What performance would non-Pt cathode catalysts need to achieve to be practical for transportation?

or

The Importance of A/cm^3

Frederick T. Wagner, Hubert A. Gasteiger and Susan Yan
General Motors Fuel Cell Activities
Honeoye Falls, NY

DOE Workshop on Non-Platinum Electrocatalysts
21-22 March, 2003
New Orleans, LA

Automotive stack performance / cost requirements

- Stack power density: ~1kW / liter
- Stack specific power: ~1 kW / kg
  - DOE 2010 targets (includes ancillaries): 0.55kW/L, 0.55kW/kg

But cost, and not just Pt cost, is the strongest driver toward small stacks (high current densities)

- DOE cost targets (FY2001 Progress Rpt., Table 4a)
  - electrodes <$5/kW ==> $\leq 0.2\ g_{Pt}$/ kW
    - 1E7 vehicles/yr doubles present Pt production
      - doable with 3-4 yr advance notice

      C. Jaffray and G. Hards, in Handbook of Fuel Cells, V. 3, W. Vielstich, A. Lamm, and H.A. Gasteiger, eds., Wiley,2003, in press.
  - membrane: ≤$5/kW, bipolar plate ≤$10/kW

Does/can Pt meet automotive requirements (including cost)?

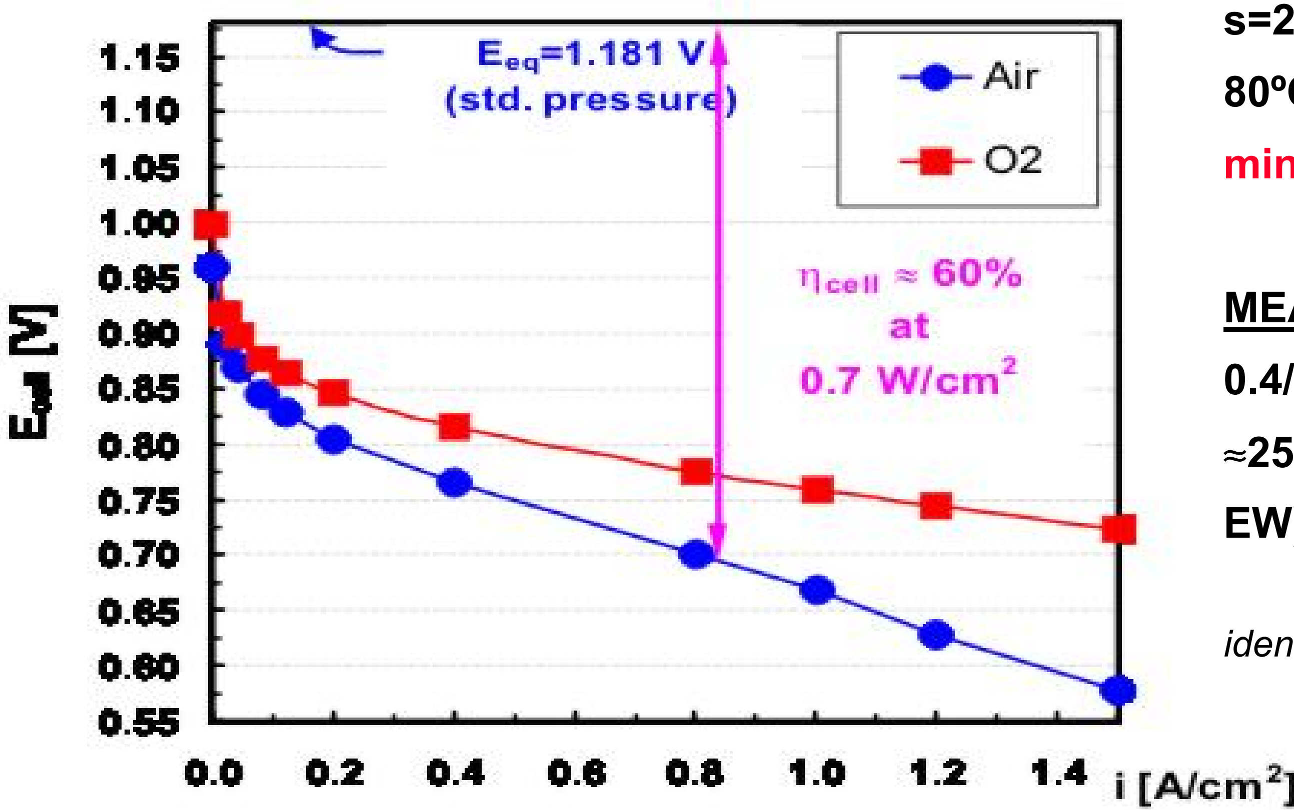
A primer on current state-of-the art Pt activities and on losses in electrodes

- Conclusions

H.A. Gasteiger and M.F. Mathias, Proceedings of the Proton Conducting Membrane Fuel Cells III Symposium, The Electrochemical Society, 2003, in press.

- $\leq$0.2g Pt / kW can be achieved if we can
  - accept getting rated power at 600-650 mV (1.5A/cm^2 on air)
  - decrease present mass transport voltage losses by ~50%
  - achieve 2x increase in catalyst activity/unit Pt
    - demonstrate durability of Pt alloy catalysts known to be more active than Pt alone

Performance of State-of-the-Art MEAs



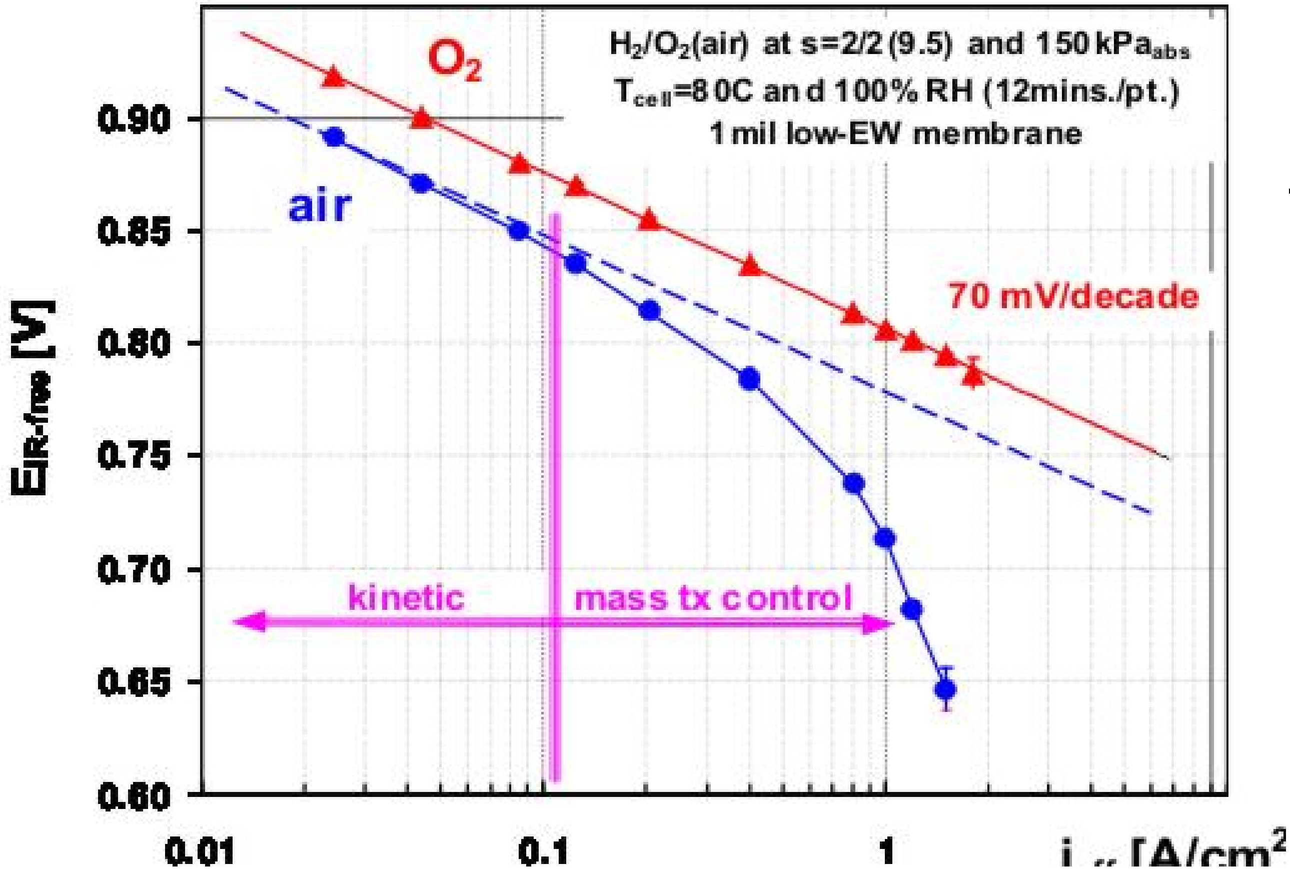
Conditions: H_2/air(O_2) at s=2/2(9.5) at 150 kPa and 80ºC (100/100%RH, 15 mins./pt.)

MEA: 50cm² active-area 0.4/0.4 mg_{Pt}/cm^2 (50%Pt/C) ≈25μm membrane (<1000 EW)

ance would be identical with 0.05mg/cm² Pt on

↳ **significant E_{cell} (i.e., η) losses at required power densities**
→ origin of E_{cell}-losses?

Voltage Losses in State-of-the-Art MEAs - 1



iR-correction:
on-line high-frequency resistance measuremts.

H electrosorption area: $45 m^2/g$ Pt

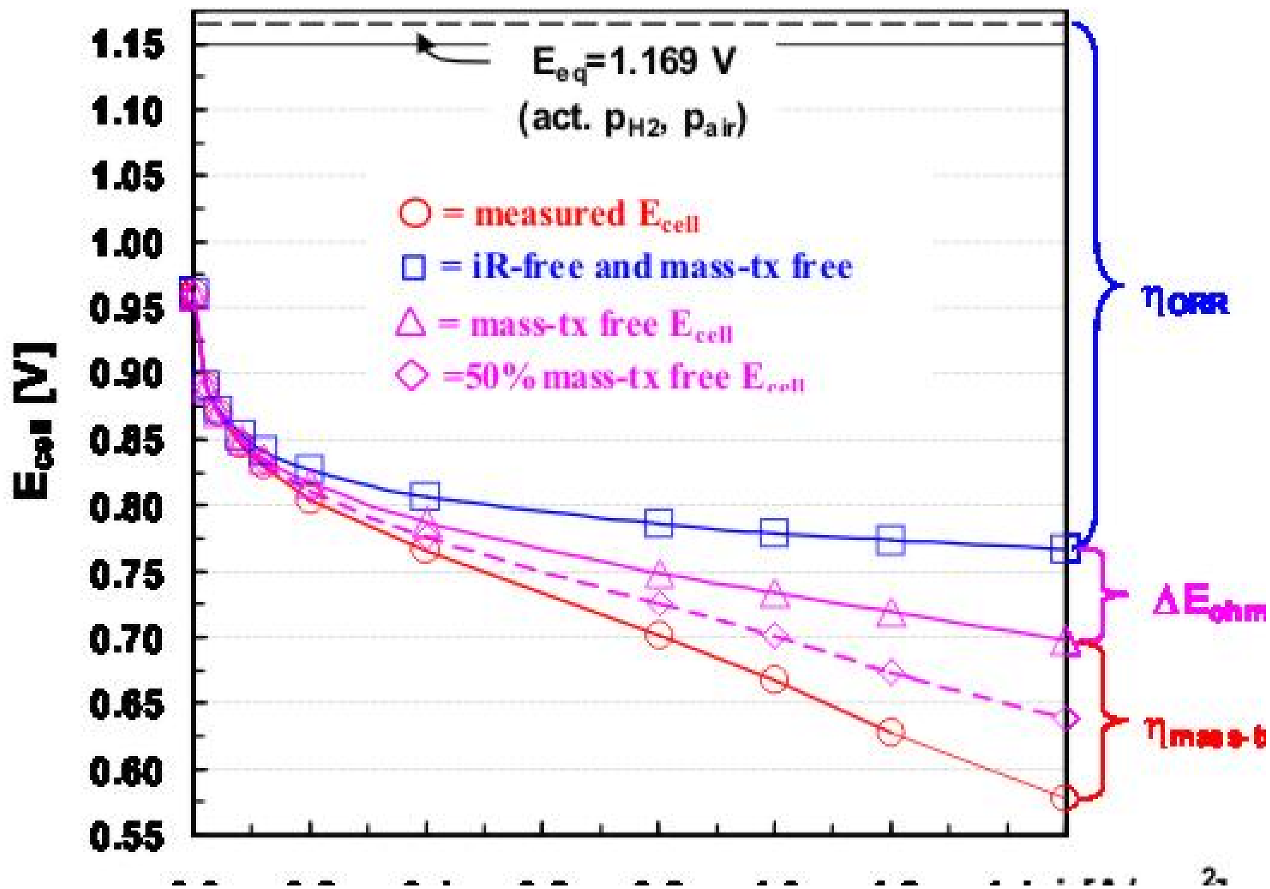
Catalyst Pt area: $60 m^2/g$

Pt utilization = 45/60 = 75%

- O_2: ≈100% kinetic losses with pure O_2 ($i_0 = 1.7 \times 10^{-8}$ A/cm$^2_{Pt}$) *)
- air: kinetically controlled only at <0.1 A/cm^2

*) H.A. Gasteiger, W. Gu, R. Makharia, M.F. Mathias, and B. Sompalli, in: *Handbook of Fuel Cells: Fundamentals, Technology, and Applications, Vol. 3*, W. Vielstich, A. Lamm, and H.A. Gasteiger, Editors, Wiley, (to be published Spring 2003).

Voltage Losses in State-of-the-Art MEAs - 2



E_{loss} at 1A/cm^2:

390 mV (78%)

50 mV (10%)

60 mV (12%)

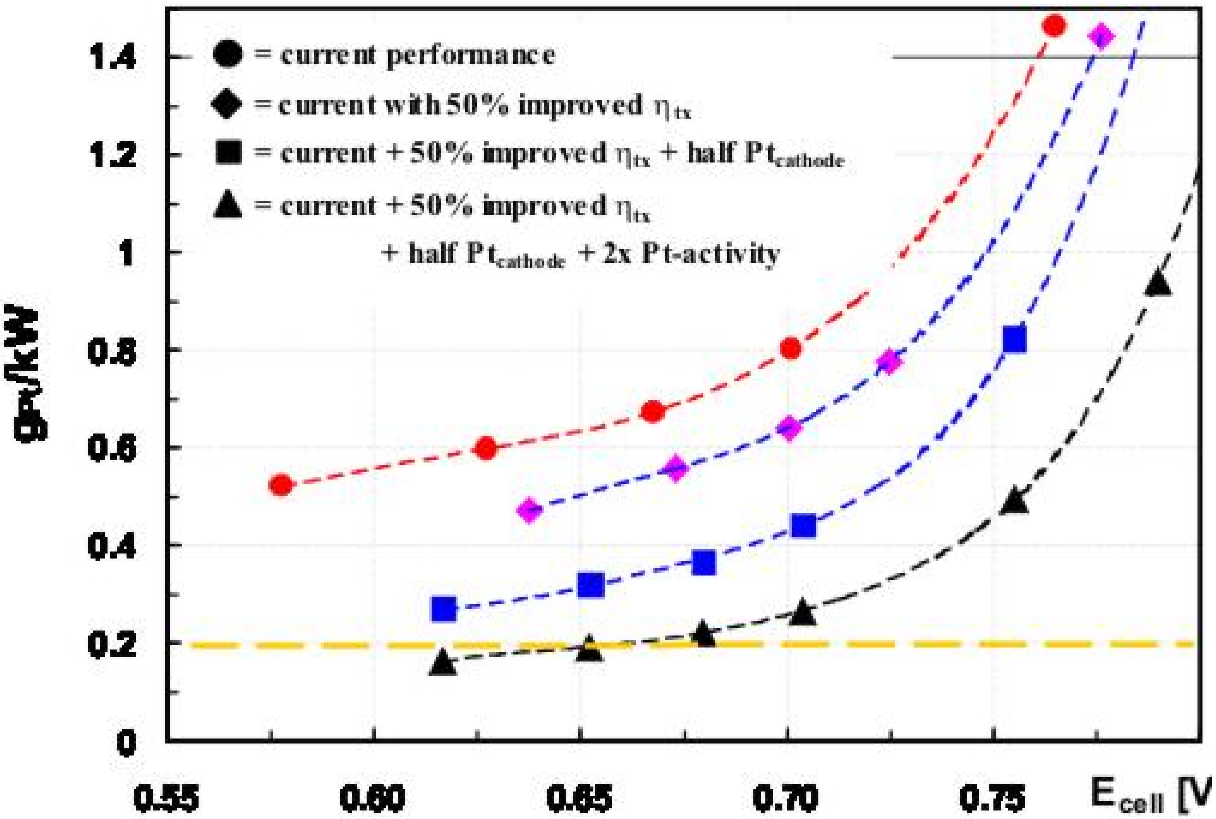
- major losses due to poor cathode kinetics (ORR)
- minor losses by ohmic resistance (50% $R_{H+,membrane}$, 50% $R_{contact}$)
- gains to be made by MEA/DM optimization (mass-tx)

Achievable Pt-Specific Power Densities (g_{Pt}/kW)

automotive requirement: **<0.2 g_{Pt}/kW (< 20g/vehicle)**

(cost and Pt-supply for millions cars/yr.)

air



current performance at **0.05/0.4 mg_{Pt}/cm^2** (for H_2/air)

50% reduced $\eta_{mass-tx}$ (MEA/DM design)

above + reduced Pt at 0.05/**0.2 mg_{Pt}/cm^2** (-20 mV f. opt. MEA)

above + new catalyst w. doubled activity (tbd)

- **automotive targets require development of x2 more active cathode catalyst**
  - → **MEA/DM optimization required but less critical**
  - **(feasibility demonstrated by UTC Fuel Cells (ECS abstracts, Fall 2002)**

Baseline Pt ORR activity: H_2/O_2

80ºC, 150 kPa, RH: 100%, 100%, stoichs 2/9.5,

0.05/0.4mg/cm^2, ~10μm catalyst layer

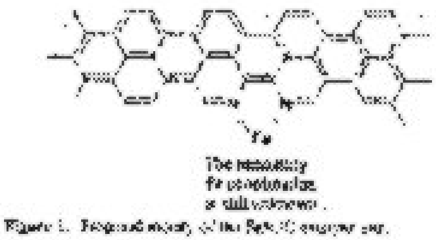
Need twice this activity for automotive

Pt H_2/O_2	A/cm^2	Turnover frequency (e^-/ site- s)	Site density (10^{20}sites / cm^3)	TF*SD ($10^{20}e^-$ /cm^3-s)	A/cm^3
Kinetic, @ 800mV$_{IR-free}$; 45m$^2_{Pt}$/g$_{Pt}$ H electro-sorption	1.26	33	2.4	79	1260
Raw data @800mV, 60m$^2_{Pt}$/g$_{Pt}$ XRD	0.55	11	3.1	34	550

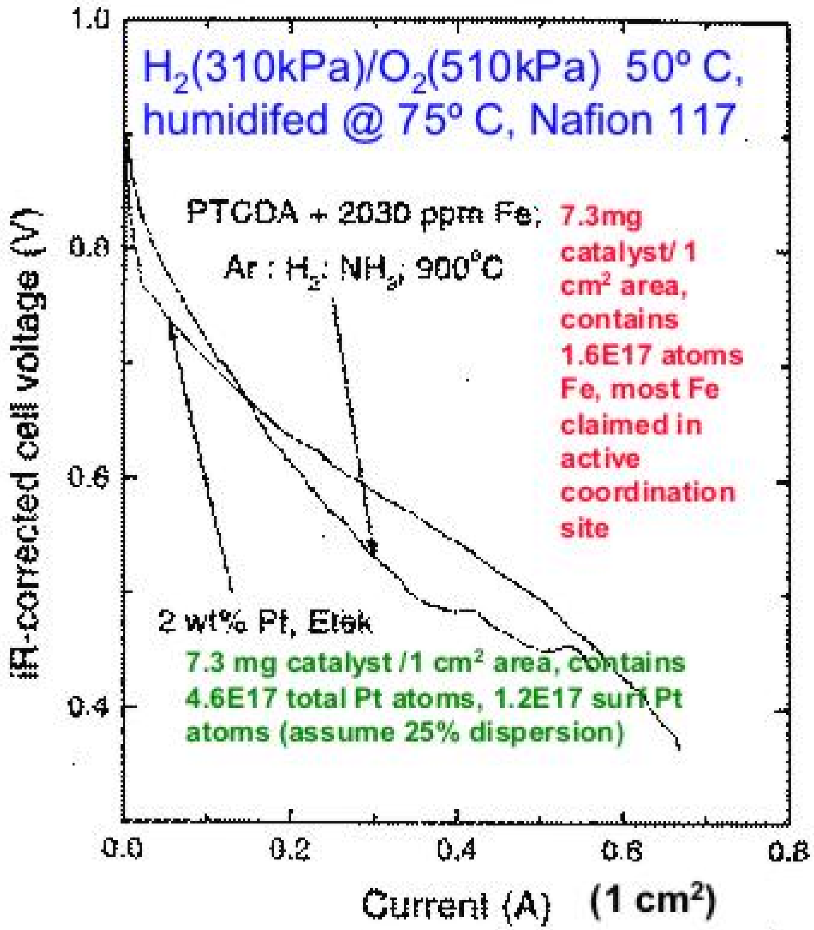
If the cathode catalyst were to cost nothing, how much could one afford to use?

Based on DOE component cost targets

- DOE cost targets in \$/kW: electrodes 5, membrane 5, plates 10
  - if zero out electrode cost
    - could afford (20/15)x larger stack if other costs scaled with area
    - more realistic: could afford 1.5x larger stack
  - transport losses rule out electrode layer thicknesses greater than 100µm (10x thicker than present)
- Pt-free catalyst could therefore occupy up to 1.5 x 10 = 15x the ***volume*** of a state-of-the-art Pt/C catalyst.
- Need 2x the activity of the current catalyst
- ***So the costless catalyst must be within 8x of current Pt on activity (turnover frequency x sites/volume).***
  - If costs/area (e.g. membrane) fell more than anticipated, volume considerations alone require activity within ~20x



An example: G. Faubert, R. Cote, J.P. Dodelet, M. Lefevre and P. Bertrand, Echim. Acta 44 (1999) 2589



@ 800 mV_{IRcorr}:

Fe/PTCDA => 0.038A/cm²

x 1e⁻/1.60E-19coul x 1/1.63E17 Fe

= 1.5 e⁻ /(Fe atom - s)

Pt / C => 0.014 A/cm²

x 1e⁻/1.60E-19coul x 1/1.2E17 surf Pt

= 0.7 e⁻ /(surface Pt atom - s)

To compare to reference conditions (150kPa, 80° C), assume 1st order in pO_2 (after subtracting P_{H2O} at cell temp.) and E_a = 6.6kcal/mole*:

TF (@ref) = TF x (103kPa/498kPa) x exp(6.6kcal/mole/R)(1/323 - 1/353)

= TF x 0.21 x 2.4 = 0.50 TF

50ºC, 510kPa => 80ºC, 150kPa would halve Pt activity

***Parthasarathy, Srinivasan, Appleby and Martin, JECS (1992) 2530**

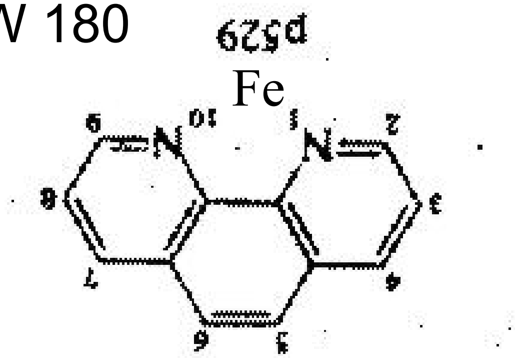
Comparison of Fe/PTCDA and Pt (Faubert et al. 1999), corrected to reference conditions, to automotive requirements

H_2/O_2	Turnover frequency @800mV$_{IR-free}$ (e^-/ site- s)	Site density (10^{20} sites / cm^3)	TF*SD (10^{20} e^- /cm^3-s)	A/cm^3 of supported catalyst
Fe/PTCDA (corrected to 80 C, 103kPa O_2) est. 180 μm thick	0.8	Est. 0.09	Est. 0.06	1.1
2% Pt (from Faubert et.al.) (corrected to 80 C, 103kPa O_2) est. 180 μm thick	0.4 (state-of-art is 33)*	Est. 0.07	Est. 0.04	0.4
Requirements High end from the more probable assumptions	1.6 to 4	3.1 or compensating higher TF	5 to12	60 to 160

*similarly suppressed Pt "reference" activities common in literature. e..g., Toda, Igarashi, Uchida and Watanabe, JECS 146 (1999)3750.

General Motors rs

o-phenanthroline
FW 180



How many Fe/PTCDA active sites should one be able to fit per cm^3?

• o-phenanthroline the smallest molecule with 2 pyridinic N sites, considered to complex with Fe to form the most active site

•our catalysts: 0.4mg C /cm^2 gives 10μm layer

=> carbon density 0.4 g /cm^3

•if polymerize and pyrolyze o-phenanthroline to same density, get 2.2E-3 moles/cm^3

= 1.3E21 active sites (2N per active site)/cm^3

•if Fe on each 2N, would be 23 weight % Fe, not 2000 ppm

With phenanthroline-like site density, activity of Fe/PTCDA could be...

	Turnover frequency @800mV$_{IR\text{-}free}$ (e^-/ site- s)	Site density (10^{20} sites / cm^3)	10^{20} e^- /cm^3-s	A/cm^3 of supported catalyst
Fe/PTCDA (corrected to 80 C, 103kPa O_2) est. 180 µm thick	0.8	Est. 0.09 ***Could be 13***	Est. 0.06 ***Could be 10***	1.1 ***Could be 170***
2% Pt (from Faubert et.al.) (corrected to 80 C, 103kPa O_2) est. 180 µm thick	0.4 (state-of-art is 33)	Est. 0.07	Est. 0.04	0.4
Requirements High end from the more probable assumptions	1.6 to 4	3.1 or compensating higher TF	5 to12	60 to 160

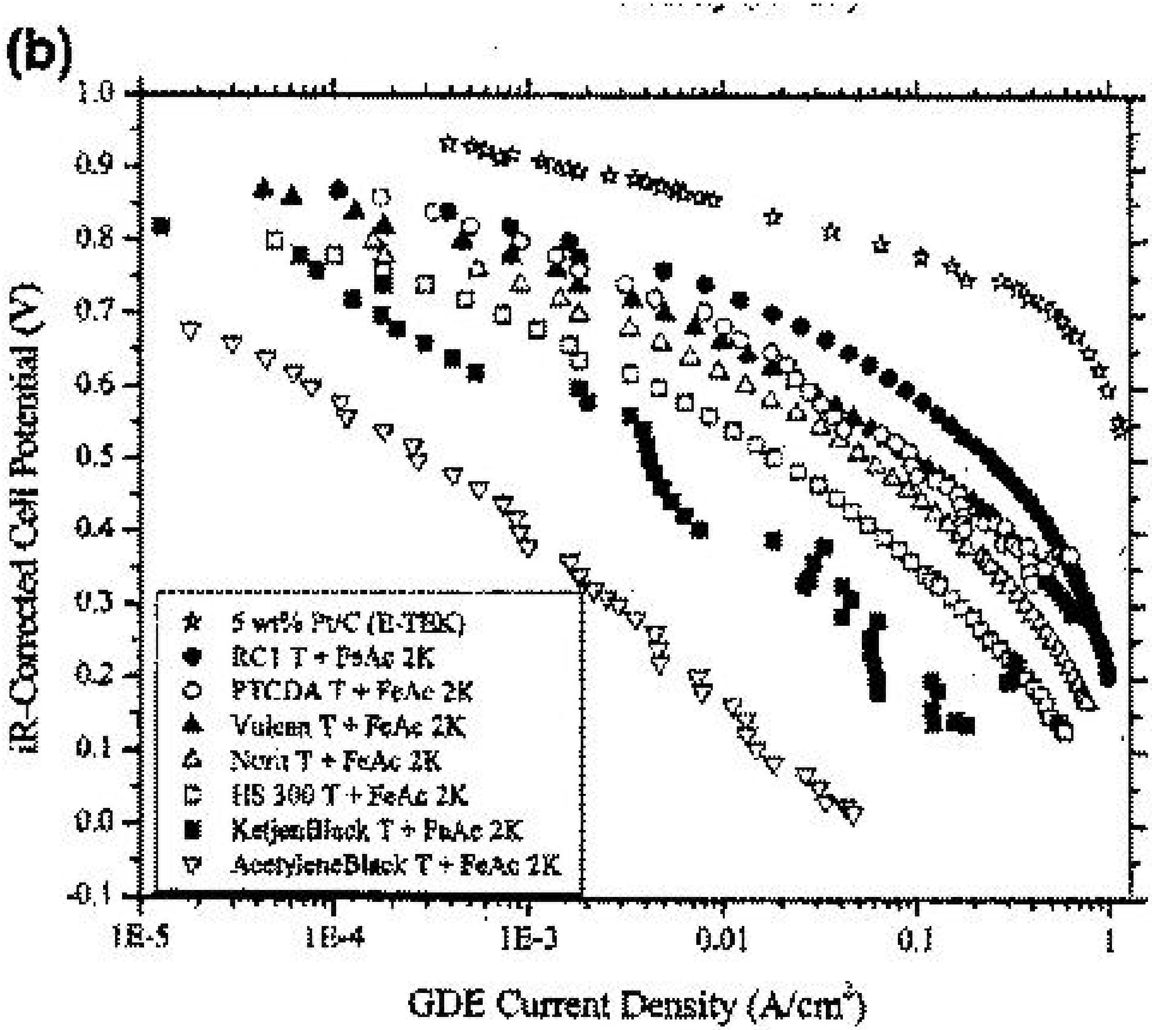


Figure 4. Tafel plots for the GDE polarization curves for selected carbons: (a) NT + FeAc 2K, (b) T + FeAc 2K.

F. Jaouen, S. Marcotte, J-P. Dodelet and G. Lindbergh, J. Phys. Chem. B 107 (2003) 1376.

H_2(310kPa)/O_2(510kPa) 80° C, humidifed @ 105° C, Nafion 117, 2.1mg catalyst/1cm^2 (~50µm)

Pt Turnover freq. 2x that in 1999 (corrected for conditions)

Fe/PTCDA Turnover freq. 1/30x that in 1999

Recommendations for cathode catalyst evaluation with automotive relevance

- Need a central laboratory to test novel electrocatalysts
  - avoid variation in reported baseline Pt activity
  - best done at a national lab
  - as milestone, samples (powder) should be sent to central lab for evaluation
- Run clean kinetic experiments (pure O_2, $E_{iR\text{-}free}$ = 800mV)
  - ≤1μm catalyst, with ionomer, on rotating disk electrode in $HClO_4$

    Paulus, Schmidt, Gasteiger and Behm, J. Electroanal. Chem. 495 (2001) 134
  - in MEA's (≤~10 μm electrode layer thickness)
    - use 1 kHz impedance or current interrupt to correct for iR
    - wait at least 15 minutes at any given condition (i.e. current density) before acquiring data
  - 80ºC, 150kPa suggested, for non-Pt compare to requirements shown on slide 11 (160 A/cm[3])
- Determine Tafel slope to check extrapolation to potential with practical full-load current density (~650 mV)

Conclusions

- A Pt-based path to automotive performance and cost exists
  - requires durability from Pt-alloy catalysts and mass transfer improvements
- Non-Pt catalysts could help with cost and Pt supply if stringent **A/cm^3** kinetic requirement could be met
- Non-Pt example (Faubert et al.):
  - initial turnover frequency from '99 paper close to plausible
  - site density needs major increase, could be possible
  - durability (beyond ~24h) still to be established
- Only once durable kinetics are established, should one start to battle mass transfer through the thicker non-Pt catalyst layers to achieve practical **A/cm^2**

Supplementary slides

DOE automotive stack cost targets

(Table 4a, FY 2001 Progress Report)

- electrodes (anode and cathode together) $5/kW
  - @$20/g Pt ($622/Tr. Oz.), allows 0.25g Pt/kW if rest of electrode were free
  - take **≤0.2g Pt/kW** as representative, to allow for some other electrode costs
  - 0.2g Pt/kW (~15g/vehicle) considered workable for Pt production for 1E7/yr vehicles, with 3-4 year advance notice to increase Pt production
    - *C. Jaffray and G. Hards, in Handbook of Fuel Cells, V. 3, W. Vielstich, A. Lamm, and H.A. Gasteiger, eds., Wiley,2003, in press.*
- membranes $5/kW
- bipolar plates (presumably also includes diffusion media) $10/kW

Proper metric of absolute catalyst activity in O_2:

Turnover Frequency x (Site 3-D Density x Layer Thickness)

- Turnover frequency (TF) = e^- transferred per surface active atom per second
- site density (SD) = active atoms per cm^3 supported catalyst
- active layer thickness (cm)

H electrosorption gives product = sites/$cm^2_{geometroc}$

- for uncorrected H_2/O_2 data @0.80 V (0.55A/cm^2), 60 m^2_{Pt}/g_{Pt} from previous slides:
  - (0.55C/1s cm^2) x (1e^-/1.6E-19C) x (1cm^2/4E-4g $_{Pt}$) x (1g_{Pt}/60E4 cm^2_{Pt}) x (1cm^2_{Pt}/1.31E15 Pt atoms) = **11 e^- / surf Pt atom-s**
  - (4E-4g_{Pt}/cm^2) x (60E4cm^2_{Pt}/g_{Pt}) x (1.31E15Pt atoms/cm^2_{Pt}) = **3.1E17 surf Pt atoms$_t$/cm^2 (10µm thick Pt-C catalyst layer)** = 3.1E20 surf Pt atoms /cm^3_{Pt-C}
- for H_2/O_2 kinetic current @0.80 $V_{iR-free}$ (1.26A/cm^2 = 1260 A/cm^3), 45m^2_{Pt}/g_{Pt} H electrosorption area
  - (1.26C/1s cm^2) x (1e^-/1.6E-19C) x (1cm^2/4E-4g $_{Pt}$) x (1g_{Pt}/45E4 cm^2_{Pt}) x (1cm^2_{Pt}/1.31E15 Pt atoms) = **33 e^- / surf Pt atom-s**
  - (4E-4g_{Pt}/cm^2) x (45E4cm^2_{Pt}/g_{Pt}) x (1.31E15Pt atoms/cm^2_{Pt}) = **2.4E17 ionically-connected surf Pt atoms$_t$/cm^2 (10µm thick Pt-C catalyst layer)** = 2.4E20 connected surf Pt atoms / cm^3_{Pt-C}

Absolute catalyst activity in air: Turnover Frequency x (Site 3-D Density x Layer Thickness) *but kinetic data should be gathered in pure oxygen*

- Turnover frequency (TF) = e^- transferred per surface active atom per second
- site density (SD) = active atoms per cm^3 supported catalyst
- active layer thickness (cm)

H electrosorption gives product = sites/$cm^2_{geometric}$

- for uncorrected H_2/air data @0.80 V (0.20A/cm^2), 60 m^2_{Pt}/g_{Pt} from previous slides:

  (0.20C/1s cm^2) x ($1e^-$/1.6E-19C) x (1cm^2/4E-4g $_{Pt}$) x ($1g_{Pt}$/60E4 cm^2_{Pt}) x ($1cm^2_{Pt}$/1.31E15 Pt atoms) = **4.0 e^- / surf Pt atom-s**

  (4E-4g_{Pt}/cm^2) x (60E4cm^2_{Pt}/g_{Pt}) x (1.31E15Pt atoms/cm^2_{Pt}) = **3.1E17 surf Pt atoms$_t$/cm² (10µm thick Pt-Ccatalyst layer)** = 3.1E20 surf Pt atoms /$cm^3_{Pt\text{-}C}$

- for H_2/air kinetic current @0.80 $V_{iR\text{-and mt-free}}$ (0.50A/cm2), 45m^2_{Pt}/g_{Pt} H electrosorption area = 500 A / cm3

  (0.50C/1s cm^2) x ($1e^-$/1.6E-19C) x (1cm^2/4E-4g $_{Pt}$) x ($1g_{Pt}$/45E4 cm^2_{Pt}) x ($1cm^2_{Pt}$/1.31E15 Pt atoms) = **13 e^- / surf Pt atom-s**

  (4E-4g_{Pt}/cm^2) x (45E4cm^2_{Pt}/g_{Pt}) x (1.31E15Pt atoms/cm^2_{Pt}) = **2.4E17 ionically-connected surf Pt atoms$_t$/cm² (10µm thick Pt-C catalyst layer)** = 2.4E20 connected surf Pt atoms / $cm^3_{Pt\text{-}C}$

If the cathode catalyst were to cost nothing, how much could one afford to use?

Based on DOE component cost targets

- If Pt = \$5/kW, membrane =\$5/kW, and bipolar plate =\$10/kW and all costs are proportional to active area, then zeroing out the Pt cost allows a 20/15x larger stack for the same cost. Bipolar plate should scale below linear with area, so say could afford a 1.5x larger-area stack -- still plausible on volume. (If BPP cost were independent of area, would be 2x)
- Current cathodes are about 10μm thick. Transport becomes more limiting with thicker electrodes; no one has ever exceeded 100μm for a successful fuel cell electrode. Take 10x as maximum layer thickness increase.
- Pt-free catalyst could therefore occupy up to 1.5 x 10 = 15x the *volume* of a state-of-the-art Pt/C catalyst.

So to give competitive cost (and acceptable stack size), the product of the turnover frequency and the active sites/volume for the costless catalyst must be no smaller than 15x less than that for the acceptable Pt solution, which in turn has 2x the activity/Pt of the current state of the art. ***So the costless catalyst must be within 8x of current Pt on activity (turnover frequency x sites/volume).***

Sensitivity considerations

– 100µm catalyst layer might easily be too thick for good mass transfer, would require higher true activities

– If membrane costs dropped well below the $5/kW level
  - stack volume (to achieve 1kW/L), rather than cost, would set the minimum costless catalyst activity, at roughly 20x lower activity (turnover frequency x site density) than current Pt

– If bipolar plate cost were essentially independent of area, minimum costless catalyst activity would be 10x lower than current Pt

– if the costless catalyst has a higher Tafel slope than the 70mV/decade for Pt at 80ºC, its activity at 0.8V must be higher than noted here to give adequate full power density

Summary: Minimum target kinetic activity for the costless oxygen reduction catalyst

- 8x to20x lower than present Pt in a purely kinetic measurement
  - for H_2/O_2 at 150kPa, 80ºC, fully humidified, IR-corrected 0.8 V vs. RHE:

    = **60 to 160 A/cm^3**

    - the higher number arises from the more probable end of the range of assumptions

    this number does not incorporate a measurement of utilization of the surface Pt (75% in baseline data), as does the TF below
  - **Turnover frequency** for above conditions (assuming the same 2.4E20 ionically [and electronically]-connected active sites per cm^3 as state-of-the-art Pt-C)

    = 1.6 to 4 e^- / (active site - second)

    - if active site volumetric density is lower than for Pt-C (likely), need proportionally higher turnover frequency

Recommendations for cathode catalyst evaluation with automotive relevance (cont'd)

- Experimental units to express results
  - $A/cm^3_{supported\ catalyst}$
    - to be practical for transportation, want at least 60 to 160
  - (catalyst layer thickness used)
- Fundamental units to express results
  - Turnover frequency (e^-/active site-second)
  - active site density (sites/ $cm^3_{supported\ catalyst}$)
    - should incorporate utilization measurement if available
    - product of the two above should exceed 5-12E20 $e^-/(cm^3\text{-}s)$
  - (catalyst layer thickness used)