Power for the Real World

## 2012 Annual Merit Review
## DOE Hydrogen and Fuel Cells and Vehicle Technologies Programs

# Catalyst Working Group Kick-off Meeting: Personal Commentary

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# 2012 Catalyst Working Group Kick-off Meeting

We all justify the concept of FC vehicles, among other things, as critical for the long term environmental health of the planet. This implies that someday they have to become a large fraction of the annual world automobile market.

**This invites Several High Level Questions**

1. Are the technological platforms we are working on now, capable of making a significant dent (> 30%) in the world's automotive markets with FC vehicles by 2030? 2050, or ever?
2. What are the ramifications for MEA production rates, quality and processing simplicity, if any technology is to be really commercially successful at such volumes?
   a) Who has responsibility for worrying about that?
   b) Is just focusing on ORR activity/durability with current technologies sufficient?
   c) Does everyone involved truly understand what high volume, ultra-low cost, totally green manufacturing means?
3. What would have the greatest impact on large scale commercialization of PEM FCV's:
   a) R&D to improve the performance of non-PGM catalysts by 2 orders of magnitude to just give equivalence to state-of-the-art 2012 PGMs (e.g. > 1.5 A/cm$^2$ at > 0.6 V on 150kPa air), if it is even possible, **or**
   b) R&D to improve the activity of state-of-the-art current PGM catalysts at 0.125 mg/cm$^2$ by 2 orders of magnitude (i.e. ~ 120 mV at 0.2 A/cm$^2$), if it is even possible?

# Re: Questions 1 and 2(c):

## ☐ Manufacturing realities for high volume, low cost MEA production

- The DOE 2015 cost targets are based on 500,000 vehicles per year (~ 3% of N. A. market)
- But just 10% of the world market in 2030 is projected to be 15 million vehicles, so

**Assume:**

- 15 million FC vehicles per year, requiring 300 MEA's/stack (vs. 400 required today). This means 4.50 billion MEA's/year have to be manufactured.
- Assuming each manufacturing line is operating at full capacity operating 3 shifts per day, or ~ 8000 hrs/year with 80% average up-time to account for maintenance, repair and lot changes of input materials, this 4.5 billion equates to 11,700 MEA's/minute.
- 1 vehicle per minute per production line => 300 MEA's/stack/minute, so 11,700 MEA's/minute and => 20 production lines each producing 10 MEA's/ second.
- Individual piece-part processing is out of the question.
- High volume roll-to-roll widths up to 1 m, with ten MEA's across the web width, each 10 cm x 30 cm, => line speeds of 20 m/min will be required to produce 10 MEA's/sec.
- Pt loadings of ~ 0.1 $mg_{Pt}/cm^2$ => electrode thicknesses will be < 2 microns requiring precision coating methods with critical limits on debris and tolerances.
- These MEA's have to be made with extraordinary quality control (one in thirty thousand defective MEAs for 1% stack failures, 1 in 300,000 for 0.1% stack failures).

# Re: Questions 1 and 2(c): (cont.)

## ☐ Manufacturing realities for high volume, low cost MEA production (cont.)

- The catalyst and catalyst/membrane integration manufacturing processes have to be simple, robust, few in number and have wide process parameter windows since the yields per step multiply. Just four sequential process steps with 90% yields would increase costs by 30% without recycling.
- Process steps for electrode formation that require, e.g. hot bonding, annealing, solvent evaporation or drying steps lasting for minutes will require proportionately long mfg. lines.
- Build-up of residues on the coaters, 8 hour shift lengths, and ability to handle jumbo roll-goods, safety and catalyst batch-size limitations will be factors affecting batch sizes, throughputs and labor costs.
- At loading targets of even 0.125 mg/cm$^2$ on MEA's with 300 cm$^2$ active areas, the above line speeds require catalyst flow through rates of 1.5 kg of Pt per hour or roughly $2 million worth of Pt per day per manufacturing line at $2K/toz.
- On site recycling of scrap will probably be justified. Ink mixing for catalyst coating of dispersions if used would have to keep pace and also require chemistries compatible with coating line speeds and quality levels.
- Safety and environmental requirements will almost certainly exclude coating catalyst with flammable solvents, and I would guess use of carbon nanotubes.
- For such reasons my own belief is that ultimately catalyst layer coating at these rates and levels of quality will be by all dry vacuum coating methods such as are already used to produce over 80% of the world's multi-layer optical film coated glass for low emissivity fenestration totaling 250 million m$^2$ already in 2005.

# Re: Question 2(a,b)

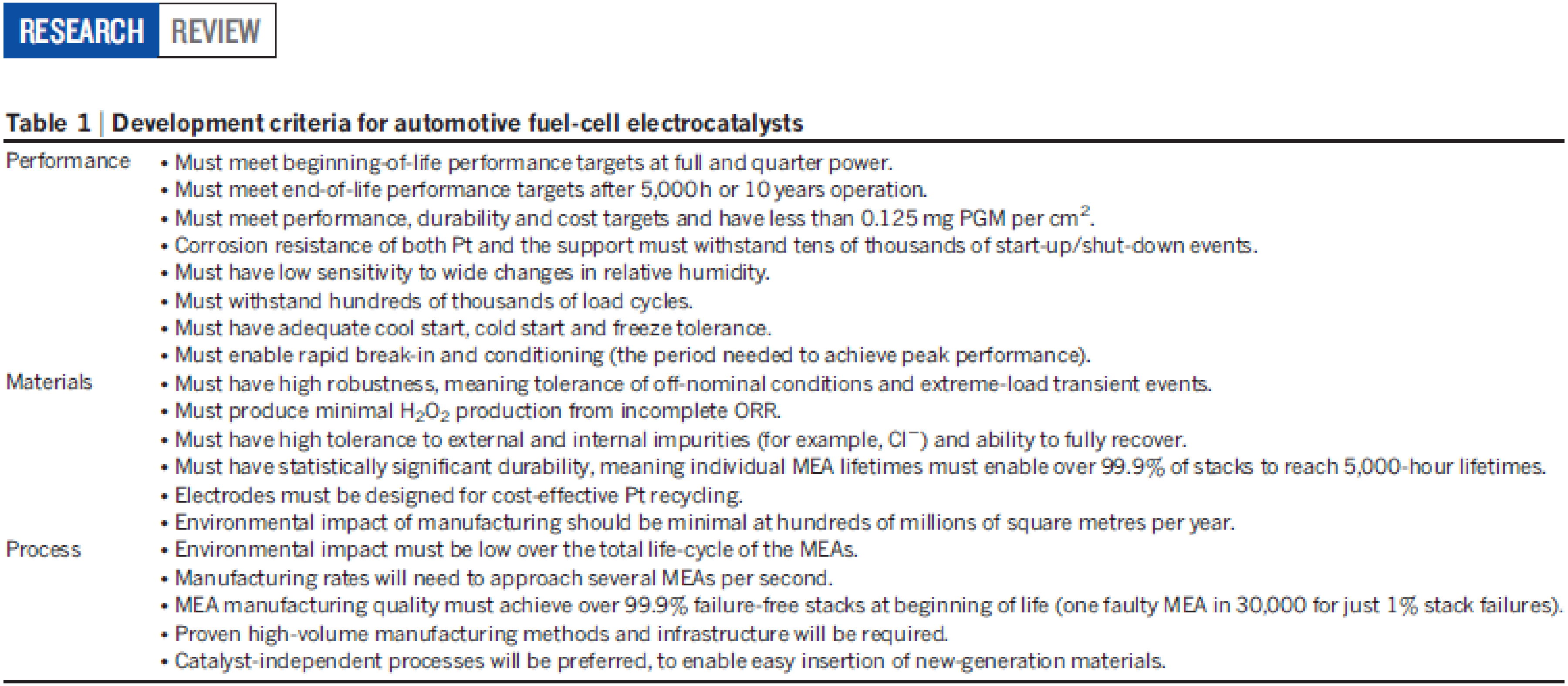

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**Table 1 | Development criteria for automotive fuel-cell electrocatalysts**

| | |
|---|---|
| Performance | • Must meet beginning-of-life performance targets at full and quarter power. |
| | • Must meet end-of-life performance targets after 5,000 h or 10 years operation. |
| | • Must meet performance, durability and cost targets and have less than 0.125 mg PGM per $cm^2$. |
| | • Corrosion resistance of both Pt and the support must withstand tens of thousands of start-up/shut-down events. |
| | • Must have low sensitivity to wide changes in relative humidity. |
| | • Must withstand hundreds of thousands of load cycles. |
| | • Must have adequate cool start, cold start and freeze tolerance. |
| | • Must enable rapid break-in and conditioning (the period needed to achieve peak performance). |
| Materials | • Must have high robustness, meaning tolerance of off-nominal conditions and extreme-load transient events. |
| | • Must produce minimal $H_2O_2$ production from incomplete ORR. |
| | • Must have high tolerance to external and internal impurities (for example, $Cl^-$) and ability to fully recover. |
| | • Must have statistically significant durability, meaning individual MEA lifetimes must enable over 99.9% of stacks to reach 5,000-hour lifetimes. |
| | • Electrodes must be designed for cost-effective Pt recycling. |
| | • Environmental impact of manufacturing should be minimal at hundreds of millions of square metres per year. |
| Process | • Environmental impact must be low over the total life-cycle of the MEAs. |
| | • Manufacturing rates will need to approach several MEAs per second. |
| | • MEA manufacturing quality must achieve over 99.9% failure-free stacks at beginning of life (one faulty MEA in 30,000 for just 1% stack failures). |
| | • Proven high-volume manufacturing methods and infrastructure will be required. |
| | • Catalyst-independent processes will be preferred, to enable easy insertion of new-generation materials. |

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- ORR catalyst activity is just one of many requirements that must be met simultaneously for successful commercialization.
- Researchers even at the fundamental level have some responsibility to ask themselves whether their approaches for new catalysts have realistic, scalable processability.

# Re: Question 2(a,b)

## Our current “Universe” of PGM heterogeneous electrocatalysts

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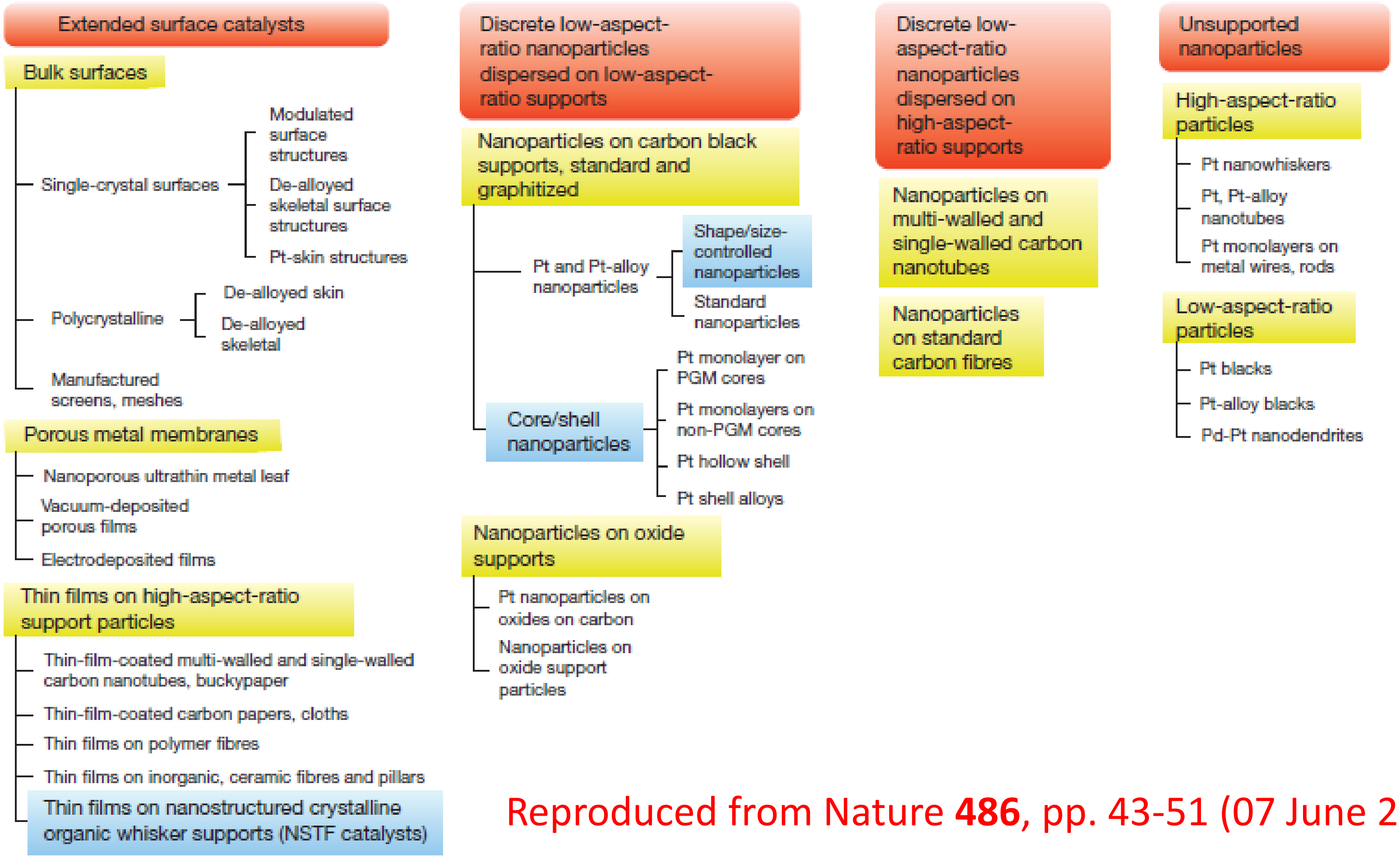

- Extended surface catalysts
  - Bulk surfaces
    - Single-crystal surfaces
      - Modulated surface structures
      - De-alloyed skeletal surface structures
      - Pt-skin structures
    - Polycrystalline
      - De-alloyed skin
      - De-alloyed skeletal
    - Manufactured screens, meshes
  - Porous metal membranes
    - Nanoporous ultrathin metal leaf
    - Vacuum-deposited porous films
    - Electrodeposited films
  - Thin films on high-aspect-ratio support particles
    - Thin-film-coated multi-walled and single-walled carbon nanotubes, buckypaper
    - Thin-film-coated carbon papers, cloths
    - Thin films on polymer fibres
    - Thin films on inorganic, ceramic fibres and pillars
    - Thin films on nanostructured crystalline organic whisker supports (NSTF catalysts)
- Discrete low-aspect-ratio nanoparticles dispersed on low-aspect-ratio supports
  - Nanoparticles on carbon black supports, standard and graphitized
    - Pt and Pt-alloy nanoparticles
      - Shape/size-controlled nanoparticles
      - Standard nanoparticles
    - Core/shell nanoparticles
      - Pt monolayer on PGM cores
      - Pt monolayers on non-PGM cores
      - Pt hollow shell
      - Pt shell alloys
  - Nanoparticles on oxide supports
    - Pt nanoparticles on oxides on carbon
    - Nanoparticles on oxide support particles
- Discrete low-aspect-ratio nanoparticles dispersed on high-aspect-ratio supports
  - Nanoparticles on multi-walled and single-walled carbon nanotubes
  - Nanoparticles on standard carbon fibres
- Unsupported nanoparticles
  - High-aspect-ratio particles
    - Pt nanowhiskers
    - Pt, Pt-alloy nanotubes
    - Pt monolayers on metal wires, rods
  - Low-aspect-ratio particles
    - Pt blacks
    - Pt-alloy blacks
    - Pd-Pt nanodendrites

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**Figure 3 | Basic platinum-based heterogeneous electrocatalyst approaches.** The four PEM fuel-cell electrocatalyst approaches (developed or under investigation) for the performance-limiting cathode ORR are shown, with Pt and Pt-alloy electrocatalysts listed according to the basic geometric structure of the catalyst particles and their supports. The main subcategories are highlighted in yellow. Catalyst approaches with the highest demonstrated activities are highlighted in blue.

# Re: Question 2(a,b)

- The current leading approaches for electrocatalysts can meet or exceed the DOE mass and specific activity targets, and will continue to improve.  Activity is no longer the key issue for the short term.

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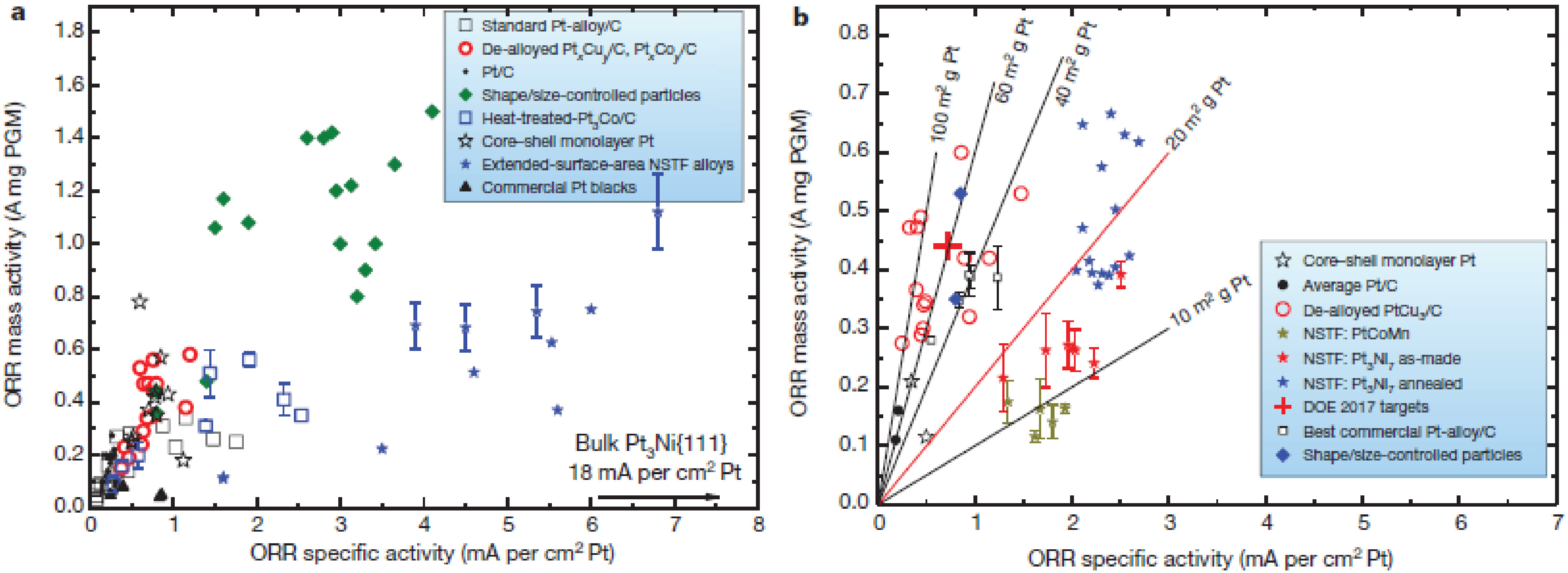

**Figure 4 | Kinetic activities of the main Pt-based electrocatalyst systems.** The ORR $A_m$ versus $A_s$ are shown for the major Pt-based electrocatalyst approaches listed in Fig. 3. **a**, Activities are measured by RDE at 900 mV for the following catalysts: standard Pt-alloys/C (refs 42, 43, 87), de-alloyed PtM$_3$/C (where M = Cu, Co) (refs 88–90), Pt/C (refs 3, 42, 44, 46–48, 50), shape- and size-controlled particles (refs 45, 47, 48, 50, 51), heat-treated Pt$_3$Co/C (ref. 42), core–shell monolayer Pt (refs 44, 56, 60, 62–64, 71), extended-surface-area NSTF alloys (refs 23,26) and commercial Pt blacks (refs 3, 48). **b**, Activities are measured in MEAs at 900 mV, 80 °C and 150 kPa saturated O$_2$ for the following catalysts: core–shell Pt monolayer (refs 49, 64), average Pt/C (refs 3, 91, 92), de-alloyed PtCu$_3$/C (refs 91–93), three extended-surface-area NSTF alloys (ref. 23), the DOE 2017 and 2015 targets, best commercial Pt-alloys/C (data from GM, 3M), and shape- and size-controlled particles (refs 46, 52). The scattering of activity values for any one type or reference represent different catalyst compositions, loadings or preparation and process treatments, not statistical variations in measurement.

# Summary

**For short term** ( 500K vehicles, present to ~ 2030?) **emerging market:**

- PGM based MEA technology approaches/platforms: (the horse has left the gate)
  - ORR for the leading contenders appears to be sufficient.
  - Durability and manufacturability to cost are key materials issues, but MEA components can't be optimized independent of one another.
  - Capital/risk management to install scaled-up capability 5 years ahead of the market is a critical business issue.
  - At 8 $g_{Pt}$/vehicle, cost and availability of PGM's is not an issue, it is just replacement and only ~ 0.5% of that needed for the rest of the (~ 100 million/year) ICE vehicles. Pt cost should not be used to justify non-PGM catalyst development, but some other justification, e.g. basic materials research.

**For long term** ( > 10M vehicles, > ~ 2030) **mature market:**

- We shouldn't assume that the same technology that is ok for short term can be scaled up to meet the volumes, cost and quality required for long term.
  - Very slim profit margins at these volumes.
  - Everything will have to be recycled in the whole manufacturing process.
  - That plus cost of quality will drive the MEA and subcomponent processes and their supply chains to utmost simplicity (as for all system component costs.)
    - ➢ It is everyone's responsibility to factor these into their R&D concepts.
  - The PGM's will be there – in use in ICE's anyway, probably leased by Anglo American or others.
  - Over 18 years since PtCo alloy first studied ….. So how long will something totally new take?
  - Should resources be applied to tweaking what approaches, platforms we have now, or strive for that "120 – 140 mV gain (miracle?) at 0.2 A/cm$^2$ " ?