R&D on Optimized Cell Performance for Operation on Reformate and Air

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Objective and Targets

- **Objective**: To achieve maximum performance in PEFCs under conditions appropriate for reformate/air operation and with methods that allow cost and efficiency targets to be met for transportation;

- Cathode targets:
  - Highest possible performance at 0.8 V or higher, maintained
- CO tolerance targets include (simultaneously):
  - Minimum air injection for CO clean-up
  - Minimum catalyst loading
  - Minimum losses due to dilution at high fuel utilization

Heightened Efforts in Industrial Outreach Since Lab Review

- **Interactions with external world**
  - Hosted 'training' visit by 3M (2 days); also visited 3M
    - Discussed MEA prep. methods, reformate/air fuel cell state of the art, segmented cell etc.
  - Visited IFC, discussion included implementing RCAs
  - Energy Partners: tested RCA; we're working directly with them to attempt to optimize for their hardware; visited, with team, 2/00
  - Plug Power: discussed similar arrangement to that with Energy Partners
  - Foster-Miller: have begun collaboration on making MEAs; initial tests at 80^{o}C = good news, bad news; pretty good HFR, disappointing performance
  - U/Wisconsin: we've corresponded about some testing later this month
  - Participated in Ford Forum discussion of Fuel Cell Manufacturing Issues
  - Starting to work with SWRI; hosted training visit
  - Collaboration underway with Virginia Tech
- **Fuel cell 'Standard Test Hardware'**

FY00 Accomplishments: Reformate Testing (as of 6/00)

- CO tolerance:

Reduction in Both Precious Metal Loading (to 0.1 mg/cm^2) and in air bleed (none for 100 ppm) since last review (different cells)

  - New reconfigured MEA allows us to tolerate 100 ppm in reformate with only 0.1 mg/cm^2 of catalyst (with air bleed)
  - New catalysts with reconfigured anode:
    - full tolerance to 500 ppm in reformate with <5% air bleed using 0.3 mg/cm^2 anode catalyst; tested for 100 hours.
    - improved transient behavior -->system start-up conditions
  - 50 ppm in reformate, sometimes higher: tolerated **without air bleeding**
  - Combined poisoning/dilution model complete

- System Start-up
  - Tests exploiting improved catalysts to assess effects of severe poisoning
  - Can we eliminate air bleeding entirely? At what cost to the system?

FY00 Accomplishments: Air Electrode Testing (as of 6/00)

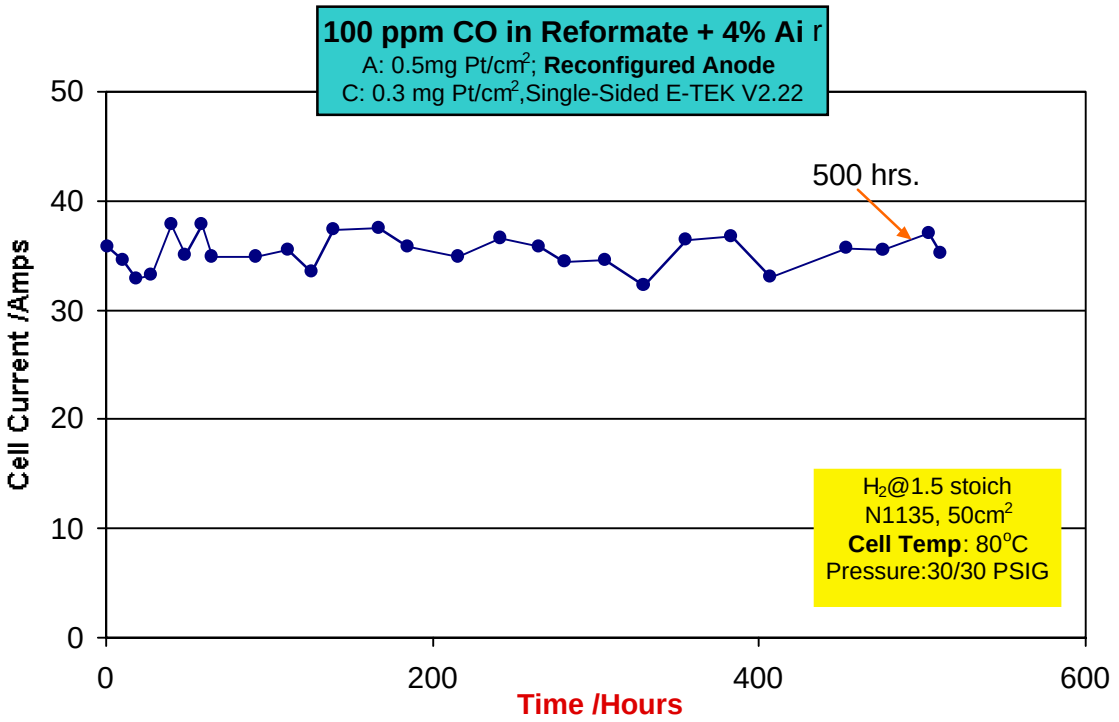
- **Stable operation of cell yielding 0.4 A/cm^2 @ 0.8 V (on H_2) demonstrated**
- Dependence of performance on catalyst loading indicates utilization problem
- Implementing studies of radically different electrode structures
- Studies of a series of alloy catalysts completed
  - Assessed stability of alloy catalysts under operating conditions

Milestones From Last Year

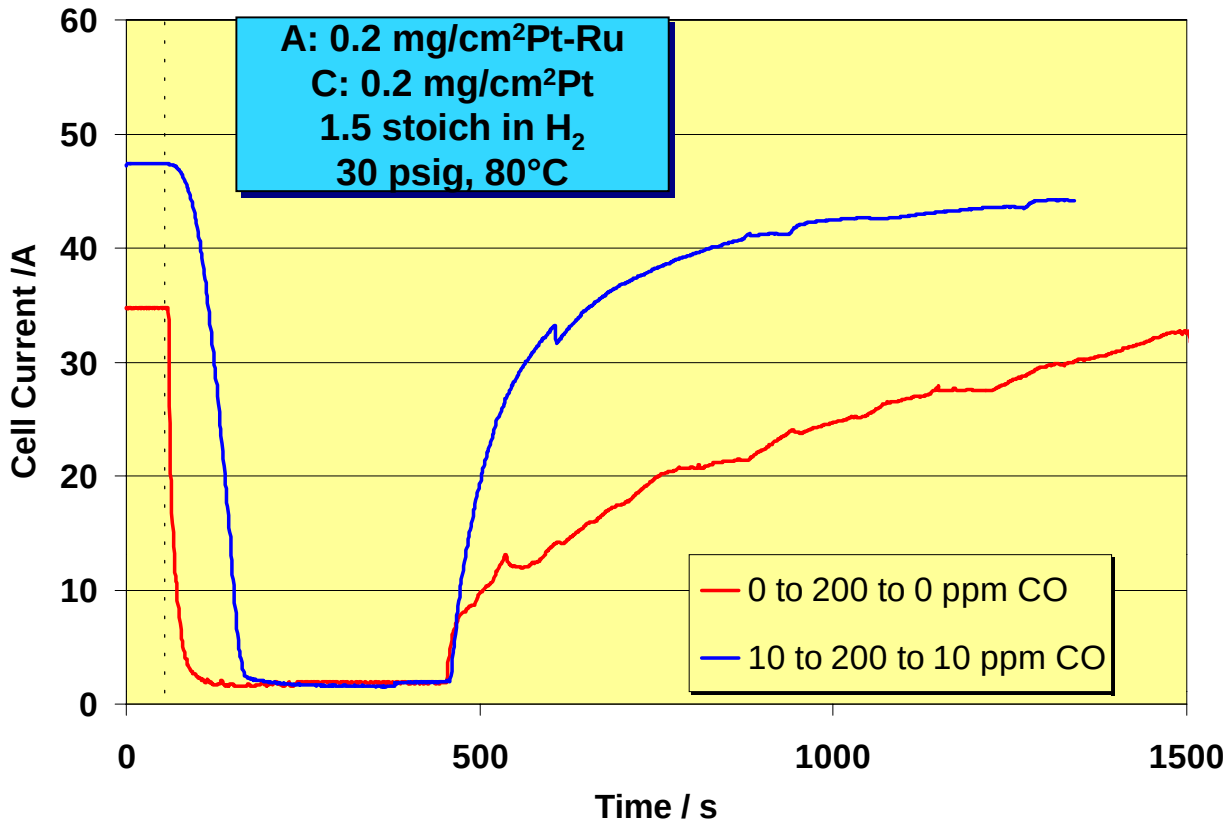
- June ‘99: 500 hour life test of 50 cm^2 cell demonstrating complete tolerance to 100 ppm, with catalyst loading of 0.5 mg Pt/cm^2 at 80^oC.
  - Status: Successfully completed.

- September ‘99:Devise optimized methods for minimizing effects of CO transients on cell performance.
  - Status:Air bleeding during transient shown to dramatically improve recovery time

Long-term Test of CO Tolerance in Reformate Using Air Bleed with Reconfigured Anode

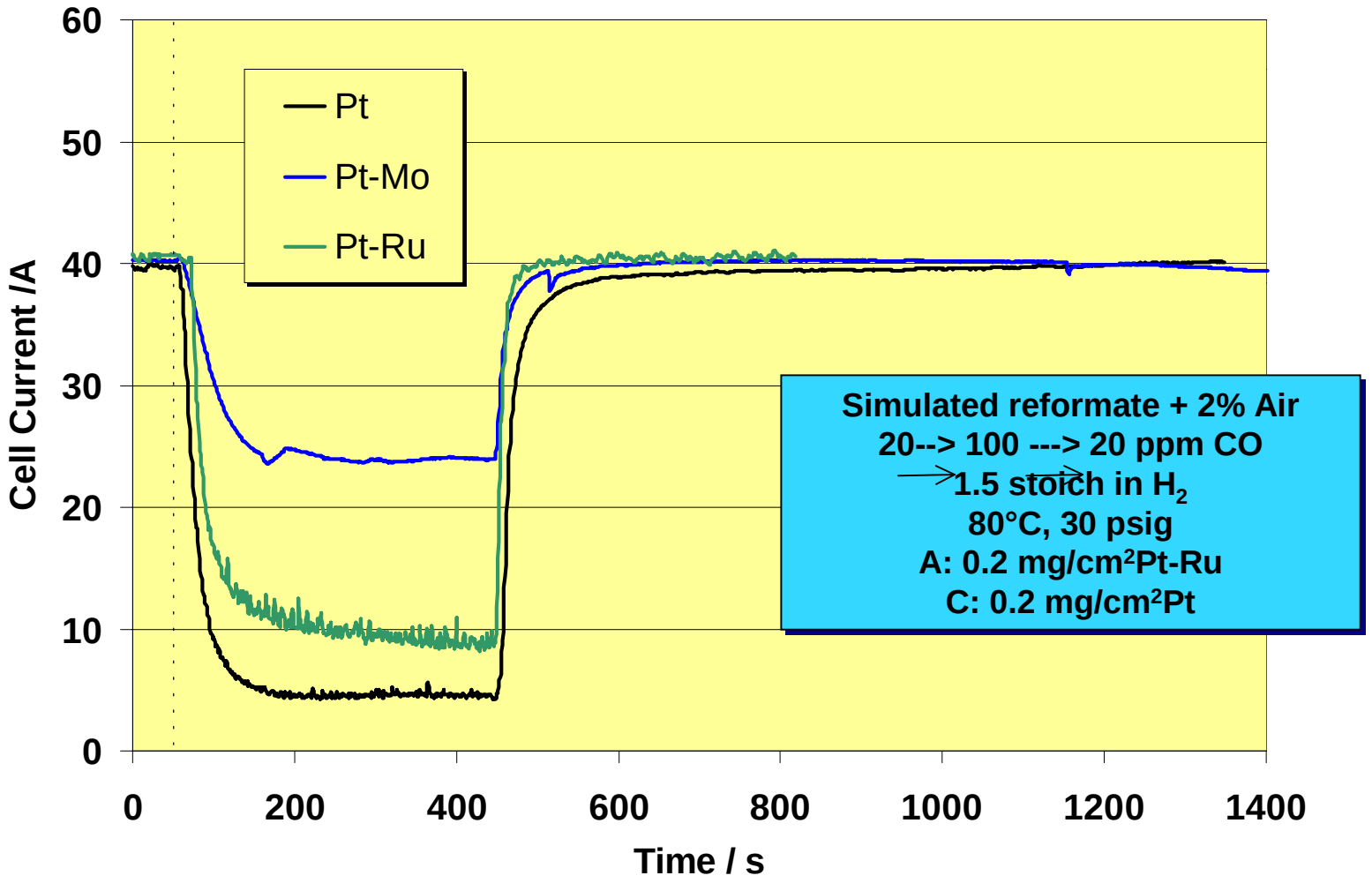


Very Sluggish Recovery on Stepping CO 10→200→10 ppm without air bleed



Conclusion: Alloy catalyst which exhibits reasonable tolerance to 10 ppm CO (without air bleed) experiences extremely long recovery time back to 10 ppm when exposed to 200 ppm CO

Enhanced Rate of Cell Recovery with Air Bleeding



Status of FY00 Milestones

- CO Tolerance
  - **Feb 00** 500 hours life test of 50 cm^2 cell demonstrating tolerance to 100 ppm CO in reformate and minimized performance loss on the hundred hour time scale. **Status: Complete**
  - **July 00** 100 hours stable performance at 500 ppm CO in reformate with advanced PtRu catalyst. **Status: Lifetests complete.**
- Cathode Performance
  - **June 00** With modified cathode, achieve 100 hours of stable cell operation with neat H_2 at 0.8V, 0.4 A/cm^2 at 80°C and 30 psig cathode/anode pressure. Catalyst loading between 0.2-0.4 mg/cm^2 to determine optimum efficiency. **Status: Complete**
  - **Sept 00** With modified cathode, achieve 100 hours of stable cell operation with reformate feed at 0.8V, 0.4 A/cm^2 at 80°C and 30psig cathode/anode pressure. Catalyst loading between 0.2-0.4 mg/cm^2 to determine optimum efficiency. **Status: Even more demanding goal!**

Focus Area 1: Improved Air Electrodes

Need for Improving the Cathode

- Drive for higher efficiency puts a renewed strong stress on improving the cathode performance

  High Efficiency = High Cell Voltage

- Need to operate at high cell voltage puts emphasis on ‘electrode kinetics’ region of polarization curve--> > 0.8 V, essentially all cathode polarization (plus a little IR loss)
- Implications:
  - Oxide coverage of catalyst
  - Relatively low current density-->tendency of cathode to dry out; dry cathode leads to poor kinetics
- Limit to cell voltage with reasonable current density.

Cathode Performance Limitations

- ORR is intrinsically slow reaction on all known catalysts.
- High current operation leads to limitations due to catalyst layer properties
  - Ionic conduction versus layer porosity trade-offs
- Most efficient operation requires pressurization of air stream
- Pressurization penalty dramatic for high flows--need to get down to <2 times stoichiometric flow

Approaches:

-- Increase catalyst loading
-- Improve ORR using Pt alloys
-- Improve ORR with new catalyst layer structures
-- Other ?

Pt Alloys Offer Dramatically Higher Performance @ High Cell Voltages

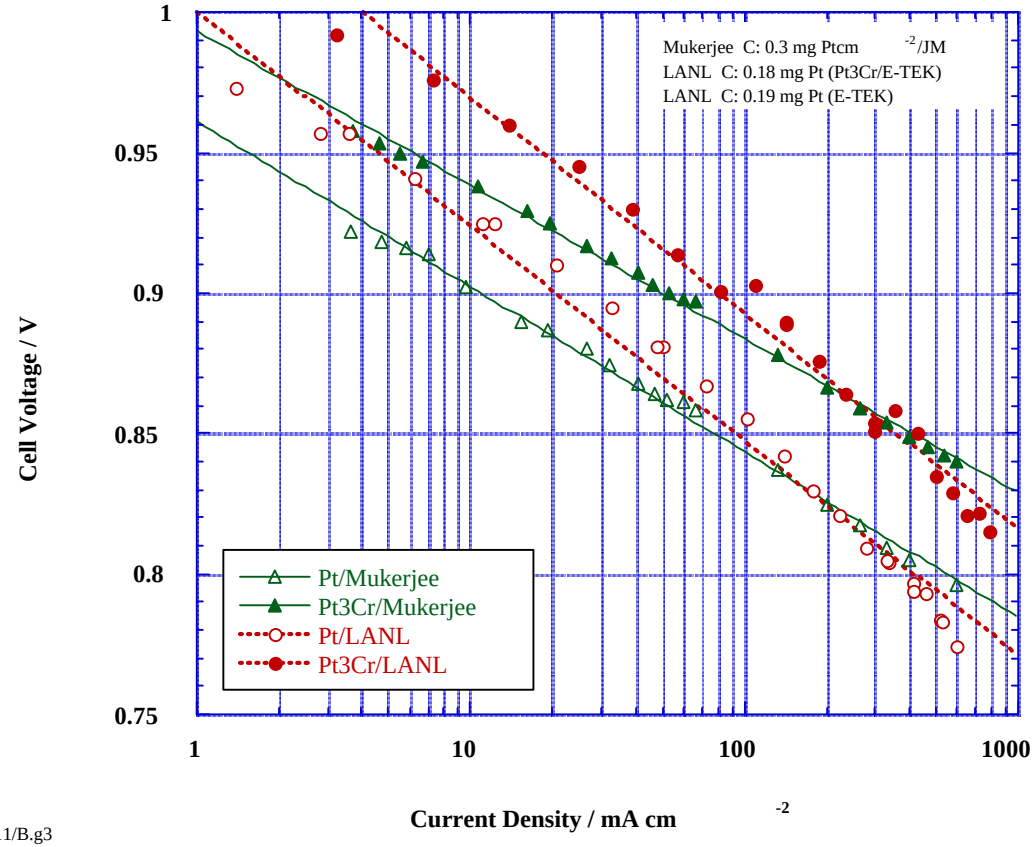
ORR / O_2

Pt and Pt-Cr 3:1

Comparison of IR Corrected Performances of JM and E-TEK Pt/C and Pt-Cr (3:1)/C FC Cathodes with 5 atm. O_2 at 95 C

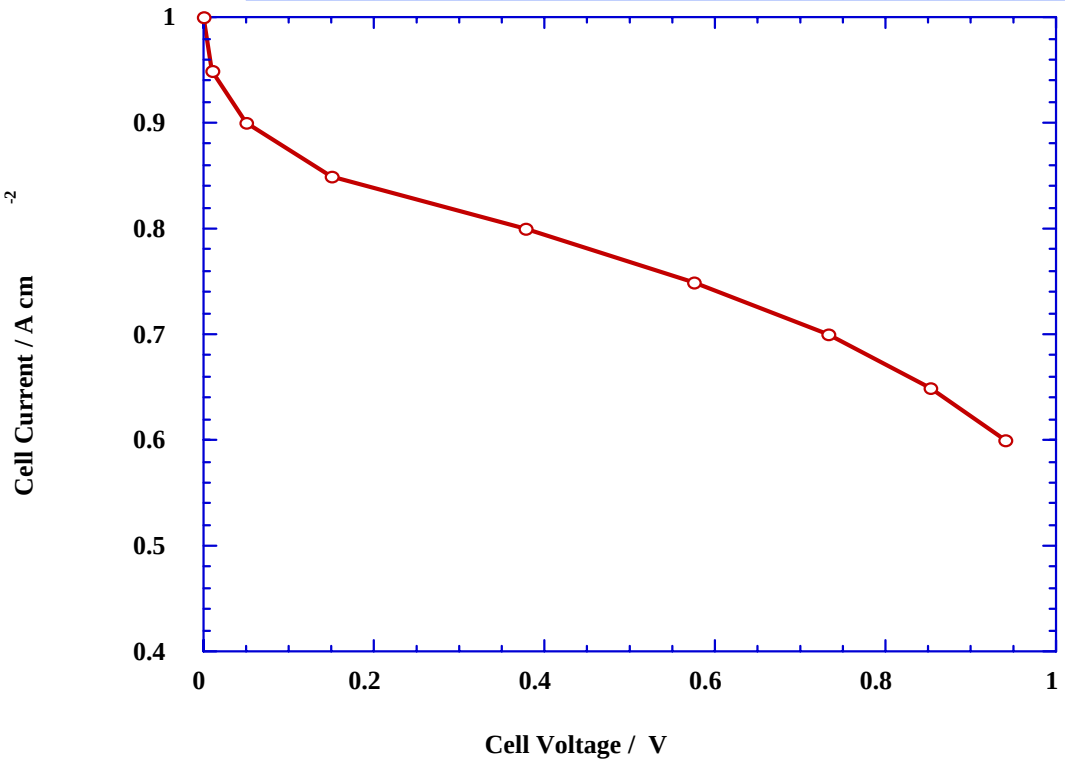
Mukerjee data normalized to 0.2 mg Pt cm^{-2}

T: Cell/H_2/O_2 : 95/105/100 C 50 cm^2



TF511/B.g3

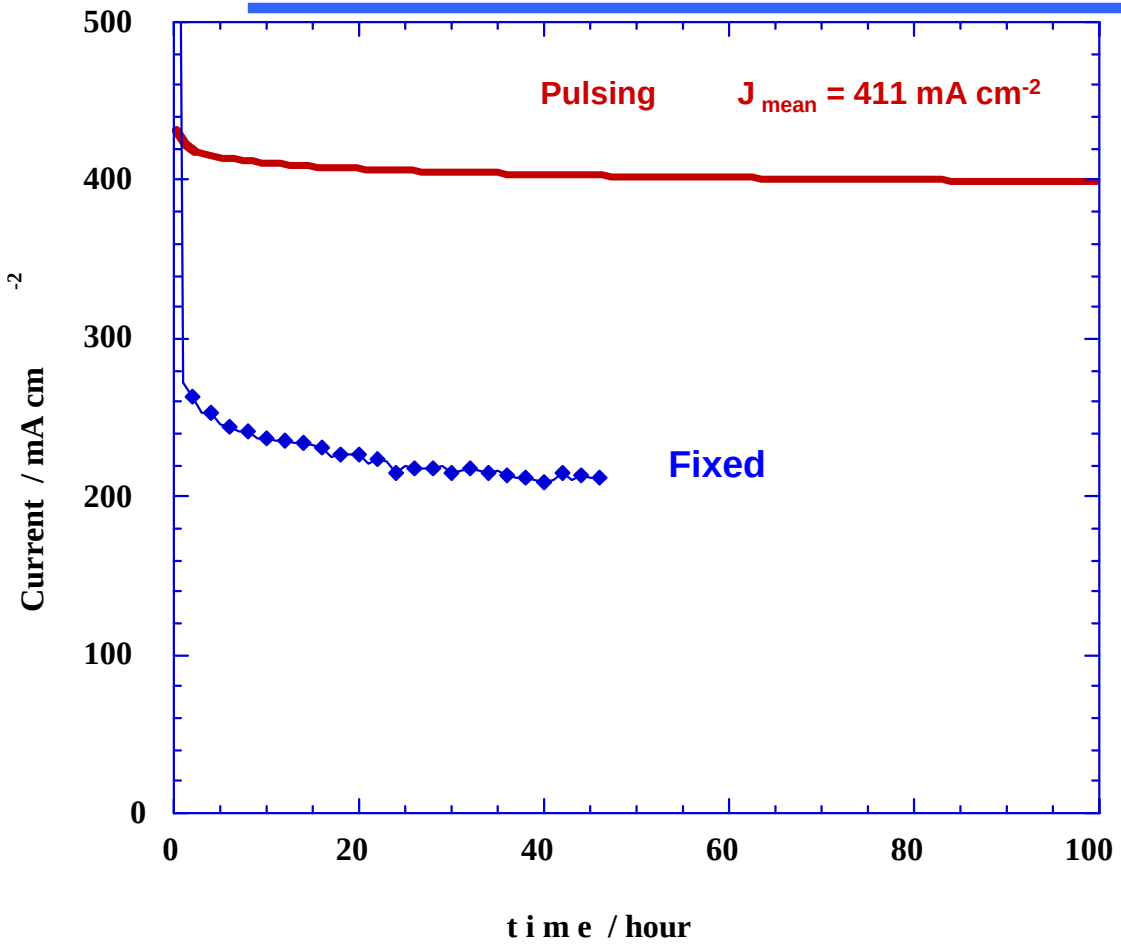
Performance at High Cell Voltages
Improvement with Alloy Catalysts

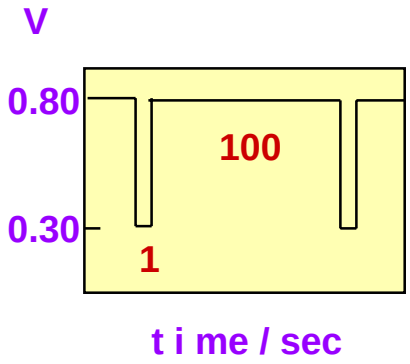


A: 0.21 mg Pt/cm² (54%Pt-Ru/C TKK)
C: 0.43 mg Pt/cm² (20%Pt_3Cr/C E-TEK)

50 cm^2; N112 ; H_2Air: 30/30 psig
HFR: 0.099 ohm cm^2 ;T= 80 °C
H_2: 1.5 stoich ; Air: 2100 sccm

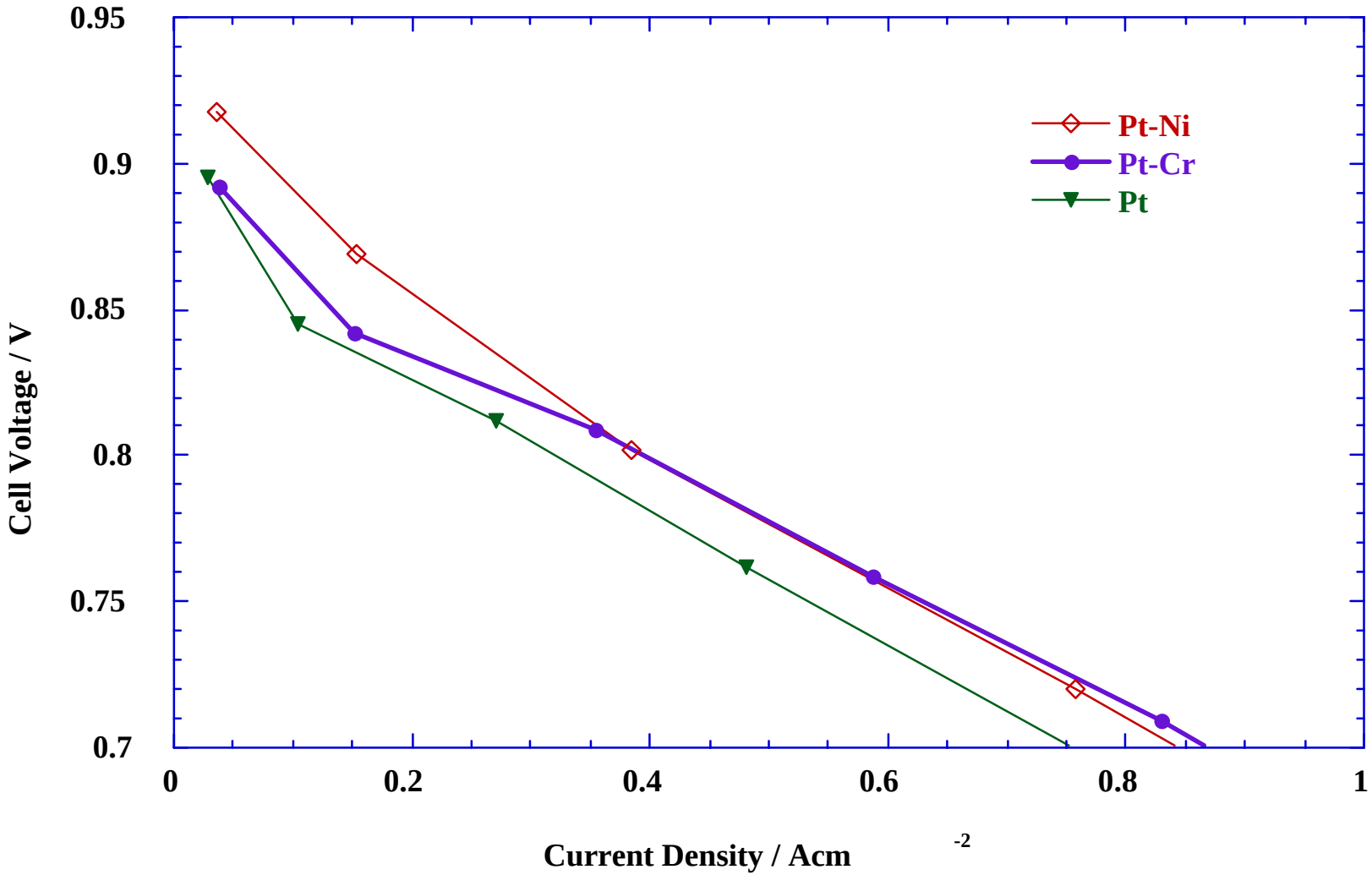
Performance at High Cell Voltage
100 hrs operation at 0.80 V / 80 °C





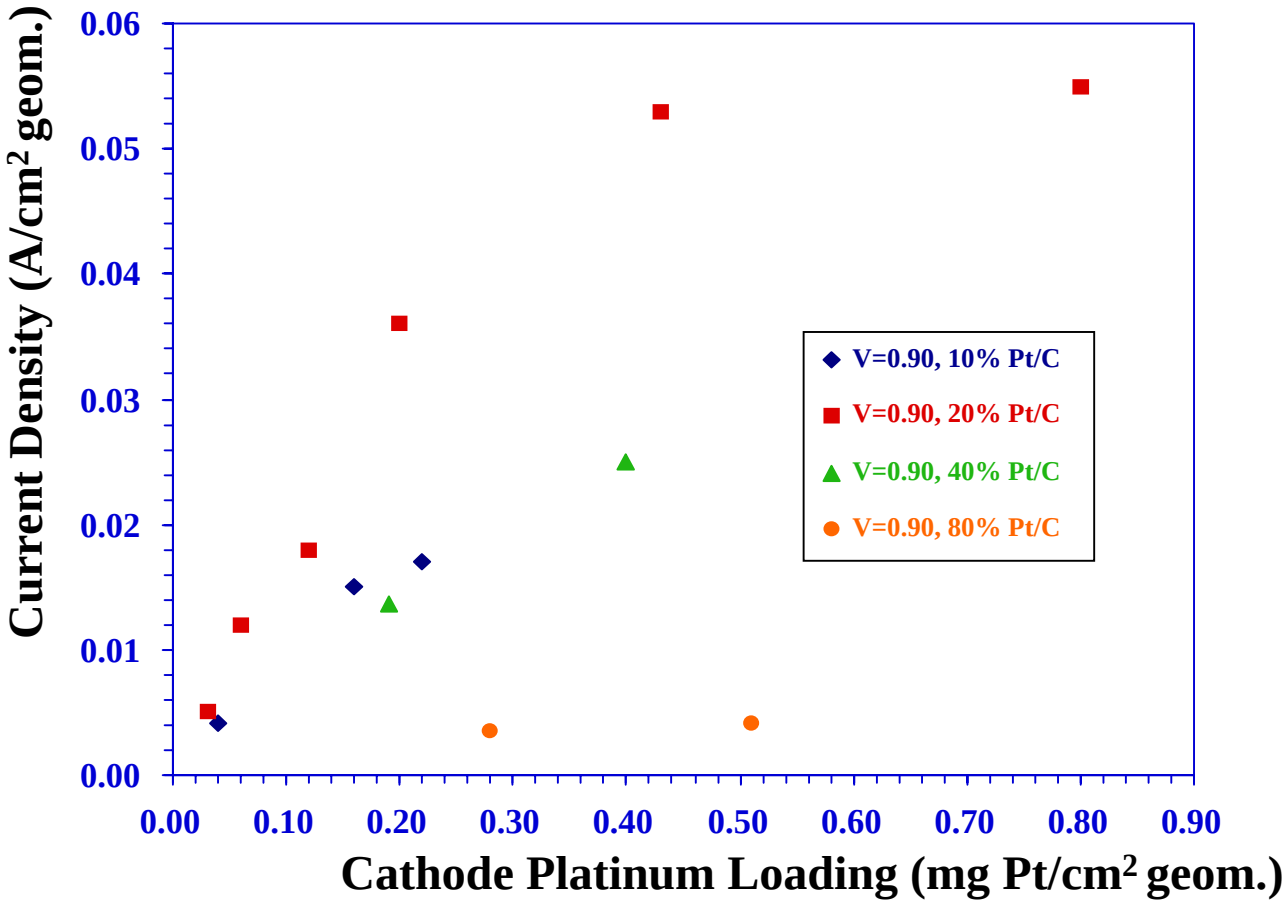
A: 0.17 mg Pt/cm² (54%Pt-Ru/C TKK)
C: 0.43 mg Pt/cm² (20%Pt_3Cr/C DmC²)
(N-112 / 50 cm²)

Performance of Cathode Catalysts



Performance at 0.9 V as a function of cathode Pt loading

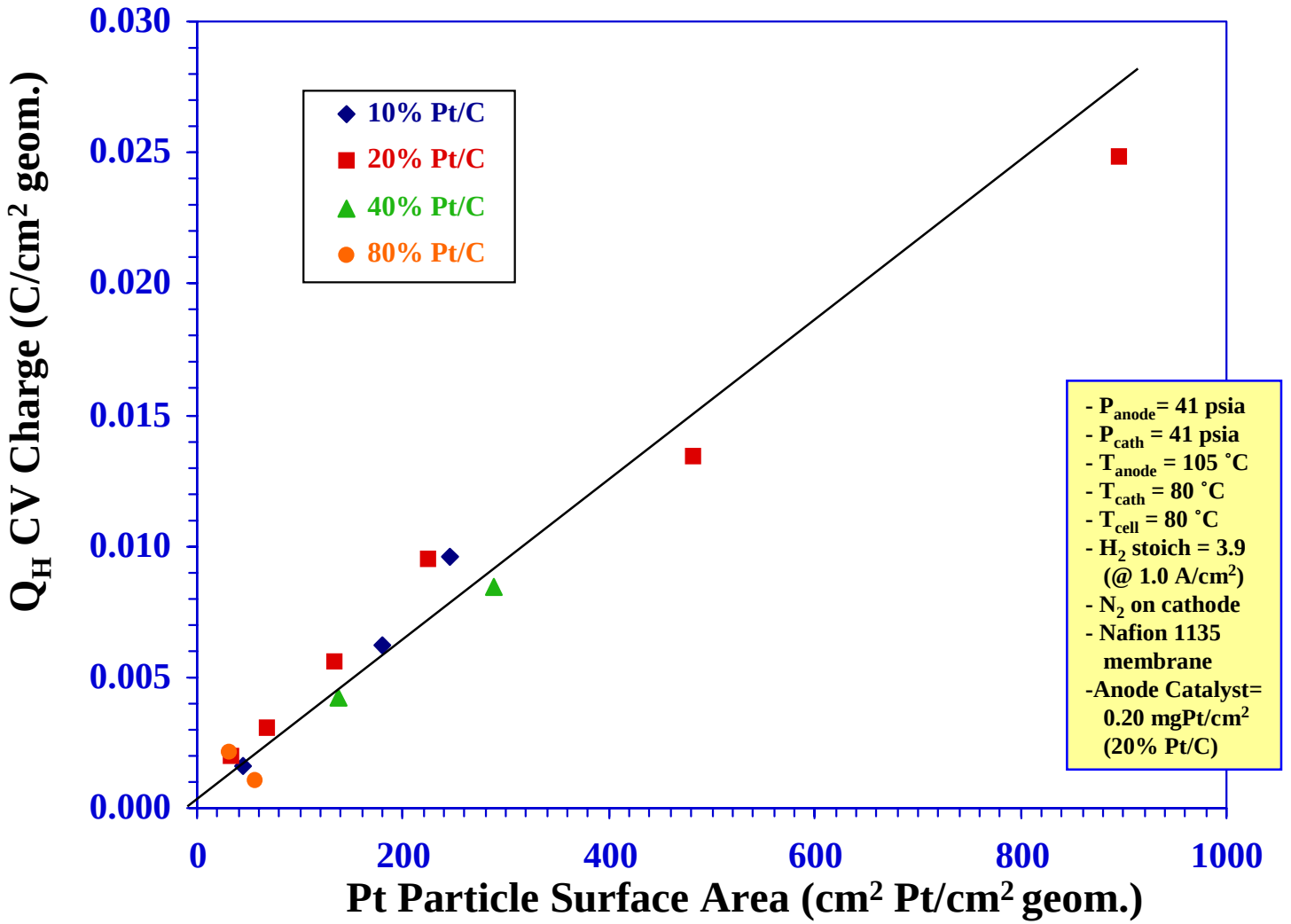
- P_{anode} = 41 psia
- P_{cath} = 41 psia
- T_{anode} = 105 ˚C
- T_{cath} = 80 ˚C
- T_{cell} = 80 ˚C
- H_2 stoich = 3.9 (@ 1.0 A/cm^2)
- O_2 stoich = 6.2 (@ 1.0 A/cm^2)
- Nafion 1135 membrane
- Anode Catalyst= 0.20 mgPt/cm^2 (20% Pt/C)



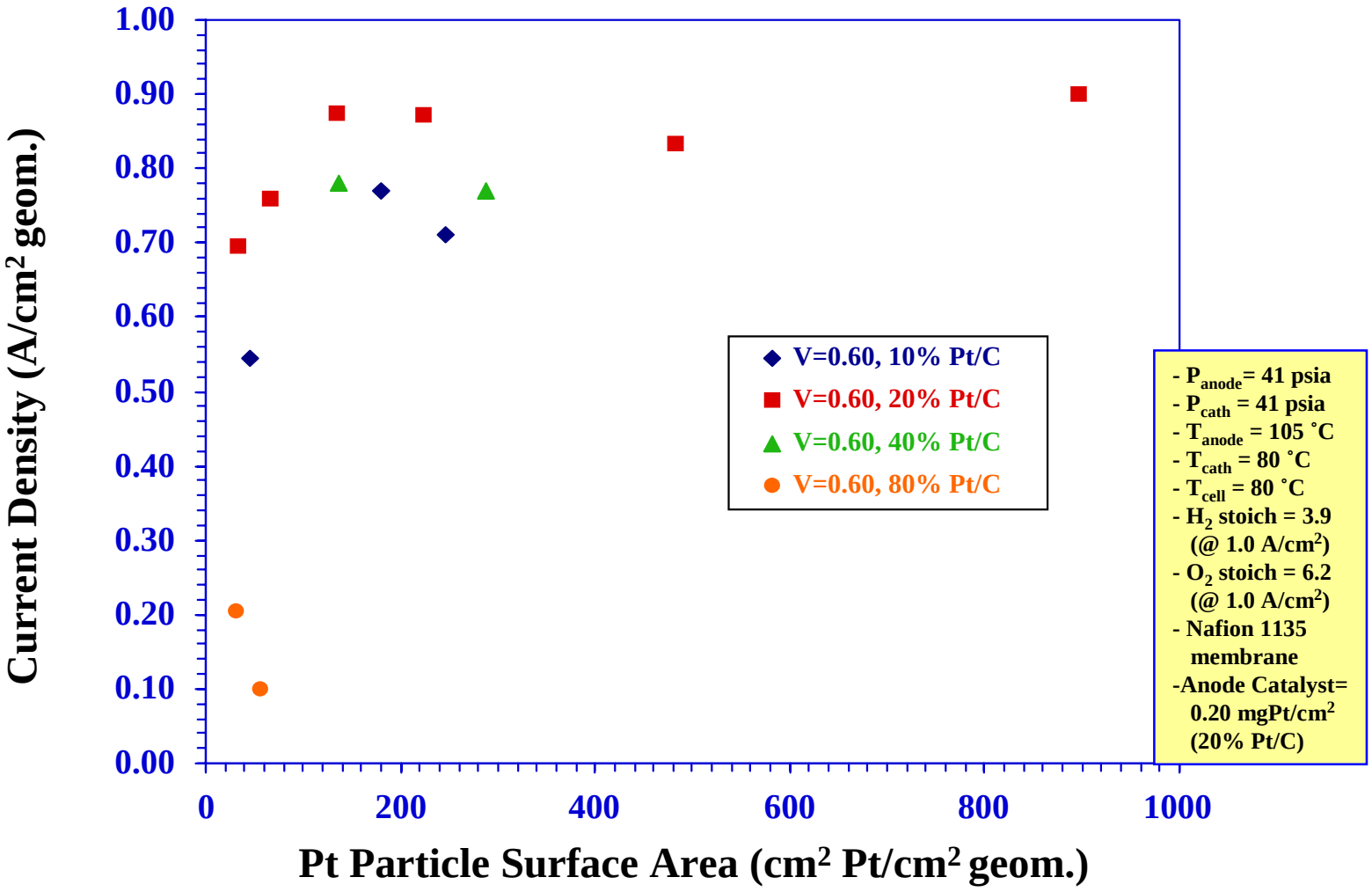
Performance at High Voltage vs Cathode Pt loading: Contributing Factors to Observed Behavior

- Intrinsic Activity of Catalyst --function of particle size (see K. Kinoshita)
- Surface Area of Catalyst
- Utilization of Catalyst--function of catalyst layer thickness, determined by proton conduction, O_2 permeability within catalyst layer
- We need to separate these effects
  - Normalize by surface area
  - 'dilute' catalyst of given type with carbon--maintains intrinsic activity while probing utilization

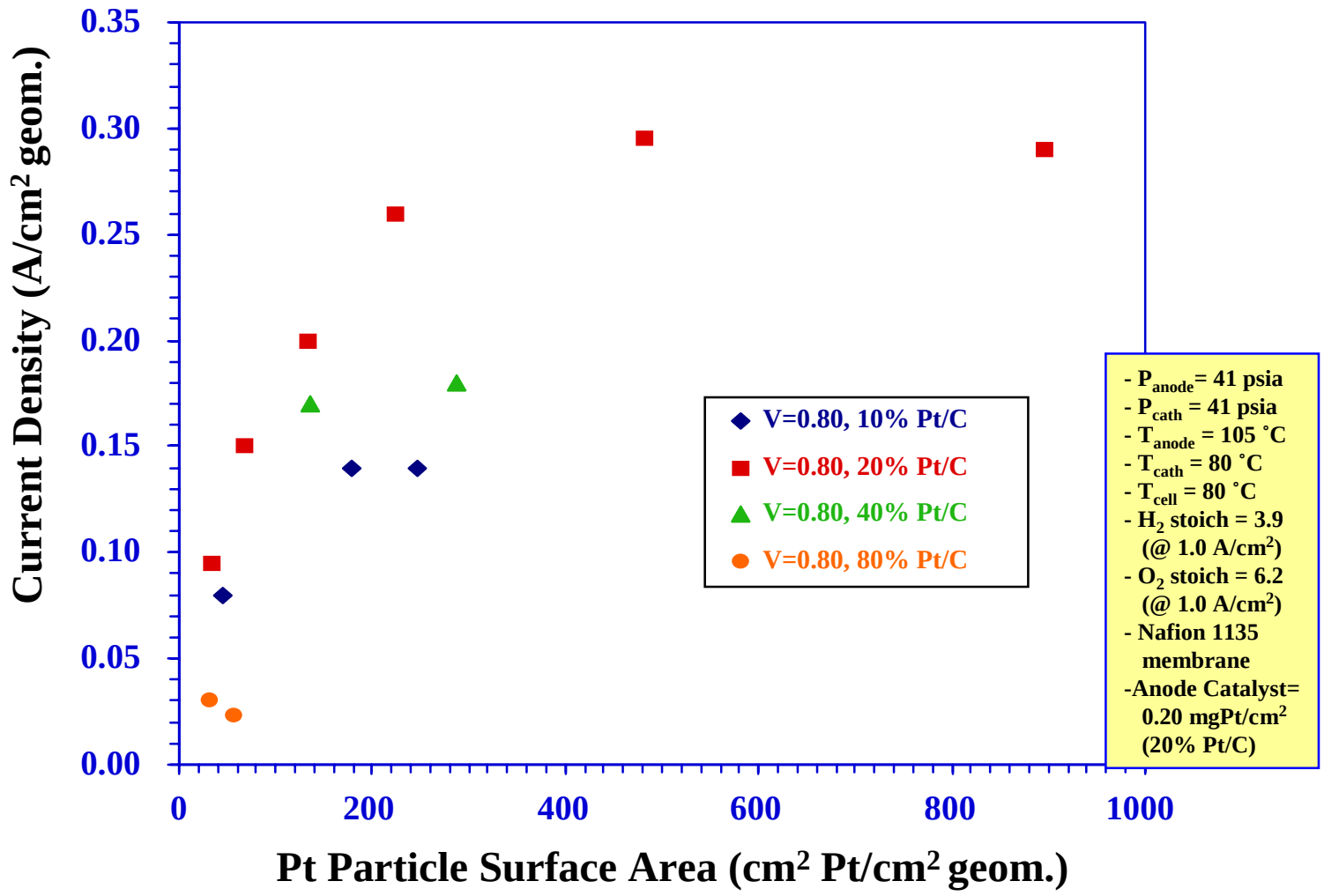
H-desorption charge from CV
Normalized by Pt particle surface area



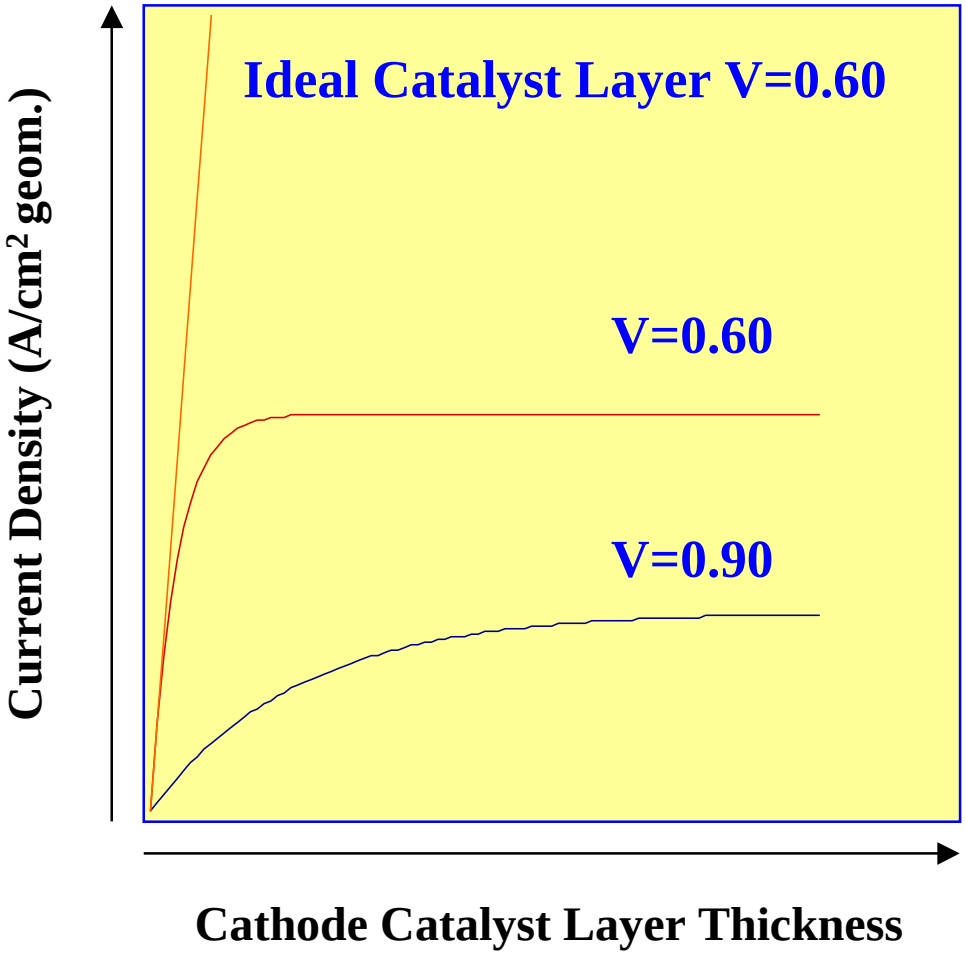
Performance at 0.6 V vs. Pt particle surface area



Performance at 0.8 V vs. Pt particle surface area



Current density profiles in cathode catalyst layer



Loss in utilization with increasing thickness occurs because of increased ionic IR loss within the catalyst layer and/or limited oxygen permeation rate.

Loss is most sharp for lower cell voltages (I.e. higher current density)

Performance vs. Cathode Pt loading: Summary of Observed Behavior

- Surface Area of Catalyst:
  - Normalized out for H-desorption but not for ORR; clear indication of significant mass transport losses above threshold loading even for high operating voltage.

- Intrinsic Activity of Catalyst:
  - 20% Pt/C apparently more active than 40%--20% has higher current density for a given loading even though 40% yields **thinner** catalyst layer.

- Utilization of Catalyst:
  - Given this catalyst layer preparation method, **there appears to be a limit to how much catalyst is actually accessed; our current estimate is that this is less than 40%**

Prospects for Improvement of Cathode Performance

- Catalyst layer far from optimized:
  - How wet does it need to be?
  - What is nature of polymer/catalyst interaction?
  - We're applying 'ink' crudely to the membrane surface--How can we fabricate more controlled structures?
- Very good alloys may be available
- Thin film catalyst layer structures changed the game: most pre-1991 work on ORR basically irrelevant
- Little gain achieved from increasing temperature, in spite of expectation
- Hydrogen cross-over effects may be non-negligible

Focus Area 2: Improved CO tolerance under Start-up Conditions

Issues for Start-up with Reformed Fuels

- Cell might see very high CO levels as balance of system comes to steady state

Approach

- Need to investigate transient behavior under severe poisoning conditions
  - Maximum tolerance needed
  - Recovery: does it require air bleeding?

CO Tolerance in Reformate-based Fuel Cells: Approaches Used to Date

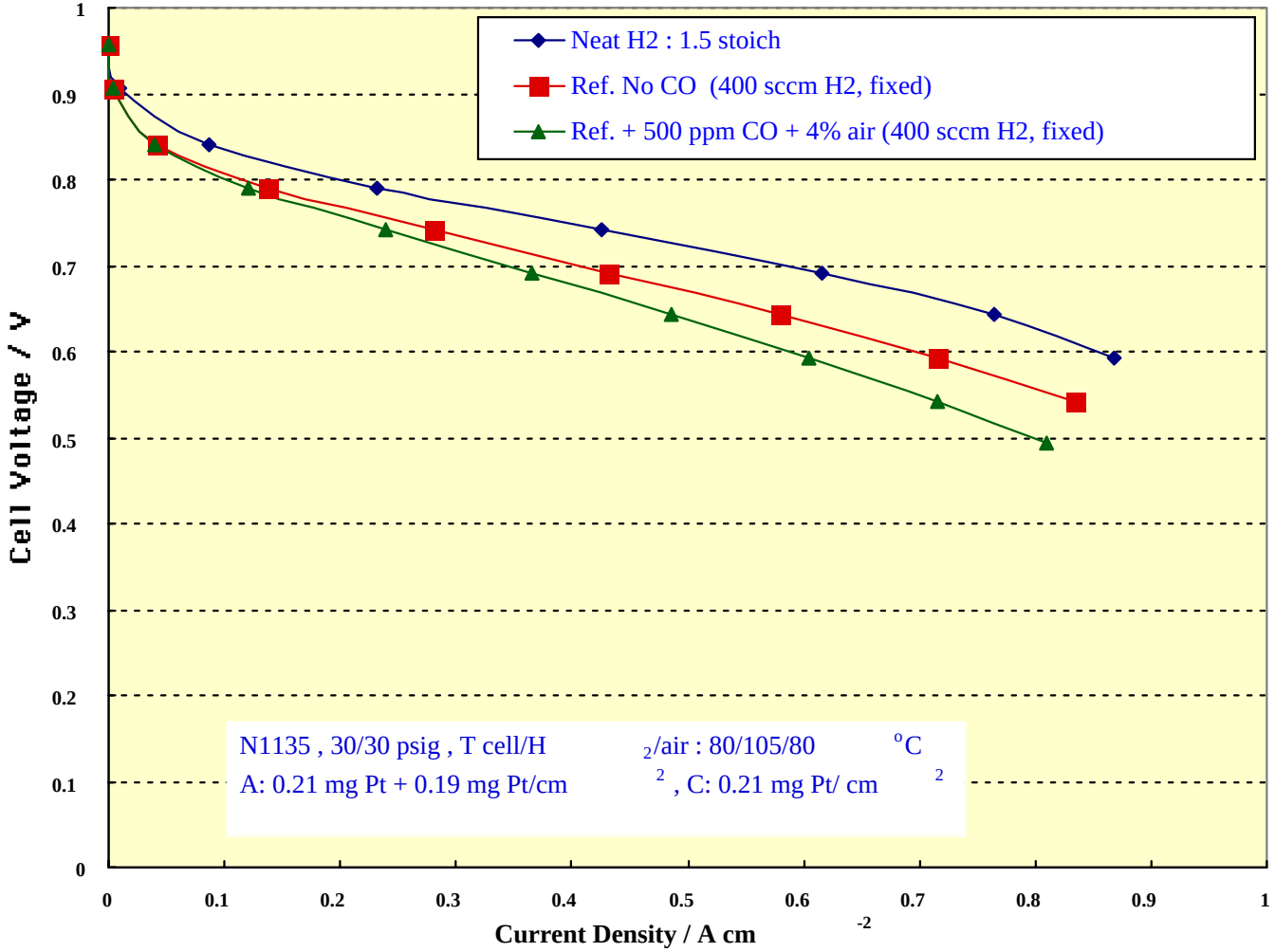
- Alloy electrocatalysts
- Air Bleeding
- Elevated Temperature

CO Tolerance: Air Bleed Impact

- System impact (ANL) of air injection
  - fuel efficiency penalty typically on the order of 2% for 5% air bleeding
  - system complexity?

- Stack operation on reformate with 100 ppm CO without any air bleed
  - typically entails dramatic performance penalty
  - however, latest improved alloy catalysts can offer full tolerance to 100 ppm CO; lifetime of such catalysts has not been fully tested

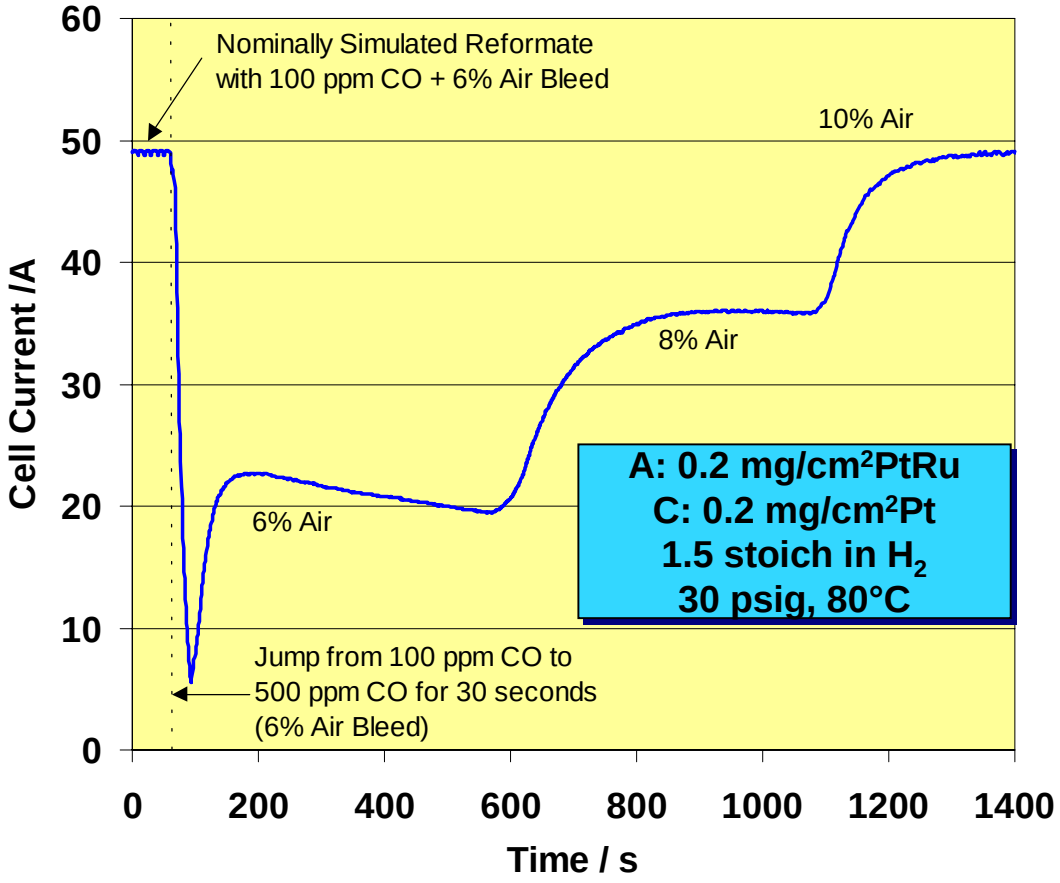
New Catalyst with Reconfigured Anode: Allows Tolerance to 500 ppm CO in Reformate



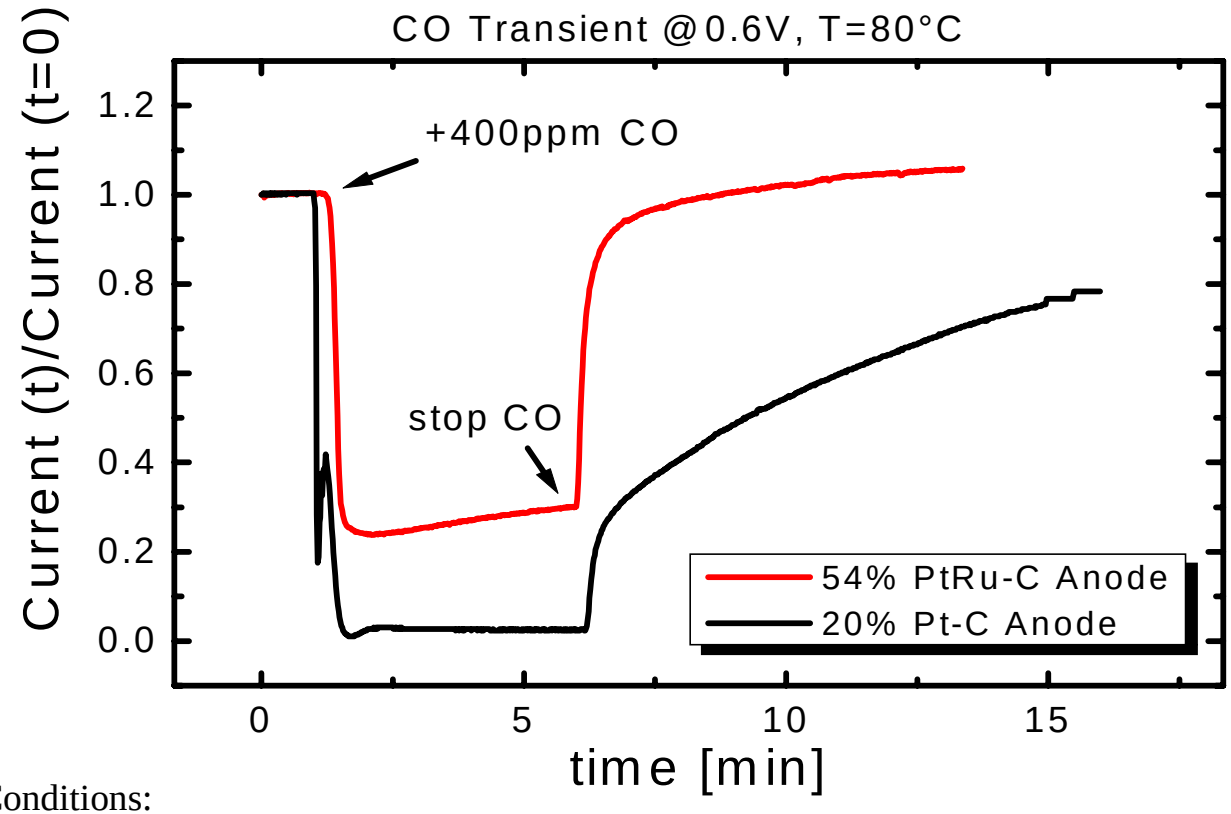
Performance Transients with Varying CO Levels: 100 ppm--->500 ppm--->100 ppm CO

- Full cell performance of 1 A cm^{-2} for inlet flow with 100 ppm CO, maintained by 6% air bleed
- CO level next spiked to 500 ppm for 30 seconds, and then returned to 100 ppm
- 6% air no longer sufficient to maintain original performance; 10% air bleed now needed

  Perhaps very few sites remain available for oxygen on exposure to 100 ppm CO



Improved Response to CO Transients with New Catalyst

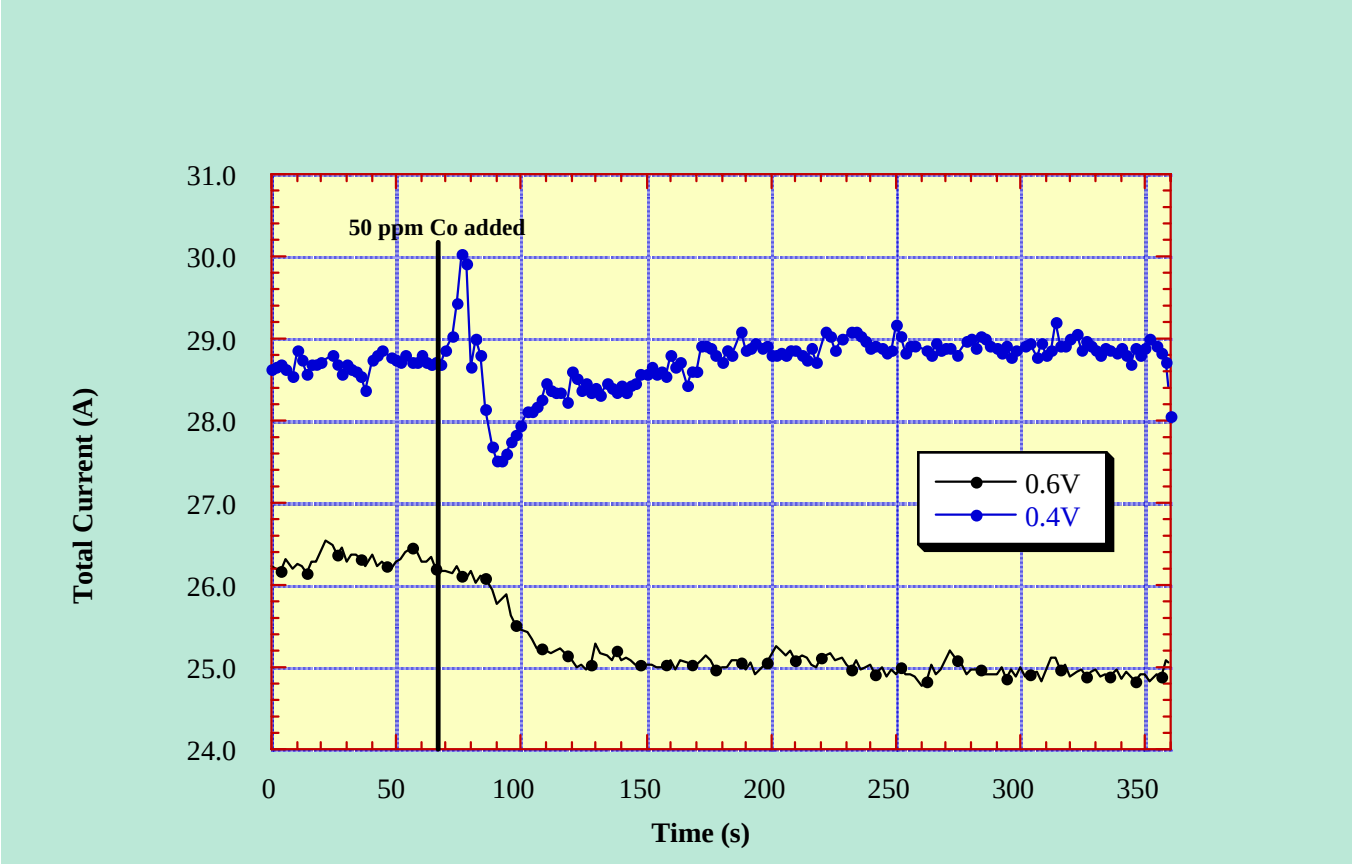


- Test Conditions:
- PtRu cell: N1135, Anode: 0.23mg/cm2 Pt (54% PtRu), Cathode: 0.23mg Pt (20% Etek), 400sccm H2, Transients @ 0.6V 80/105/80 30/30,Backings: A: DS, C: SS
- Ptcell, N1135; A: 0.18mg/cm2 Pt, C: 0.16mg/cm2 Pt (20% Etek) 80/105/90 30/30 Transients @0.6V flows equal to PtRu cell, Backing: A and C DS:

Possible Modes of Operation during Start-up

- use air bleed only to smooth out transient CO spikes during start-up or power transients
- eliminate air bleed during start-up by operating at lower cell voltage

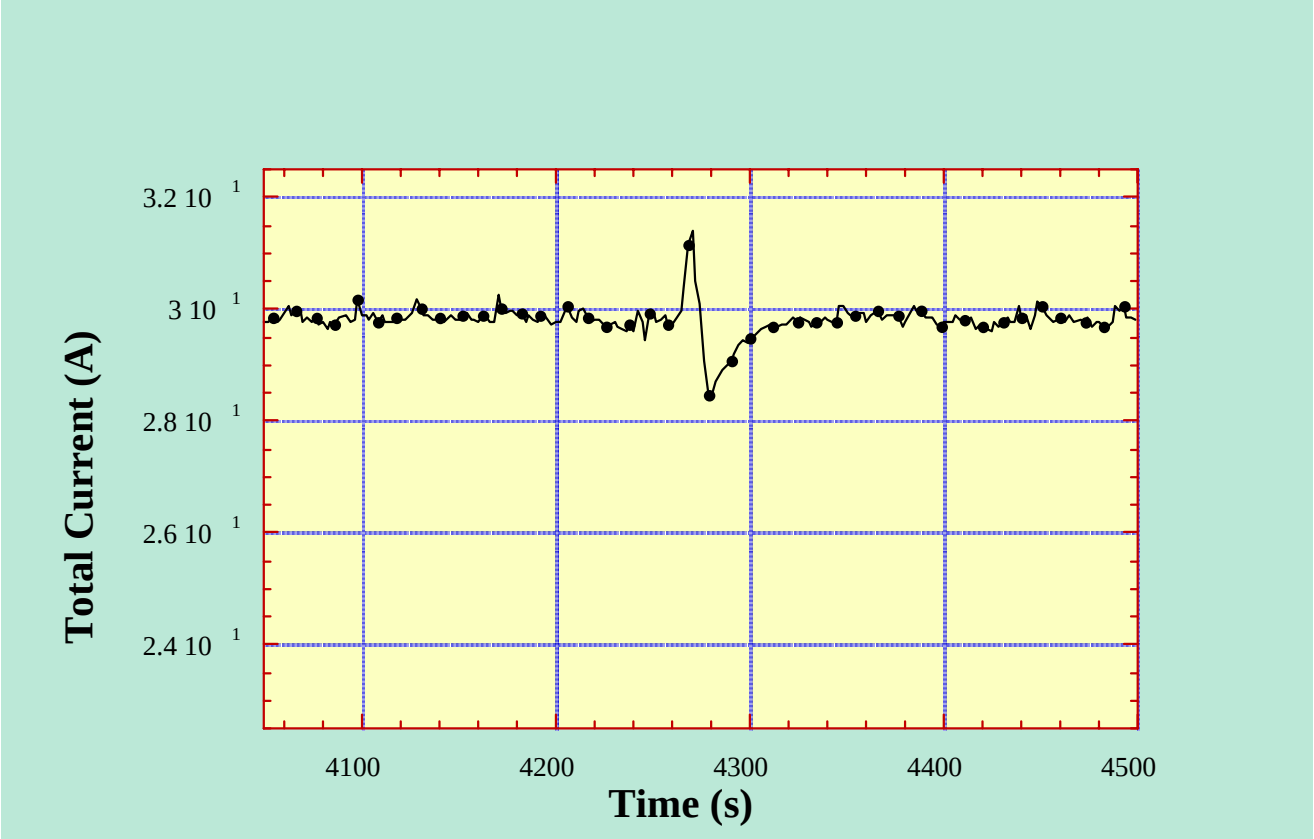
Effect of 50 ppm CO Pulse For Two Different Cell Voltages



Test Conditions:

PtRu cell: N1135, Anode: 0.22mg/cm2 Pt (54% PtRu), Cathode: 0.26mg PtCr (20% Etek),, Transients @ 0.6V 80/105/80 30/30,Backings: A: SS, C: DS ETEK; H2@1.3 stoich for 1 A/cm2,

Effect of 100 ppm CO Pulse
Cell Voltage held @ 0.4V



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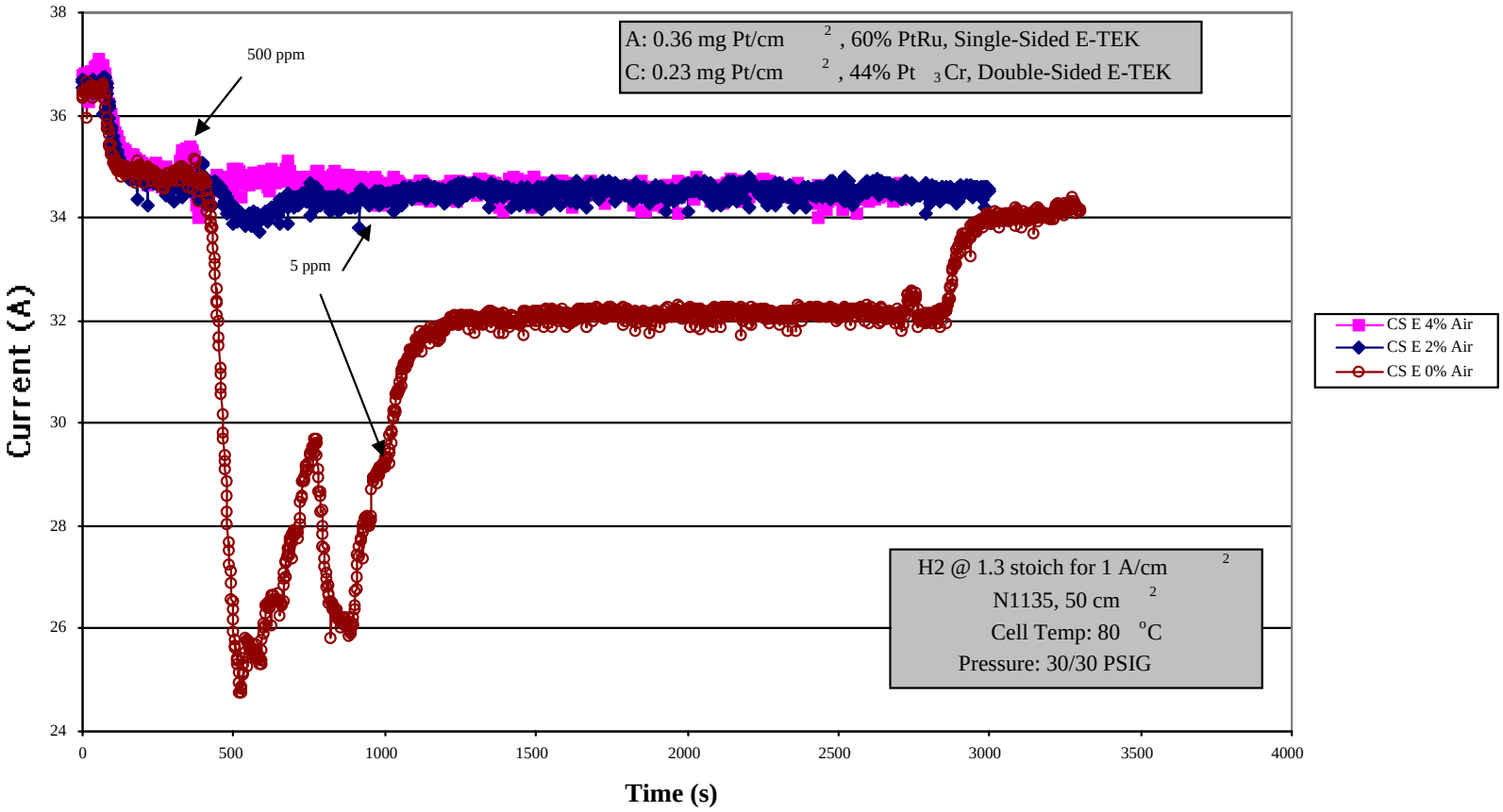
Simulated Start-up: Effect of Air Bleeding



CO stepped from 500 ppm to 50 ppm @ 75 ppm/min;
then from 50 ppm to 5 ppm @ 15 ppm/min

Prospects for Improvements for Reformate Operation

- Strong Need for Two Parallel Paths:
- 1. Continued improvement of alloys/reconfigured anode (RCA) /air bleeding level for ordinary T operation
  - Cause for optimism: some RCA structures show very efficient use of air bleeding--our present RCA is not optimized; we continue to work on additional *selective* catalysts for chemical CO oxidation; incorporation into anode shows promising results.
- 2. High T membranes
  - Cause for optimism: excellent CO tolerance obtained at 120^{o}C and even better in the 150 to 180^{o}C range (w. doped PBI) ; decent, but not completely adequate, lifetime obtained even with Nafion
  - Need for enhanced effort in this area.

Summary and Highlights

- Demonstrated 100+ hour stability for operating at 0.4 A/cm^2 @ 0.8V

- Lowered air bleeding level for to 0.5% or lower for full tolerance to 100 ppm
- Demonstrated significant tolerance to 500 ppm CO in reformate
- Completed modeling of combined CO and dilution effects

- Substantial work continues to document transient and ‘down-the-channel’ effects using new segmented cell approaches

- Many substantial industrial interactions

Future Plans

Cathode work:overall goal of increasing achievable current density at 0.8 V

- Improved cathode catalysts
- Vary catalyst layer and backing compositions to improve hydration
- Experiment with elevated temperature operation/alternate hydration methods
- Guidance from cathode modeling
- Catalyst layer with controlled nanostructures

Anode work:overall goal of minimizing effects of dilution and CO

- Improved anode catalysts, reconfigured anodes and effectiveness of air injection for ever higher CO tolerance
- Improved catalyst layer composition to further minimize dilution effects, increase fuel utilization
- Improved start-up
- Further clarification of long term effects of higher levels of CO
- **Implement new activity related to high temperature membranes**

Future Plans II

Practical studies of Critical Impact

- MEA durability issues: accelerated lifetest protocols, 'brute force'testing, materials evolution modeling
- Break-in effects
- New MEA fabrication approaches

Diagnostics

- Complete segmented cell development; make design/specs available to companies; implement additional probes for local temperature etc.
- Increased attention to diagnosing long-term performance limitations.

Industrial Interactions

- Extensive, direct interaction with industrial partners to implement best strategies in stacks
- Continued MEA development with outside parties
- Implement Web site to allow rapid updating of DOE partners on current work, receive 'instant feedback'on our stuff

Appendix

Subtasks: Improved Air Electrode

- **Subtask 1.1 Alloy Electrocatalysts.**
- **Subtask 1.2. Air Electrode Catalyst Layer Optimization**
- **Subtask 1.3. Modified Air Cathode Water Management Schemes for operation near 0.8V.**
- **Subtask 1.4 Backing layer and Flow Field Optimization.**

Subtasks: Reformate Tolerance

- **Subtask 2.1. Further lowering of anode catalyst loading for tolerance of 100 ppm CO tolerance in reformate with minimized air bleed.**
- **Subtask 2.2 Segmented cell tests to investigate distribution of CO poisoning effects to optimize anodes with non-uniform catalyst distributions.**
- **Subtask 2.3 Study Cold Start**
- **Subtask 2.4. High Utilization**
- **Subtask 2.5. Further investigate PtRu catalyst that enables tolerance to 500 ppm CO in reformate, with 4% air bleed, in short term tests.**
- **Subtask 2.6. Tests on supplier membranes; high temperature operation**
- **Subtask 2.7. Novel CO removal method (Allied-Signal)**