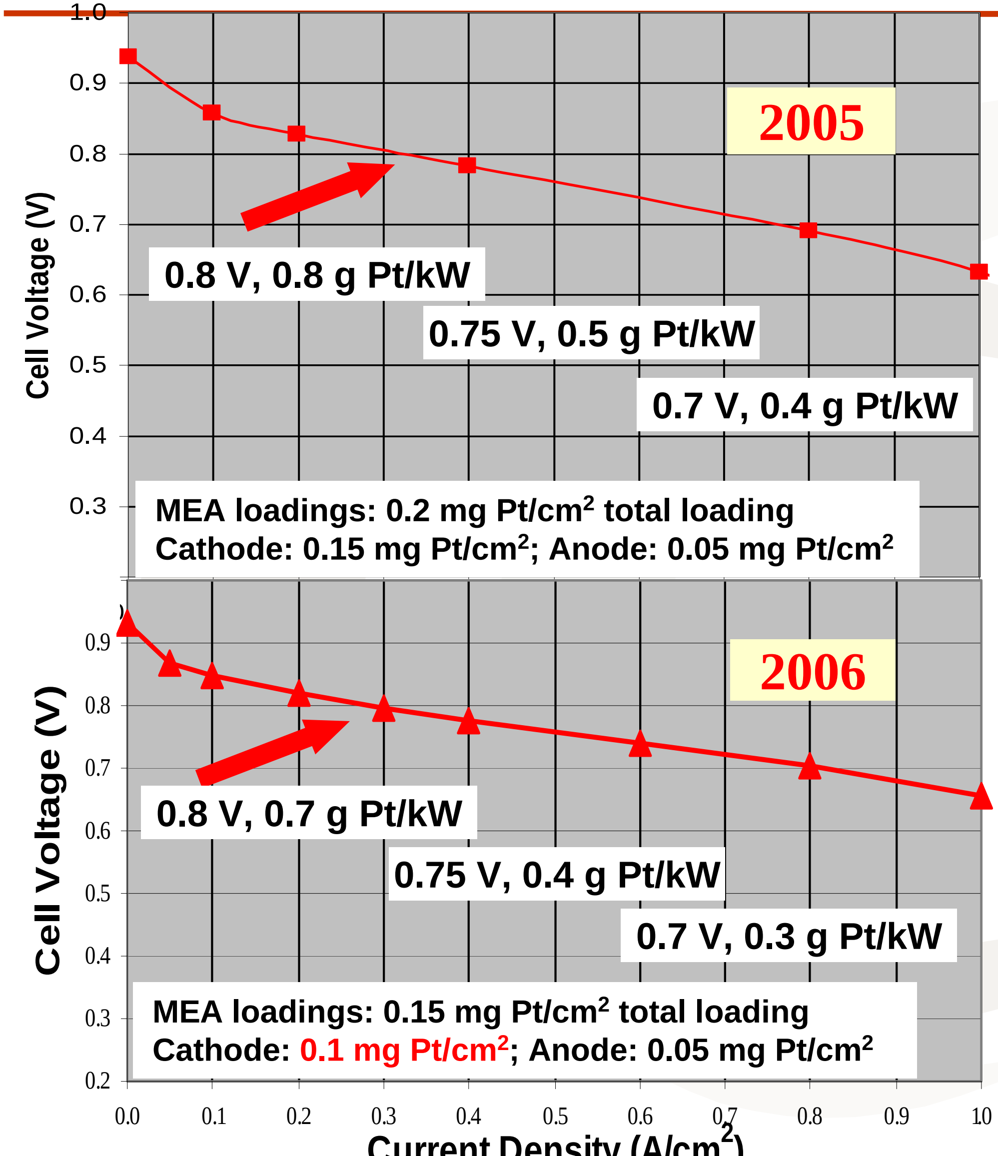
	A(%)	B (%)	Pt (%)
A	33	23	44
B	29	25	46
C	30	27	43
Whole area	31	20	49
Expected	25	25	50

nm scale



	A (%)	B (%)	Pt (%)
1	22	22	56
2	17	11	72
3	16	11	73
4	22	18	60
Expected	25	25	50

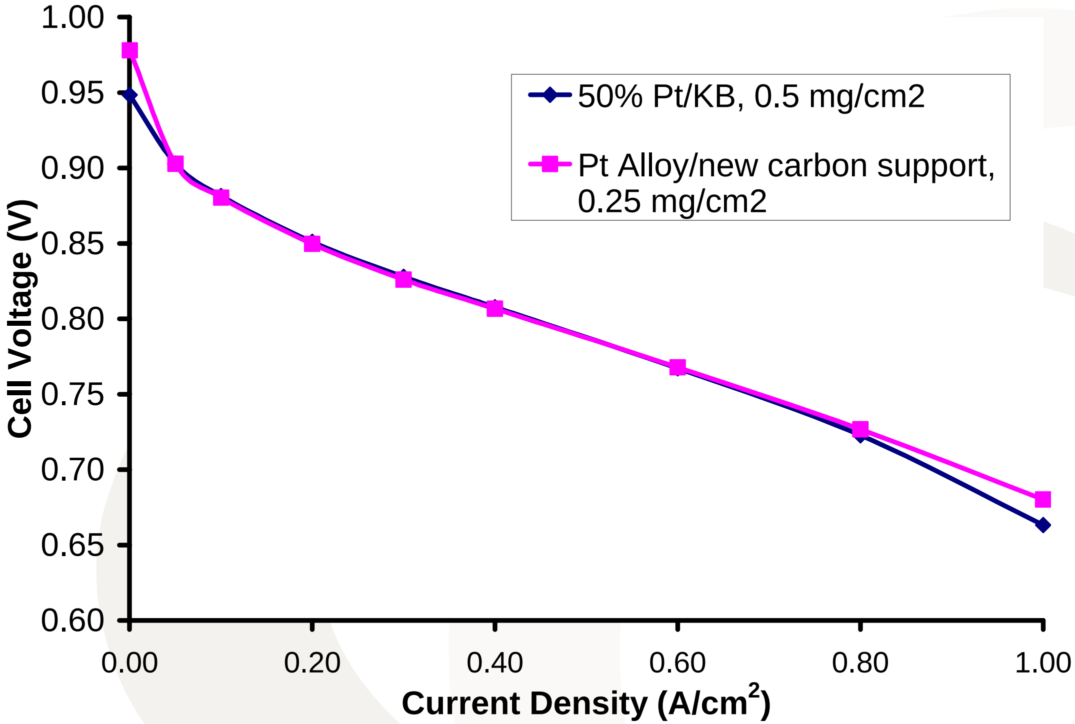
Best Single Cell MEA Performance



Test Conditions:

- ✓ 50 cm² MEA
- ✓ Nafion™ 112
- ✓ 80ºC, 1.5 H_2/2.5 air at 1A/cm²
- ✓ 100% RH, 30 psig, 10min/point,
- ✓ Non IR corrected

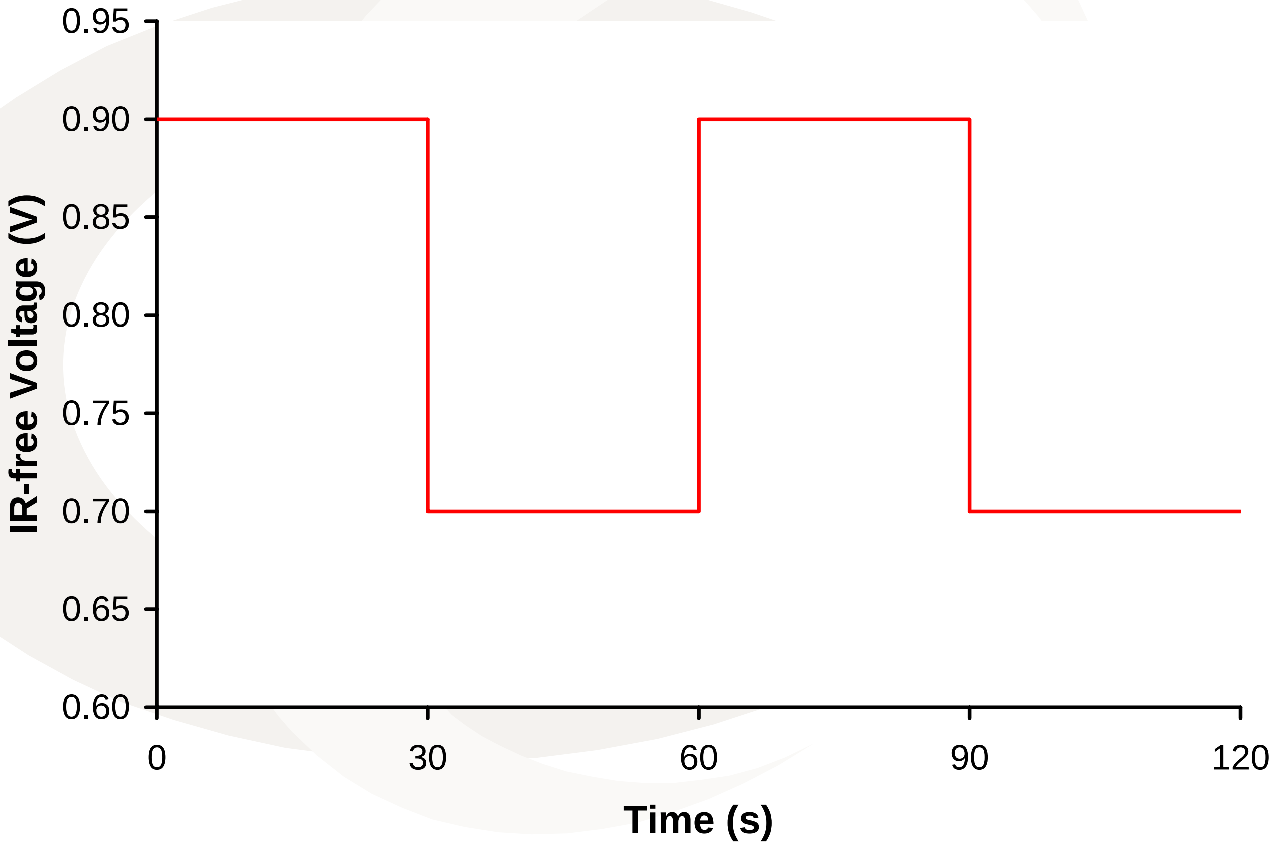
High Metal Loading Pt Alloy Catalyst on High Surface Area Carbon Support



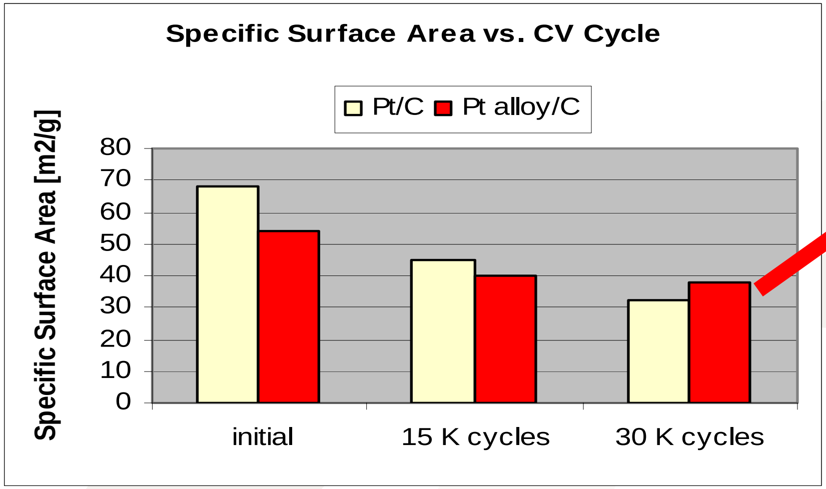
- *Similar high absolute performance at approximately half of the Pt content*
- *Mass activity measured at 0.9V (IR-free) in pure hydrogen and oxygen with reactant flow set at stoichiometry of 2 and 9.5, respectively (9 psi back pressure) corresponds to 0.24 A/mg Pt.*
- *New carbon support is more corrosion resistant than conventional carbon.*

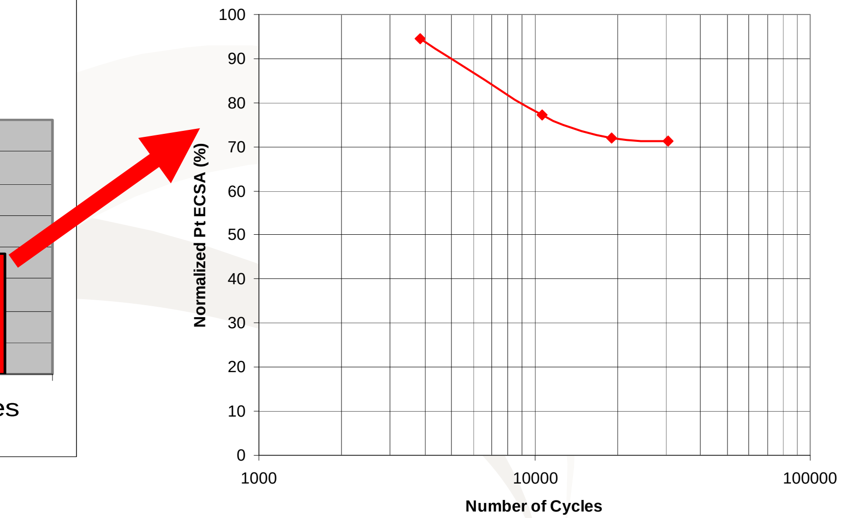
Long-Term Durability Study Under Cycling Protocols

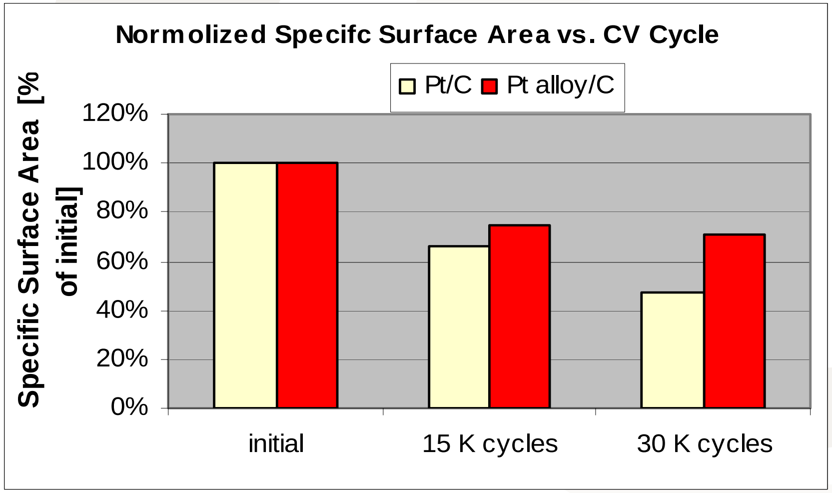
- The test consists of cycling a 25 cm^2 MEA under H_2/air at 80°C and 100% RH between 0.7 and 0.9 V IR-free voltage (30 s hold at each potential) combined with periodical evaluation of the Pt surface area using cyclic voltammetry and performance.



Long-Term Durability Study – Cycling Protocols

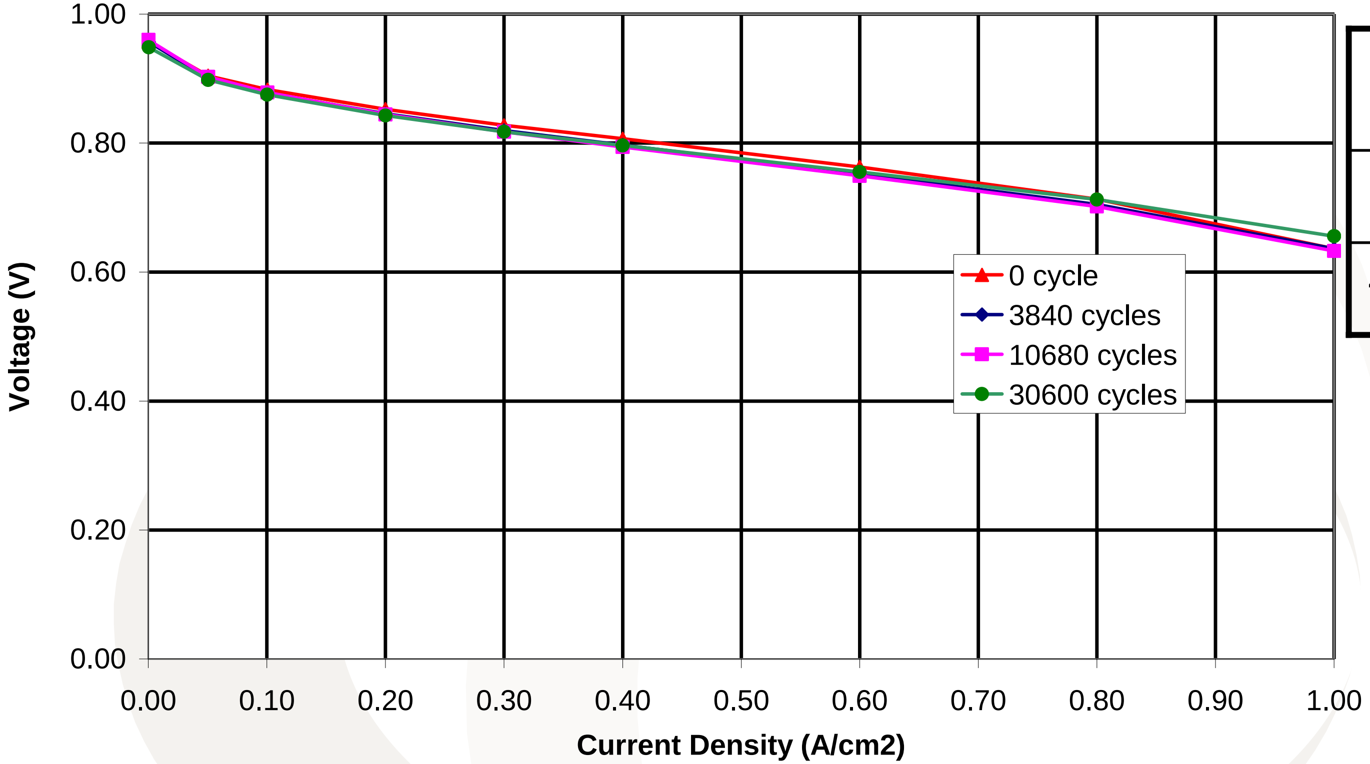






- **Pt alloy catalyst shows better durability under cycling protocols than Pt/C.**
- **Further analysis of the alloy durability with post mortem analysis of structural changes in progress.**

Long-Term Durability Study – Cycling Protocols



	Voltage loss (mV)
50 mA/cm^2	6
400 mA/cm^2	13

Test conditions:

- Single MEA 50 cm^2 test cell, Nafion 112
- Cell temperature 80C
- Anode/cathode constant flow rates = 510/2060 mL/min H_2/air (1.5H_2/ 2.5 air stoich at 1 A/cm^2)
- 30 psig pressure on both anode and cathode
- 100% humidification of gases, 80C dew point

Conclusion

- Demonstrate effectiveness of combinatorial platform combined with systematic production scale up for discovery of highly active Pt alloy compositions.
- Demonstrate better durability of Pt alloy catalyst under cycling protocols than Pt/C.
- Durable Pt alloy catalyst with further activity enhancement on corrosion-resistant carbon is needed for automotive fuel cell commercialization.

Acknowledgements

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