DOE Hydrogen Program

Highly Dispersed Alloy Cathode Catalyst for Durability

Sathya Motupally

June 10, 2008

UTC Power
A United Technologies Company

Project ID # FC5

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HIGHLY DISPERSED ALLOY CATALYST

DOE Hydrogen Program

Timeline

- Start – May 1, 2007
- End – April 30, 2010
- 33% Complete

Budget

- Total project funding
  - DOE share - $6.278M
  - Cost share - $2.860M
- DOE Funding received in FY07
  - $200K
- DOE Funding for FY08
  - $1,600K

Barriers

A. Performance
- Increase catalyst activity

B. Cost
- Reduce Pt metal loading

C. Durability
- Increase cyclic durability

Partners

- Johnson Matthey Fuel Cells
- Texas A&M University
- Brookhaven National Laboratory

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Technical Contributors

UTC Power:

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Objective

Develop structurally and compositionally advanced cathode catalyst that will meet DOE 2010 targets for performance and durability

DOE 2010 and 2015 Technical Targets

Characteristics	DOE 2010 Target	DOE 2015 Target
Pt group metal (total content) [g/kW]	0.3	0.2
Pt group metal (total loading) [mg/cm^2]	0.3	0.2
Mass activity @ 900mV [A/mg]	0.44	0.44
Specific activity @ 900mV [μA/cm^2]	720	720
Cyclic durability @ <80°C / ≥80°C [h]	5000/2000	5000/5000
ECA Loss [%]	<40	<40
Cost [$/kW]	5	3

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Milestones

Month/Year	Milestone or Go/No-Go Decision
August 2008	Milestone: Bench scale dispersed alloy catalyst formulation
September 2008	Go/No-Go decision: Verification of down-selected dispersed alloy catalyst
October 2008	Milestone: Bench scale core/shell catalyst formulation
November 2008	Go/No-Go decision: Verification of down-selected core/shell catalyst

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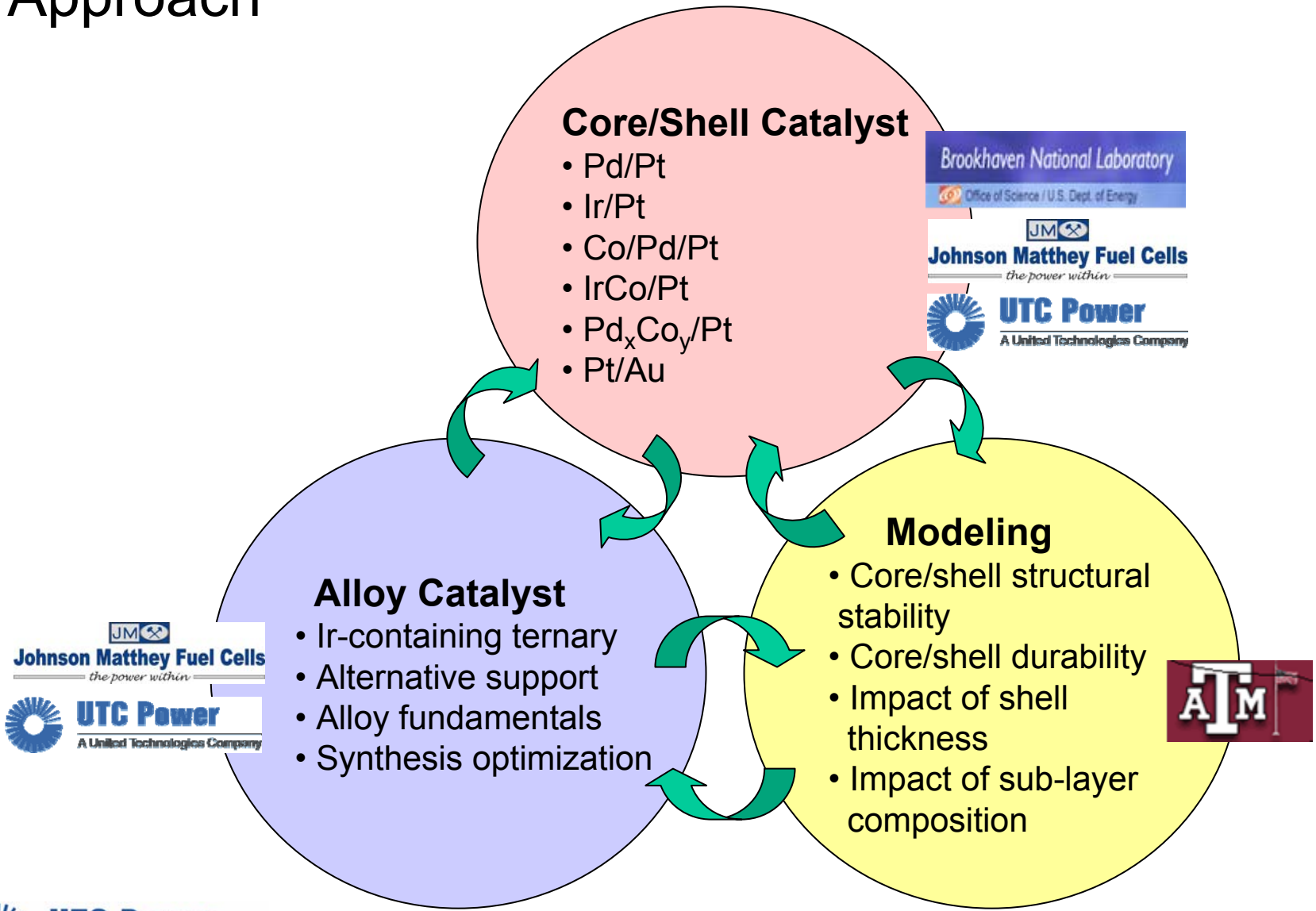
Approach



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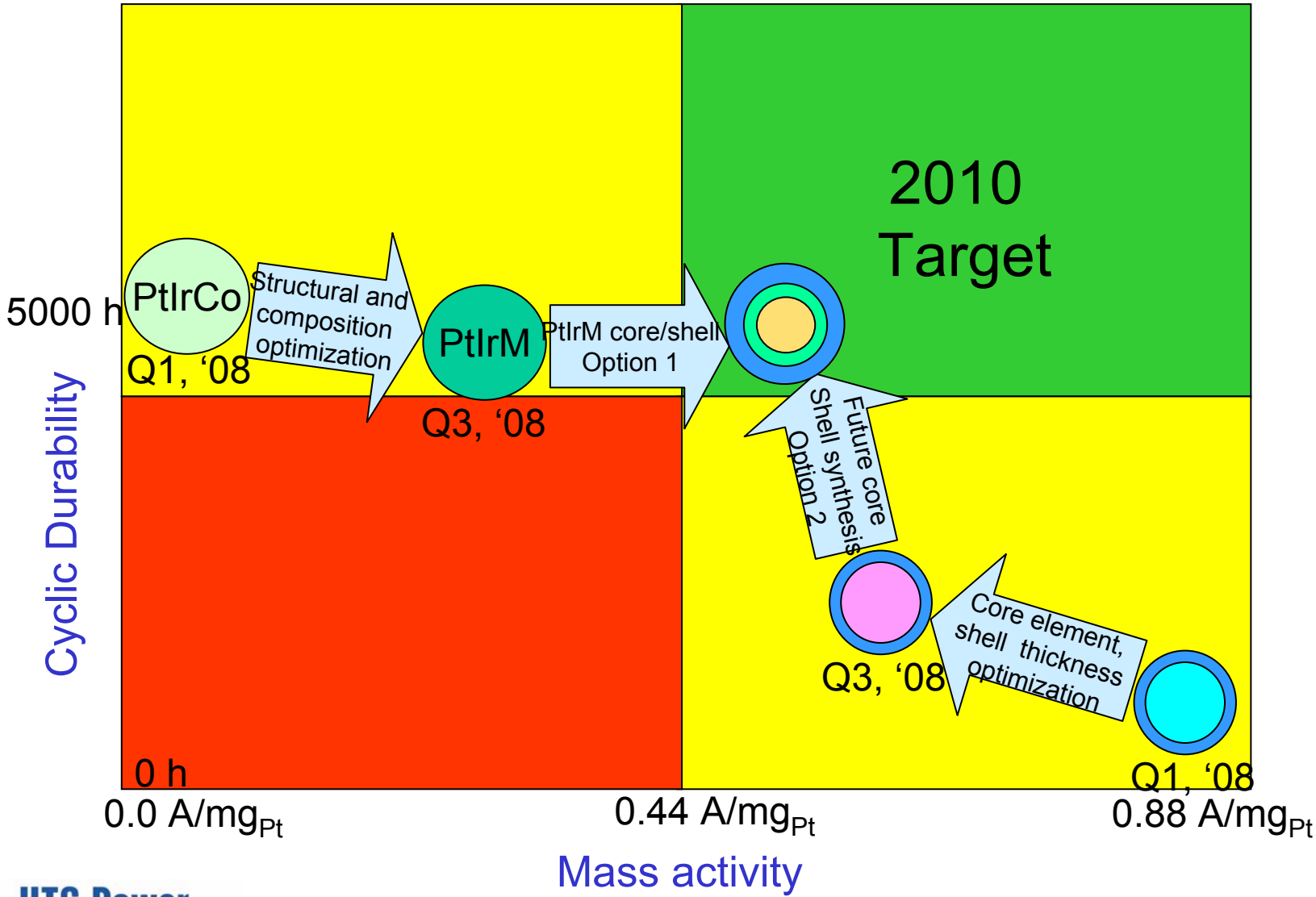
Strategy



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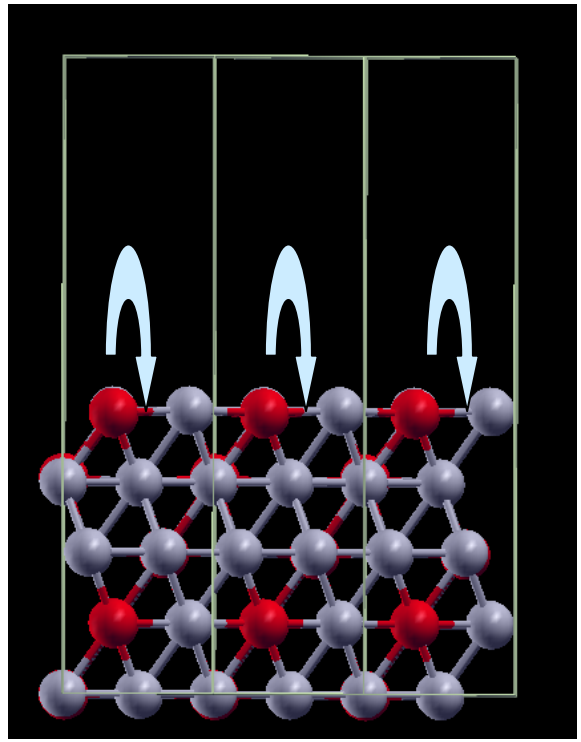
Modeling – Segregation energies for Pt_3M alloys

Atomic radius, experimental surface energy (E_{surf}) of M and calculated segregation energy (E_{segr}) of Pt in Pt_3M(111)

M	Atomic radius (Å)	E_{Surf} (J/m^2)	E_{segr} (eV) in Pt_3M
Pt	1.39	2.475	
Ag	1.44	1.250	0.15
Co	1.25	2.550	-0.61
Cr	1.28	2.300	0.06
Cu	1.28	1.825	-0.17
Fe	1.26	2.475	-0.41
Ir	1.36	3.000	-0.54
Mn	1.27	1.600	0.12
Mo	1.39	3.000	-1.30
Ni	1.24	2.450	-0.38
Pd	1.37	2.050	-0.03
Re	1.37	3.600	-2.08
Rh	1.34	2.700	-0.35
Ru	1.34	3.050	-0.83
Ti	1.47	2.100	0.68
V	1.34	2.550	-0.31



Surface Segregation Model for Pt_3M Alloys

Y. Ma and P. Balbuena, Surface Sci. 602, 107-113, (2008)

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CORE/SHELL STABILITY

Effects of Oxygen on Pt segregation

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E_{seg}(eV)	Pt_3Ir(111)	Pt_3Co(111)	Pt_3Fe(111)	Pt_3Ni(111)
Under 0.25 ML of O	-0.04	0.14	0.45	0.20
Without adsorption	-0.54	-0.61	-0.41	-0.38

E_{seg}: surface segregation energy
Positive E_{seg}: core/shell structure energetically unfavorable

- Segregation behavior changes in the presence of oxygen
- Most transition metals change from Pt surface segregation in the absence of oxygen to anti-segregation with oxygen

IMPACT OF CORE/SHELL ON Pt DISSOLUTION

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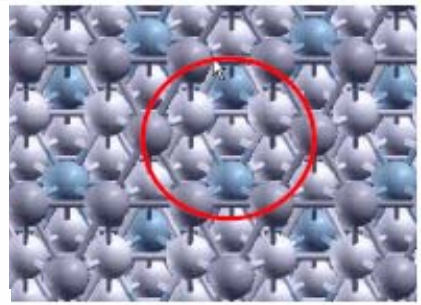
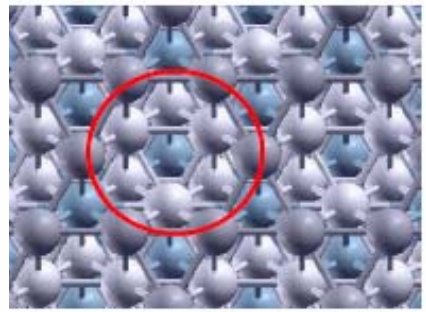
Potential shift with monolayer Pt shell in vacuum

System		μ_{Pt} (eV)	$\Delta\mu$ (eV)	ΔU (V)
Pt		-6.98	0	0
Pt(shell)-Pd(core)		-7.38	-0.40	0.20
Pt(shell)-Co(core)		-5.90	1.08	-0.54
Pt(shell)-Pd_3Co (core)	CVT1	-7.39	-0.41	0.21
	CVT2	-7.38	-0.40	0.20
Pt(shell)-Pd_3Fe (core)	CVT1	-5.96	1.02	-0.51
	CVT2	-5.97	1.01	-0.51



CV1



CV2

In vacuum –
Pd and Pd_3Co cores increase Pt stability (positive potential shift) whereas Co, and Pd_3Fe cores decrease stability

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IMPACT OF CORE/SHELL ON PT DISSOLUTION

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Potential shift with monolayer Pt shell with oxygen

0.25 monolayer of oxygen

System		μ_{Pt} (eV)	$\Delta\mu$ (eV)	ΔU (V)
Pt (0 ML)		-6.98	-0.72	0.36
Pt (0.25ML)*		-6.26	0	0
Pt(shell)-Pd(core)		-6.42	-0.16	0.08
Pt(shell)-Pd_3Co (core)	CVT1	-6.46	-0.20	0.10
	CVT2	-6.46	-0.20	0.10
Pt(shell)-Pd_3Fe (core)	CVT1	-4.88	1.38	-0.69
	CVT2	-6.49	-0.23	0.12

In the presence of oxygen –
Pt becomes less stable compared with in vacuum
Pd and Pd_3Co cores can increase Pt stability

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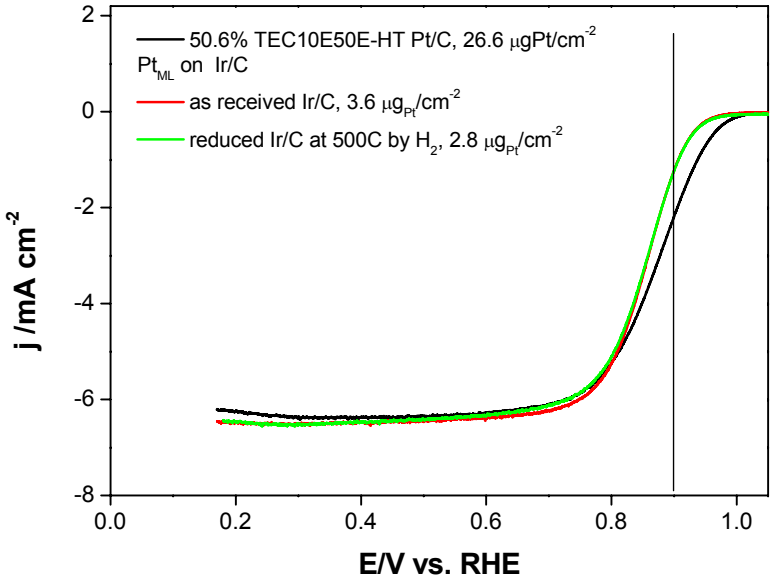
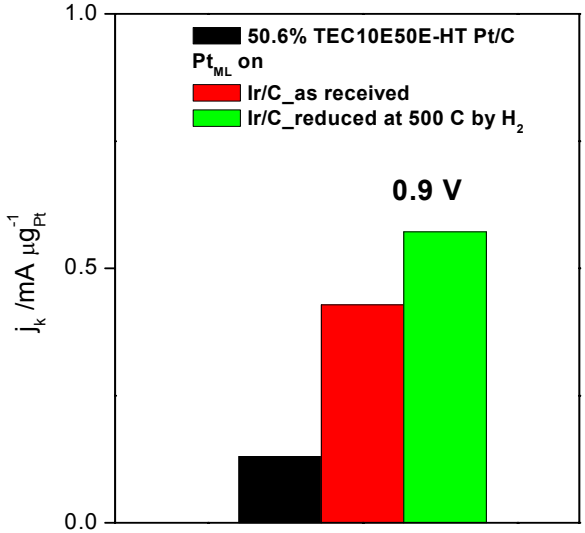
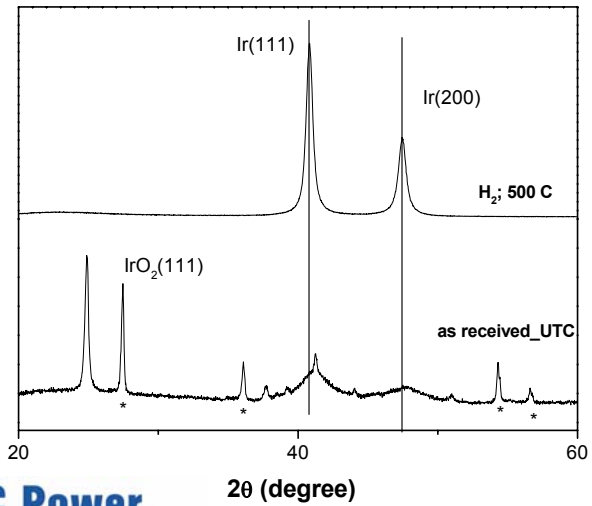
CORE/SHELL IMPACT ON ACTIVITY

Ir/Pt Core/Shell – As received and H2 annealed



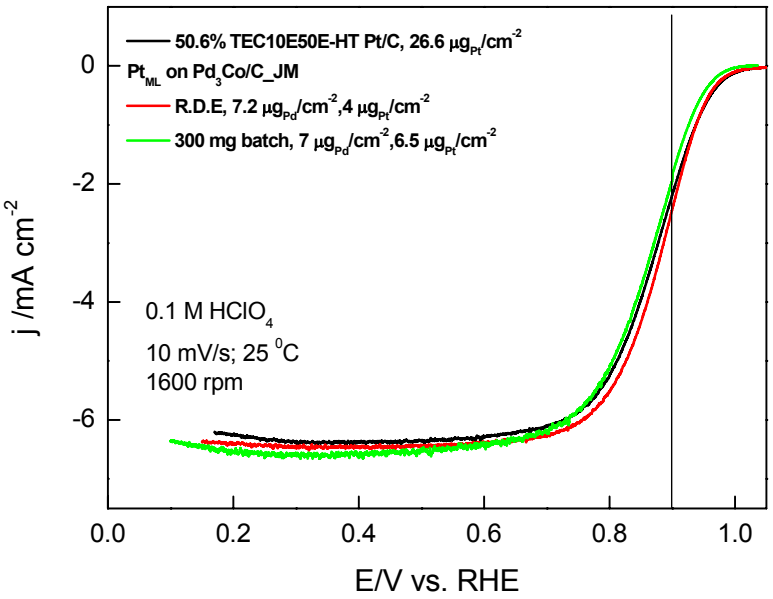


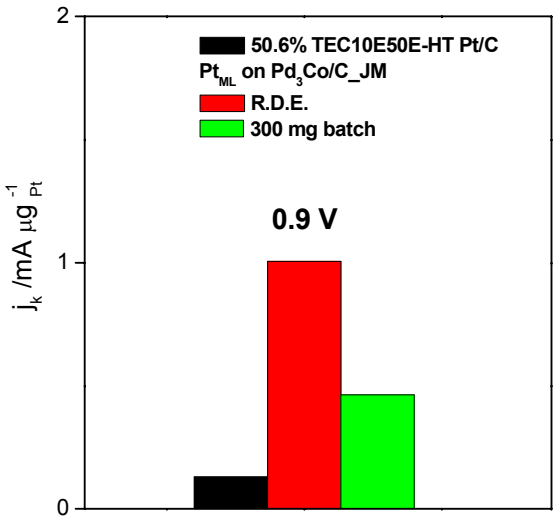


- Oxide observed in the as-received state
- Reduction using hydrogen leads to further increase in mass activity

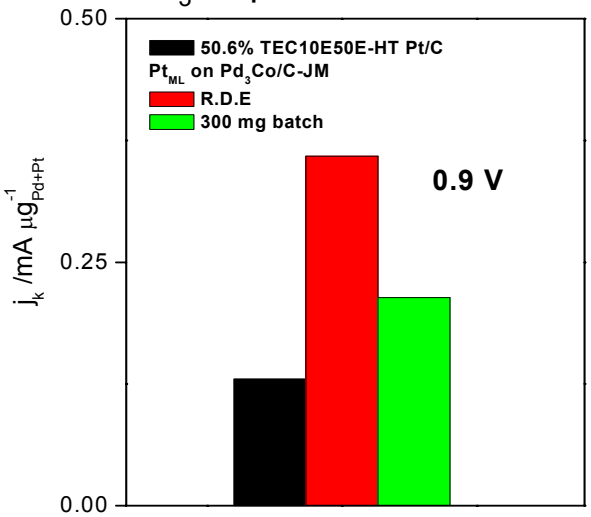
CORE/SHELL IMPACT ON ACTIVITY

Pd_3Co/Pt Core/Shell





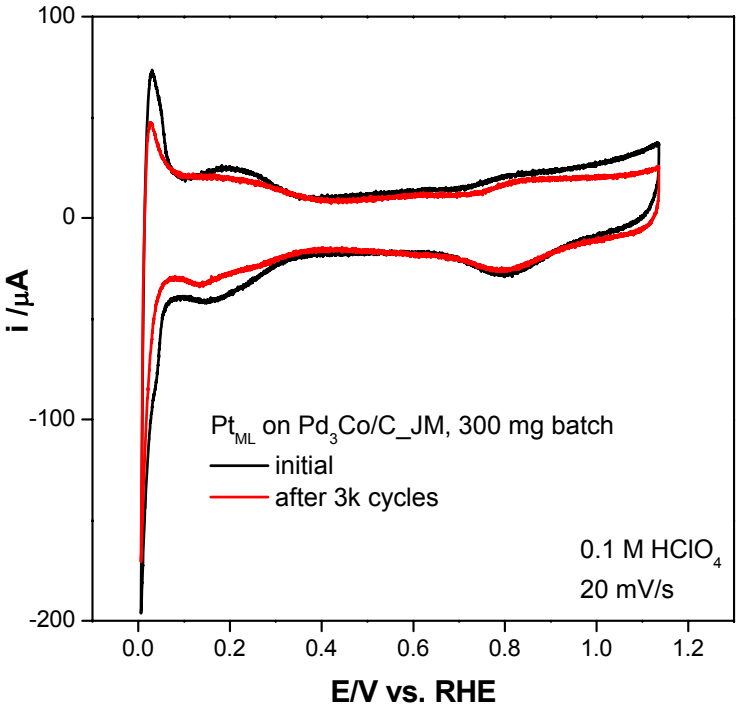
Pd_3Co particle size: 5.5 nm

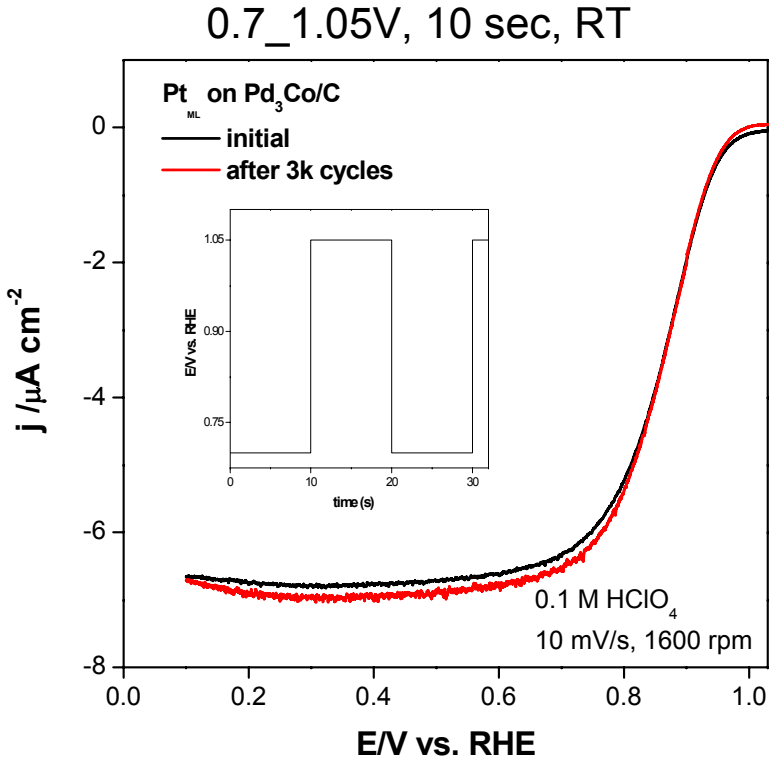


- Pd_3Co core gives the highest activity among all the Pd-Co alloys – 7x
- Chemistry for 20g scale-up underway
- Mass activity normalized by 5 y average spot price ratio of PGM metals equals 0.70 mA/μgPGM and 0.38 mA/μgPGM for RDE and 300mg methods, respectively.

CORE/SHELL IMPACT ON ACTIVITY

Pd_3Co/Pt Core/Shell





- Pd_3Co/Pt core/shell cyclic resistance - no apparent activity loss after 3000 cycles

HIGHLY DISPERSED ALLOY CATALYST

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Alternative Ir containing alloys

40% Pt_2IrFe

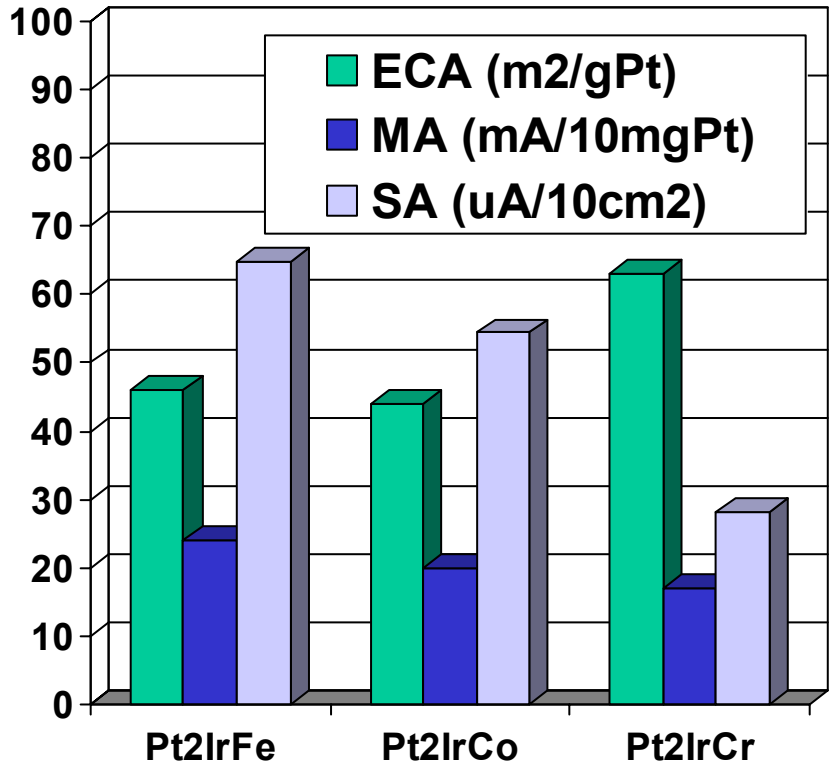
ICP: 38.3% wt. Pt, 17.1%Ir, 7.0%Fe
ECA: ~46 m^2/g Pt
Mass Activity: ~0.24 A/mg Pt
Specific Activity: ~649 $\mu A/cm^2$

40% Pt_2IrCr

ICP: 39.2%Pt, 17.8%Ir, 4.4%Cr
ECA: ~63 m^2/g Pt
Mass Activity: ~0.17 A/mg Pt
Specific Activity: ~281 $\mu A/cm^2$

40% Pt_2IrCo = Baseline

ICP: %Pt; %Ir; %Co
ECA: ~44m^2/gPt
Mass Activity: ~0.20 A/mgPt
Specific Activity: ~544 $\mu A/cm^2$



SUMMARY AND FUTURE WORK

DOE Hydrogen Program

- Modeling
  - Impact of oxygen on Pt dissolution and structural stability for various core/shell systems has been quantified
- Core/Shell(Pt) Catalyst
  - A number of elemental and alloy cores have been evaluated; Pd_3Co and Ir cores lead to the highest improvement in ORR
- Alloy Catalyst
  - Various PtIrX alloys have been synthesized and tested to understand activity and durability trade-off
- Future Work (2008)
  - Pd_3Co/Pt, Ir/Pt core/shell durability and scale-up optimization
  - Ir_xCo_y alloy cores
  - Validate modeling results on core/shell stability and durability
- Future Work (2009)
  - Down-select optimum catalyst from dispersed or core-shell catalyst
  - Validate full scale single-cell fuel cell