AFCC AUTOMOTIVE FUEL CELL COOPERATION®

Pt-Co/C Catalysts: PEMFC Performance and Durability

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Slides presented by James Waldecker of Ford to the

DOE Catalysis Working Group Meeting on June 16, 2014

- Why are we looking at Pt-Co/C catalysts for PEM Fuel Cells even after so many years since the introduction?

- What trade offs in Pt-Co alloy characteristics can yield better performance and durability than Pt/C?
  - Pt:Co atomic ratio
  - Particle size
  - Metal loading

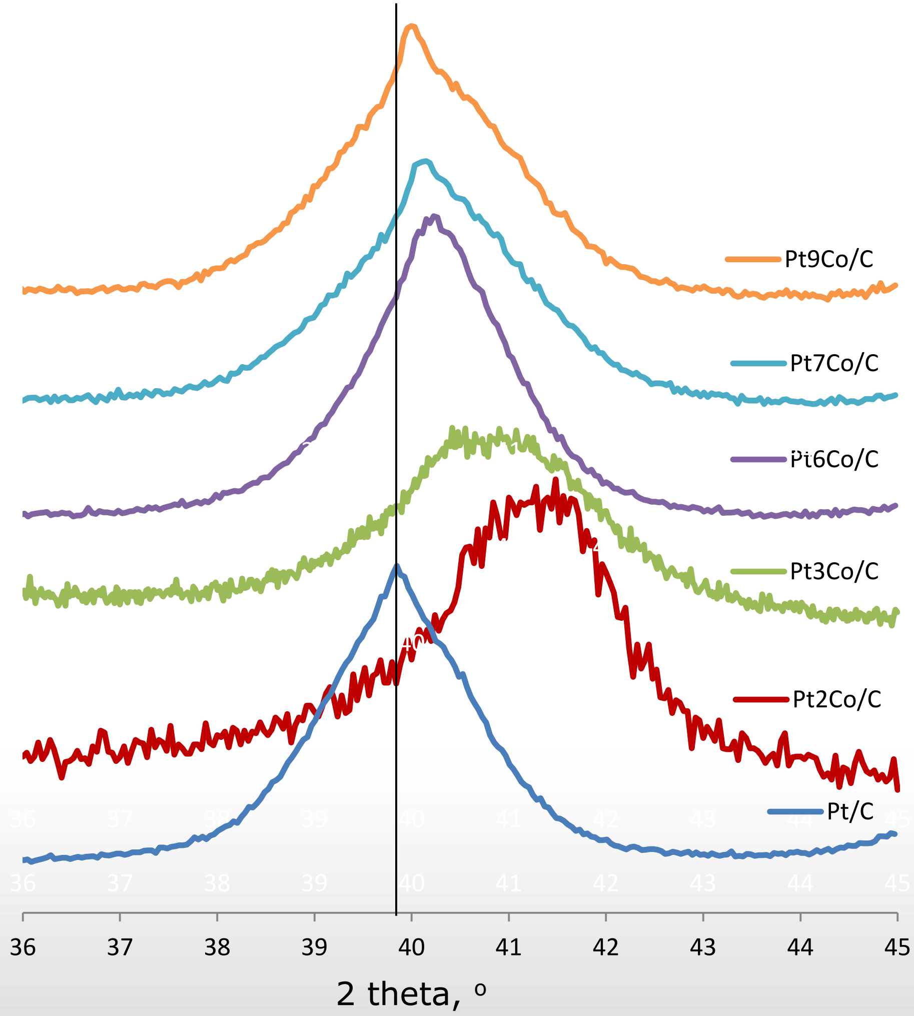
- What causes the performance to drop during accelerated stress test?

Pt-Co/C catalysts

Catalyst	Pt wt%	Co wt%	Pt/Co atomic ratio	XRD crystallite size, nm	Catalyst surface area, m^2/g
Pt/C	52.5	-	-	4.9	358
Pt_2Co/C	47.0	6.9	2.1	4.2	333
Pt_3Co/C	28.8	3.1	2.8	3.3	514
Pt_4Co/C	31.5	2.3	4.1	3.2	438
Pt_6Co/C	48.6	2.5	5.9	4.9	350
Pt_7Co/C	30.1	1.3	7.0	3.9	521
Pt_9Co/C	30.3	1.0	9.2	3.9	508

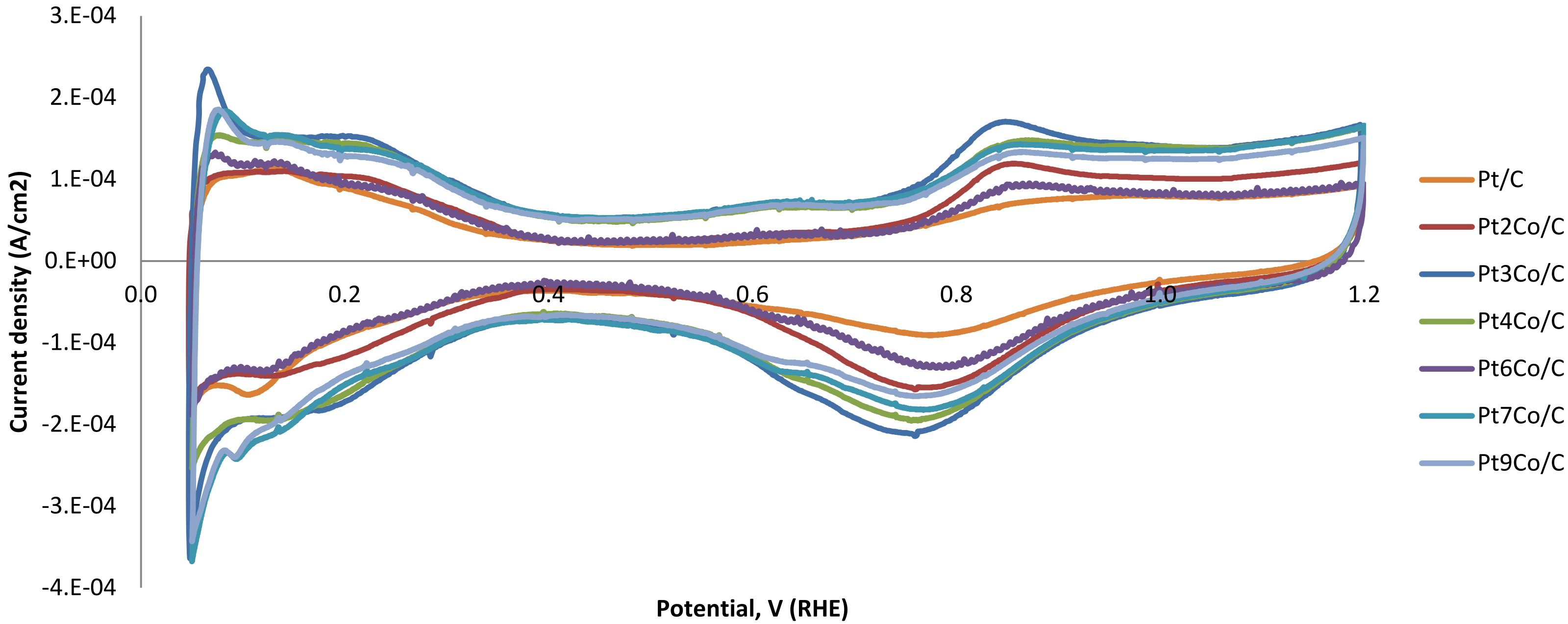
- Pt:Co atomic ratio – 2:1 to 9:1
- Alloy particle size – 3 to 5 nm
- Metal loading – 30 & 50 wt%

XRD



- All catalysts show disordered fcc structure
- Positive shift in the (111) peak position for Pt-Co/C catalysts indicate alloying of Co with Pt
- Pt_2Co/C & Pt_3Co/C show slightly broader distribution

RDE

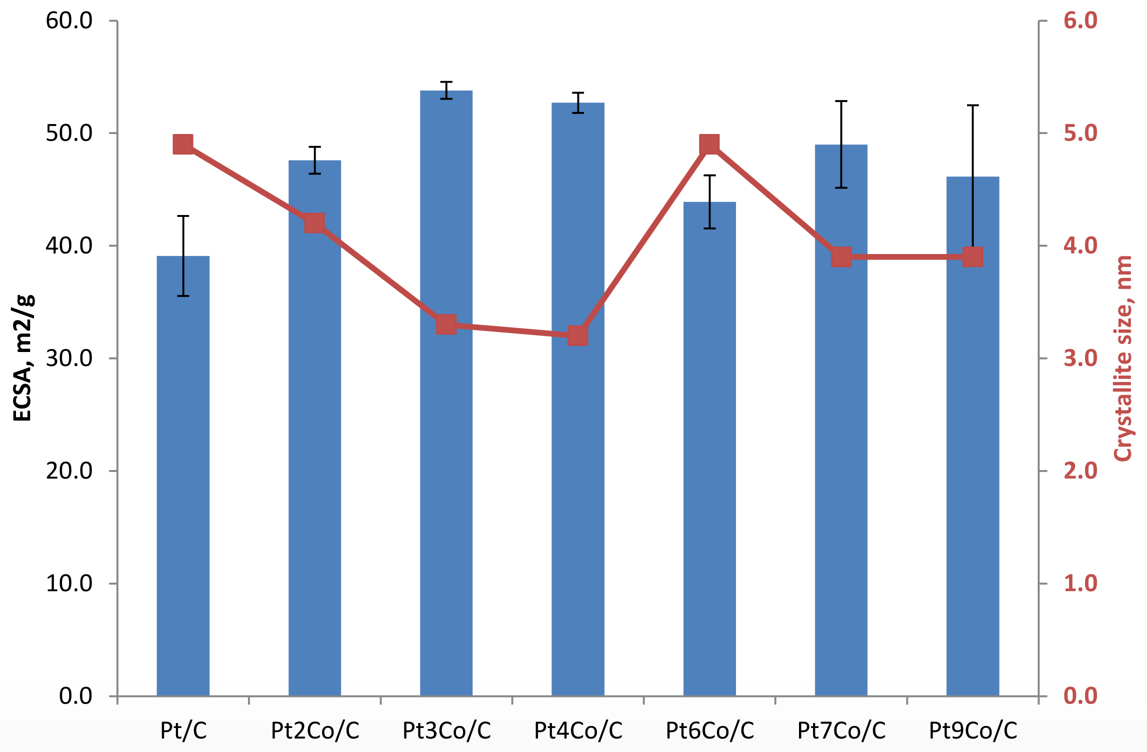


Pt loading on GC disk: ~10 μg/cm^2
0.1M $HClO_4$, 35 ^oC

Scan rate: 20mV/s

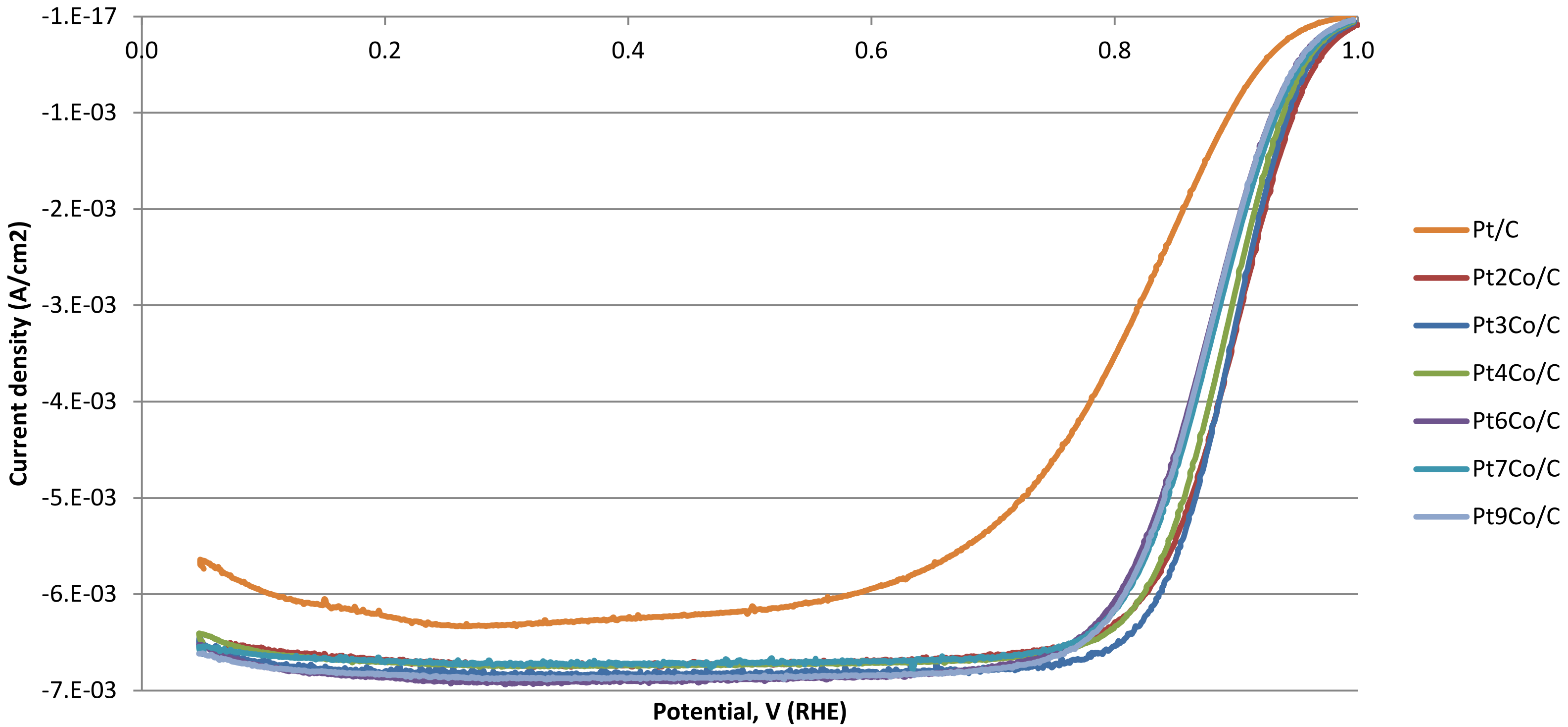
- ❑ Increased double layer capacitance for 30wt% catalysts compared to 50 wt% catalysts
- ❑ 30wt% catalysts show enhanced Hydrogen adsorption/desorption peaks

ECSA



- Good co-relation between XRD crystallite sizes and ECSAs measured in RDE

ORR

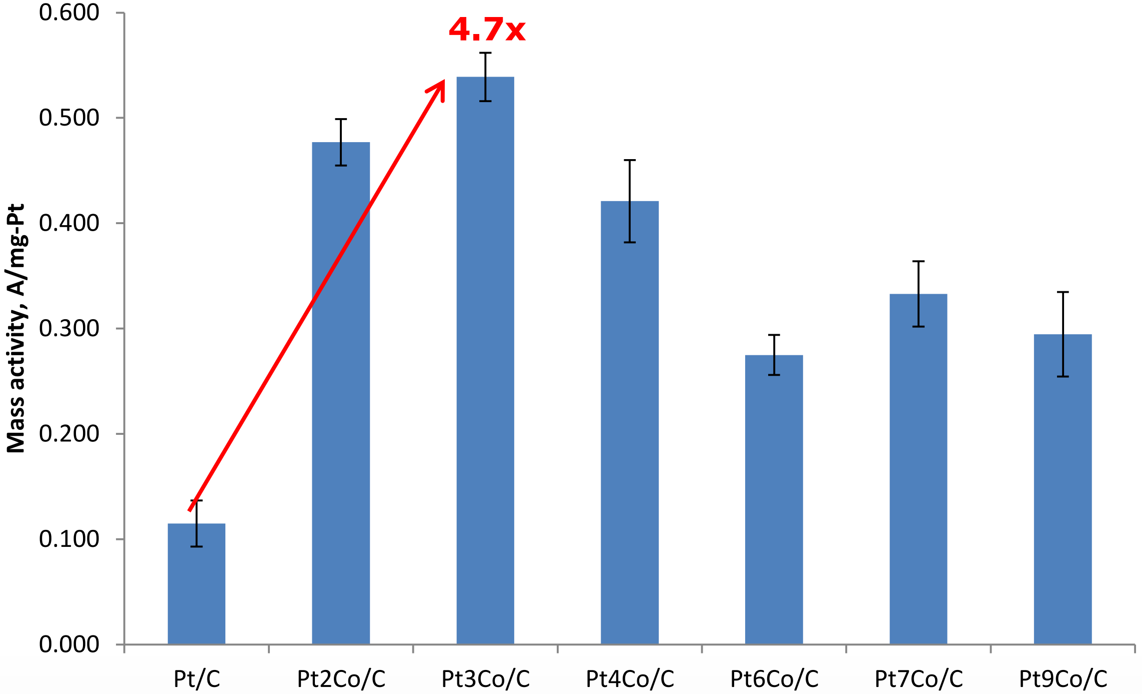


Scan rate: 5mV/s (Anodic), 2000 RPM

Pt loading on GC disk: ~10 μg/cm^2
0.1M $HClO_4$, 35 ^oC

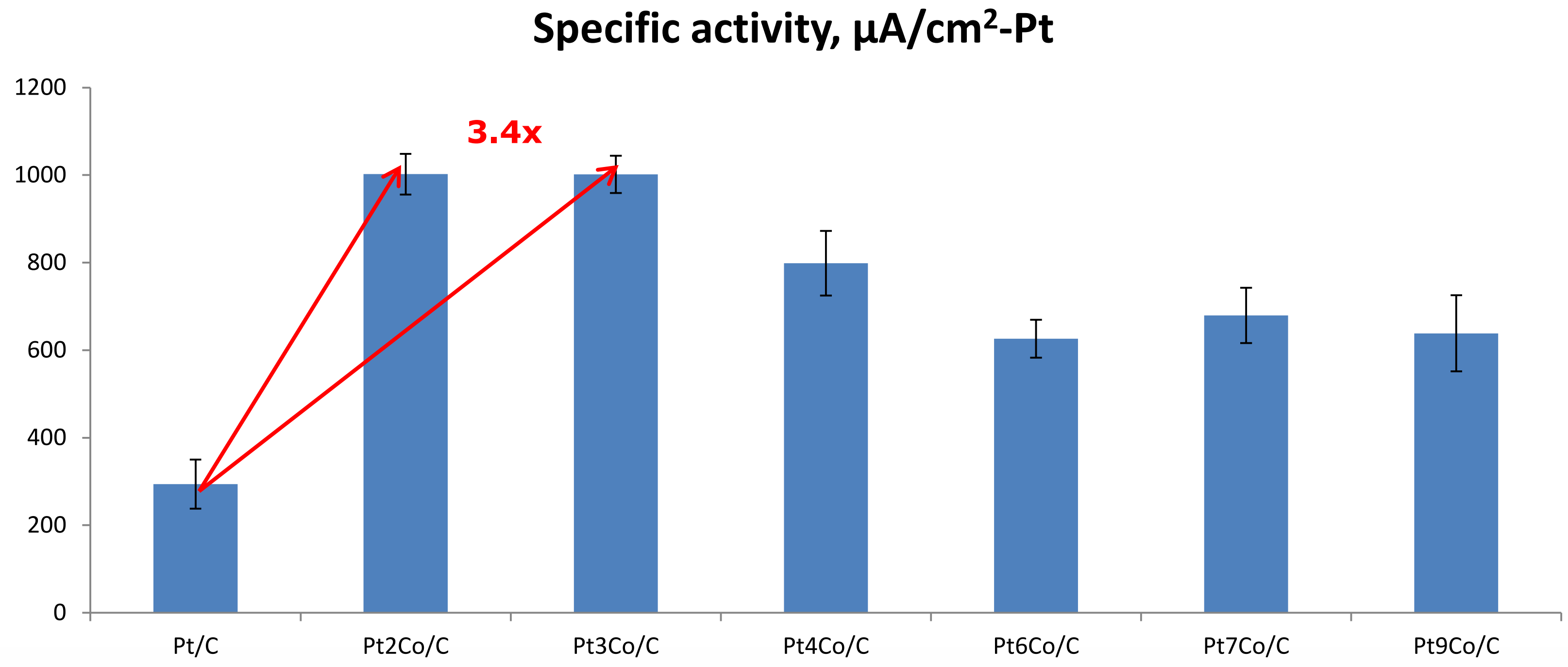
- Pt-Co/C catalysts clearly show higher oxygen reduction activity over Pt/C
- Limiting current densities are close to theoretical calculation at 2000 RPM

Pt Mass activity



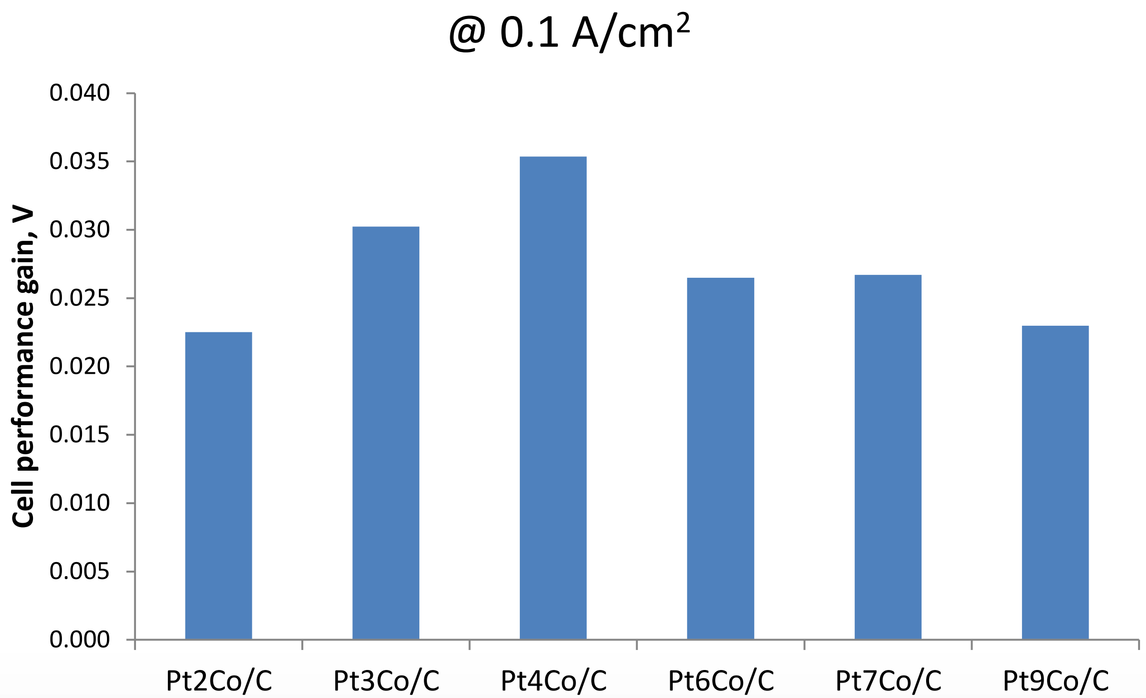
- Surprisingly catalysts with low Co (atomic ratios 6:1 to 9:1) show about 2.5x activity compared to Pt

Specific Activity



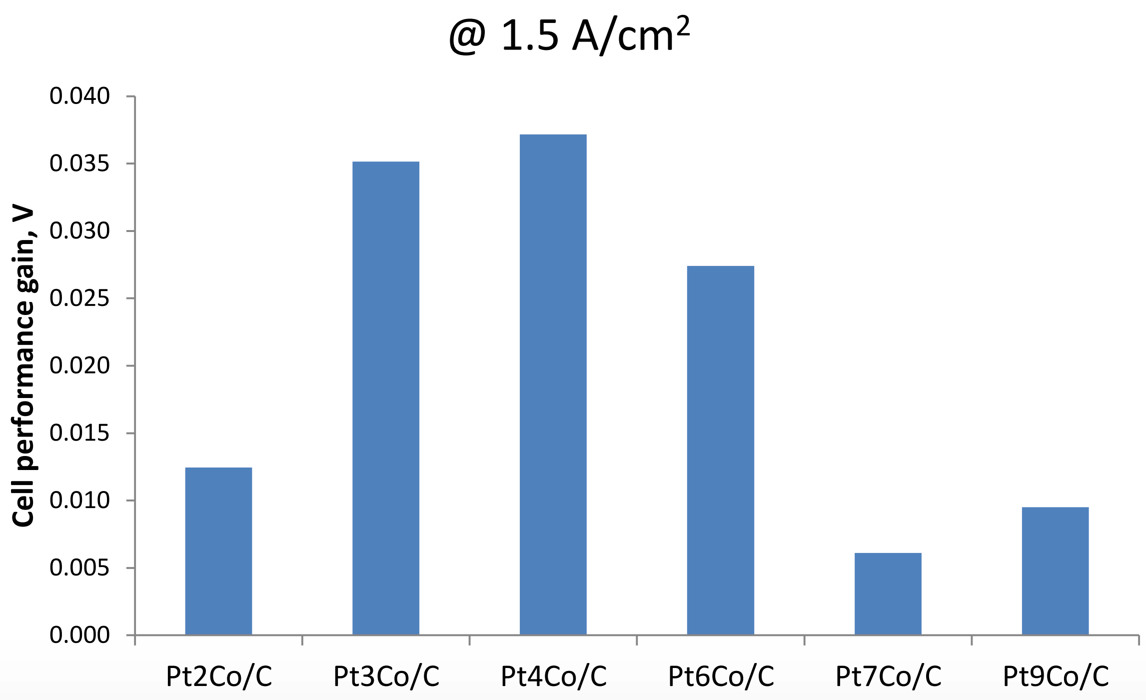
- ❑ Highest Pt specific activity of about 1000 µA/cm^2-Pt is observed for Pt_2Co/C & Pt_3Co/C
- ❑ Alloying small amount of Co with Pt (Pt:Co atomic ratio of 6:1 to 9:1) increase specific activity by 2x compared to Pt

Fuel Cell Performance



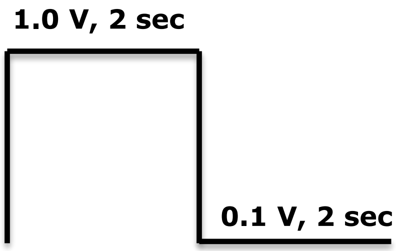
- In fuel cells (~50cm^2 active area), peak performance improvement observed for Pt_4Co/C unlike Pt_3Co/C in RDE
- 3.6x improvement in activity for Pt_4Co/C over Pt in RDE translates to 35mV improvement in fuel cell performance

Fuel Cell Performance

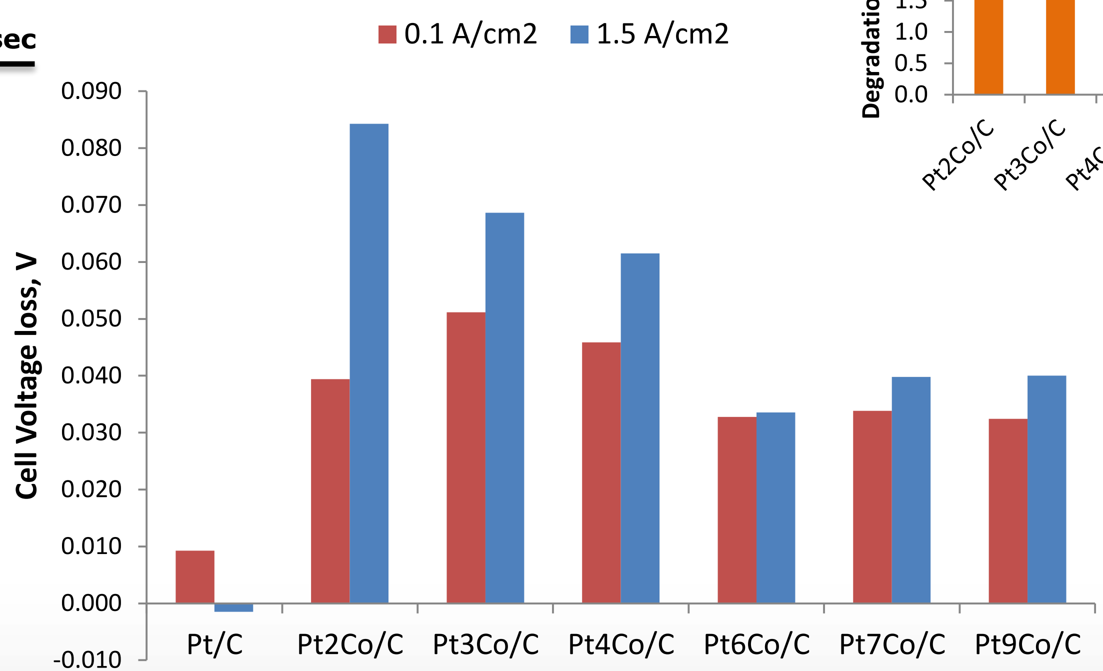


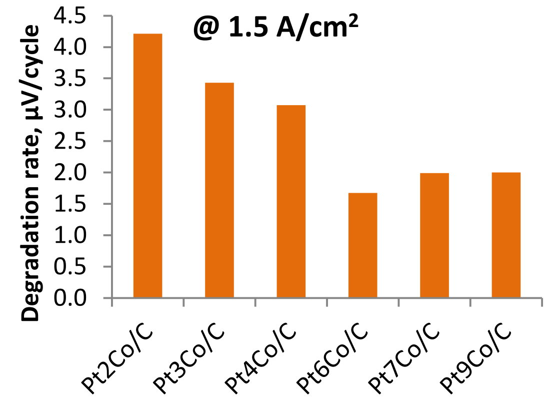
- Unexpectedly Pt_2Co/C, Pt_7Co/C & Pt_9Co/C show smaller improvement over Pt/C at 1.5 A/cm^2

Accelerated stress test



AST: 20,000 cycles





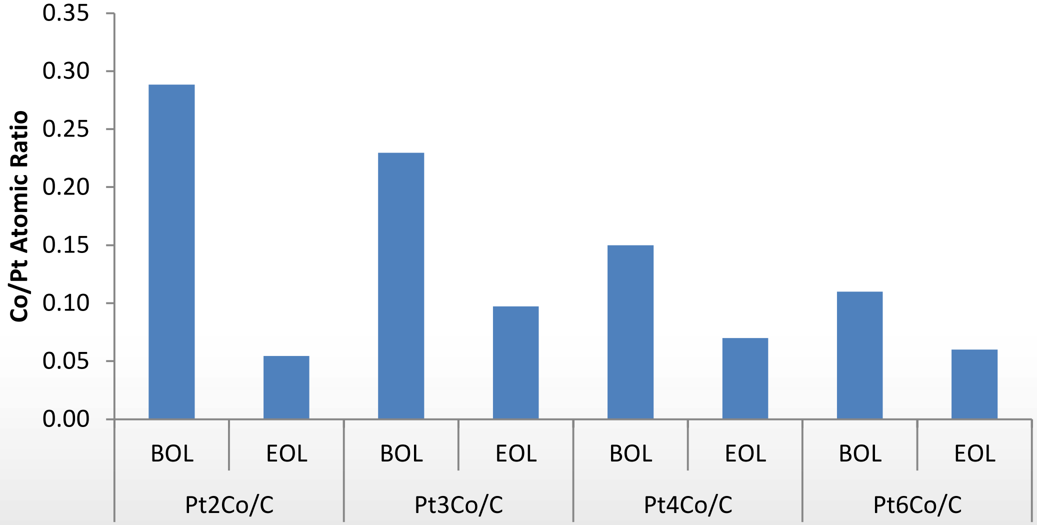
- Catalysts with Pt:Co atomic ratios -2:1 to 4:1 show slightly higher voltage losses at 0.1 A/cm^2
- Also for these catalysts significantly additional voltage losses are observed at 1.5 A/cm^2

Characterizations

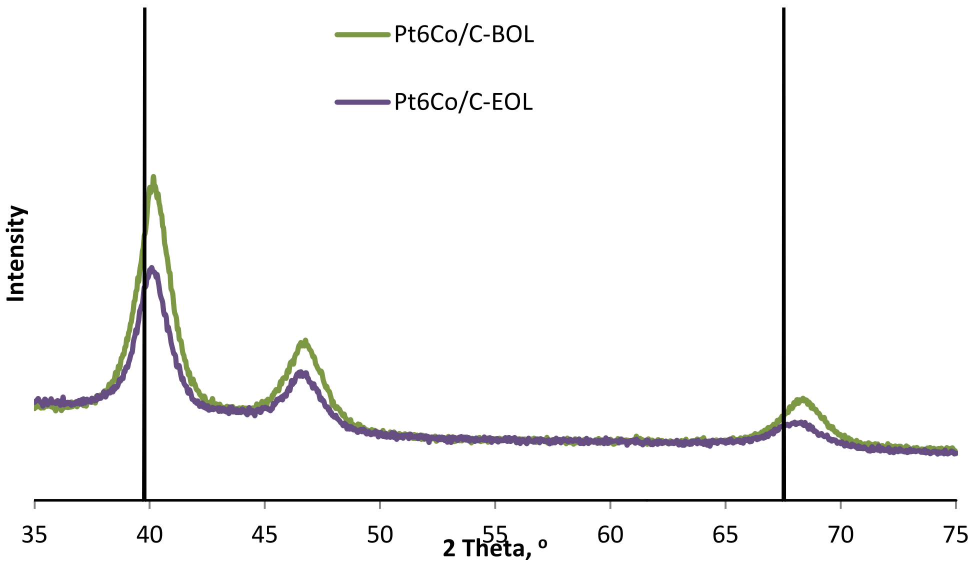
BOL & EOL MEA samples

- ❑ Catalyst layer thickness
- ❑ Catalyst surface species
- ❑ Particle size
- ❑ Ohmic resistance
- ❑ PITM
- ❑ Dissolution of Co

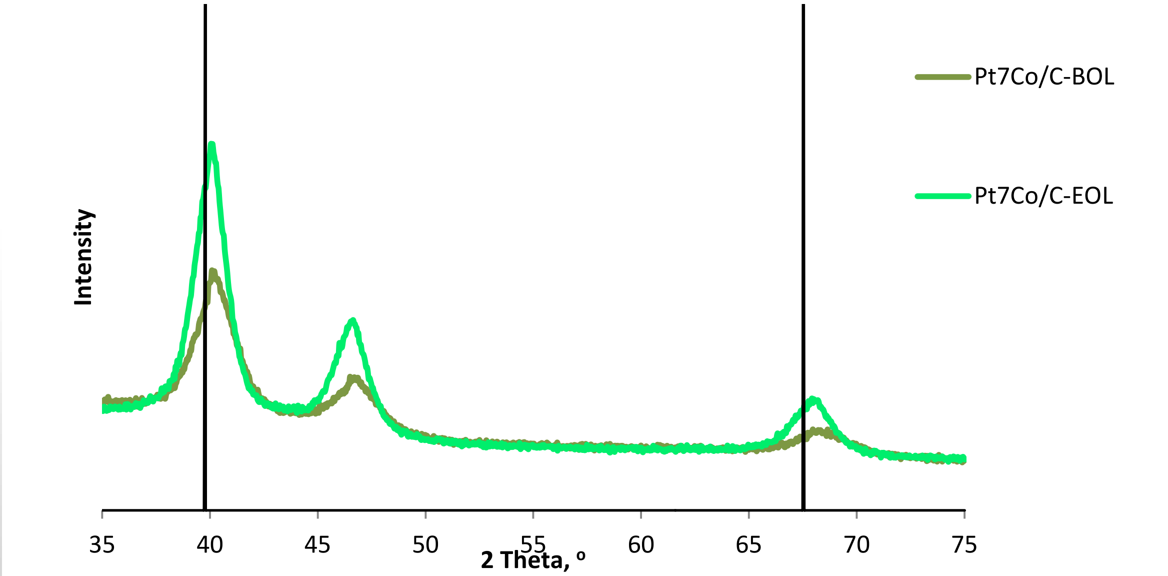
- ❑ EDX analysis exhibits catalysts with higher Cobalt ratios show massive loss of Cobalt after 20,000 voltage cycles



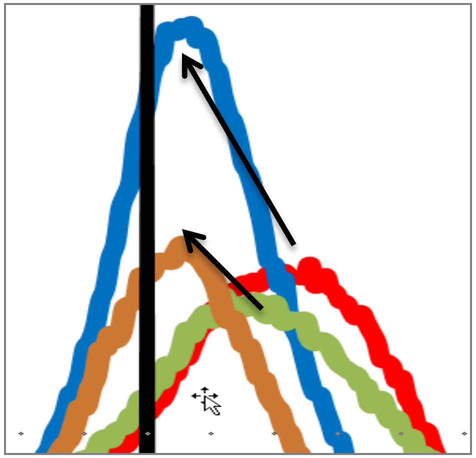
Structural characterization



- Smaller negative shift in peak position observed for EOL samples show leaching of Co



Structural characterization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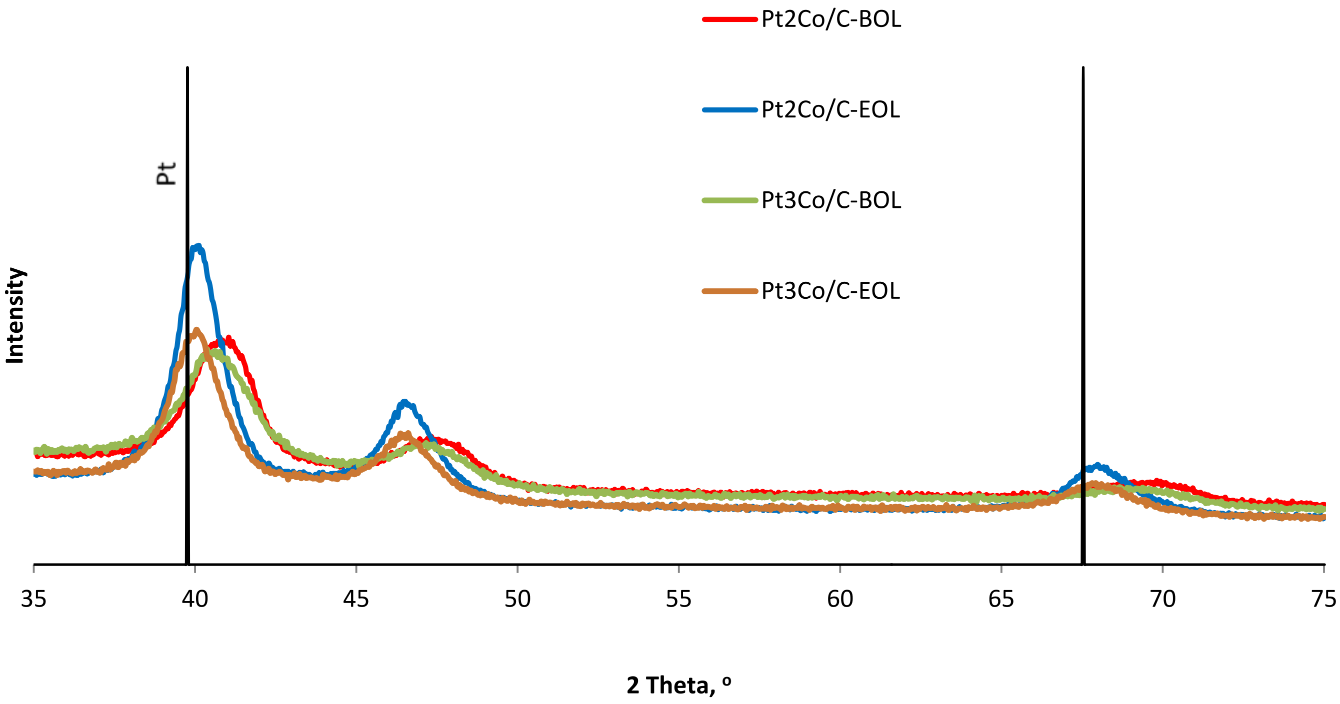

- Significant shift (negative) in peak positions observed for Pt_2Co/C & Pt_3Co/C EOL samples show extensive dissolution of Co

Summary

- 35mV improvement in performance observed for Pt_4Co/C over Pt/C at low and high current densities
- Of all the changes in catalyst properties, dissolution of Co seems to have a key contribution in cell performance losses (AST: 20,000 cycles, 0.1-1.0V)
- At 1.5 A/cm^2, catalysts with higher cobalt ratios such as Pt_2Co/C, Pt_3Co/C & Pt_4Co/C show additional performance losses after voltage cycling; this is attributed to leached Co related water management issues
- Further optimization of alloy durability and performance is possible but trade-offs are needed depending on the intended operating conditions. Pt-Co/C catalysts are still a significant consideration for fuel cell vehicles.