

2016 AMFC Workshop

4/1/16, Phoenix, AZ

AMFC Challenges: Electrocatalysis

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Engineering



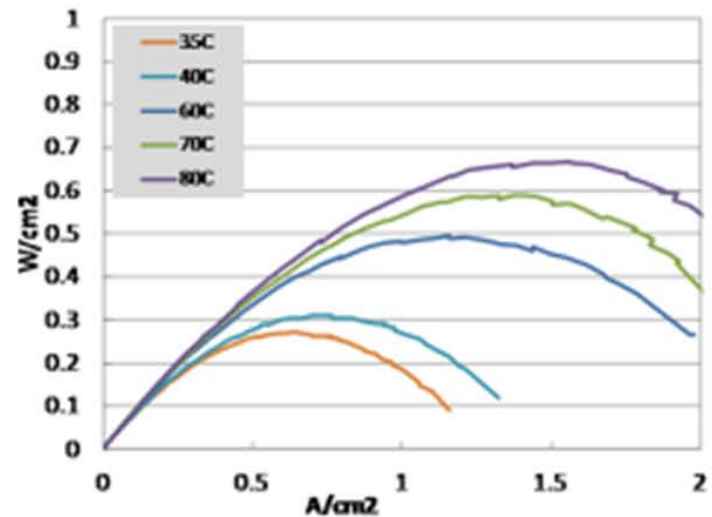
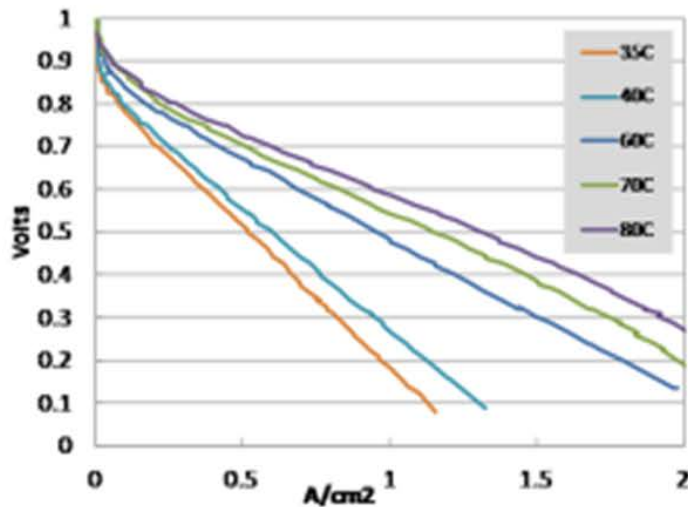
HEMFC: ORR Catalyst Activity

- Current status:
 - Numerous PGM-free catalysts can match Pt/C by activity in RDE, but with much higher mass loading (e.g. 10x loading) [1]
 - A PGM-free catalyst with activity matching Pt/C in high performance MEA has been demonstrated with **H₂/air**[2]
- Research targets:
 - Demonstrate PGM-free catalysts with activity matching Pt/C by RDE, at same volume/mass loading (a standard protocol is desirable)
 - **Demonstrate PGM-free catalysts with activity matching Pt in high performance MEA (e.g. 500 mW/cm² peak power density, 80 °C, H₂/O₂) (a standard protocol is desirable)**

1. Hoon T. Chung, Jong H. Won & Piotr Zelenay NATURE COMMUNICATIONS | DOI: 10.1038/ncomms2944
2. Dekel et al. PRiME 2012, Hawaii

HEMFC: ORR Catalyst Activity

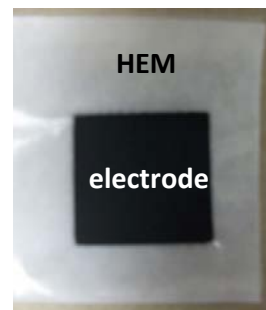
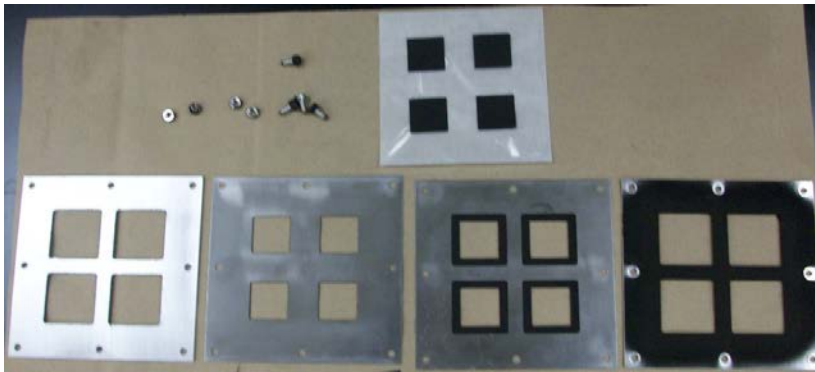
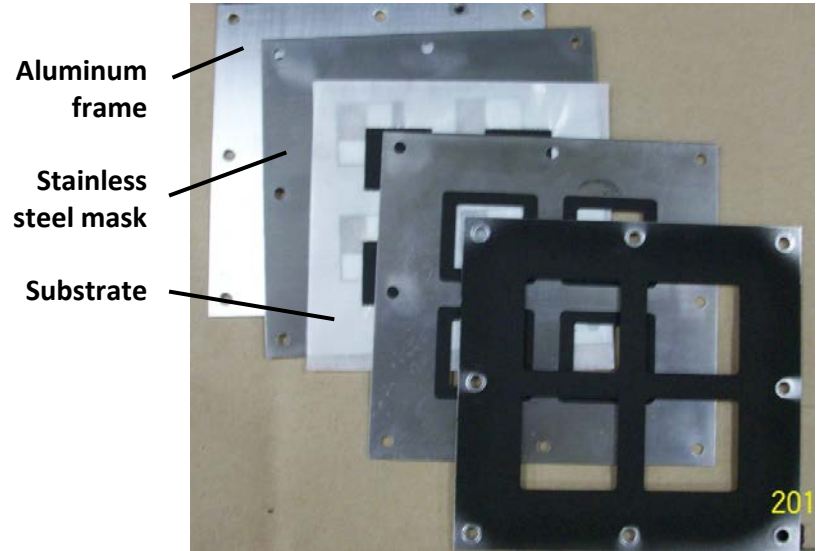
Early studies on non-Pt cathode catalysts



Pt anode / zero-Pt cathode, H₂ / air → 0.8V @330mA/cm² (680mW/cm²)

Dekel D.; Carisma 2012, Copenhagen, Denmark 2012
 Dekel D.; PRiME 2012, 222nd ECS Meeting, Honolulu, Hawaii 2012

Sono-Tek programmable electrode sprayer



730 peak power density at 80 °C, 100% RH, H₂/O₂, 250 kPa, Tokuyama membrane and ionomer

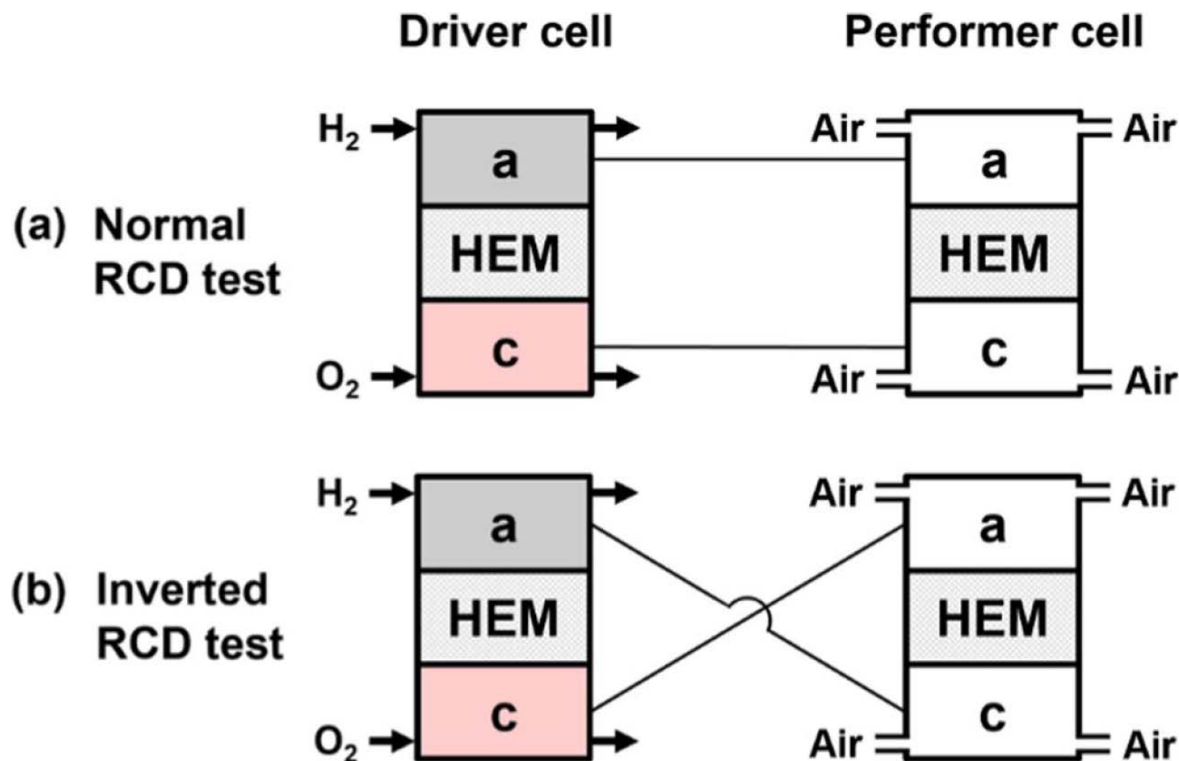
HEMFC: ORR Catalyst Durability

- Current status:
 - Carbon based PGM-free catalysts have better durability than Pt/C by RDE (by DOE RDE protocol for catalyst and support in acids)[1]
- Research needs
 - A standard RDE protocol is desirable
 - A standard MEA protocol is desirable
 - Carbon is undesirable due to possible reverse current delay, which may be managed by using a HOR catalyst with no ORR activity[1]

1. Kaspar ... Yan, *Journal of The Electrochemical Society*, **163** (5) F377-F383 (2016)

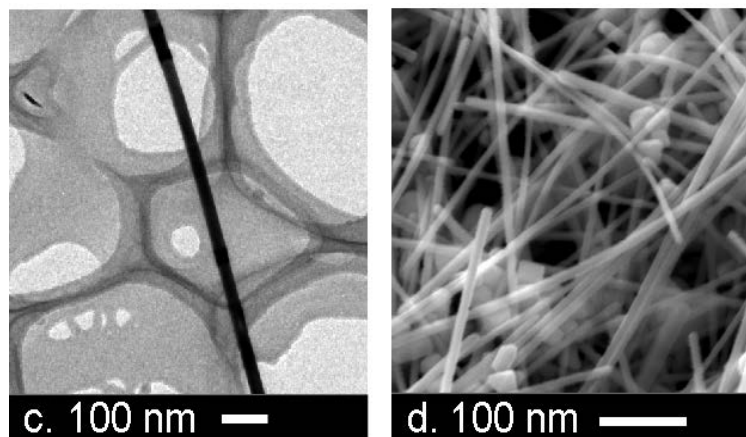
2. Wittkopf ... Yan, unpublished results

Reverse Current Decay (RCD) in HEMFC

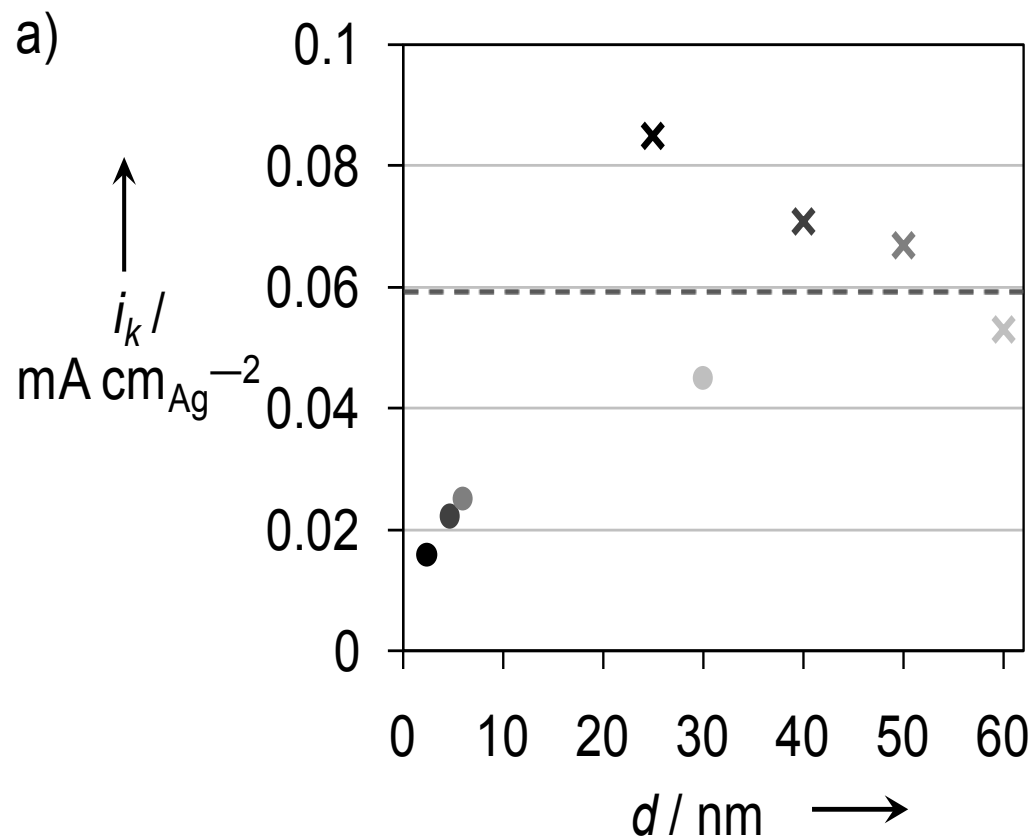


- RCD occurs on Pt/C cathode if anode catalyst has ORR activity
- PGM-free HOR catalyst should have no ORR activity
- **Carbon support should be avoided for HOR catalyst as carbon has ORR activity**

AgNW ORR Catalyst in base



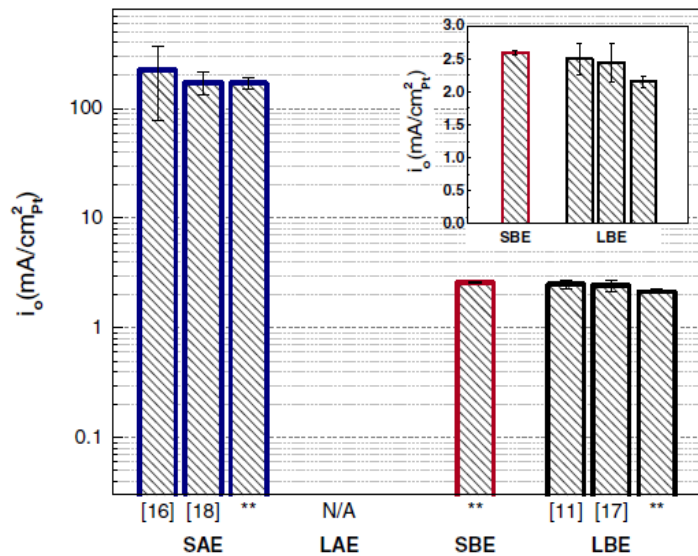
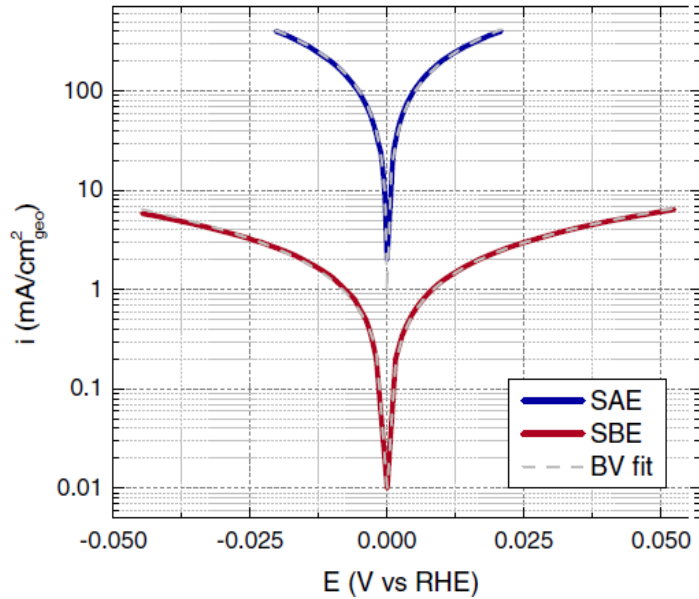
- Much higher specific activity than AgNP
- May offer better mass transport and better ionomer distribution in catalyst layer
- No carbon support corrosion



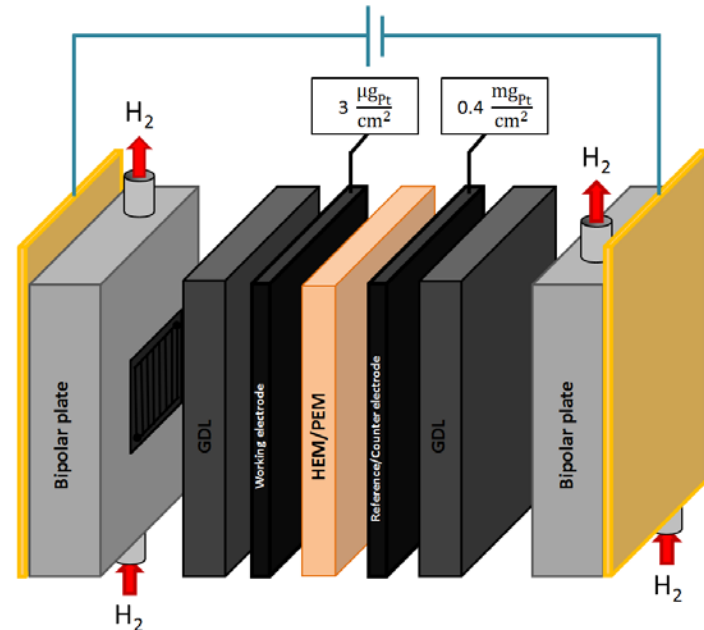
HEMFC: HOR Catalyst

- Current status:
 - PMG-free catalyst activity and stability
 - With exchange current density of 1/20 of that of Pt/C by RDE [1,2]
 - Passivate at 0.1 V vs RHE
 - A puzzle: PGMs are ~100 times less active in base than in acid [4]
- Research needs:
 - Understand why activity of PGMs is slower in base
- Research targets
 - PGM-free catalysts with activity matching Pt/C by RDE, at the same volume/mass loading (a standard protocol is desirable) and stable up to 0.3 V vs RHE (a standard protocol is desirable)
 - **PGM-free catalysts with activity matching Pt in high performance MEA (e.g. 500 mW/cm² peak power density, 80 °C, H₂/O₂) and stability (a standard protocol is desirable)**

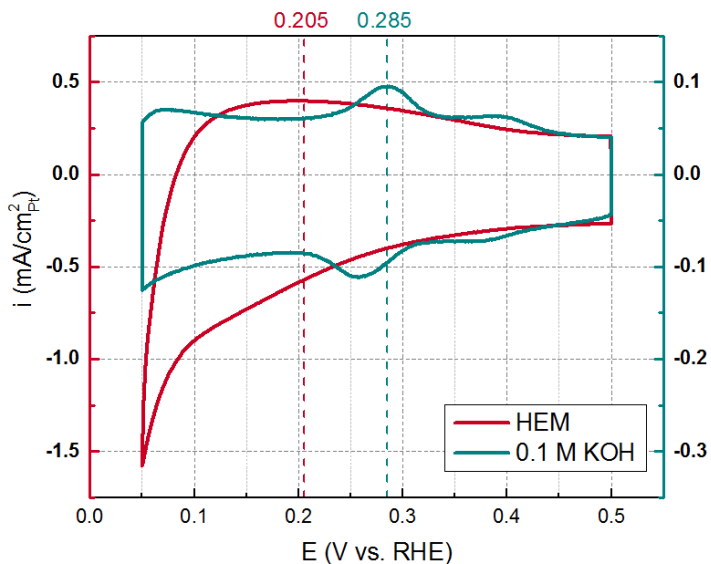
1. Sheng ... Yan. *Energy & Environmental Science* **2014**, 7, 1719-1724.
2. Zhuang ... Yan, *Nat Communications* **2016**, 7.
3. Woodroof ... Yan, *Electrochemistry Communications* **2015**, 61, 57–60
4. Durst ... Gasteiger, *Energy & Environmental Science* **2014**, 7, 2255-2260.



HOR Activity H₂ Pump vs RDE



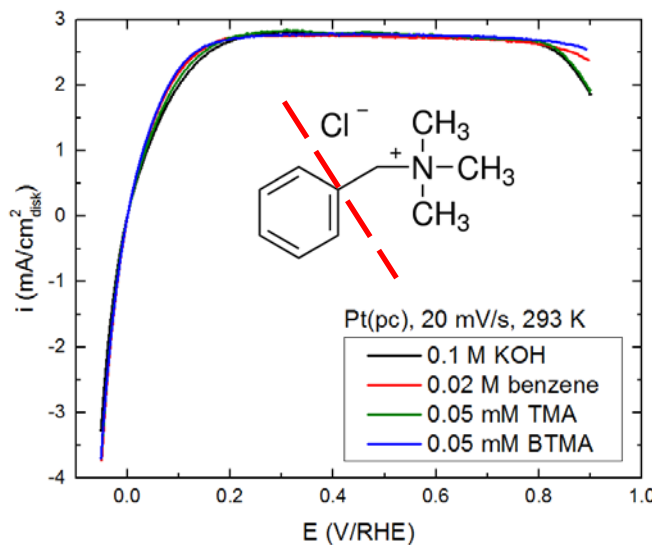
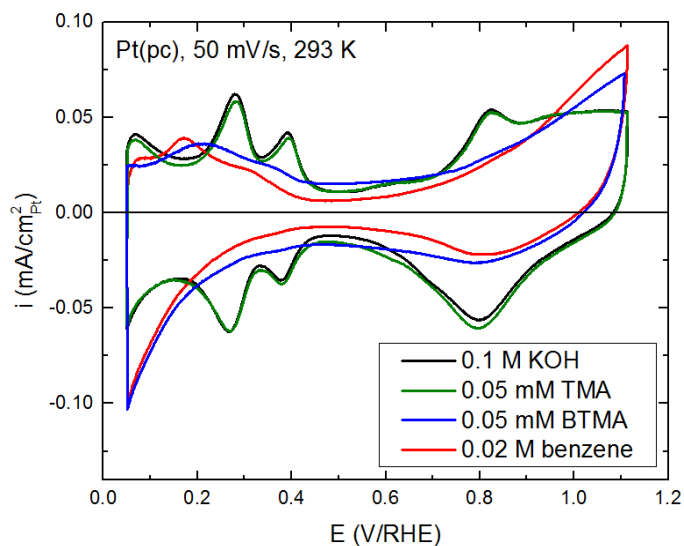
| Electrolyte | ECSA (m ² _{Pt} /g ² _{Pt}) | i_0 (mA/cm ² _{Pt}) |
|-------------|--|---|
| LAE | 96 | - ^a |
| LBE | 58 | 2.15 ± 0.09 |
| SAE | 97 | 171 ± 21 |
| SBE | 23 | 2.60 ± 0.03 |



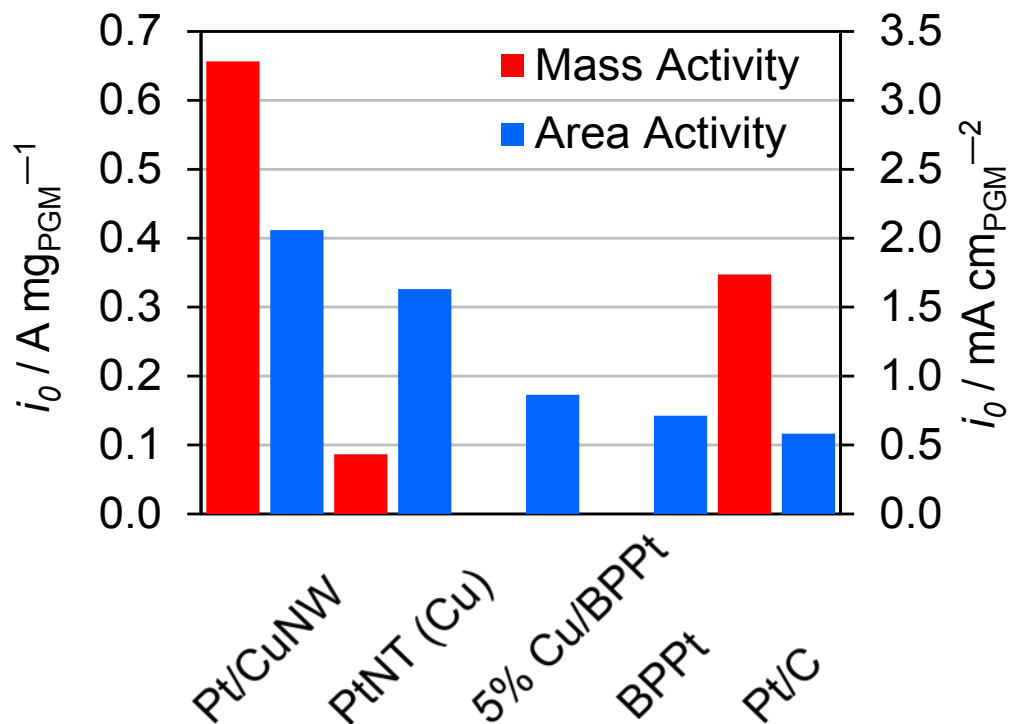
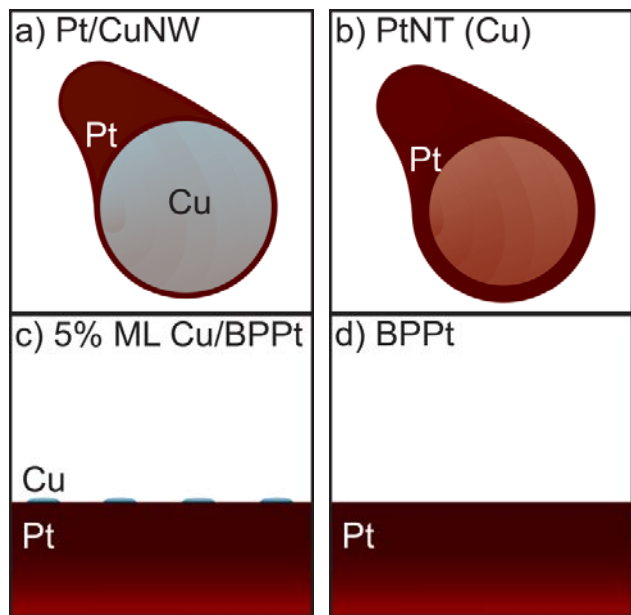
Cation adsorption onto Pt hinders ORR

What about HOR?

- In situ CV in H₂ pump looks different from liquid KOH. why?
- Due to BTMA? Yes.
- Which part of BTMA: TMA or benzene?
- Not TMA because it has no impact on CV.
- It is benzene; benzene adsorbs at > 0.3 V vs. RHE.
- However, adsorption of benzene, BTMA, or TMA does NOT significantly affect HOR activity.



HEMFC: HOR particle size effect



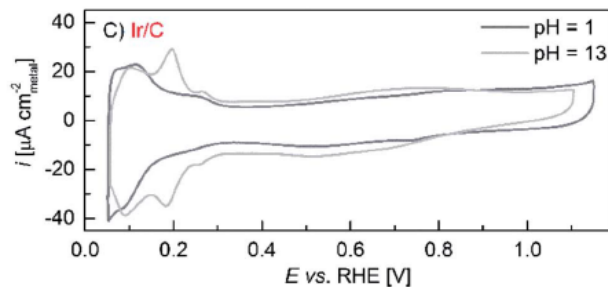
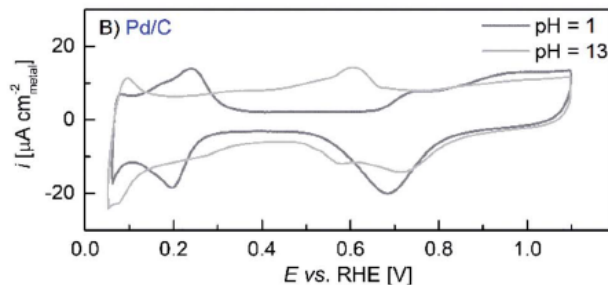
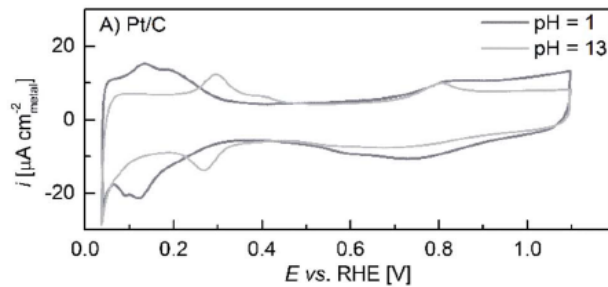
Extended surface Ir and Pd have higher HOR activity in base
Lattice strain helps Pt HOR activity in base

Pd: Zheng, ... Xu, Yan, *JECS*, **2016**

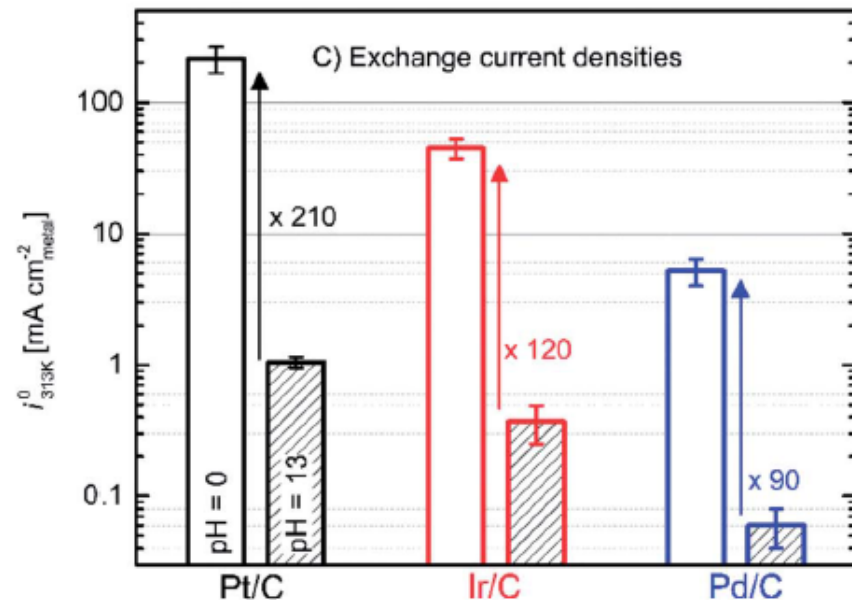
Ir: Zheng, Zhuang, Xu, Yan, *ACS Catal.* **2015**, 5, 4449–4455

Pt: Alaj, Pivovar, Yan, *J. Am. Chem. Soc.* **2013**, 135, 13473–13478

HEMFC: HOR catalyst is a major barrier



- H_{upd} peak locates at higher potential at pH = 13 than pH = 1



$$\frac{r_{pH=0}}{r_{pH=13}} \approx \exp[\Delta E_{\text{binding}}/RT]$$

$$\Delta E_{\text{binding}} = F\Delta E_{H-UPD} \approx 12.5 \text{ to } 13.5 \text{ kJ/mol}$$

$$\frac{r_{pH=0}}{r_{pH=13}} \approx 120 - 200$$

PGMs are ~100 times less active in base than in acid

Fundamentals: Reaction mechanisms and kinetics

Reaction mechanism:

| | Acid | Base |
|-----------|--|--|
| Overall | $H_2 \leftrightarrow 2H^+ + 2e$ | $H_2 + 2OH^- \leftrightarrow 2H_2O + 2e$ |
| Tafel | $H_2 + 2 * \leftrightarrow 2H_{ad}$ | $H_2 + 2 * \leftrightarrow 2H_{ad}$ |
| Heyrovsky | $H_2 + * \leftrightarrow H_{ad} + H^+ + e$ | $H_2 + OH^- + * \leftrightarrow H_{ad} + H_2O + e$ |
| Volmer | $H_{ad} \leftrightarrow H^+ + e + *$ | $H_{ad} + OH^- \leftrightarrow H_2O + e + *$ |

Reaction kinetics:

| Pathway | Rate equation |
|---|---|
| Tafel (RDS)-Volmer | $i_k = i_{0,T} \frac{\exp\left(\frac{2F}{\eta RT}\right) - 1}{[\theta_H^0 + (1 - \theta_H^0) \exp\left(\frac{F}{\eta RT}\right)]^2}$ |
| Tafel – Volmer (RDS) or Heyrovsky-Volmer (RDS) | $i_k = 2 i_{0,V} \left[\frac{\theta_H}{\theta_H^0} \exp\left(\frac{\alpha_V F}{\eta RT}\right) - \frac{1 - \theta_H}{1 - \theta_H^0} \exp\left(\frac{(\alpha_V - 1)F}{\eta RT}\right) \right]$ |
| Heyrovsky(RDS)-Volmer | $i_k = 2 i_{0,H} \left[\frac{1 - \theta_H}{1 - \theta_H^0} \exp\left(\frac{\alpha_H F}{\eta RT}\right) - \frac{\theta_H}{\theta_H^0} \exp\left(\frac{(\alpha_H - 1)F}{\eta RT}\right) \right]$ |
| Diffusion as RDS | $\eta = -\frac{RT}{2F} \ln\left(1 - \frac{i}{i_{l,a}}\right) + \frac{RT}{2F} \ln\left(1 - \frac{i}{i_{l,c}}\right)$ |

Reaction pathway

| Catalyst | Electrolyte | Pathway | Observation | Ref |
|---------------------|--|---------------------------|--|---------------------------------------|
| Pt | 96 wt% H ₃ PO ₄ | Tafel (RDS)-Volmer | Similar reaction kinetic rates between HOR and H ₂ -D ₂ exchange reaction | Vogal et al. 1975 |
| Pt | 0.1 M H ₂ SO ₄ | Tafel(RDS)-Volmer | An additional HOR limiting current attributed to the limiting rate of Tafel step | Chen et al. 2004; Wang et al. 2006 |
| Pt/C, Ir/C, Pd/C | H ₂ -pump in a PEMFC configuration/ 0.1 M KOH | Volmer (RDS) | Butler-Volmer fitting ($\alpha_a + \alpha_c = 1$) yields $\alpha_a \approx 0.5$ | Durst et al. 2014 |
| Pt/C | 1 M HClO ₄ | Tafel(RDS)-Volmer | ΔG_{+H}^0 (294 meV) > ΔG_{+T}^0 (195 meV) > ΔG_{-V}^0 (177 meV) (fitted from a dual pathway model) | Elbert et al. 2015 |
| Pt/C | 1 M KOH | Tafel-Volmer(RDS) | ΔG_{+H}^0 (475 meV) > ΔG_{-V}^0 (352 meV) > ΔG_{+T}^0 (305 meV) (fitted from a dual pathway model) | Elbert et al. 2015 |

W. Vogel, L. Lundquist, P. Ross and P. Stonehart, *Electrochimica Acta*, 20, 79 (1975).

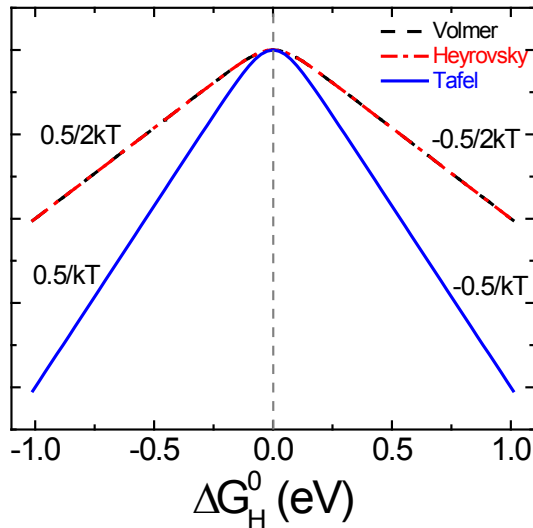
S. Chen and A. Kucernak, *The Journal of Physical Chemistry B*, 108, 13984 (2004).

J. X. Wang, T. E. Springer and R. R. Adzic, *Journal of The Electrochemical Society*, 153, A1732 (2006).

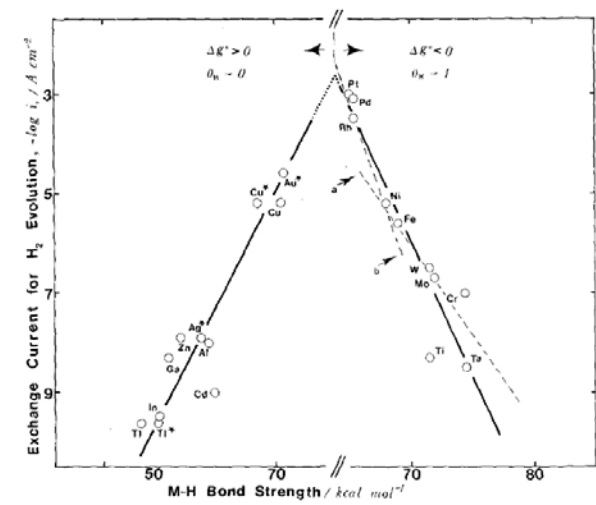
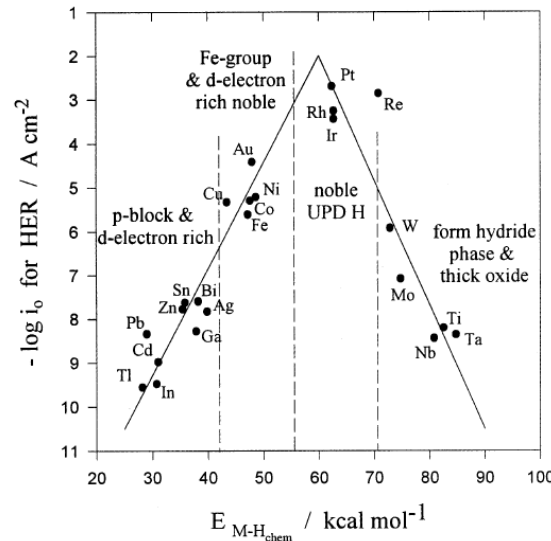
J. Durst, A. Siebel, C. Simon, F. Hasche, J. Herranz and H. A. Gasteiger, *Energy & Environmental Science*, 7, 2255 (2014).

K. Elbert, J. Hu, Z. Ma, Y. Zhang, G. Chen, W. An, P. Liu, H. S. Isaacs, R. R. Adzic and J. X. Wang, *ACS Catalysis*, 6764 (2015).

Volcano Plot



- Theoretical foundation
- Gas phase measured M-H bond strength



Hydrogen binding energy (HBE) is the descriptor

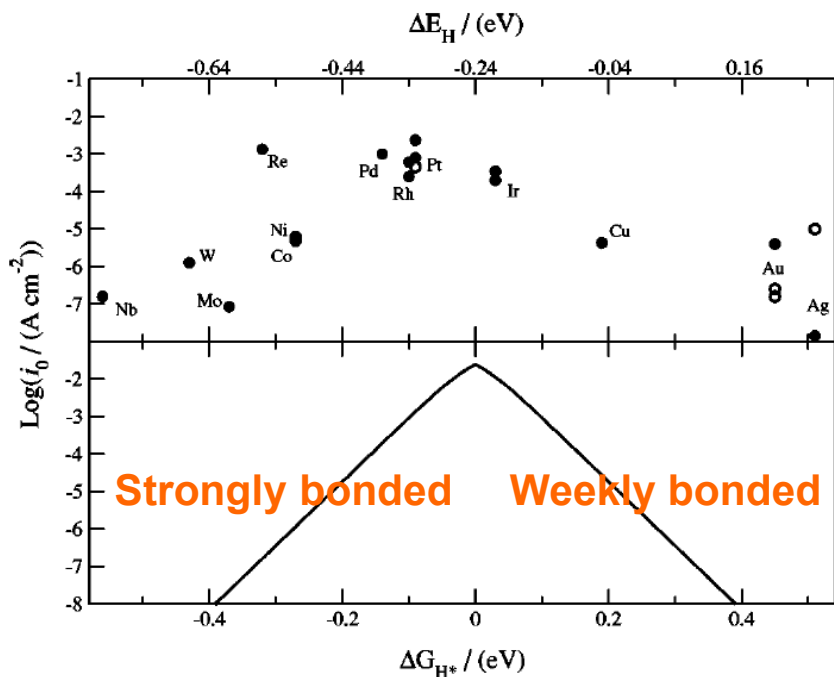
Parsons, R. *Transactions of the Faraday Society* **1958**, 54, 1053-1063.

Conway, B. E.; Tilak, B. V. *Electrochimica Acta* **2002**, 47, 3571-3594.

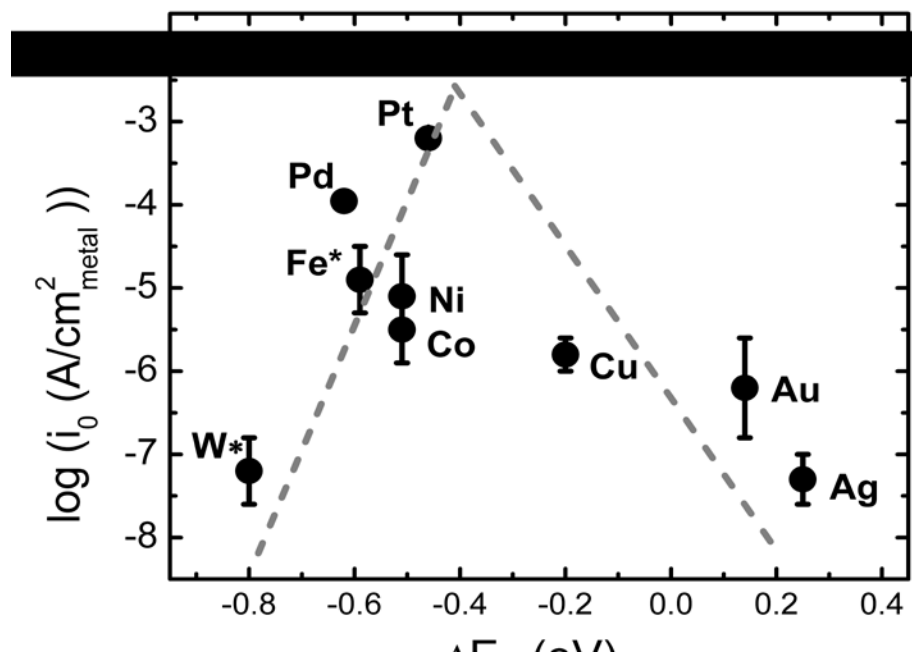
Trasatti, S. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1972**, 39, 163-184.

Volcano plots – DFT calculated HBE

Acid



Base



- Volcano plots obtained in both acid and base when HER exchange current densities were correlated to DFT-calculated HBE
- HBE is the descriptor for activity

HOR/HER measurement methods

- Rotating disk electrode [1]
 - Not possible at low pHs for some PGMs
- Ultramicroelectrode (UME) [2]
- Scanning electrochemical microscopy (SECM) [3]
- H₂-pump [4,5]
- Floating electrodes [6]
- Hanging-strip GDL method [7]

[1] Sheng, W.; Gasteiger, H. A.; Shao-Horn, Y. *Journal of The Electrochemical Society* **2010**, *157*, B1529-B1536.

[2] Chen, S.; Kucernak, A. *The Journal of Physical Chemistry B* **2004**, *108*, 13984-13994.

[3] Zhou, J.; Zu, Y.; Bard, A. J. *Journal of Electroanalytical Chemistry* **2000**, *491*, 22-29.

[4] Durst, J.; Siebel, A.; Simon, C.; Hasche, F.; Herranz, J.; Gasteiger, H. A. *Energy & Environmental Science* **2014**, *7*, 2255-2260;

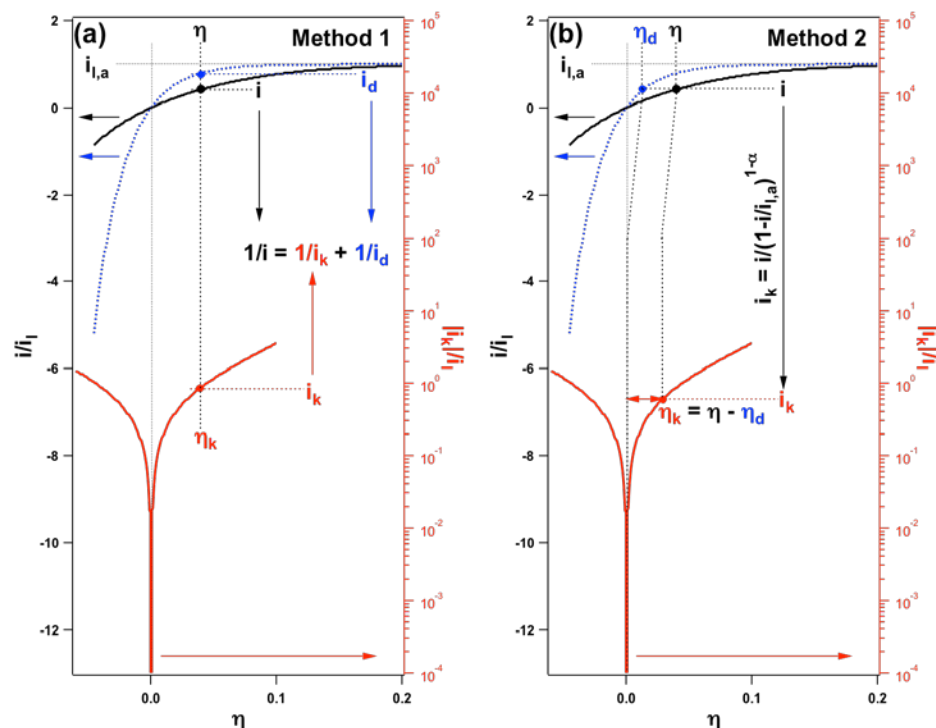
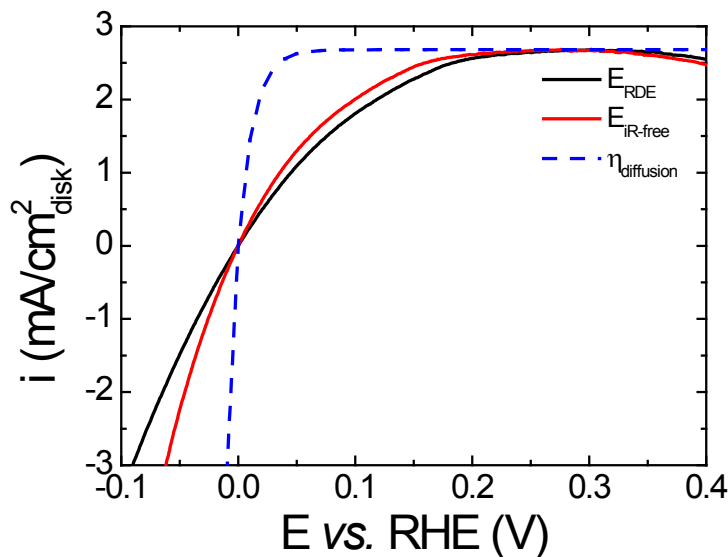
[5] Woodroof, M. D.; Wittkopf, J. A.; Gu, S.; Yan, Y. S. *Electrochemistry Communications* **2015**, *61*, 57-60.

[6] Zalitis, C. M.; Kramer, D.; Kucernak, A. R. *Physical Chemistry Chemical Physics* **2013**, *15*, 4329-4340.

[7] Wang, J. X.; Zhang, Y.; Capuano, C. B.; Ayers, K. E. *Scientific Reports* **2015**, *5*, 12220.

RDE: Kinetic current determination

$$\eta_{diffusion} = -\frac{RT}{2F} \ln\left(1 - \frac{i_d}{i_l}\right)$$

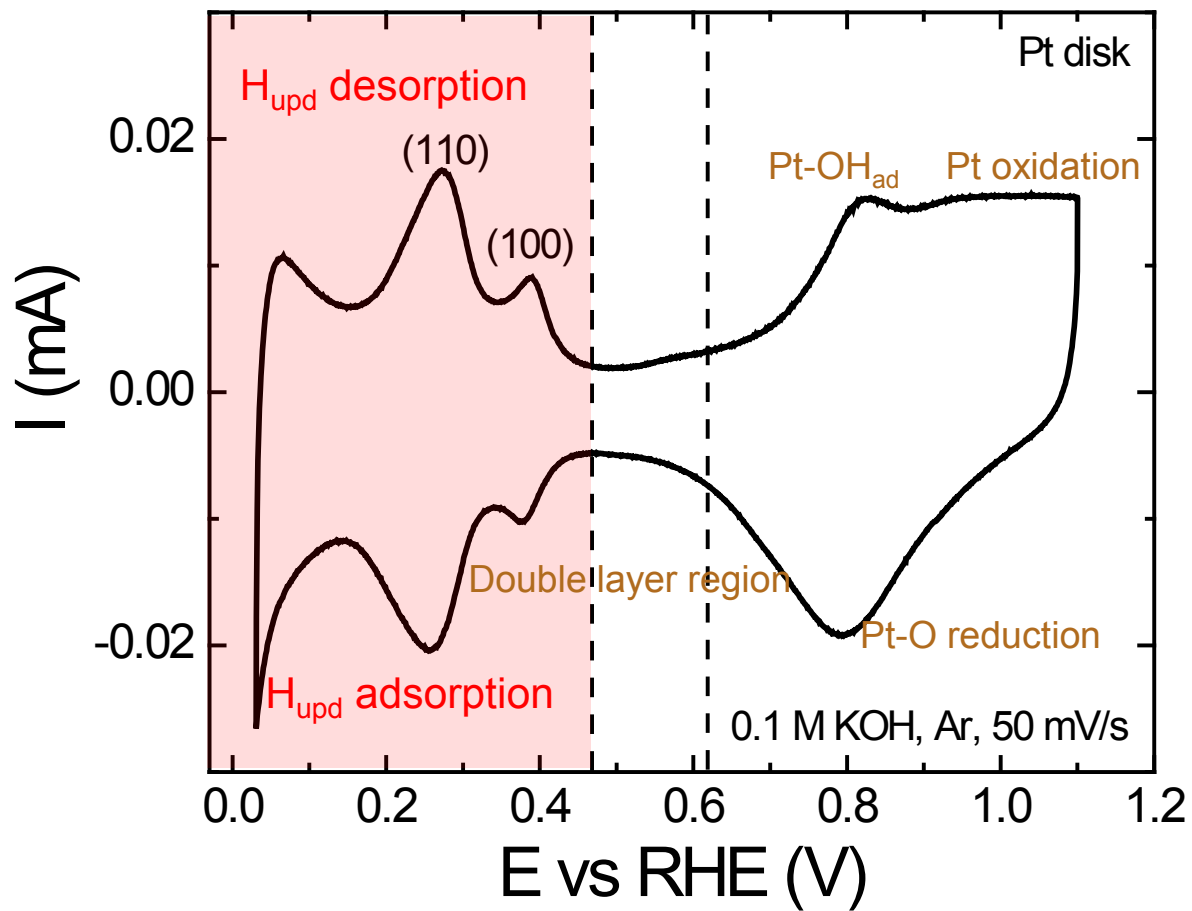


- Measured current is a convolution of kinetic current and diffusion current
- **How to determine kinetic current?**
- **Both HOR and HER branch needs correction**

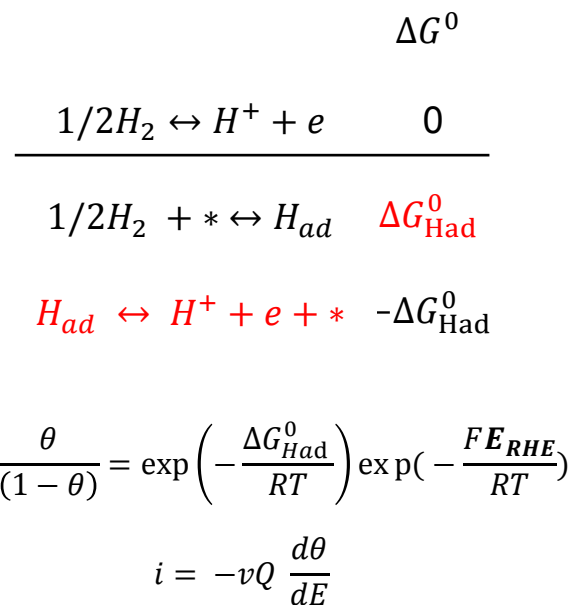
Why HOR is slower in base?

- Existing hypothesis
 - HBE is higher in base
 - OHad facilitates HOR in base
- HBE measurement
 - DFT
 - Gas phase adsorption
 - Both do not capture effects of solvent and electrolyte

Determine **apparent HBE** experimentally from CV



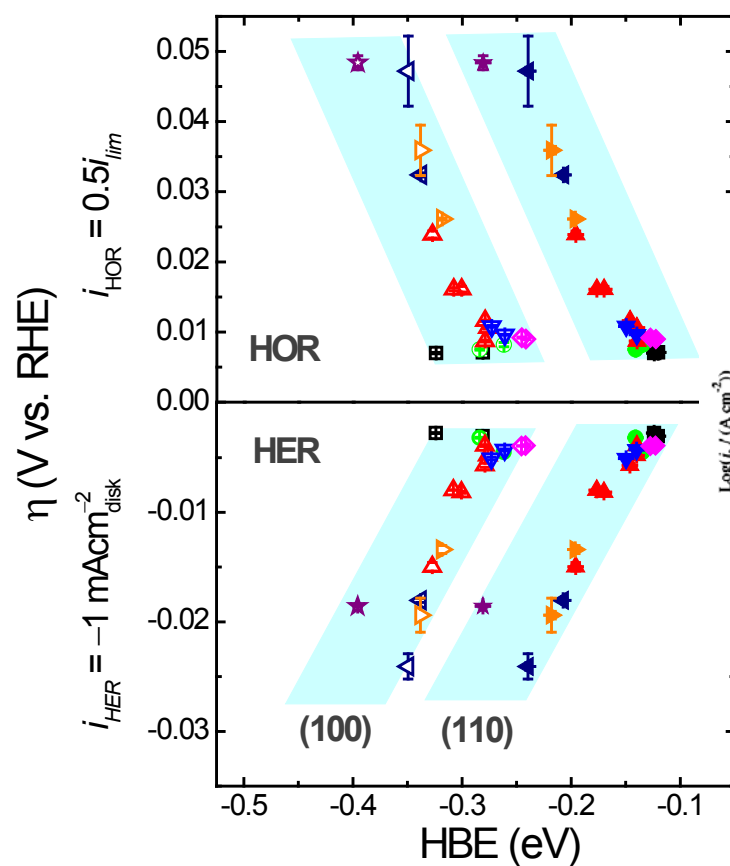
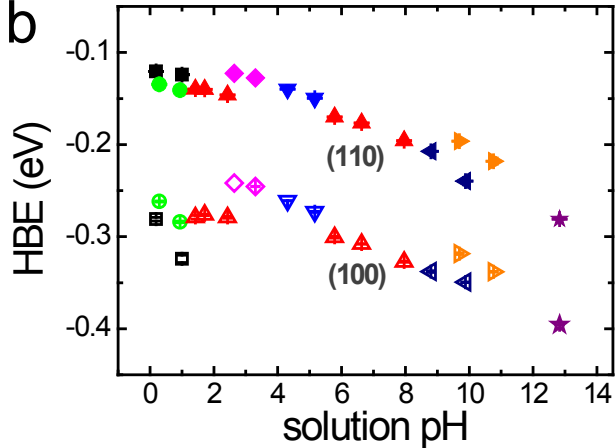
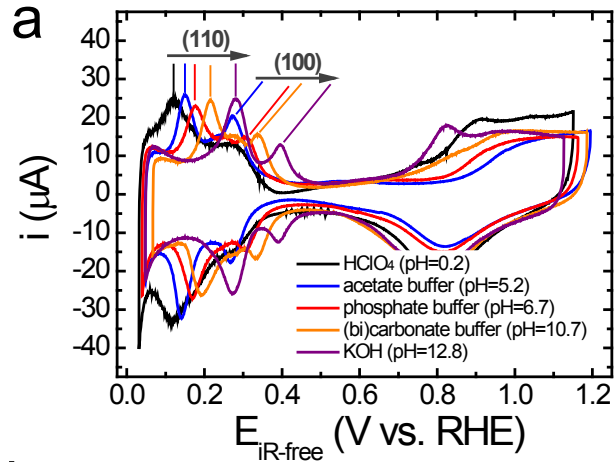
- Higher H_{upd} peak potential \rightarrow higher HBE



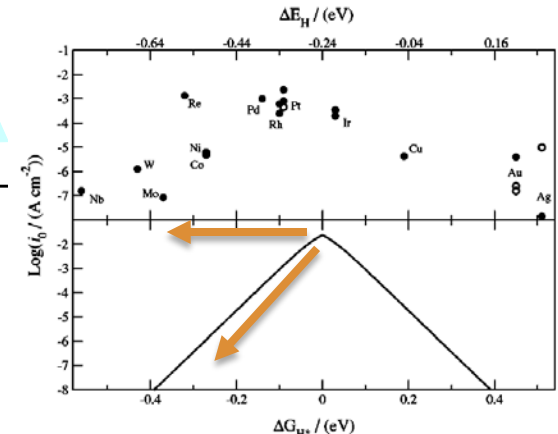
$$E_{peak,RHE} = -\frac{\Delta G_{Had}^0}{F}$$

$$HBE = -E_{peak}F - \frac{1}{2}S_{H_2}^0$$

pH-dependent HBE and activity in a broad pH range (Pt disk)



- Volcano plot in acid
- Almost zero overpotential for HOR on Pt



- As pH increases, HBE on Pt goes up
- So activity goes down which makes sense

- HBE increases as pH increases
- HOR/HER activity correlates well with HBE

i_0 and E_{peak} on Pt/C, Ir/C, Pd/C, Rh/C

- Arrhenius Equation**

$$i_0 = K \exp\left(-\frac{E_a}{RT}\right) \quad (1)$$

E_a is the activation energy

- Brønsted-Evans-Polanyi (BEP) principle**

$$E_a = E_0 + \beta \Delta H \quad (2)$$

E_0 is the activation energy of a reaction of the same class,
 ΔH is the enthalpy of reaction,
 β characterizes the position of transition state along the reaction coordinate ($0 \leq \beta \leq 1$)

- Relationship between ΔH and E_{peak}**

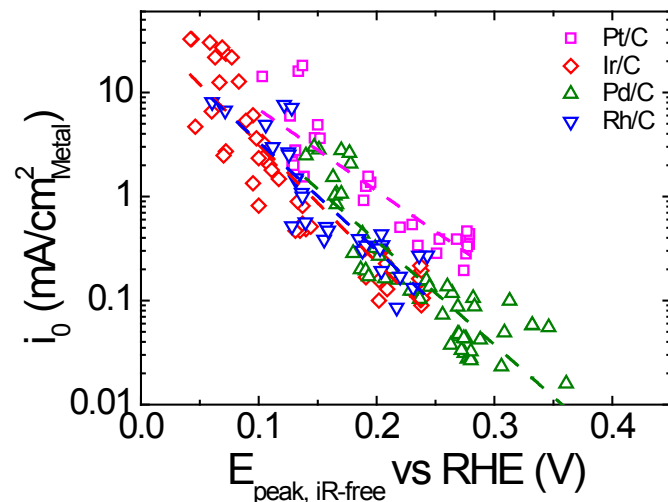
$$\Delta H_{H,desorption} = FE_{peak} + \frac{1}{2}TS_{H_2}^0 \quad (3)$$

$$i_0 = K \exp\left(-\frac{E_0 + \beta(FE_{peak} + \frac{1}{2}TS_{H_2}^0)}{RT}\right)$$

$$= \boxed{K \exp\left(-\frac{E_0 + \frac{1}{2}\beta TS_{H_2}^0}{RT}\right)} = A \exp\left(-\frac{\beta FE_{peak}}{RT}\right)$$

$$i_0 = A \exp\left(-\frac{\beta FE_{peak}}{RT}\right) \quad \text{or}$$

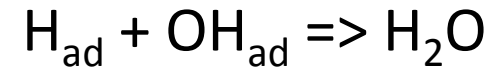
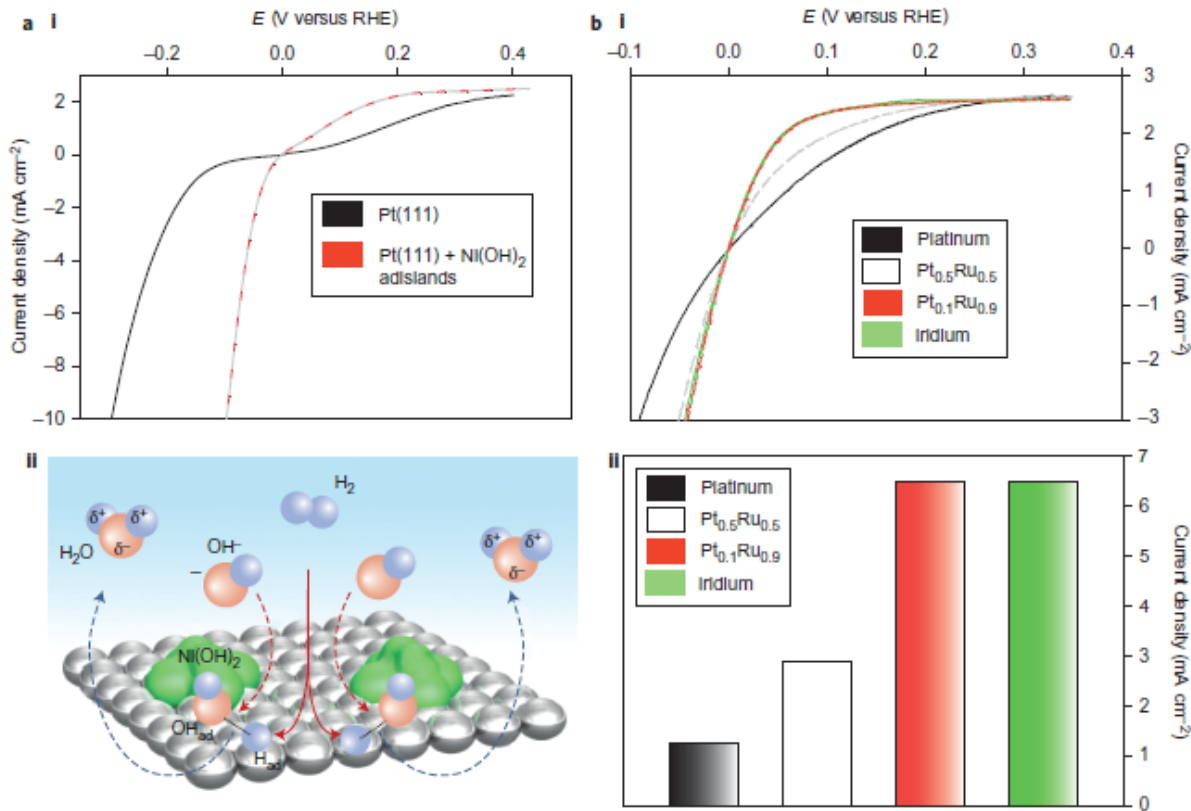
$$\log(i_0) = \log(A) - \frac{\beta FE_{peak}}{2.303 RT}$$



| $i_0 = A \exp\left(-\frac{\beta FE_{peak}}{RT}\right)$ | | |
|--|---------|----|
| | β | A |
| Pt/C | 0.5 | 59 |
| Ir/C | 0.8 | 68 |
| Pd/C | 0.6 | 37 |
| Rh/C | 0.6 | 36 |

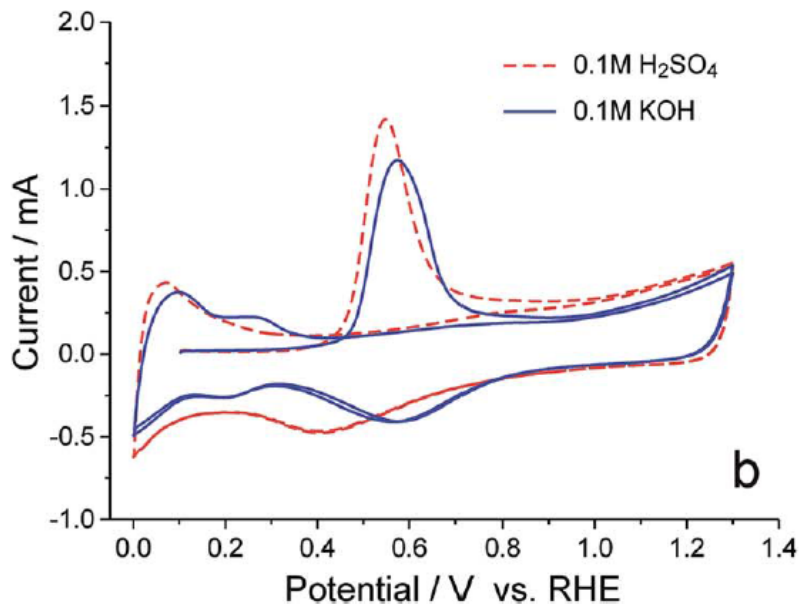
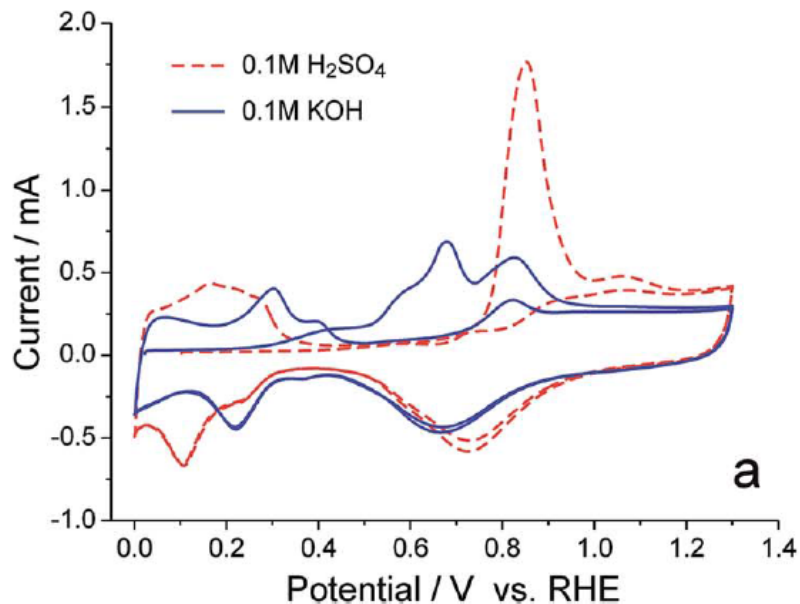
- **Activation energy correlates to HBE**
- **Correlation between HOR/HER activity and E_{peak} (or HBE) is independent of PGMs**

OH_{ad} promotes HOR in base



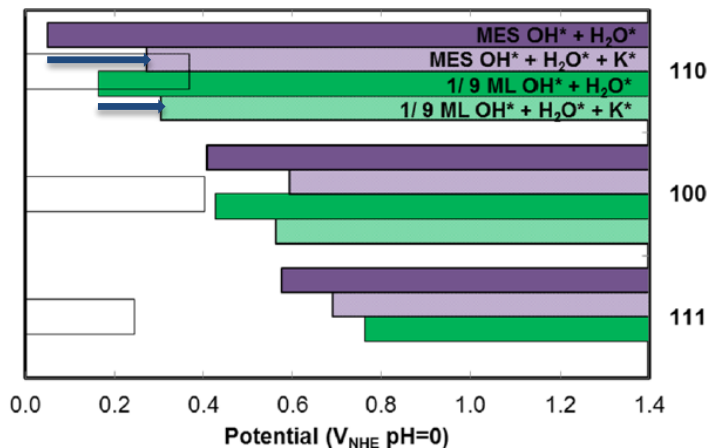
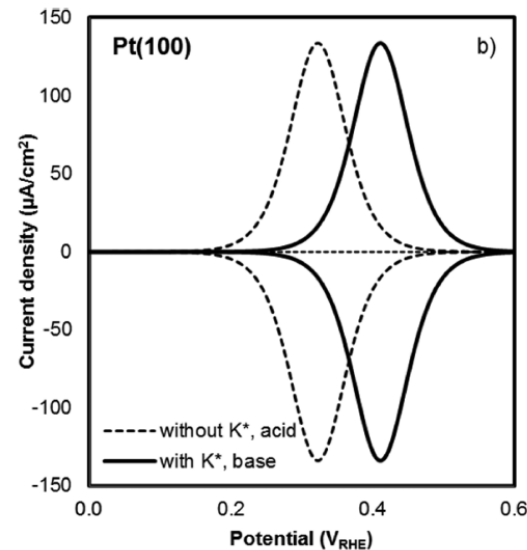
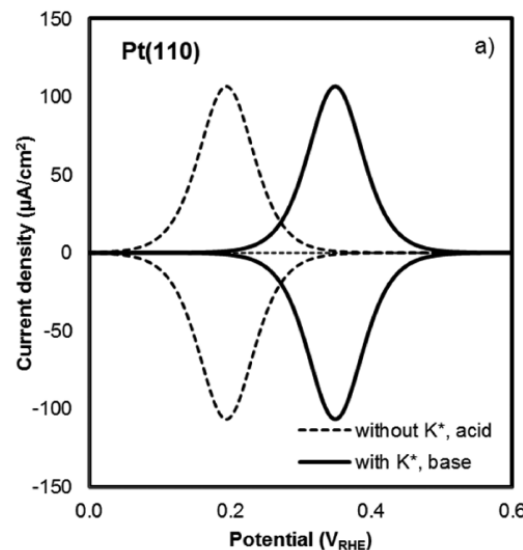
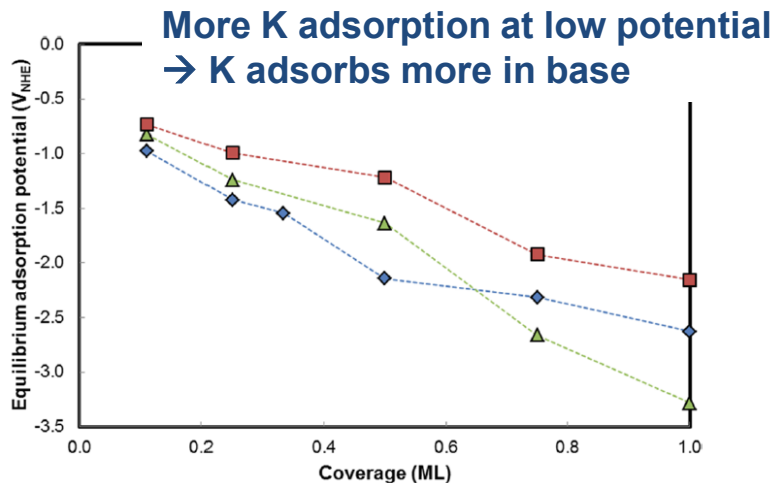
- Adsorbed OH_{ad} promotes HOR by facilitating removing H_{ad}

Improved HOR activity on PtRu: oxophilic effect?



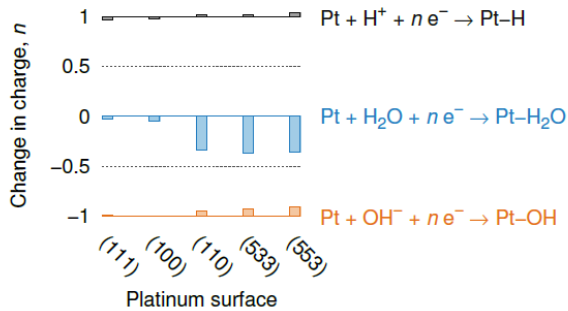
- Earlier CO onset potential on Pt in base than in acid
 - **Stronger OH binding on Pt in base than in acid,**
 - **which contradicts that HOR is slower in base**
- Earlier CO onset potential on Pt than on PtRu in base
 - Contradicts that Pt is a worse HOR catalyst than PtRu in base
- Better activity on PtRu cannot be explained by the **oxophilic effect**, but can be explained by **HBE**

$E_{\text{peak,upd}}$ vs pH: Coadsorption of K and OH



- The interaction of K and OH weakens OH adsorption strength
 - With K⁺ (or base), H_{upd} peak shift to more positive potential
- Higher pH leading to weaker OH adsorption is inconsistent with CO stripping data

$E_{\text{peak,upd}}$ vs pH: : Partial water oxidation



$$\text{Peak shift relative to RHE} = 59 - \frac{59}{n} \text{ mV/pH}$$

$$E = E_0 + \frac{RT}{nF} \ln[\text{H}^+]$$

| Species | Surface | Site | n |
|-----------------|---------|--------|-------|
| OH ⁻ | 111 | atop | -0.99 |
| | 100 | atop | -1.00 |
| | 110 | atop | -0.94 |
| | 533 | atop | -0.92 |
| | 553 | atop | -0.91 |
| H ⁺ | | atop | 0.97 |
| | 111 | fcc | 0.97 |
| | | hcp | 0.97 |
| | 100 | atop | 0.98 |
| | 110 | atop | 1.02 |
| | 533 | bridge | 1.02 |
| Water | | atop | 1.04 |
| | 553 | bridge | 1.02 |
| | 111 | atop | -0.03 |
| | 100 | atop | -0.04 |
| | 110 | atop | -0.34 |
| | 533 | atop | -0.37 |
| | 553 | atop | -0.36 |

| # waters | n | Shift (mV/pH unit, relative to RHE) |
|----------|------|-------------------------------------|
| 1 | 1.39 | 17 |
| 2 | 1.34 | 15 |

| System | Shifts [mV vs RHE / pH unit] | | | | | |
|----------|------------------------------|------------------|---------------------|----|-------------------------|----|
| | Experiment | | SaLSA ³⁰ | | LinearPCM ²⁷ | |
| | 0.1M | 0.2M | 0.1M | 1M | 0.1M | 1M |
| (553) | | 10 ⁵ | | | | |
| 110 step | 10 ¹² | 11 ¹¹ | 14 | 16 | 15 | 17 |
| (533) | | 10 ⁵ | | | | |
| 100 step | 8 ¹² | 11 ¹¹ | 14 | 16 | 15 | 17 |
| (110) | | | 11 | 13 | 14 | 16 |

- Partial water oxidation leads to $n > 1$ electron transfer
 - H_{upd} peak shift of $(59-59/n)$ mV/pH

Partial water oxidation at edge sites

Apparent HBE



$$\Delta G_{Had,app}^0 = \Delta G_{Had,vac}^0 - \Delta G_{H_2O}^0$$

$\Delta G_{H_2O}^0$ changes with pH and weaker water adsorption strength leads to stronger apparent HBE

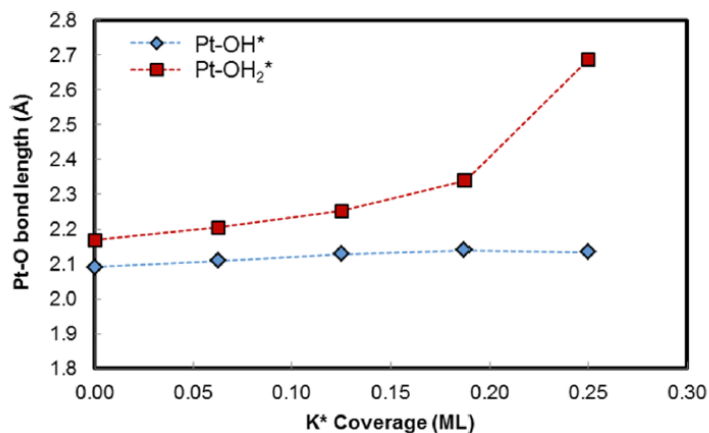


Figure 10. Pt–O bond length (Å) for adsorbed hydroxide and adsorbed water as a function of K* coverage (ML).

McCrum, I. T.; Janik, M. J. *The Journal of Physical Chemistry C* **2016**, *120*, 457-471.

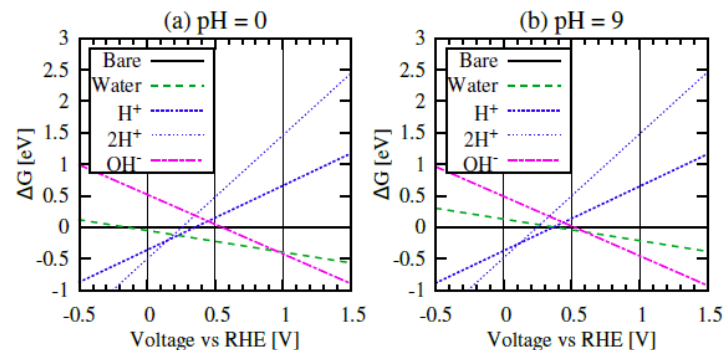


Fig. 4 Gibbs free energies of H⁺, water and OH⁻ adsorbed on the atop sites of the step edge of Pt(110), relative to the bare surface in (a) acid conditions, pH = 0 and (b) basic conditions, pH = 9. Free energies are estimated from calculations at 0 V vs SHE and include vibrational and entropic contributions (see Methods section for details).

Schwarz, K.; Xu, B.; Yan, Y.; Sundararaman R.; Physical Chemistry Chemical Physics, Submitted

Ni showed low HOR activity in base

| Catalyst | Evaluation | Activity | Ref |
|----------------------------|---------------------------------------|---|-------------------|
| Ti-containing Raney Ni | Alkaline fuel cell (6 M KOH) | $i_0 = 3 \text{ mA/cm}^2$ for Ti-Raney Ni; $i_0 = 0.4 \text{ mA/cm}^2$ for pure Raney Ni; | Mund et al. 1977 |
| Cr-doped Raney Ni | Alkaline fuel cell (6 M KOH) | $k = 1.3 \times 10^{-3} \Omega\text{cm}^3$ for Cr-Raney Ni; $k = 4.5 \times 10^{-3} \Omega\text{cm}^3$ for nondoped Raney Ni; (k: interfacial resistance) | Kenjo et al. 1985 |
| Raney Ni with carbon black | Alkaline fuel cell (6 M KOH) at 80 °C | Carbon black increases the diffusivity of OH ions at the electrode | Shim et al. 1998 |
| Cr-doped Ni | Solid HEMFC (Ag as cathode catalyst) | Peak power density $\approx 50 \text{ mW/cm}^2$ (Ni loading = 5 mg/cm ² , and Ag loading = 1 mg/cm ² , at 60 °C and 1.3 atm backpressure) | Lu et al. 2008 |
| Ni | Solid HEMFC (Ag as cathode catalyst) | Peak power density $\approx 78 \text{ mW/cm}^2$ (Ni loading = 5 mg/cm ² , and Ag loading = 0.5 mg/cm ² , at 70 °C) | Gu et al. 2013 |

K. Mund, G. Richter and F. V. Sturm, Journal of The Electrochemical Society, 124, 1 (1977).

T. Kenjo, Journal of The Electrochemical Society, 132, 383 (1985).

J.-P. Shim, Y.-S. Park, H.-K. Lee and J.-S. Lee, Journal of Power Sources, 74, 151 (1998).

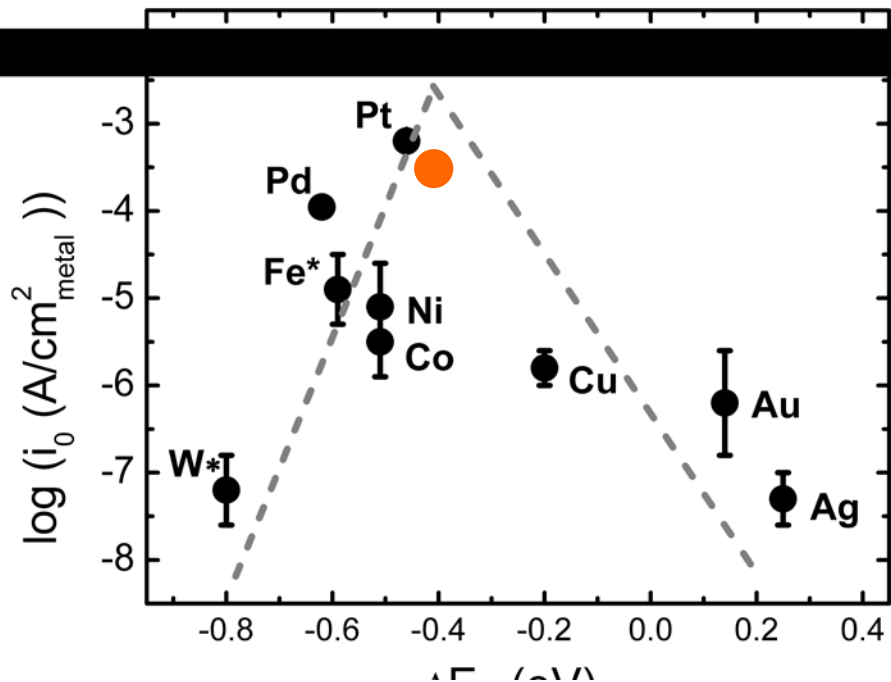
S. Lu, J. Pan, A. Huang, L. Zhuang and J. Lu, Proceedings of the National Academy of Sciences of the United States of America, 105, 20611 (2008).

S. Gu, W. Sheng, R. Cai, S. M. Alia, S. Song, K. O. Jensen and Y. Yan, Chem. Commun., 49, 131 (2013).

Weakened Ni-HBE on CoNiMo

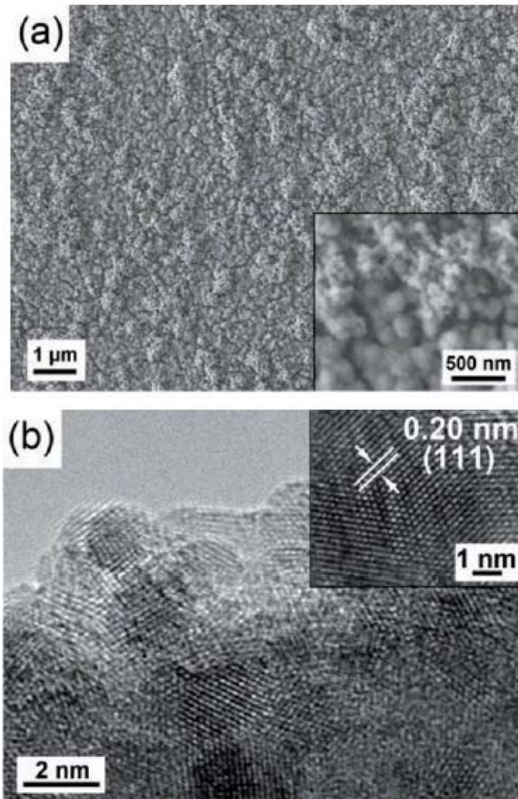
Table 2 Hydrogen binding energies from DFT calculations for the most energetically favorable binding site for each surface

| | Mo (110) | Ni (111) | Ni _{ML} /Mo (110) | CoNi/Mo (110) | Pt (111) |
|--|-------------|-------------|-------------------------------|------------------|-------------|
| Binding energy (eV) | -0.70 | -0.51 | -0.40 | -0.43 | -0.46 |
| Binding energy (kJ mol ⁻¹) | -67.6 | -49.5 | -38.6 | -41.6 | -44.7 |
| Binding site | Bridge | fcc | Bridge | Bridge | fcc |
| Bond length (Å) | 1.90 | 1.71 | 1.64 | 1.66 | 1.87 |
| Bond angle | 44.8 | 42.5 | 38.4 | 37.7 | 39.0 |



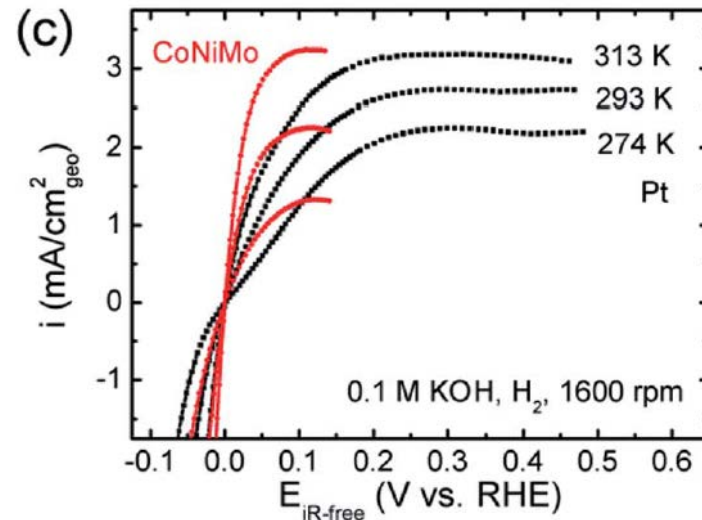
- Higher HOR/HER activity of CoNiMo due to weakened Ni-HBE

Alloying Ni with Co and Mo (CoNiMo)



CoNiMo film prepared by electrodeposition.

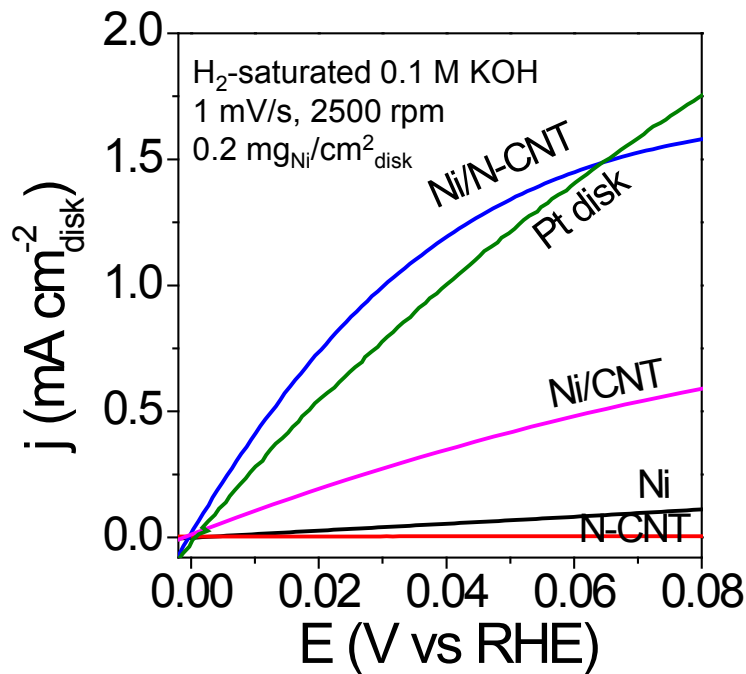
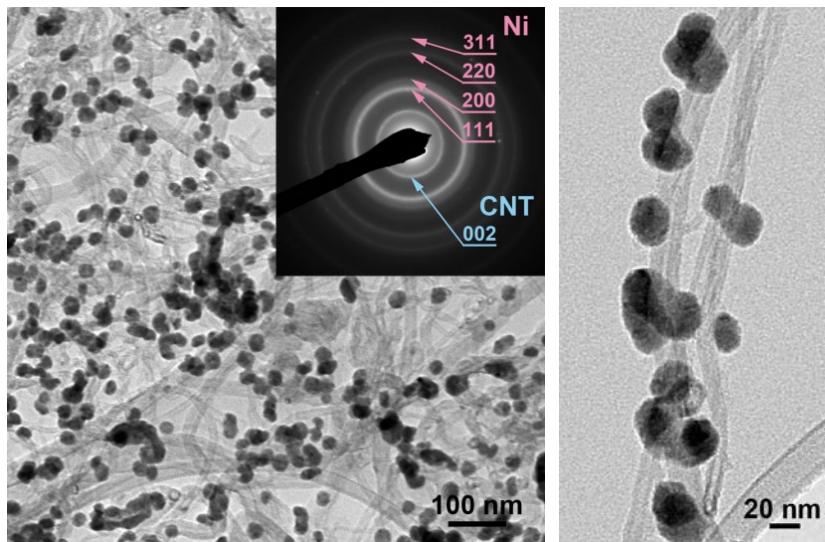
Co: Ni: Mo = 0.12: 5.10 : 1



| | i_0 (mA/cm ² _{metal}) | $i_{k,0.05\text{ V}}$ (mA/cm ² _{metal}) |
|---------|--|--|
| Pt disk | 0.61 ± 0.05 | 1.44 ± 0.13 |
| CoNiMo | 0.015 ± 0.002 | 0.044 ± 0.005 |
| Ni | - | 0.002 |

CoNiMo outperforms Pt disk with higher loading

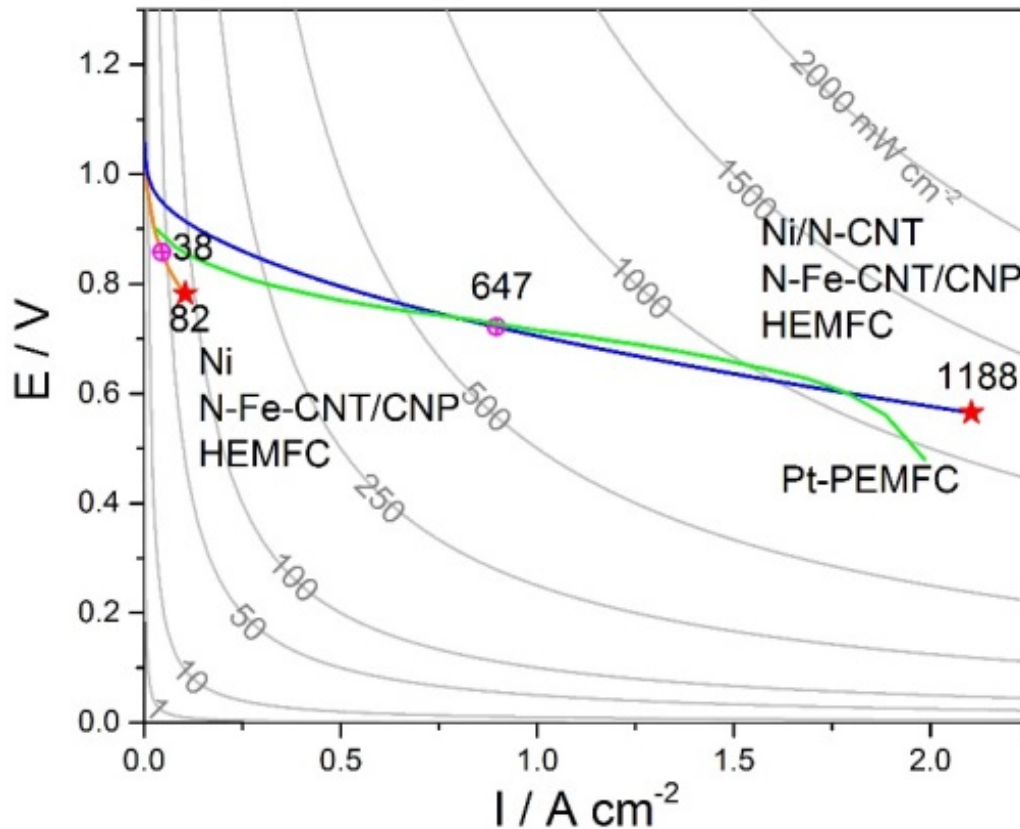
Tuning Ni activity by support (Ni/N-CNT)



| | i_0 ($\text{mA}/\text{cm}^2_{\text{metal}}$) | $i_{m,0.05 \text{ V}}$ (mA/mg_{Ni}) |
|----------|---|--|
| Ni/N-CNT | 0.028 | 9.3 |
| Ni/CNT | 0.0092 | 1.9 |
| Ni | 0.0013 | 0.28 |

- Ni/N-CNT > Ni/CNT >> Ni
- Ni/N-CNT with a loading of $0.5 \text{ mg}_{Ni}/\text{cm}^2_{\text{disk}}$ outperforms a Pt disk

Simulated fuel cell performance



Simulated polarization curves of Ni/N-CNT HEMFC (blue line) and Ni HEMFC (orange line). Anode catalyst is Ni/N-CNT or Ni with a loading of 5 mg_{Ni}/cm². Cathode catalyst is N-Fe-CNT/CNP (5 mg/cm²) and cell resistance is 0.07 Ω cm² and cell temperature is 80 °C. The circles stand for the cell operating at 0.1 V overpotential on anode side and the stars at 0.15 V. The numbers are the peak power density. The green line is state-of-the-art PEMFC with 0.15 mg Pt /cm².

Summary

- ORR
 - PGM-free ORR catalysts of adequate activity exist
 - MEA tests are now a preferred tool for screening for true performance
- HOR
 - PGM-free catalysts need higher activity
 - But more importantly higher stability
 - Stable up to at least 0.2 V, preferably 0.3 V, and ideally > 0.4 V
 - Demonstrate PGM-free catalysts with activity matching Pt/C in high performance MEAs
- Apparent HBE is the sole descriptor for monometallic PGMs
- OH_{ad} might be at play for PGM alloys
- Water plays a critical role in explaining why HOR on PGMs is slower in base and is likely also important for PGM-free catalyst design

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