Tuning the Stability of $PtCu_3$/C ORR Electrocatalyst by Gold Decoration & Gold Doping

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Introduction: Carbon supported Pt alloy electrocatalysts are not stable during proton exchange membrane (PEM) fuel cell operating conditions. We hereby present an effective strategy of about 1%$_{atomic}$ gold addition to a $PtCu_3$/C oxygen reduction reaction (ORR) electrocatalyst that reduces the rate of two key degradation mechanisms – corrosion of carbon support & removal of less noble metal without any trade-off in ORR activity.[1] The addition of gold results in either **gold decoration** or **gold doping** of the $PtCu_3$/C ORR electrocatalyst.

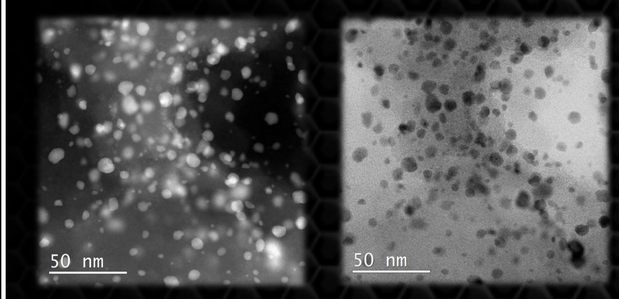
Synthesis

As prepared ($PtCu_3$/C)
- Galvanic displacement (GD) of K_2PtCl_4 with Cu/C
- 5 mM $KClO_4$ (aq), RT, CO purge
- Annealing: 600 °C, Ar, 12h
- 2 grams batch

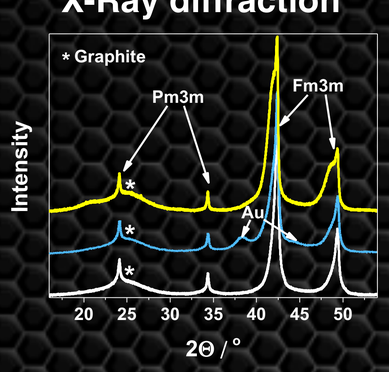
CO annealed
- Annealing of $PtCu_3$/C in CO, 500 °C, 3h

Gold decorated
- GD of $HAuCl_4$ with superficial Cu on $PtCu_3$/C
- 5 mM $KClO_4$ (aq), RT, Ar purge
- 100 mg batch

Gold doped
- Annealing of Gold decorated $PtCu_3$/C in CO, 500 °C, 3h

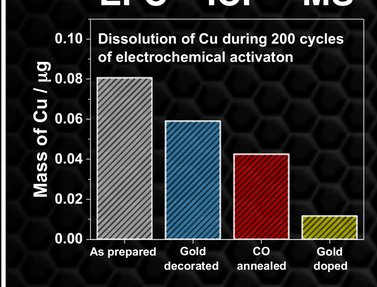


X-Ray diffraction

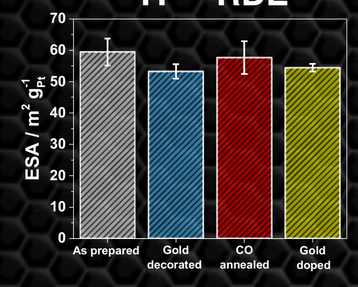


Electrochemical activation (all samples)
- 0.05 – 1.2 V_{RHE}, 300 mV, 200 cycles, 0.1M $HClO_4$

EFC – ICP – MS



TF – RDE



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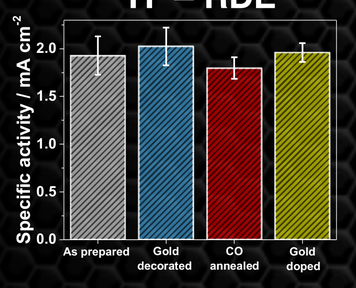

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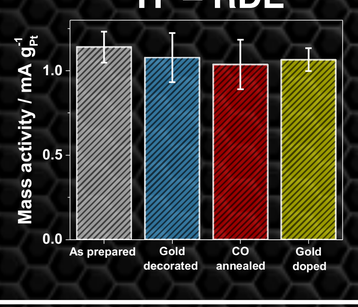
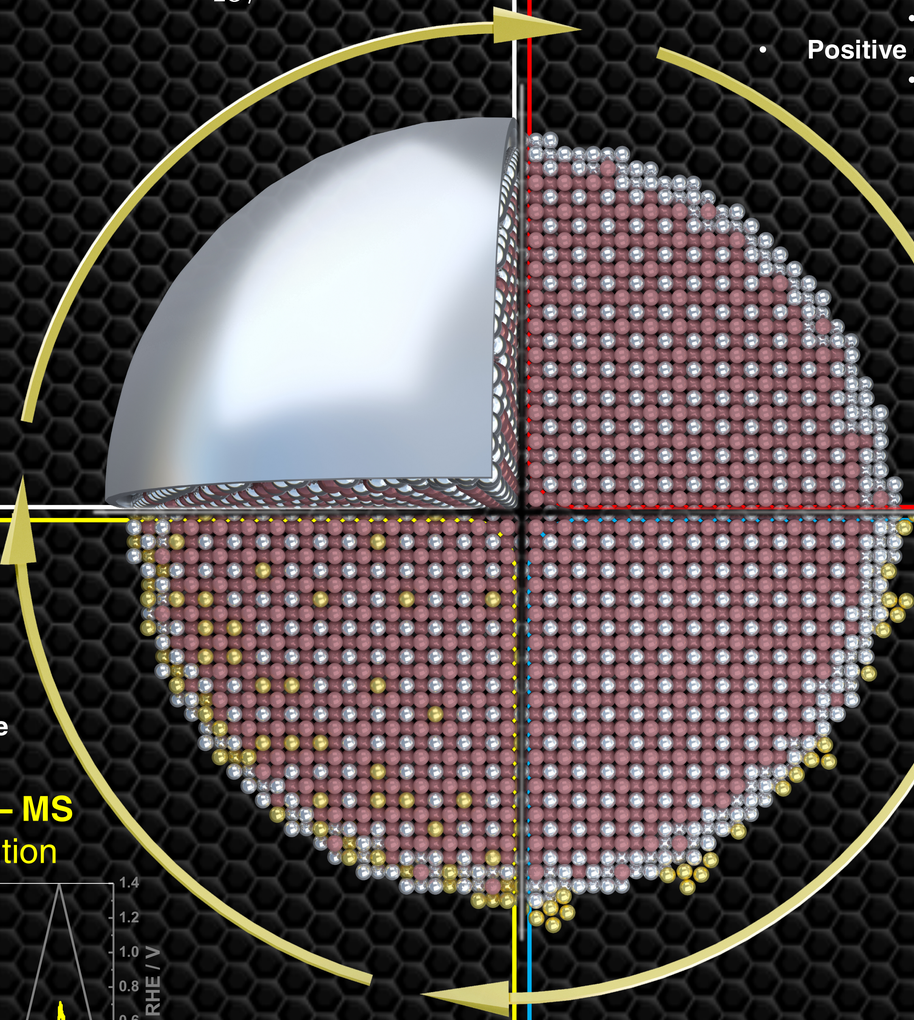
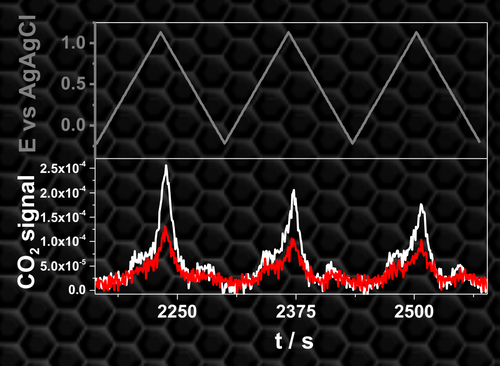


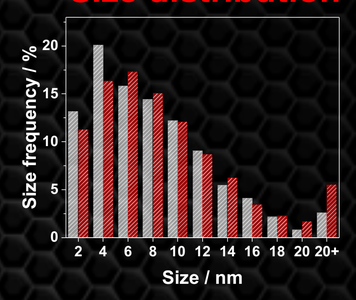


Effect of CO annealing

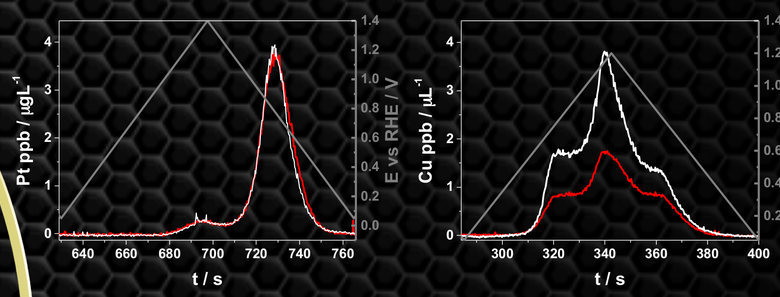
SFC – OLEMS *In-situ* monitoring of carbon electrooxidation
- Positive effect on carbon corrosion
- Appropriate annealing procedure is crucial to carbon stability
  - Possible effect on surface chemistry of carbon support
  - Comparison of ESA and size distributions before and after CO annealing makes the effect of lower contact area of NPs with carbon support due to NPs sintering insignificat to the observed difference in CO_2 signal



Size distribution

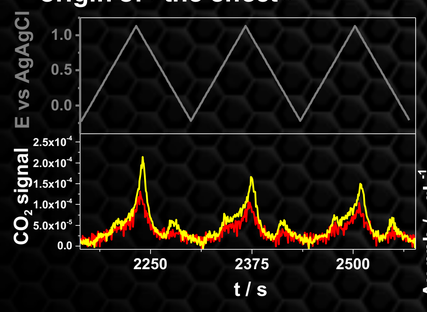


EFC – ICP – MS *In-situ* monitoring of dissolution of metals
- No effect on dissolution of platinum
  - This supports the claim on NPs sintering and contact area
- Positive effect on retention of Cu
  - Better Pt-skin uniformity due to Pt segregation by annealing in carbon monoxide atmosphere



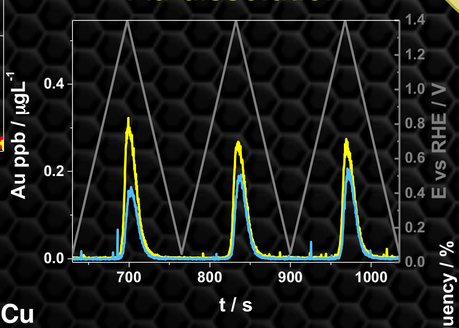
Effect of gold doping

SFC – OLEMS
- Inhibition of carbon corrosion is lost
- This supports the evidence that gold decoration is the origin of »the effect«

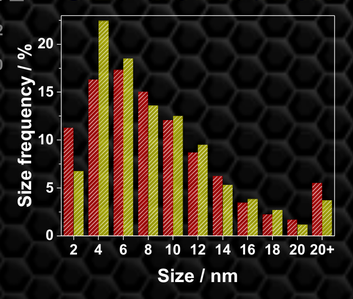


EFC – ICP – MS
- Positive effect on retention of Cu
  - Considerable effect on dissolution of Cu during electrochemical activation cycles
  - Less dissolution during slow cycles
- Slight increase in anodic[3] and only visible shift in cathodic dissolution of Pt.[4]
  - Higher Cu retention and more Pt-Cu coordination destabilizes Pt[3] in comparison to gold decoration
  - We can observe the same destabilization when comparing Au dissolution of gold decorated & gold doped samples

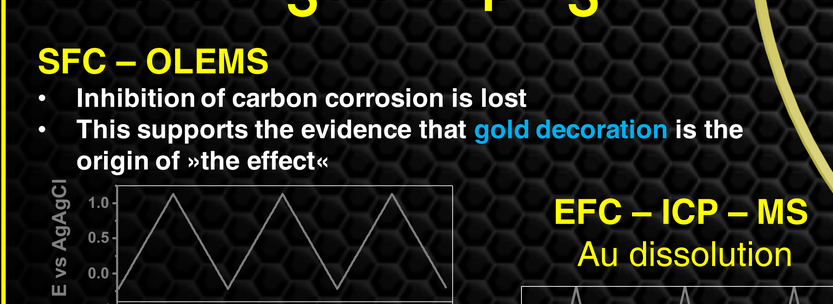
EFC – ICP – MS
Au dissolution



Size distribution

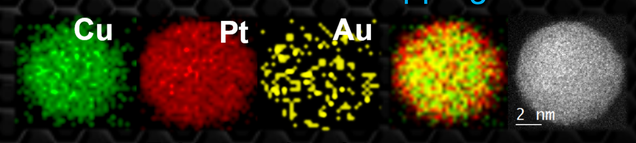


TEM
chemical mapping



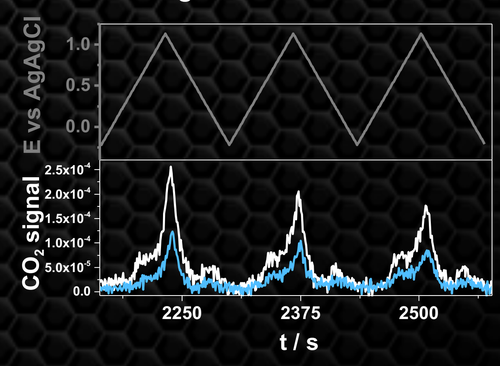
Effect of gold decoration

TEM chemical mapping

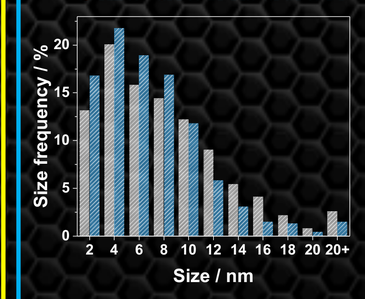


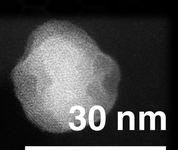
- Evidence of Pt rich surface
- Evidence of gold decoration

SFC – OLEMS
- Gold decoration considerably inhibits carbon corrosion
- The origin of the effect could be:
  - Lower contact area between NPs and carbon support
  - Gold decoration of Pt defects
  - Gold decoration of carbon surface

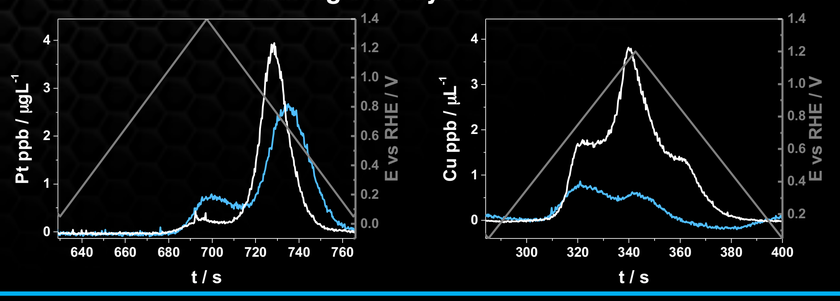


Size distribution





EFC – ICP – MS
- Increase in anodic and decrease in cathodic dissolution of Pt
- Gold decoration was shown to decrease Pt oxide formation[2]
- Positive effect on retention of Cu
  - Less dissolution during electrochemical activation cycles
  - Less dissolution during slow cycles
- GD with Au induces Cu dealloying



Conclusion:

In summary, we have successfully addressed two major corrosion mechanisms, i.e. corrosion of carbon support by and removal of less noble metal without a trade-off in ORR activity. We have demonstrated that **gold decoration** may be the key approach towards inhibition of carbon corrosion, while **gold doping** has a major effect on copper retention.

References:

1. Gatalo M. et. al. ACS Catal., **2016**, 6 , 1630–1634
2. Zhang J. et. al. Science, **2007**, Vol. 315, Issue 5809, 220-222
3. Jovanovic P. et. al. *J. Power Sources*, **2016**, accepted manuscript
4. Cherevko S. et. al. *J. Electrochem. Soc.* **2016**, vol. 163, Issue 3, 228–233

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