Are we there yet? *No!*
Pt-alloy catalysts

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General Motors Global Product Development,

Fuel Cell Activities

Present to the DOE DWG-CWG

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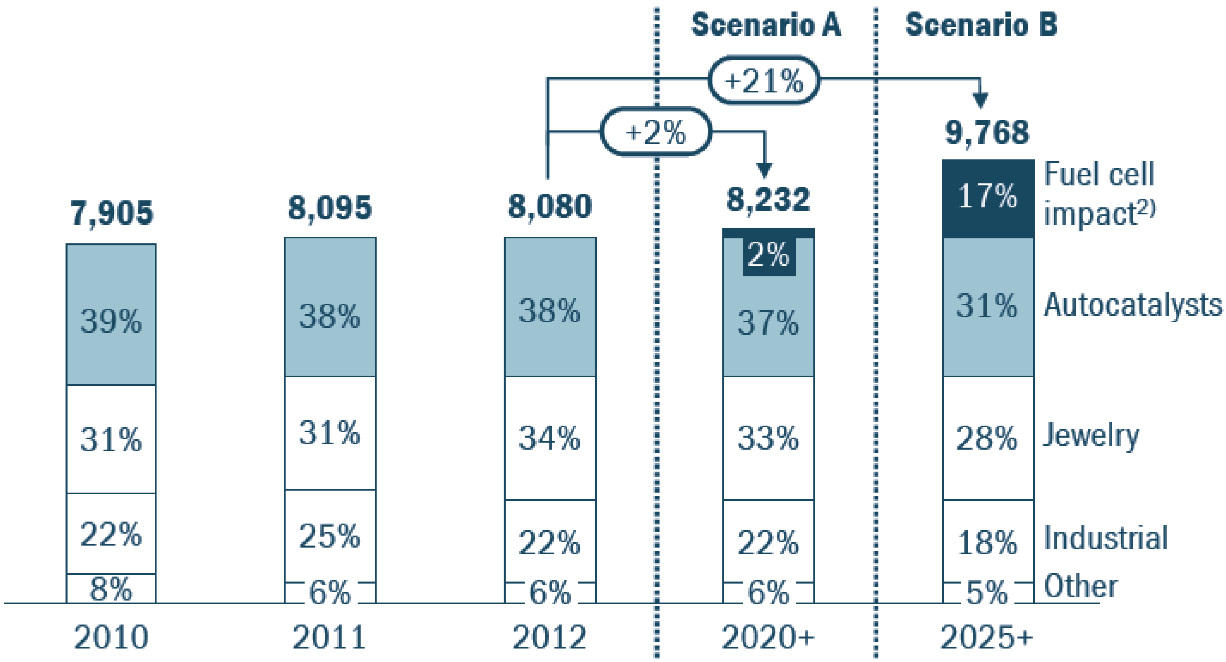
Outline

- Catalyst long-term targets
- Low PGM cathode
- Pt surface area loss
- Catalyst support

Long-term Catalyst Targets

Platinum demand[1)] by application ['000 oz]



Comments

Scenario A:
Next-generation technology will reach 0.15 mg/cm² platinum load in the MEA – By 2020, a global production volume of 300,000 vehicles is assumed

Scenario B:
FCEVs will improve significantly in costs and required platinum load decreases to <0.10 mg/cm² in the MEA. FCEVs become a global success story with a yearly production volume of 5 million units

1) Excluding movement in stocks 2) Underlying assumption: 300,000 FCVs with each 16 g platinum in Scenario A, 5 million FCVs each with <10 g platinum/vehicle in Scenario B

Source: Johnson Matthey; Roland Berger

Roland Berger study, 2013

- Even at 10 g-Pt/veh, Pt demand/supply will shift, putting pressure on Pt price.
- Need to cut Pt usage to the replacement level of IC engines (2-8 g-Pt/veh).
- Can we get people to use less Pt for jewelry?

Beyond 2020

Table 5. Technical Targets for Electrocatalysts *From FCTT Roadmap, June 2013*

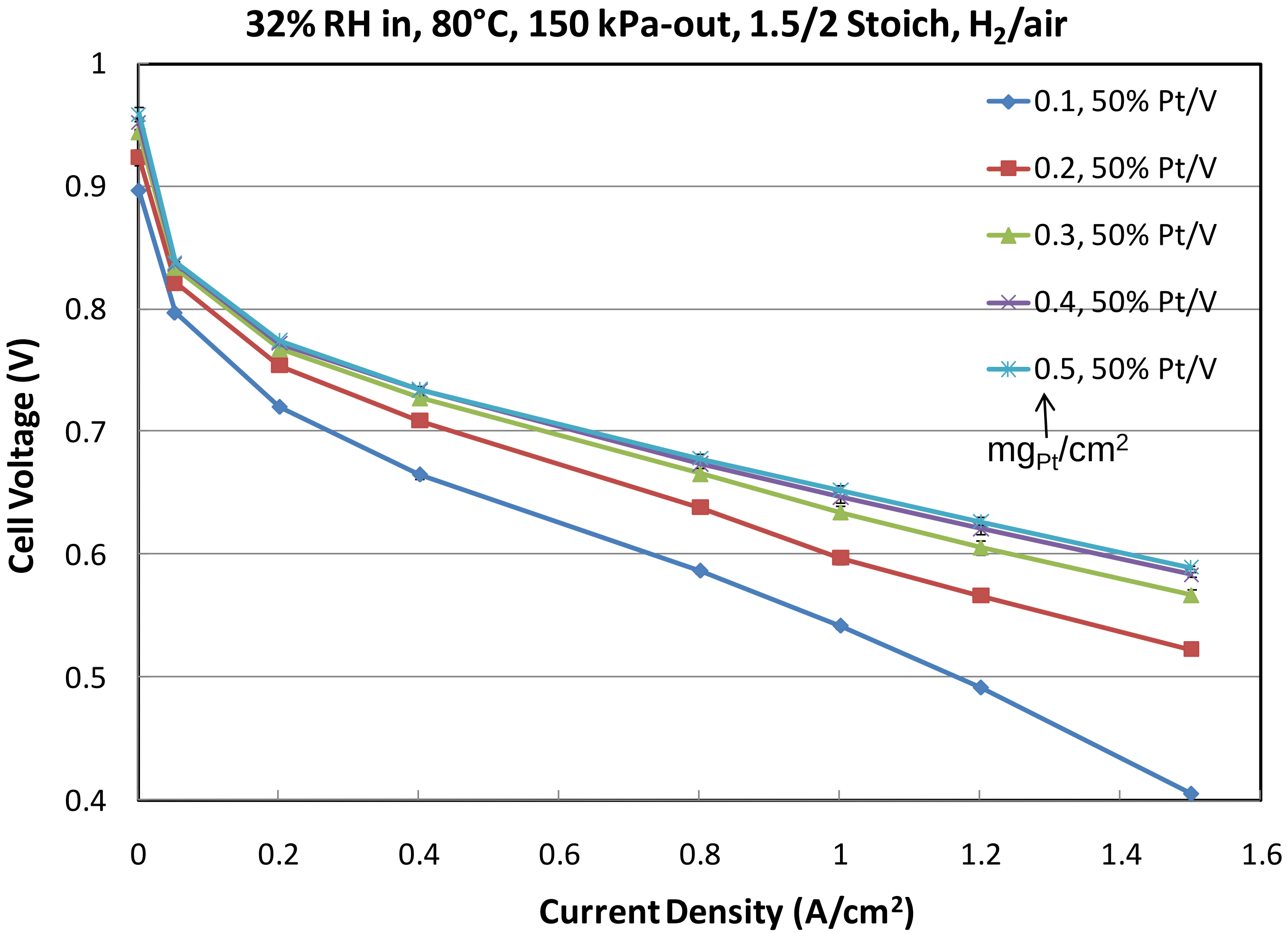
Characteristic	Units	Status	2020 Target
Platinum group metal (PGM) total content[a]	g/kW rated	0.14[b]	0.125
PGM total loading[a]	mg PGM/cm^2 electrode area	0.15[b]	0.125
Mass activity[f]	A/mg$_{PGM}$ @ 900 mV$_{iR\text{-}free}$	0.47-0.67[b]	0.44

→ 11.25 g-PGM/veh

- In the long term, we will need to continue cutting PGM (especially Pt) usage down to IC engine level (2-8 g-Pt/veh) → <0.08 g$_{Pt}$/kW (>36% reduction from current target)
    - ➢ Increase ORR mass activity (0.8 A/mg$_{Pt}$??) to maintain efficiency
    - ➢ Increase ECSA (>100 m^2/g$_{Pt}$) for high power performance
    - ➢ Increase current density at rated power by improving mass transport
- NEDO by 2030 aims for <5 g$_{Pt}$/veh,

Low PGM cathode

Low-loaded catalysts (Pt or Pt-alloy) give unexpectedly worse performance at high current density in air

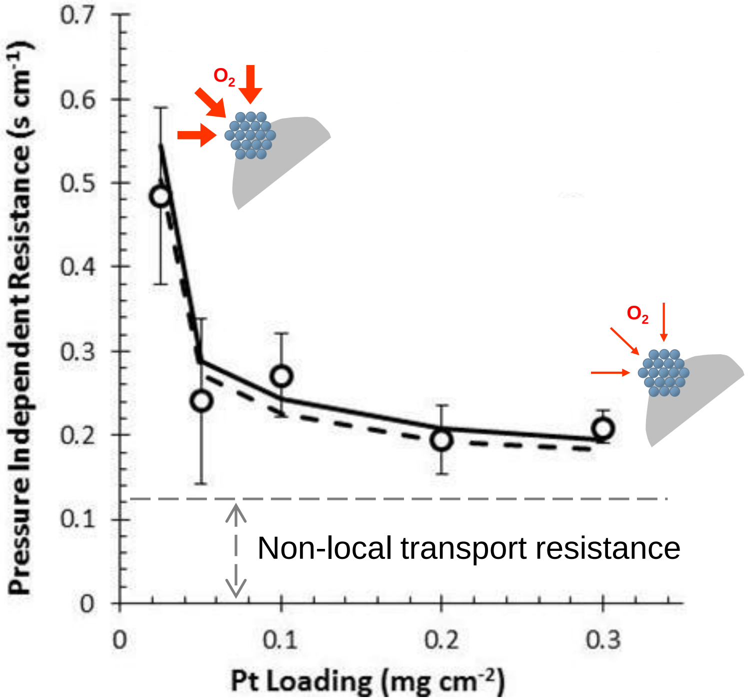


- From simple kinetics (constant 70mV/decade Tafel slope, expect parallel curves, 20 mV lower for each halving of loading
- Expect transport losses to be less for lower-loaded (thinner) electrodes

GM

Data here and to follow from T. Greszler, S. Kumaraguru, N. Subramanian, B. Litteer, Z. Liu and R. Makharia, Fuel Cell Seminar, 28 Oct 2008 [GM]

Effect of *local* O_2 transport resistance increases with decreasing Pt surface area



Inverse of roughness factor

$$R_{O_2}^{P,ind} = R_{O_2}^{Knudsen} + \frac{A_{electrode}}{A_{Pt,surface}} R_{O_2}^{local}$$

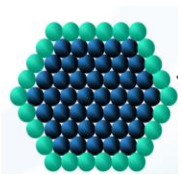
- Owejan *et al.*, J. Electrochem. Soc. (2013) F824.
- Greszler *et al.*, J. Electrochem. Soc. (2012) F831.

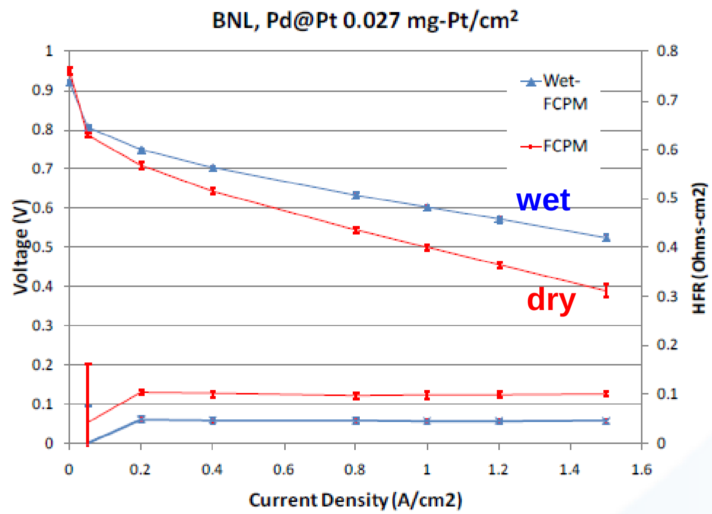
- Voltage at high current density will decrease quickly if Pt roughness factor is lower than a certain value.

High Pt ECSA of Pt ML catalyst enables excellent high-power performance at very low loading

GM data from Adzic et al. 2012 AMR

H_2/air fuel cell polarization curves of Pt/Pd/C





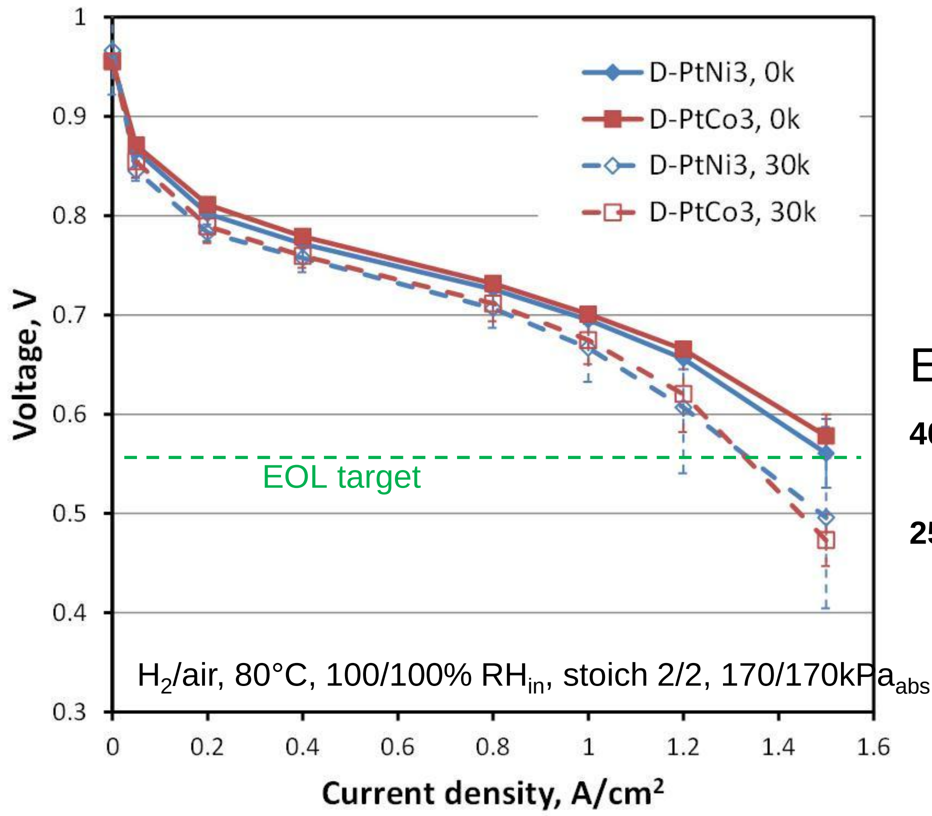
- The ORR activities comparable to literature were reproduced in MEA and RDE.
- Very impressive fuel cell performance with low Pt loading was observed on (at least) Pt/Pd/C.
- Poor performance of two other catalysts are most likely due to their thick cathodes.
- Future tests with higher metal contents preferred

A. Kongkanand, J. Zhang, F. Wagner

H_2/Air, 80° C, 65%RH, 150kPa; 100%RH, 170kPa; **27μgPt/cm²**

- Long-term target (<8 g-Pt/veh) can be achieved, even with current understanding of local O_2 transport, if Pt ML catalysts become mature.

State-of-the-art Pt alloy at 0.1 mg/cm^2



Pt loading: **0.1** mg_{Pt}/cm^2
Nafion NR211 membrane

ECSA

40 m^2/g_{Pt}

25 m^2/g_{Pt}

- After aging, Pt ECSA loss causing high-power performance loss.
  → Must find ways to mitigate ECSA loss

ECSA loss / Pt dissolution

ECSA loss, Pt dissolution

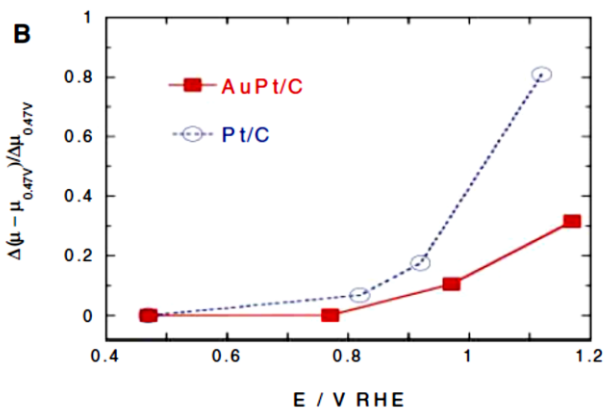
- Even with good Pt alloy with durable ORR activity, Pt dissolution remains a concern.
- Especially on low-loaded cathode, Pt dissolution causes ECSA loss, and in turn high power performance loss.

Mitigate Pt dissolution

1. Materials solution
   Example: Au cluster on Pt surface

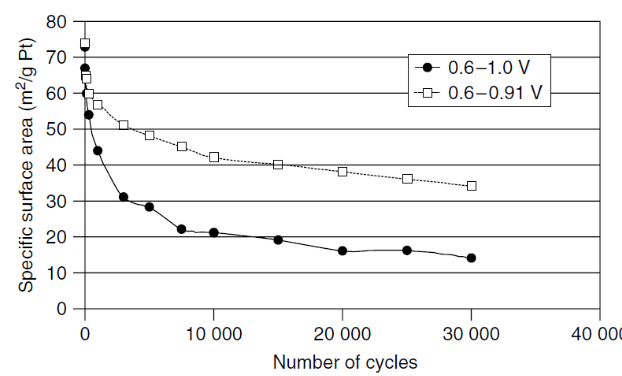
2. Operational solution
   Example: lowering upper voltage limit

Au cluster on Pt/C mitigate Pt oxidation



Zhang et al. Science 2007

Limit upper voltage can lower ECSA loss



Wagner et al. Handbook of Fuel Cells Ch.16

Understanding gap: Pt dissolution accelerates under O_2

Matsumoto et al., JPCC 2011

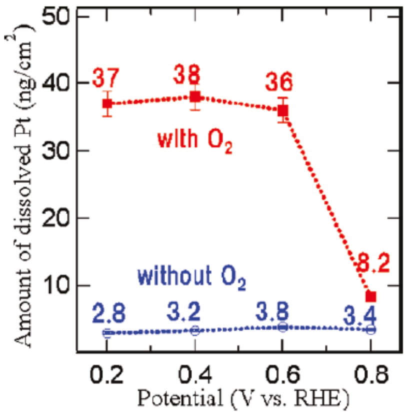
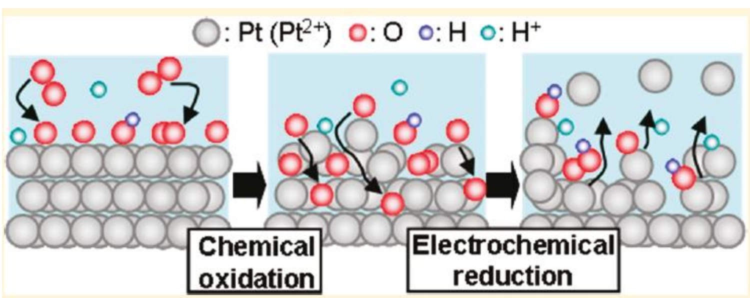
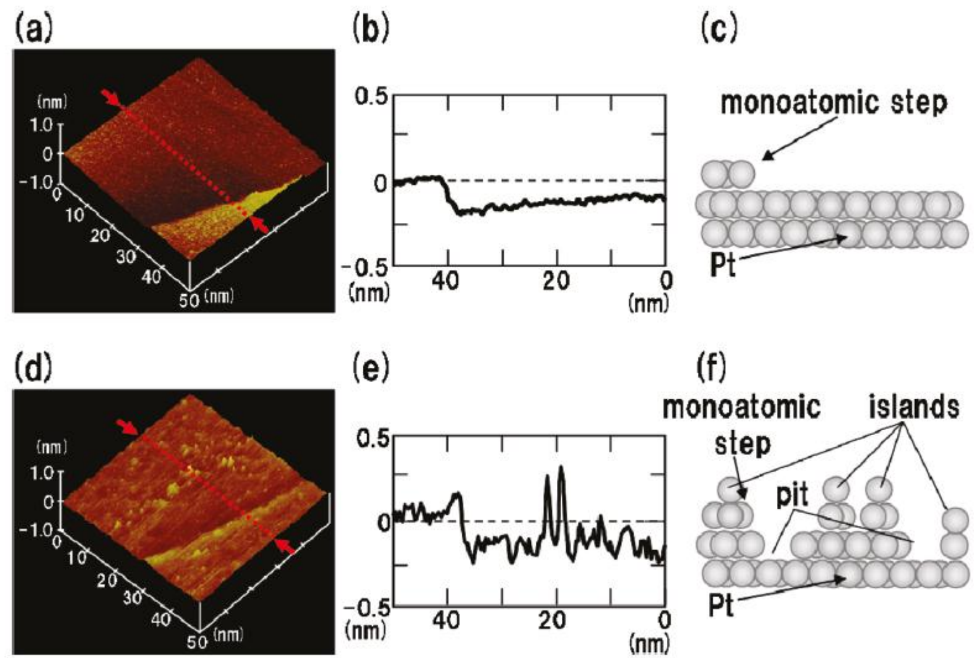


Figure 4. Amount of dissolved platinum in constant potential polarization experiments under N_2 (blue) and O_2 (red). Overall polarization time was 50 h.

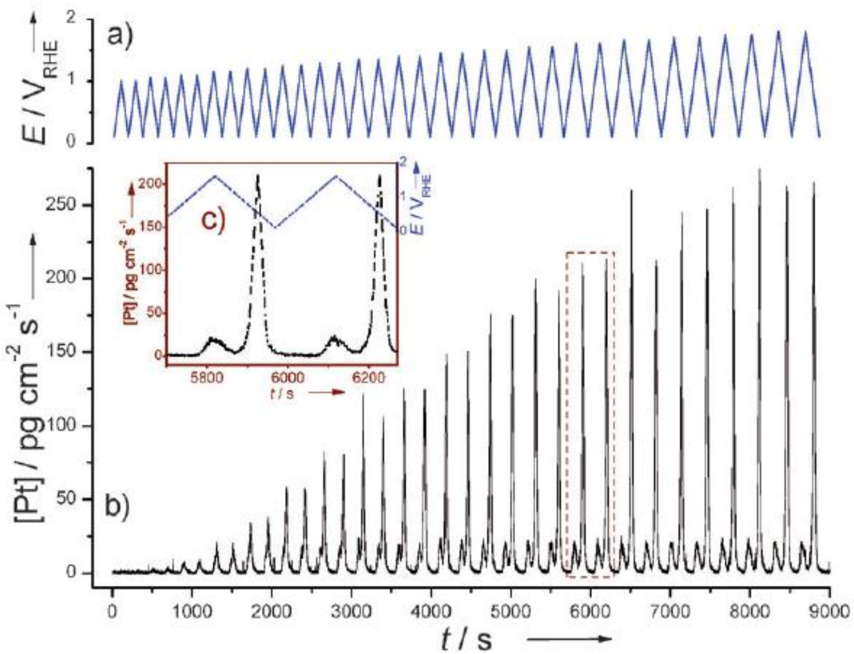




- In presence of O_2, place-exchange occurs even at low potential, causing cathodic dissolution of Pt.
- GM confirmed sub-surface oxygen at low potential on Pt/C *(JPCC 2012)*
- What does this mean to us? How can we better avoid Pt dissolution?

New tools: Realtime-resolution electrochemical ICP-MS

Mayrhofer and coworkers, Angew. Chem. 2012



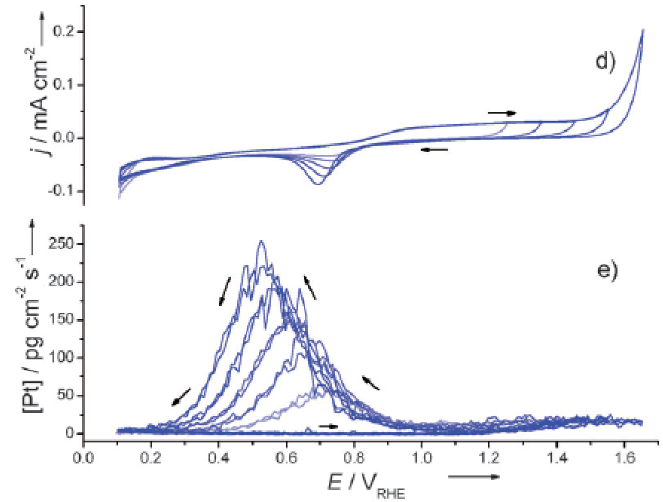


Figure 1. a) The applied experimental sequence in 0.1 M $HClO_4$, consisting of two cyclic voltammograms with a scan rate of 0.01 Vs^{-1} for each potential window that always start from +0.1 V_{RHE} to an upper potential limit between +1.0 and +1.8 V_{RHE} raised in steps of 0.05 V_{RHE}. b) Corresponding time-resolved dissolution profile of Pt presented on the same time axis as in (a). c) A magnification on the region around 6000 s. d) Representative cyclic voltammograms with e) their corresponding mass-spectrometric voltammograms.

- Measure Pt dissolution in real time.
- Enable more detail mechanistic study to guide selection of operating condition.
- Help develop new catalysts.

Catalyst support

Catalyst Support

- Support forms a foundation for catalyst deposition, one cannot independently do support development without thorough knowledge of catalyst deposition.
- Such knowledge is held confidential by suppliers. Therefore, ***cathode*** catalyst support development should be left for private sector.
- ***Anode*** catalysts have less stringent requirements and are an area of great importance by offering potential saving by eliminating certain system controls and cell voltage monitoring.
- It is more easy to avoid high-voltage exposure on the cathode than on the anode.

Anode: Area of interest

1. Corrosion resistant support for anode
2. Anode catalysts with a high Pt surface area, or the removal of PGM all together

Future Foci

- Cathode catalyst
  - → High ECSA
    - ➢ More-aggressive core-shell alloy catalysts
    - ➢ Monolayer catalysts
- Anode catalyst
  - → High ECSA on corrosion-resistant support
- Learn to mitigate Pt dissolution.
  - → Materials solution
  - → Mechanistic study to guide operation