Performance and Durability of Advanced Automotive Fuel Cell Stacks and Systems with Dispersed Alloy Cathode Catalyst in Membrane Electrode Assemblies

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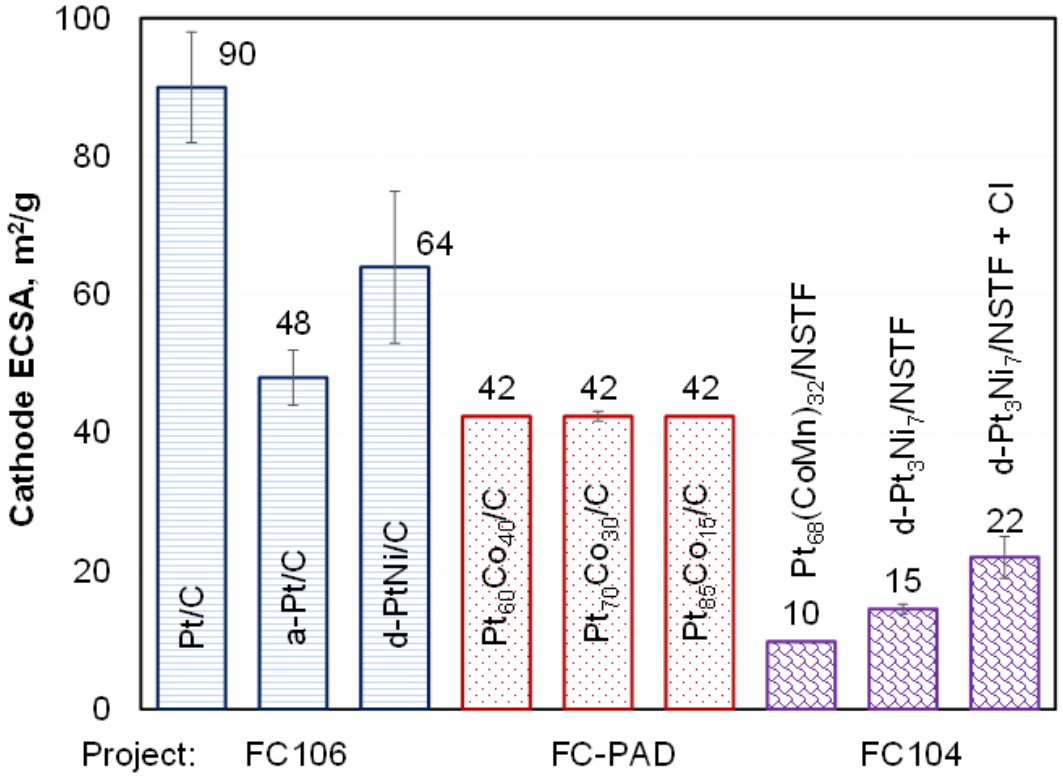
Performance and Durability of Advanced Automotive PEMFC Stacks and Systems with Dispersed Alloy Cathode Catalyst in MEAs

Collaborations with 3M, JMFC/UTRC, Ballard, FC-PAD and GM

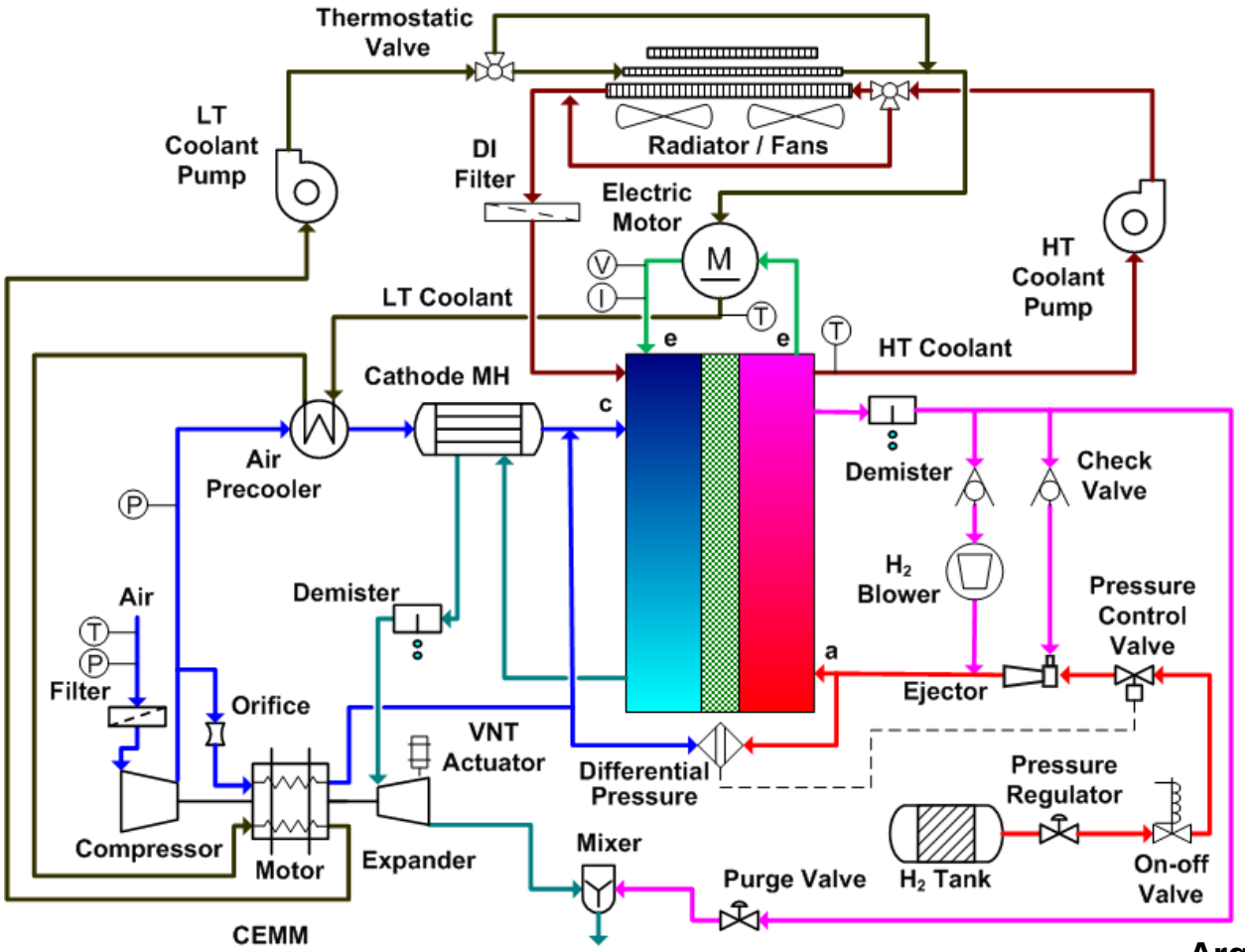
1. Dispersed Pt/C: JMFC, Ballard
2. Annealed Pt/C (a-Pt/C): JMFC
3. De-alloyed PtNi/C (d-PtNi/C): JMFC
4. Dispersed PtCo/C alloy: EWii, Umicore, GM
5. Ternary $Pt_{68}(CoMn)_{32}$/NSTF: 3M
6. De-alloyed Pt_3Ni_7/NSTF: 3M
7. De-alloyed Pt_3Ni_7/NSTF with cathode interlayer (CI): 3M



System Perspective of Catalyst Performance and Durability

Performance: Optimized performance and cost of 80 kW_e net fuel cell system subject to $Q/\Delta T$ = 1.45 kW/^oC constraint

Durability: Acceptable loss in ECSA for 10% derating in system power at EOL



Argonne 2016 FCS

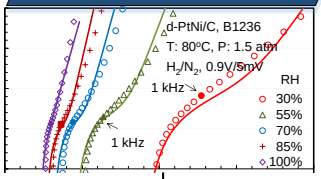
ΔT: Stack coolant exit T – Ambient T

From Differential Data to Integral Cell Model

1.1 Differential Cell Data

Variables: P, T, RH, X_{O2}, i

1.2 EIS Data



CCL Conductivity

σ_c (T, RH)

2. Overpotential Breakdown

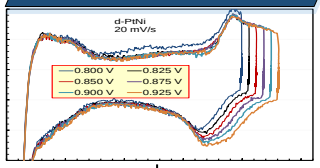
η_s^c, η_s^a, iR_Ω^m, iR_Ω^c, η_m

3. η_m Correlation

i_L(P, T, RH, X_{O2})

η_m(P, T, RH, X_{O2}, i/i_L)

1.3 CV Data



PtO_x Formation

Θ(E)

4. Expanded Polarization Data

5. Mass Transfer Resistance

R_m (P, T, RH, X_{O2}, E, i)

FC-PAD

Gas Resistance

R_g(P,T,RH,X_{O2})

GDL Resistance

ε_τ^d, ε_τ^w(E, i), δ_l/δ_d

6. Resistance Breakdown

R_d: Pressure Dependent

R_{cf}: Pressure Independent

CCL Resistance

R_{cf} (T, RH, E, i)

7. Integral Cell Model

1+1D or 2+1D

Operating Conditions

Cell Design

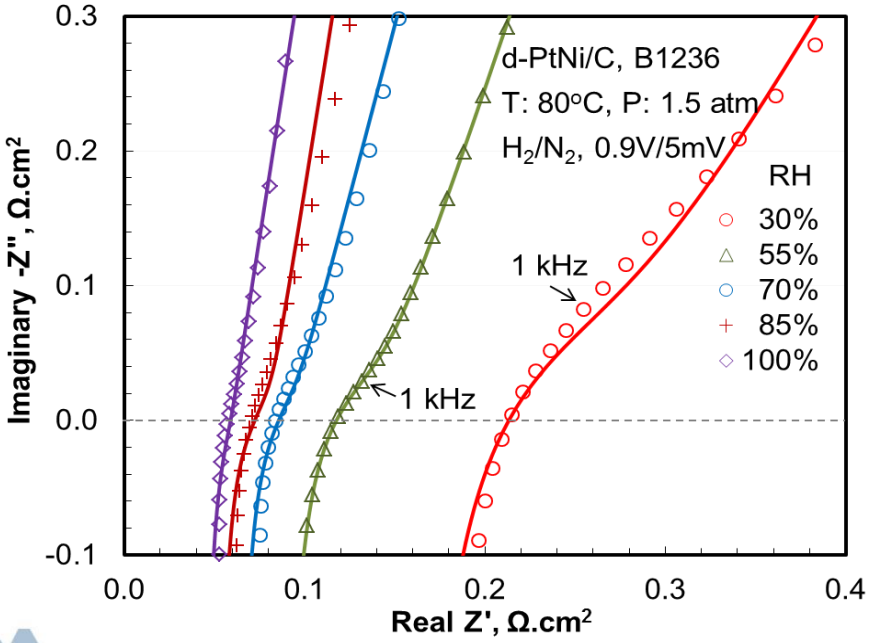
Electrode Resistance

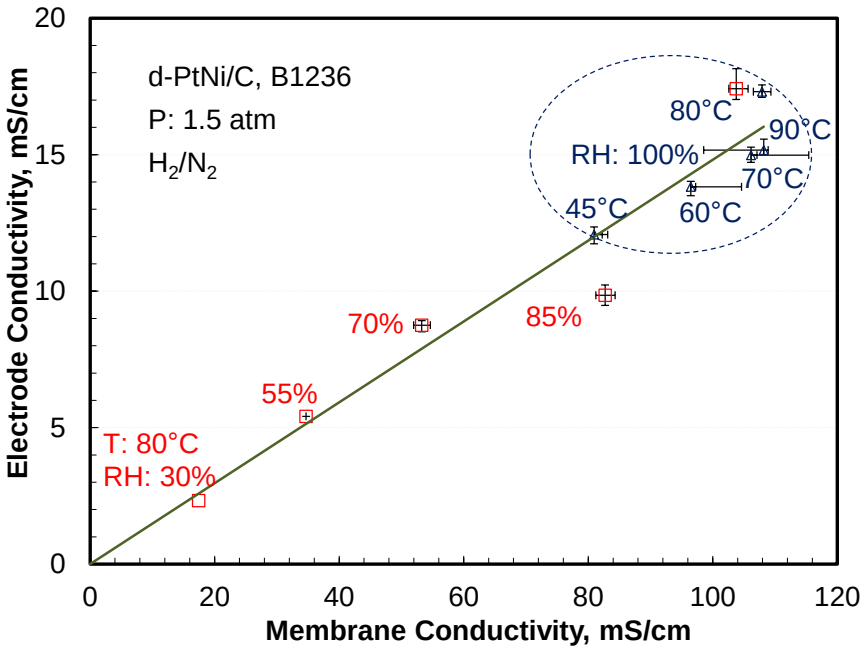
UTRC 12.25-cm^2 active area cell, triple serpentine flow channels, fixed flow rate 1(a) / 3(c) slpm, 5 minutes hold per point

- JMFC Catalyst: d-PtNi/C, 0.1 mg/cm^2 Pt loading, 60 m^2/g$_{Pt}$ ECSA (A_{Pt})
- BOL diagnostics: H_2-pump, H_2-xover, CV, EIS

Electrode conductivity (σ_c) from Galvanostatic impedance data for H_2/N_2 at 0.4 to 0.925 V with 5 mV perturbation

- ZVIEW transmission line model (100 repeat units)
- σ_c has similar temperature and RH dependence as σ_m: $\sigma_c = \sigma_m f(\varepsilon_i, \tau)$

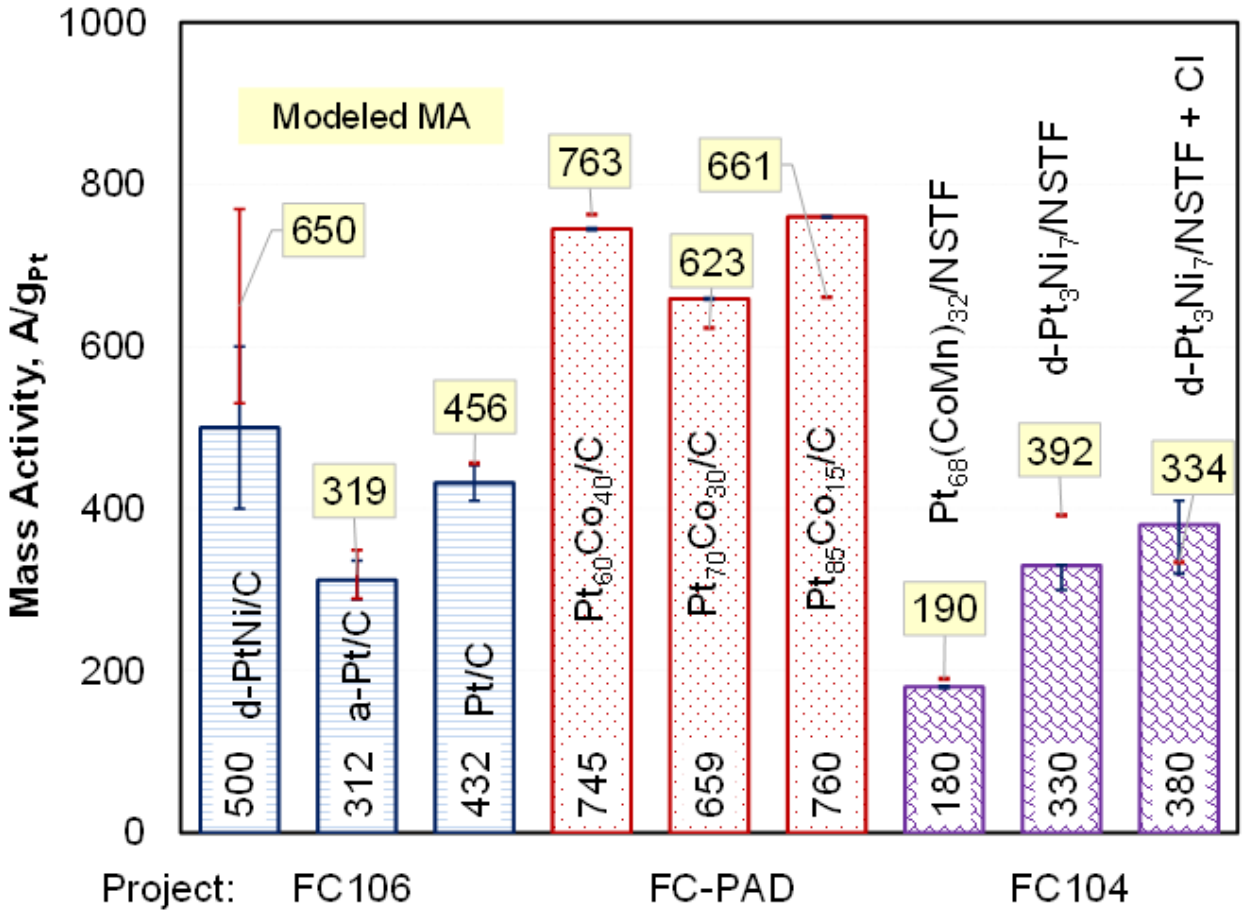




σ_m; Membrane conductivity; ε_i : Ionomer volume fraction; τ; Tortuosity for ion conduction

Kinetics of ORR on SOA Catalysts

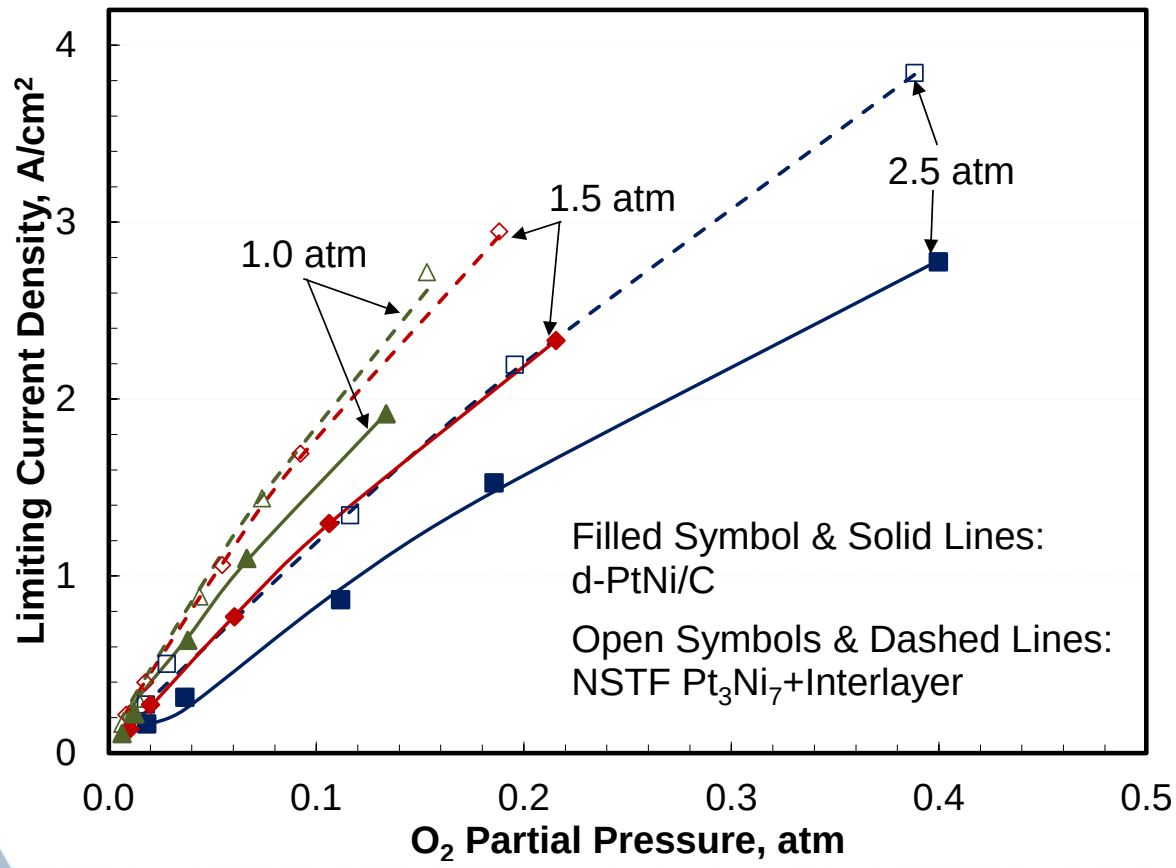
- d-PtNi/C has 2X modeled mass activity of a-Pt/C that has nearly the same particle size
- d-PtNi/C and PtCo/C alloy have comparable mass activities
- Both d-PtNi/C and PtCo/C alloy systems meet the mass activity targets of 440 A/g_{Pt}



Limiting Current Density

- Definition of mass transfer overpotential

  $\eta_m = E_N - E - iR_\Omega^m - \eta_c - \eta_a$
- i_L defined as current density at which η_m = 450 mV
- Limiting current densities are higher are higher in NSTF MEAs than in dispersed catalyst MEAs with nearly same Pt loading

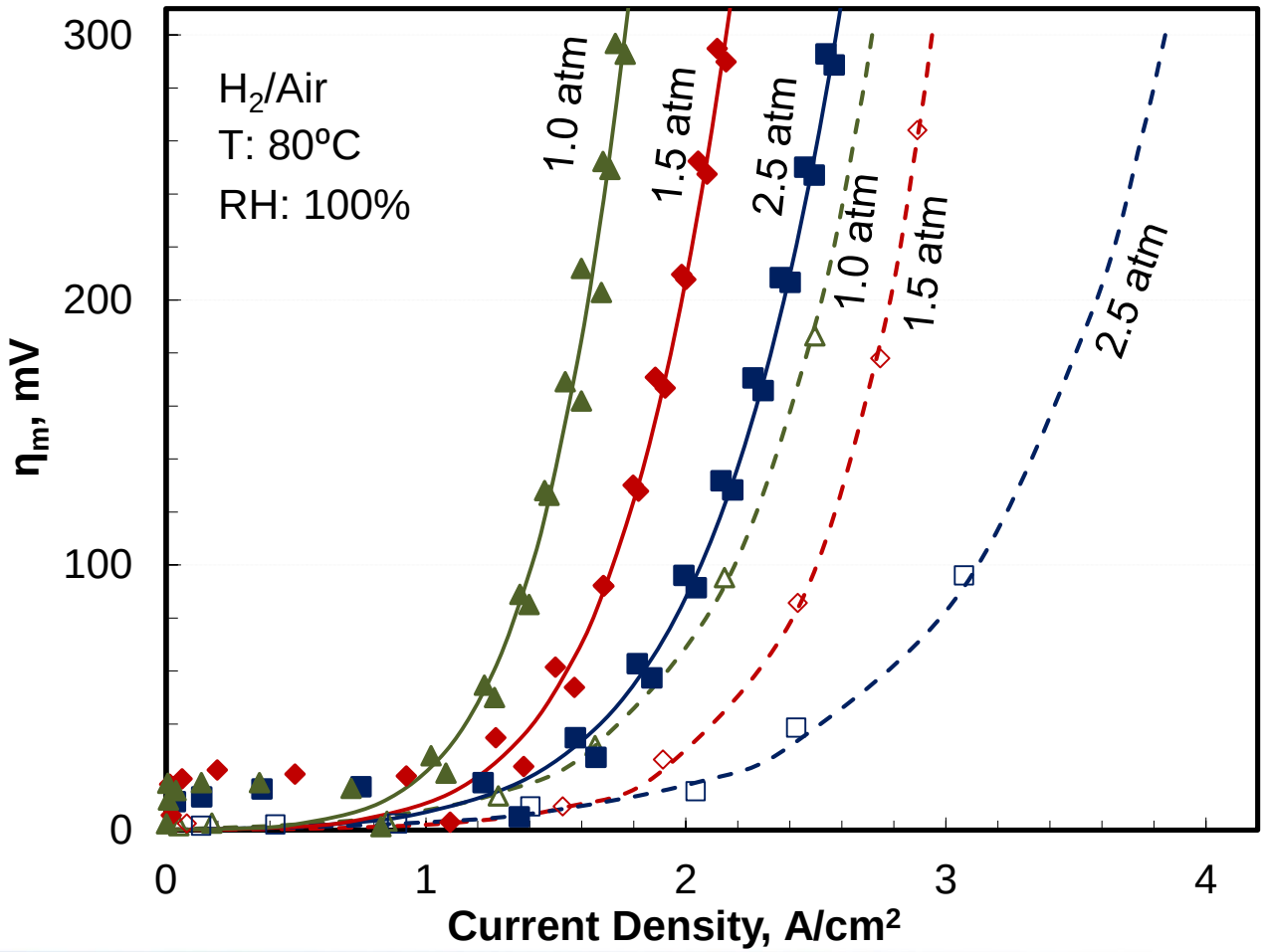


Illustrative results at 100% RH and 80°C

- Liquid water likely present in the electrode and diffusion media

Mass Transfer Overpotentials

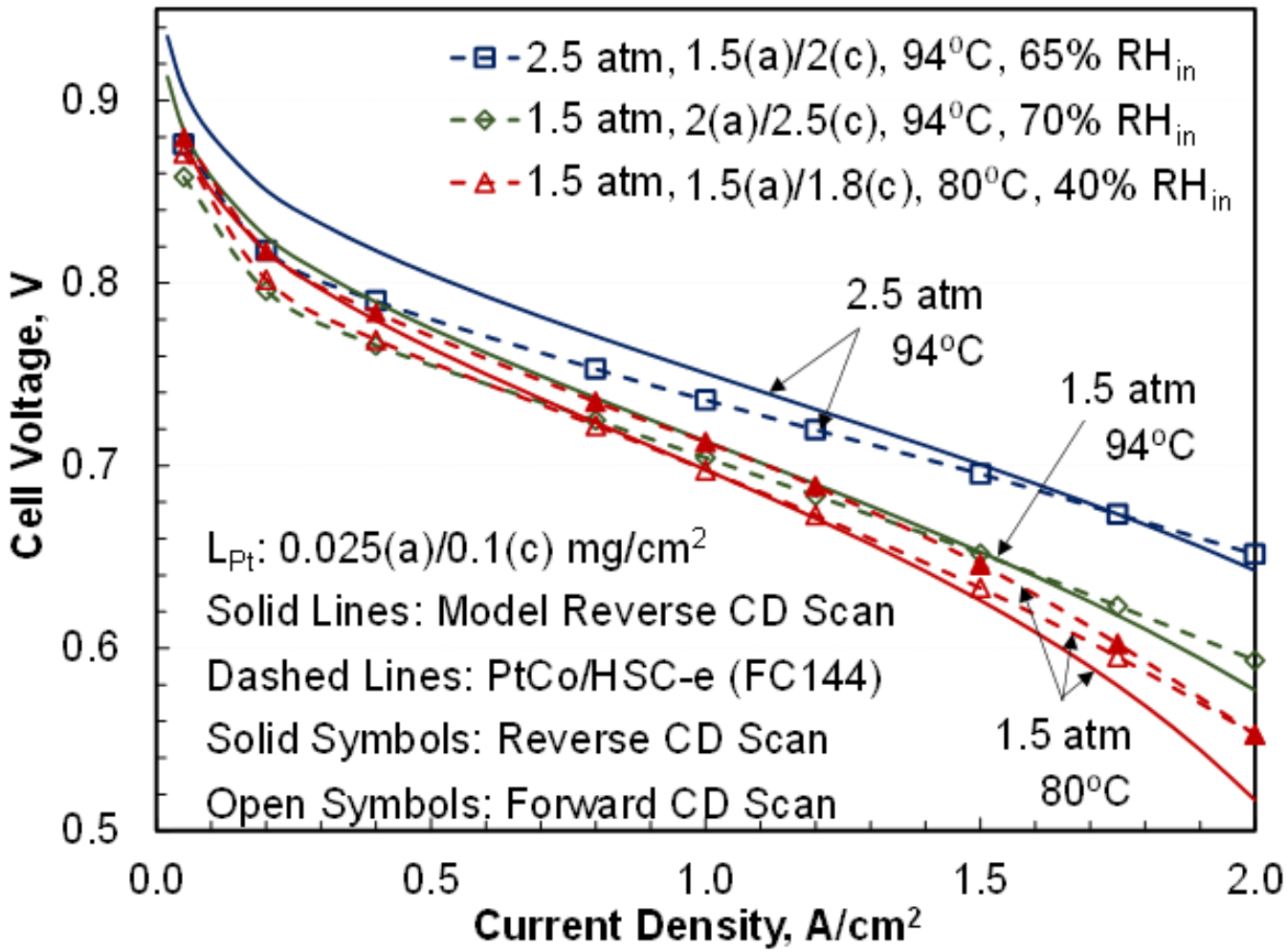
- Mass transfer overpotentials are smaller in NSTF MEAs than in dispersed catalyst MEAs with nearly same Pt loading
- However, cold start and robustness are still outstanding issues for NSTF MEAs even with the cathode interlayer



Model Calibration against SOA MEA Data

GM data reported in FC144 (2017) under conditions relevant to Q/ΔT constraint, 1.5 and 2.5 atm outlet pressure, 94°C, 40-70% inlet RH, $\Delta T_c = 0$

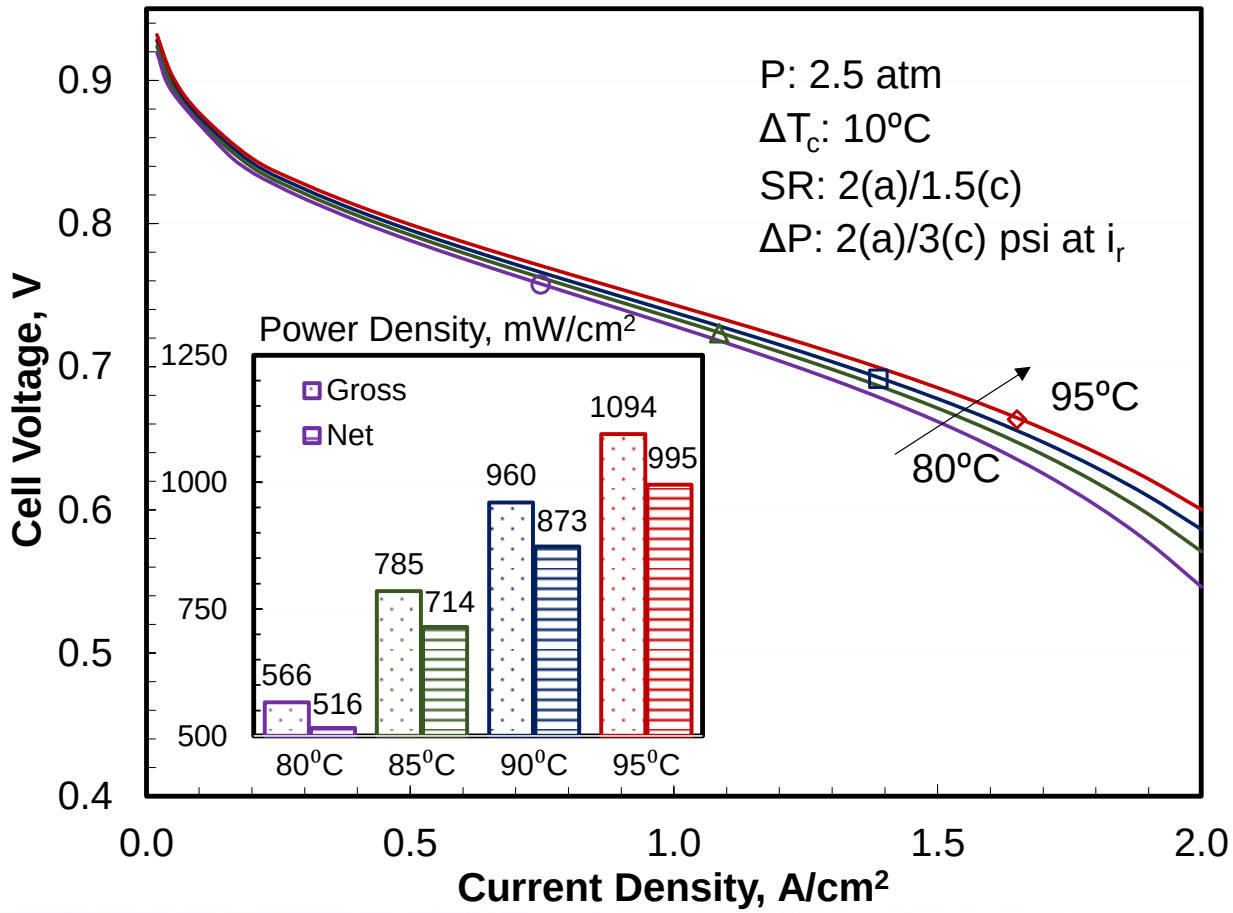
- GM PtCo/HSC(e) cathode, 0.1 mg/cm^2 Pt loading
- Model data as solid lines for d-PtNi/C, reverse current density (CD) scan



Impact of Q/ΔT Constraint

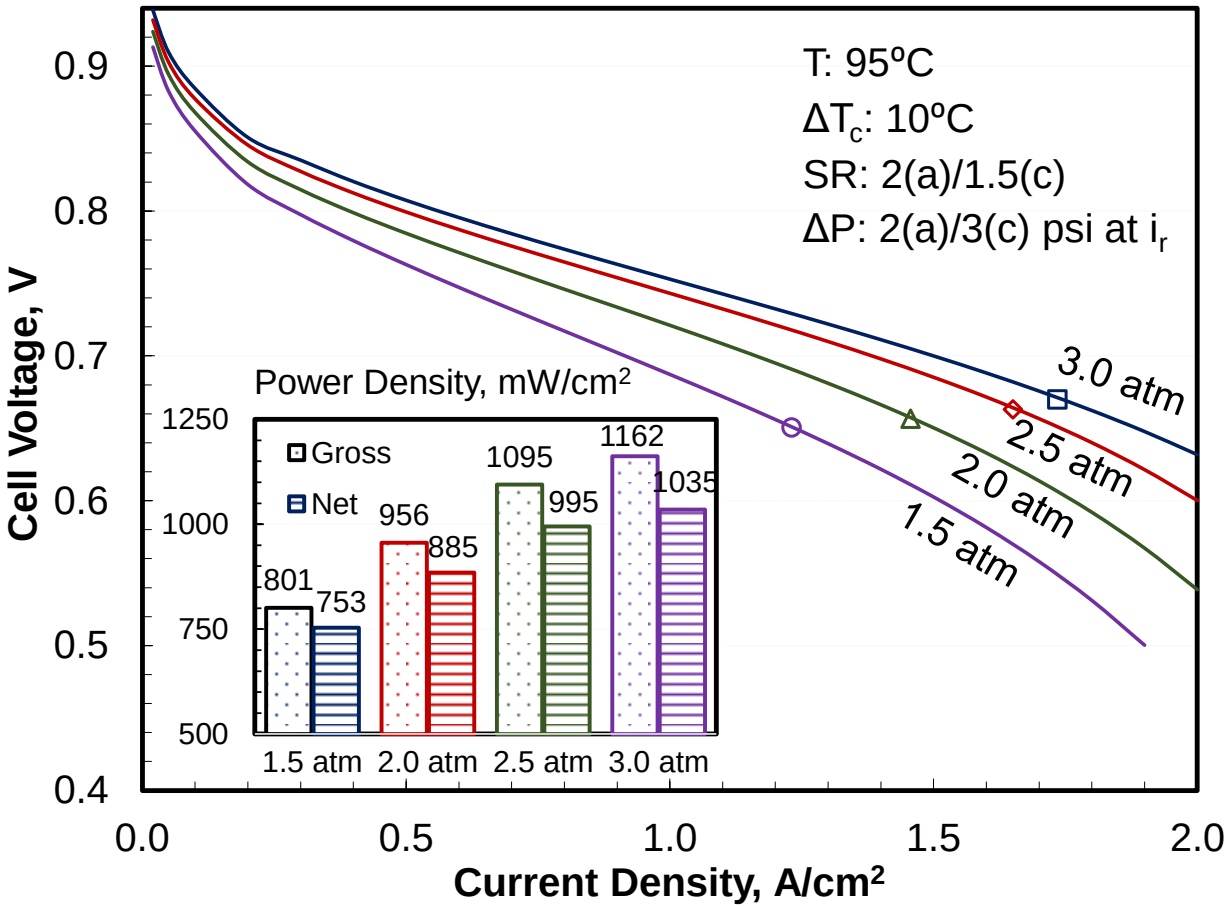
Modeled optimal beginning of life (BOL) performance of FCS, d-PtNi/C cathode catalyst subject to Q/ΔT=1.45 kW/°C constraint: 0.125 mg/cm^2 total Pt loading; 850 EW, 14-μm chemically-stabilized, mechanically-reinforced membrane, 2.5 atm inlet pressure, SR(c) = 1.5

- Because of Q/ΔT constraint, the required cell voltage at rated power is higher at lower operating temperatures: 757 mV at 80°C, 663 mV at 95°C
- 95°C or higher operating temperature required for >1000 mW/cm^2 power density



Desired Operating Pressures

- Q/ΔT constraint: Higher cell voltage at rated power required for higher operating pressures: 651 mV at 1.5 atm, 670 mV at 3 atm, 95ºC, SR(c)=1.5
- Because of the dependence of mass transfer overpotential on $P(O_2)$ and RH, 2.5 atm or higher stack inlet pressure required for >1000 mW/cm^2 power density

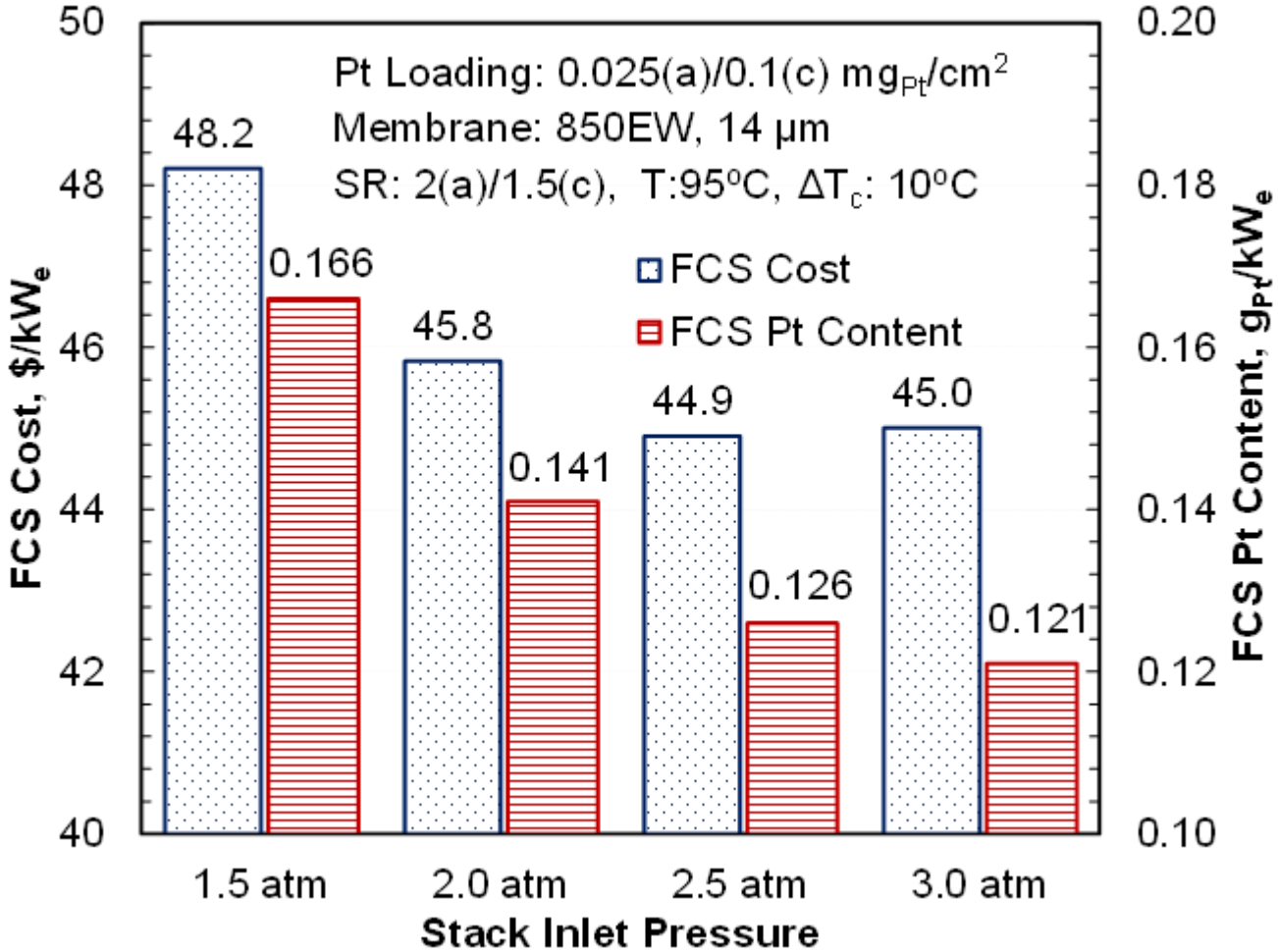


MEA parameters as in previous slide

Projected Performance of Automotive FCS with SOA Cathode Catalyst

Projected FCS cost and Pt content: 44.9 $/kW$_e$ at 2.5 atm, and 0.126 g_{Pt}/kW_e at 2.5-atm stack inlet pressure, 95°C stack temperature, SR(c)=1.5

- 0.125 g_{Pt}/kW_e ultimate target for stack PGM content exceeded by ~10%
- Optimum exit RH: ~100% at 2.5 atm, <60% at 1.5 atm

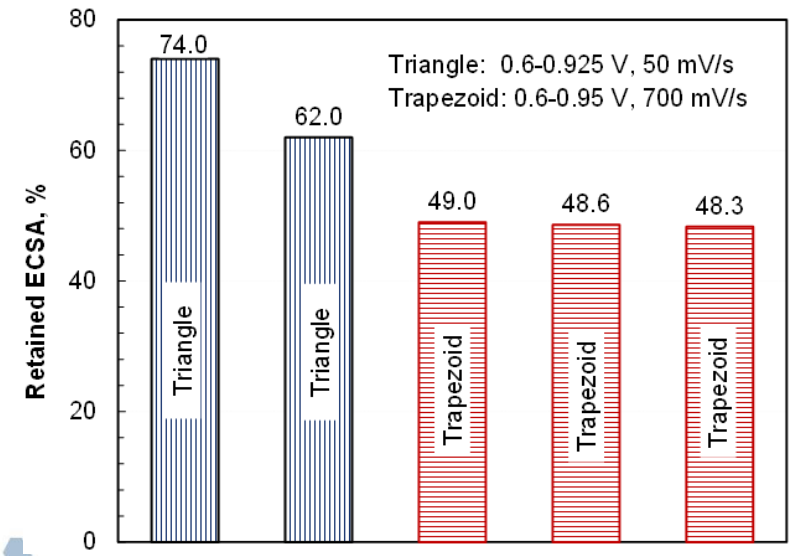


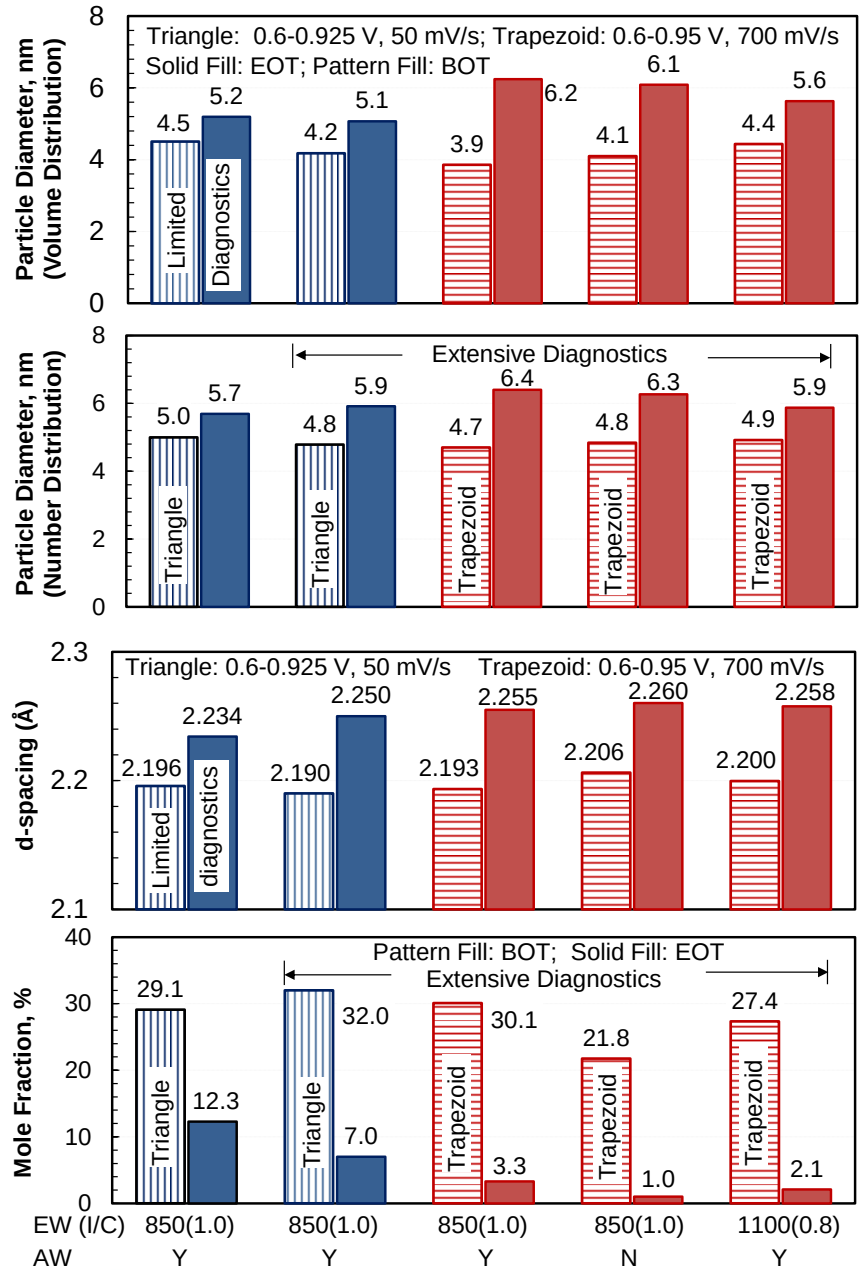
Cost correlations from Strategic Analysis (SA), 500,000 units/year, no H_2 blower

Stability of d-PtNi/C Electrode under Cyclic Potentials

30,000 Catalyst AST cycles

- Measured ECSA loss higher on trapezoid cycles (0.6-0.95 V, 700 mV/s) than on triangle cycles (0.6-925 V, 50 mV/s)
- Faster ECSA loss with extensive intra-cycle diagnostics
- WAXS indicates extensive leaching of Ni that depends on duty cycle[1]
- ECSA loss correlates with growth in particle size and leaching of Ni





WAXS data from N. Kariuki and D. Myers (ANL)

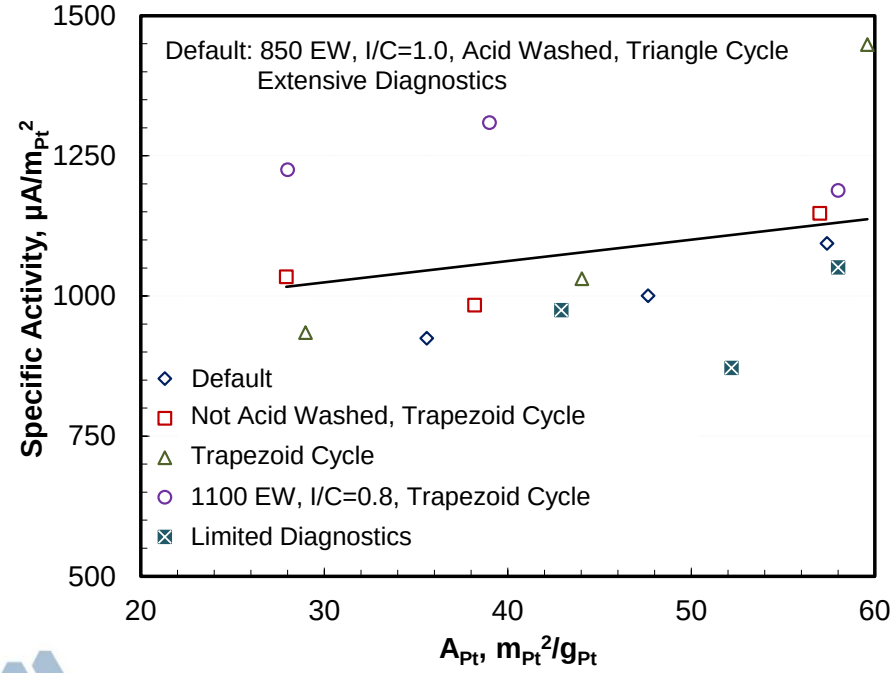
ORR Activity of Degraded d-PtNi/C Electrode

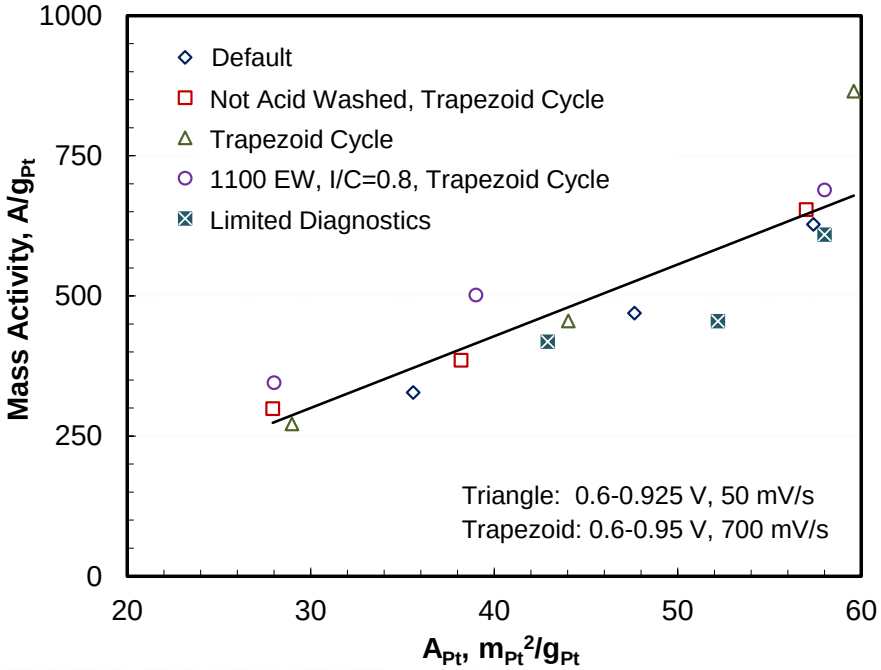
Even with extensive Ni leaching, the catalyst retains its high specific activity

- <10% decrease in specific activity with >90% Ni loss

Losses in mass activity and ECSA (A_{Pt}) are correlated

- However, some loss in ECSA is due to Ni leaching out from the alloy catalyst
- ECSA loss depends on the potential cycle, upper potential limit and electrode pretreatment

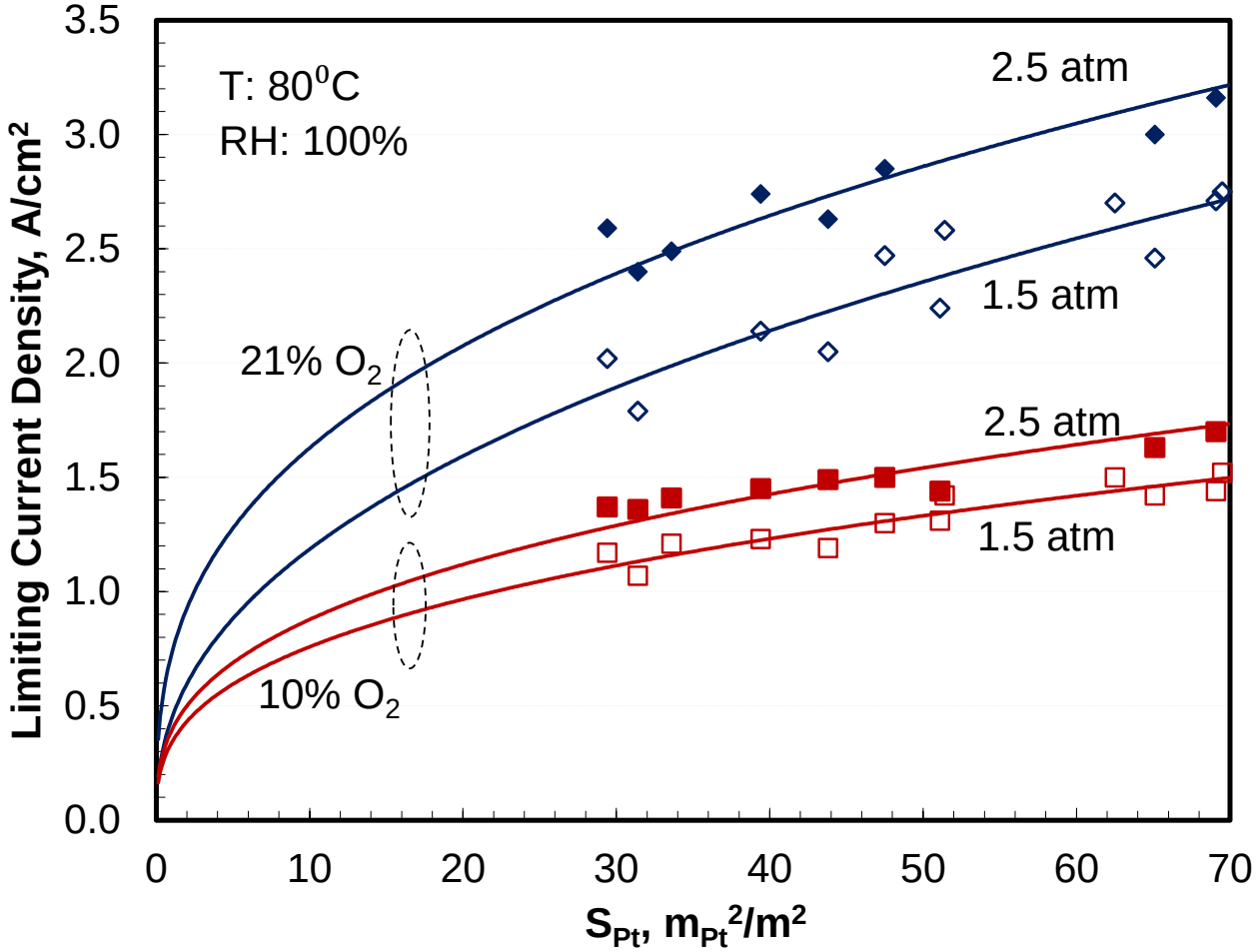




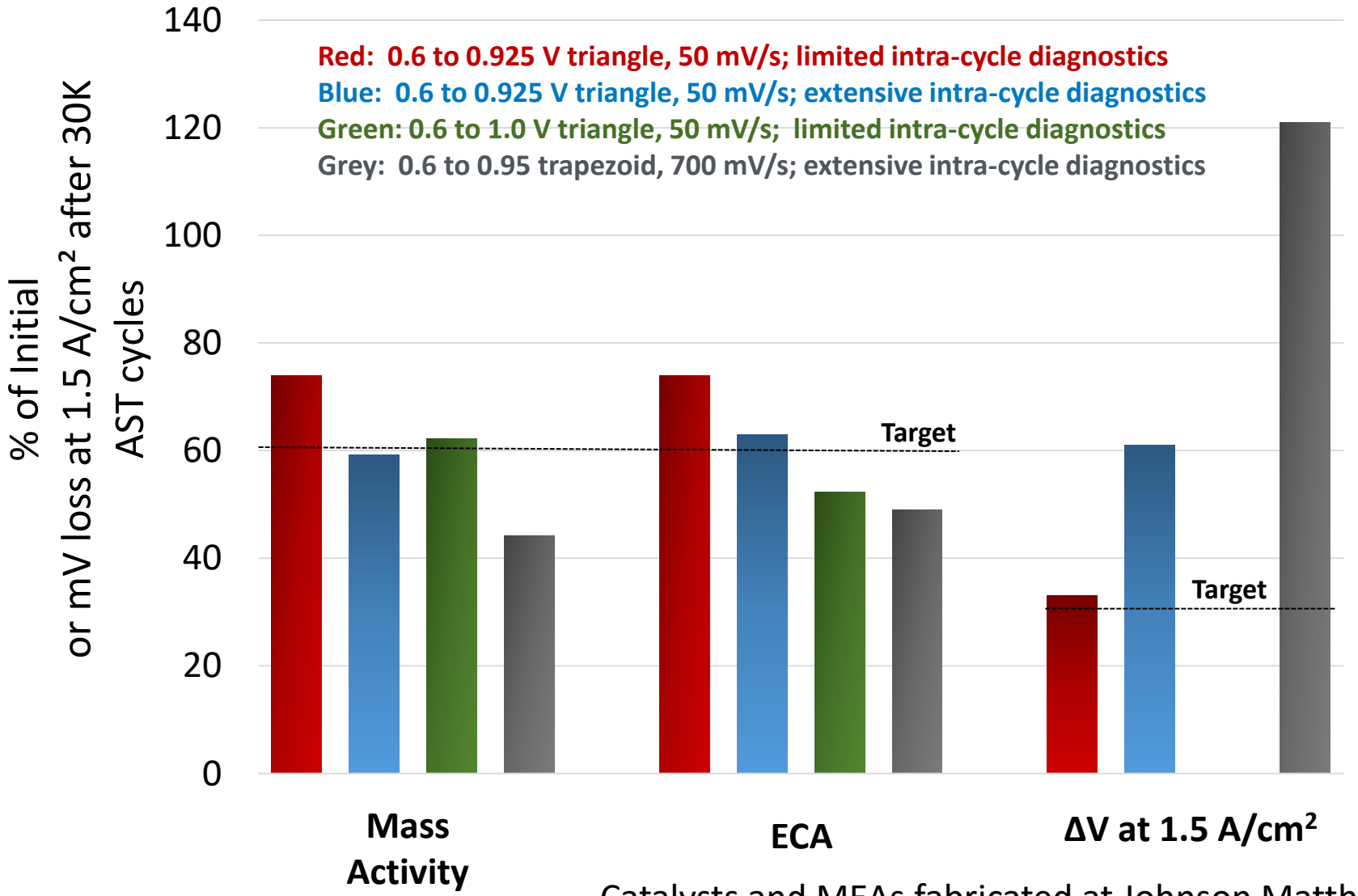
Oxygen Mass Transport in Degraded d-PtNi/C Electrode

As a corollary to the O_2 transport resistance in fresh electrodes, limiting current density in degraded electrode may be correlated with changes in Pt surface roughness (m_{Pt}^2/m^2)

$$S_{Pt} = A_{Pt} L_{Pt}$$



Effect of catalyst accelerated stress tests (AST) and intra-cycle diagnostics on de-alloyed PtNi/C cathode performance loss

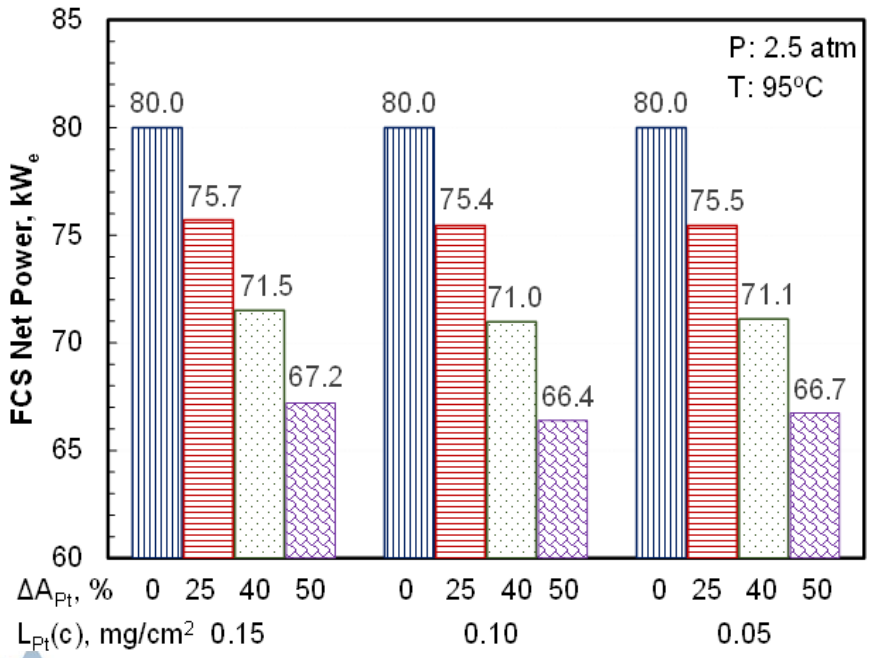


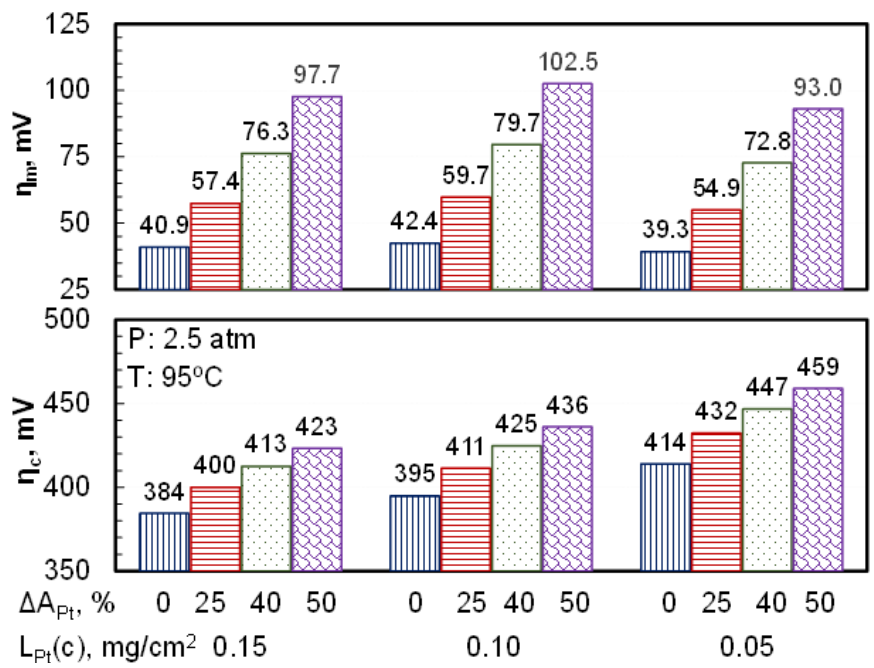
Catalysts and MEAs fabricated at Johnson Matthey; MEAs cycled and tested at UTRC

Projected FCS Performance Degradation

To meet the target of 10% derating in net FCS power over lifetime, the acceptable ECSA loss (ΔA_{Pt}) is limited to <40% for $L_{Pt}(c)$=0.1 mg/cm^2

- Small dependence of acceptable ECSA loss on Pt loading (L_{Pt}) although Pt loading may affect ECSA loss over cyclic potentials and startup/shutdown
- Regardless of Pt loading, increase in kinetic and mass transfer overpotentials contribute equally to voltage loss
- Additional degradation mechanisms involving other components (membrane, catalyst support) and fuel/air impurities to be included in future work





Performance and Durability of Advanced Automotive PEMFC Stacks and Systems with Dispersed Alloy Cathode Catalyst in MEAs Summary and Conclusions

Projected performance of automotive FCS with SOA cathode catalyst and support (high surface-area carbon with tailored PSD), subject to $Q/\Delta T = 1.45$ kW/^{o}C constraint

- Exceeds target of 1000 mW/cm^2 stack power density (PD) with target PGM loading (0.125 g-Pt/cm^2 total)
- Preferred operating conditions at rated power: >2.5 atm stack inlet pressure, higher than 95°C coolant exit temperature, 1.5 cathode stoichiometry
- Projected FCS cost at high volume manufacturing: \$45-50/kW$_e$ at 100K/500K units/year
- Projected FCS Pt content: 0.126 g_{Pt}/kW_e

Projected durability of alloy catalyst in automotive FCS

- Transition metal leaches from the catalyst during operation
- Possible to satisfy the targets of mass activity, ECSA, and voltage losses on accelerated stress tests with limitations on wave form, scan rate and upper potential
- Target of 10% decrease in FCS power at EOL can be met by limiting ECSA loss to 40%

Cell-to-Stack Derating in Power Density

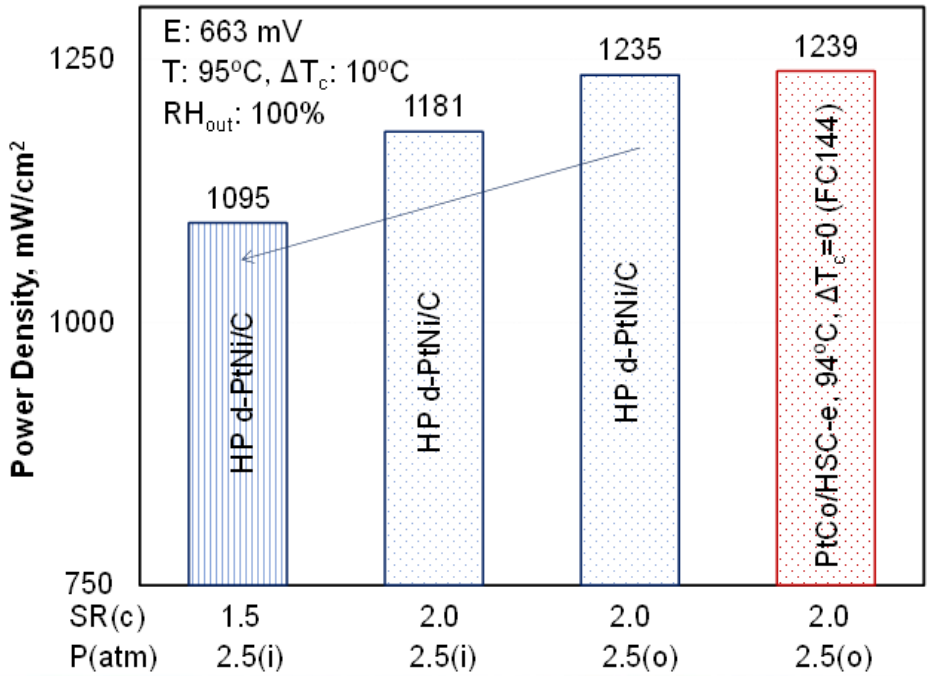
High performance stack with d-PtNi/C cathode catalyst, 10°C rise in coolant T (ΔT_c)

- 0.025(a)/0.1(c) mg/cm^2 Pt loading
- 850 EW, 14-μm (dry) chemically-stabilized, reinforced membrane, ~42 mΩ.cm^2 HFR[(1)]
- 20% higher i_L reflecting thinner GDL, improved high surface-area carbon support (FC144)
- 47 mΩ.cm^2 electrode sheet resistance (δ_c/σ_c) at 100% RH

Sources of Cell-to-Stack Derating in Power Density at Q/ΔT Relevant Conditions

2.5-atm Stack Inlet P, 95°C Stack T[(2)]

- Operating pressure, 2.5 atm inlet (i) vs. 2.5 atm outlet (o): 4.4%
- Air stoichiometry (SR(c)), 1.5 vs. 2.0: 7.3%
- Total derating: 11.3%

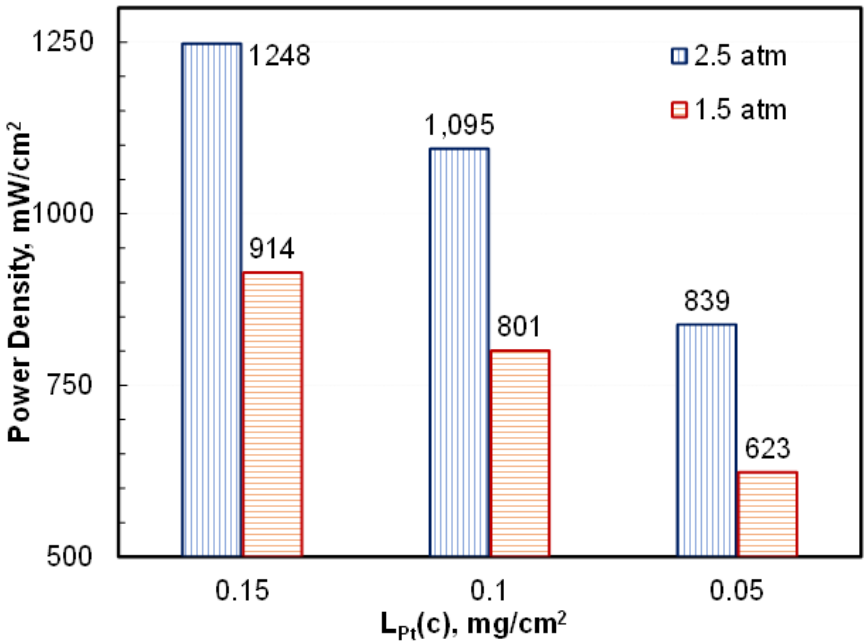


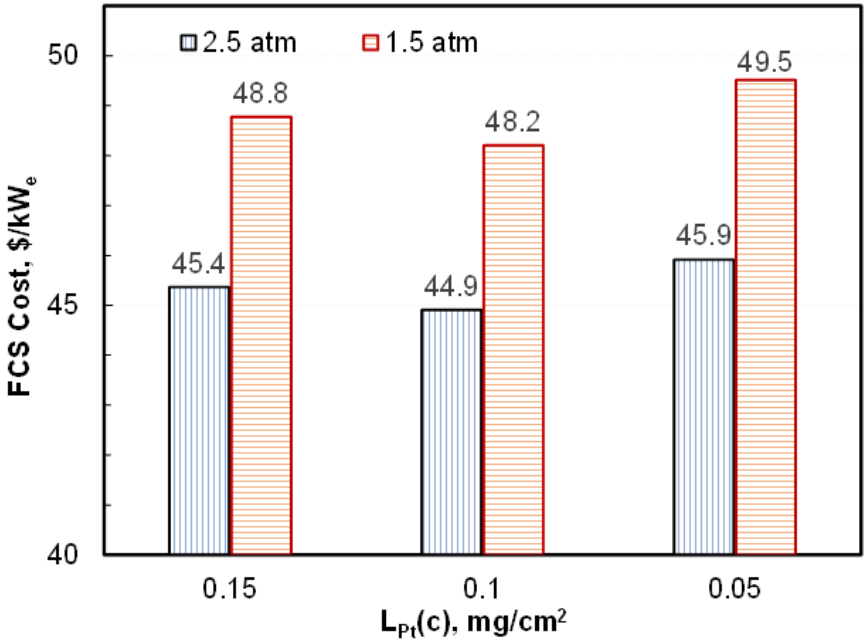
[(1)]High-frequency resistance for 2.5-atm conditions; [(2)]Bipolar plate temperature at coolant exit

Optimum Pt Loading in SOA Cathode Electrode

Small differences in FCS cost may favor >0.10 mg/cm^2 Pt loading in cathode

- 33% higher power density at 0.15 mg/cm^2 Pt loading in cathode partially offsets the increased cost of Pt





***Conditions as in slide 10, Q/ΔT=1.45 kW/°C, 95°C stack T, ΔT_c = 10°C**