Effect of thermodynamics, kinetics, and mass transfer on dissolution of electrocatalysts

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Outline

- Motivation
- Dissolution quantification
- Mechanism

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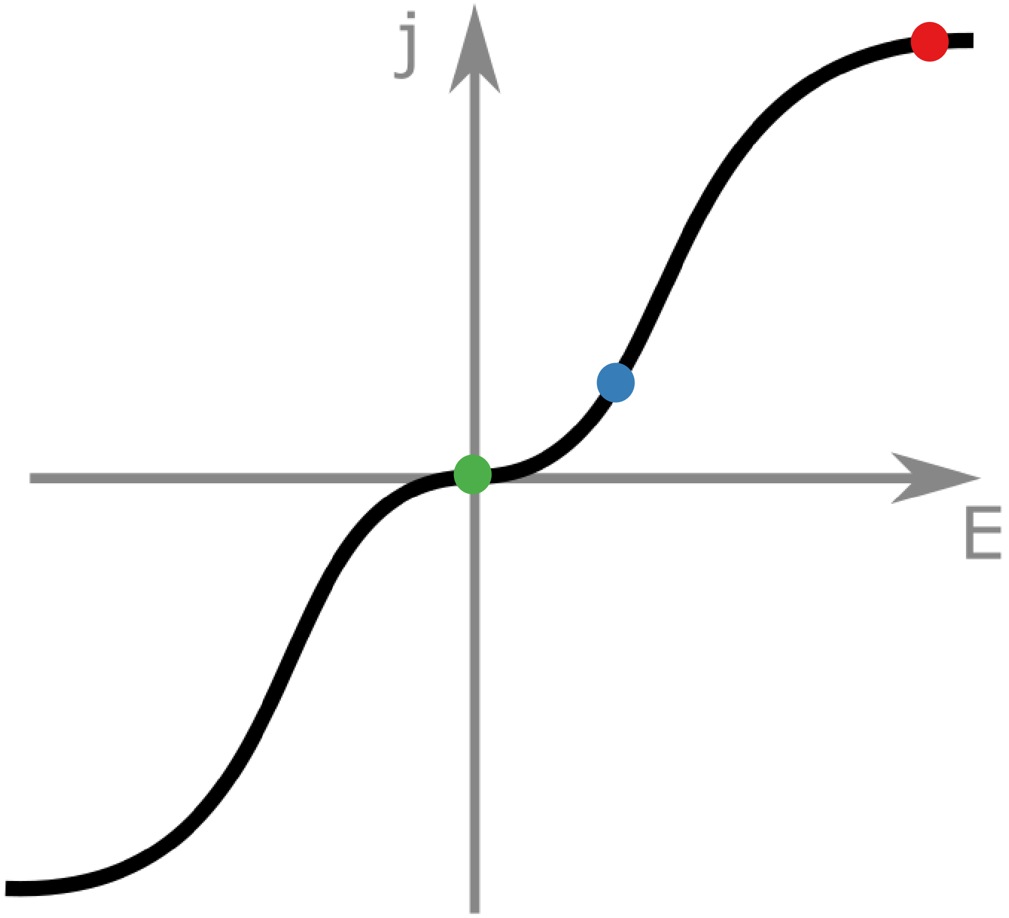
- Dissolution quantification
- Thermodynamics
- Kinetics
- Mass transfer
- Mechanism

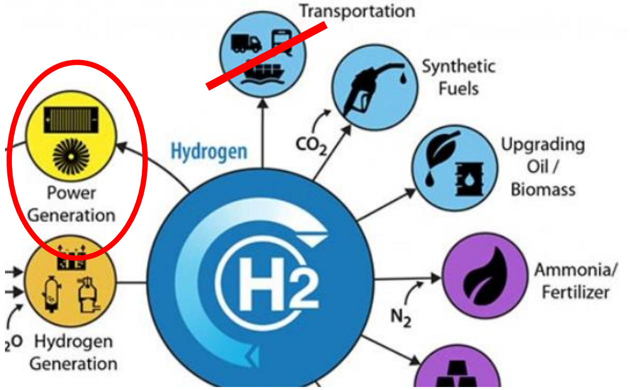
← Literature



Motivation: Why do we need to study dissolution?

Technology	Anode	Cathode	Potential Dissolution	[Ref]
PEMFC	Pt	Pt, FeNC	Pt, Fe	1, 2, 3
PEMWE	Ir	Pt	Ir	4, 5, 6
AEMFC	PtRu, NiMo, …	FeNC, Ag	Ru, Mo, Fe, Ag	7
AEMWE	NiFe, CoFe, …	Pt, NiMo	Fe, Mo	8
Alcohol FCs	PtRu	Pt	Pt, Ru	9
CO_2 Electrolysis	Ir, Pt, Ni, …	Cu, Ag, …	Ir, Ni, Cu, Ag	10,11
Aq. batteries		$Na_2NiFe(CN)_6$	Ni, Fe	12

[Ref]
[1] T. Fuchs, …, J. Drnec, O.M. Magnussen Nature Catalysis 3 (2020) 754-761
[2] D.J.S. Sandbeck, .. , J. Kibsgaard, … ACS Catalysis 10(11) (2020) 6281-6290
[3] A. Pedersen, …, I.E.L. Stephens, F. Maillard EES (2024) In press
[4] S. Geiger et al. Nature Catalysis 1 (2018) 508-515
[5] S. Czioska, …, J.-D. Grunwaldt ACS Catalysis 11(15) (2021) 10043-10057
[6] R.A. Krivina, …, S.W. Boettcher ACS Catalysis13 (2023)902–915
[7] Y.-P. Ku et al. JACS 144(22) (2022) 9753–9763
[8] M. Schalenbach et al. Electrochimica Acta 259 (2018) 1154-1161
[9] A. Kormanyos et al. ACS Materials Au 4(3) (2024) 286-299
[10] J. Vavra, …, R. Buonsanti Nature Catalysis 7 (2024) 89-97
[11] A. Vass, …, C. Janáky ACS Energy Letters 6 (2021) 3801–3808
[12] X. Lamprecht, …, A. Bandarenka ACS Applied Materials & Interfaces 14(2) (2022) 3515–3525

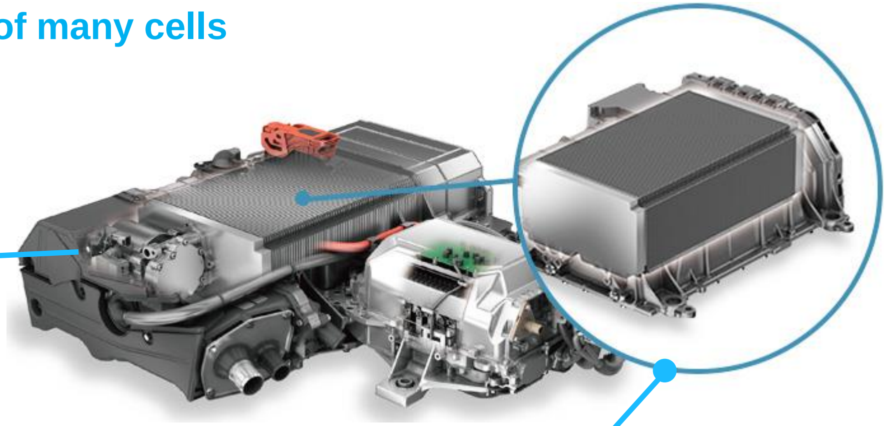


https://www.nrel.gov

Platinum in PEMFC

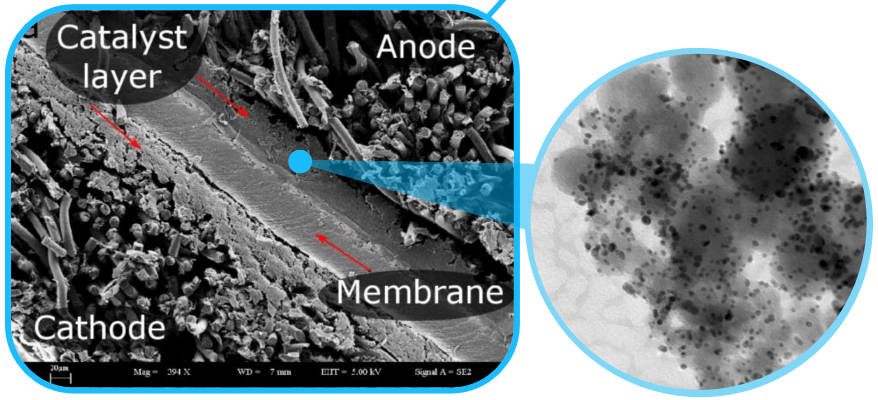
Fuel cell car

Stack of many cells

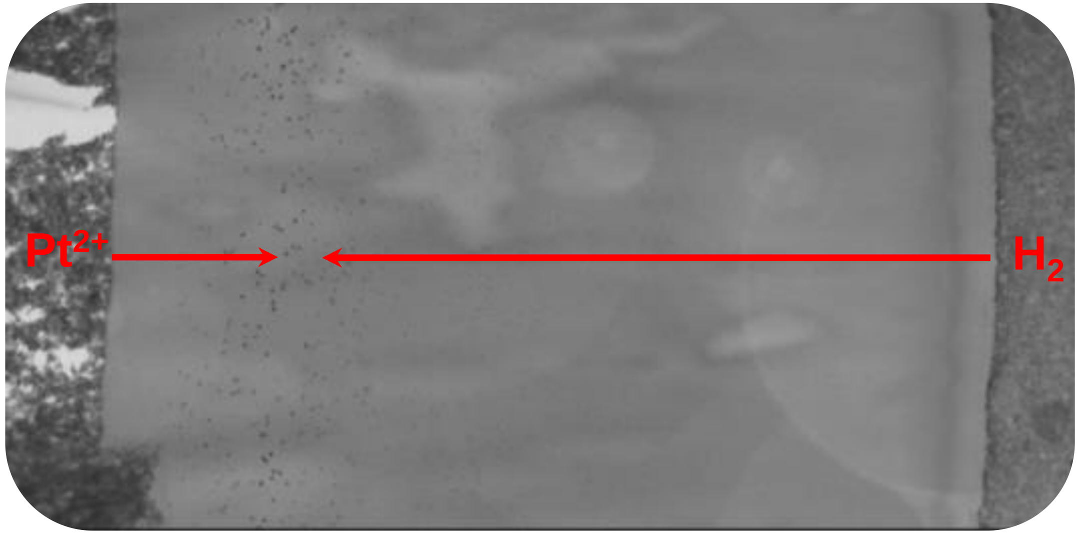


Membrane electrode assembly (MEA)

Catalyst – Pt/C



Cathode Membrane Anode



Quantify (Do we care?)
Understand (When? Why? How?)
Mitigate (Operational and/or material solutions)

[1] C. Baldizzone Thesis, Ruhr-University Bochum, 2015, pp. 150

From: E. Guilminot et al. J. Electrochem. Soc., 154 (2007) B96-B105

How to approach? Dissolution, Leaching, Corrosion, …

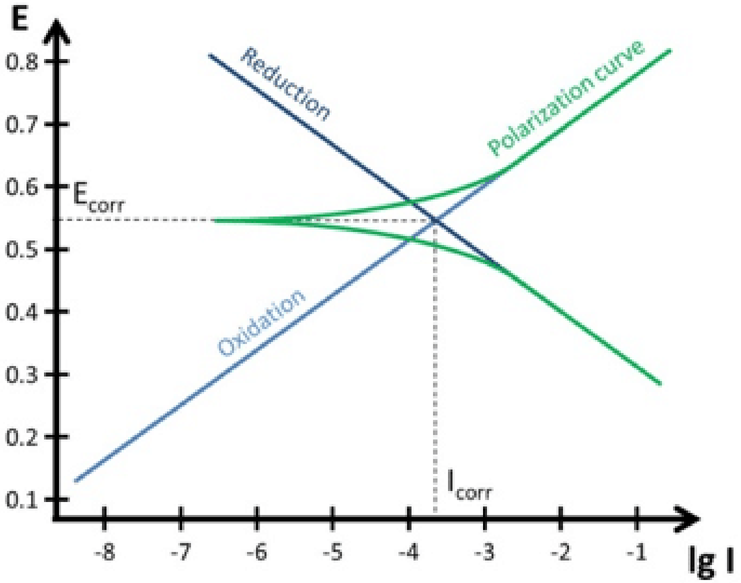
https://www.icorr.org/world-corrosion-science/

…, we know that the **Romans** covered copper utensils with a thin layer of tin to prevent corrosion.
… **Robert Boyle** published two papers which served to introduce corrosion science in **1675**.

How to quantify electrocatalyst dissolution?

In-situ

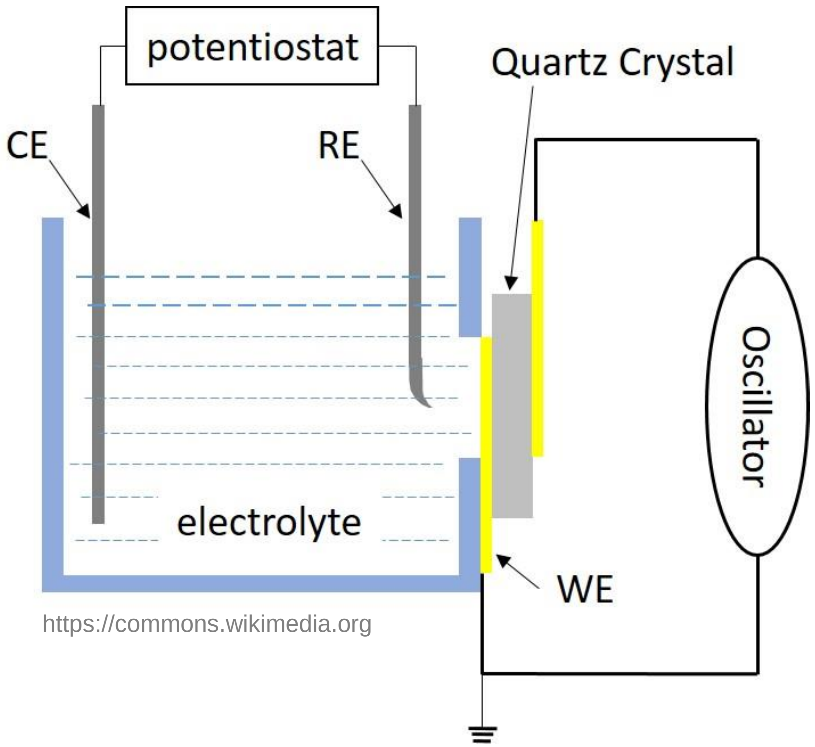
Electrochemistry (Evan's diagram)



https://assets.palmsens.com

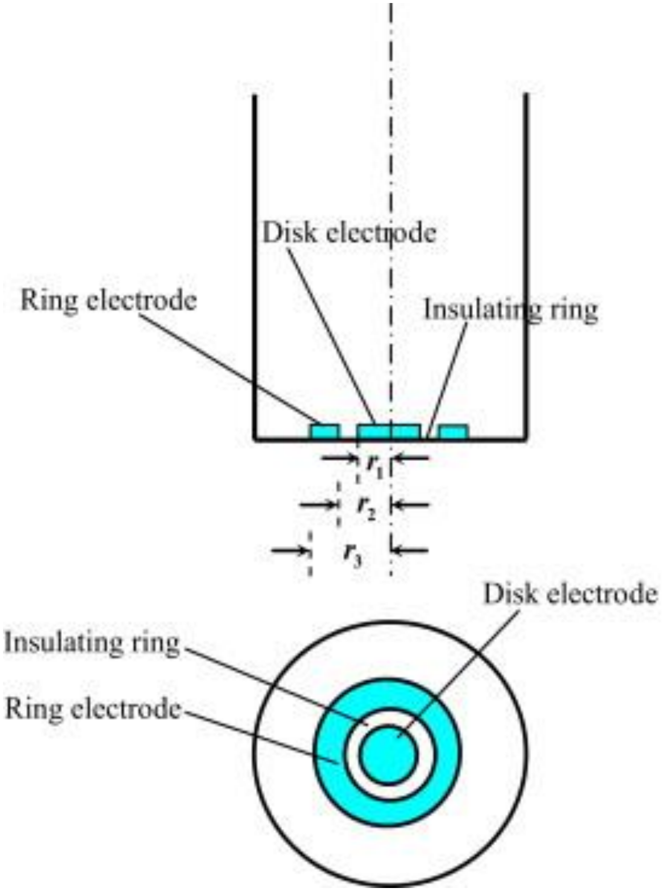
1 Monolayer 400 ng cm^{-2} (nA cm^{-2})
Dissolution selectivity < 0.01%

Electrochemistry + EQCM



https://commons.wikimedia.org

Electrochemisry + RRDE



https://doi.org/10.1016/B978-0-444-63278-4.00006-9

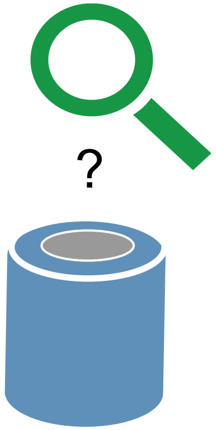
Pros:
- dissolution rate
- cheap

Cons:
- not selective

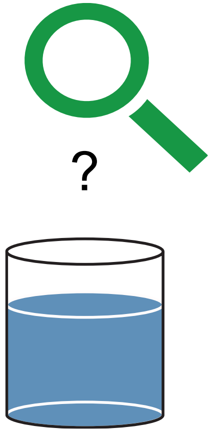
How to quantify electrocatalyst dissolution?

Ex-situ

Electrode:
- SEM, TEM,…
- EDX, XPS,…
- gravimetry



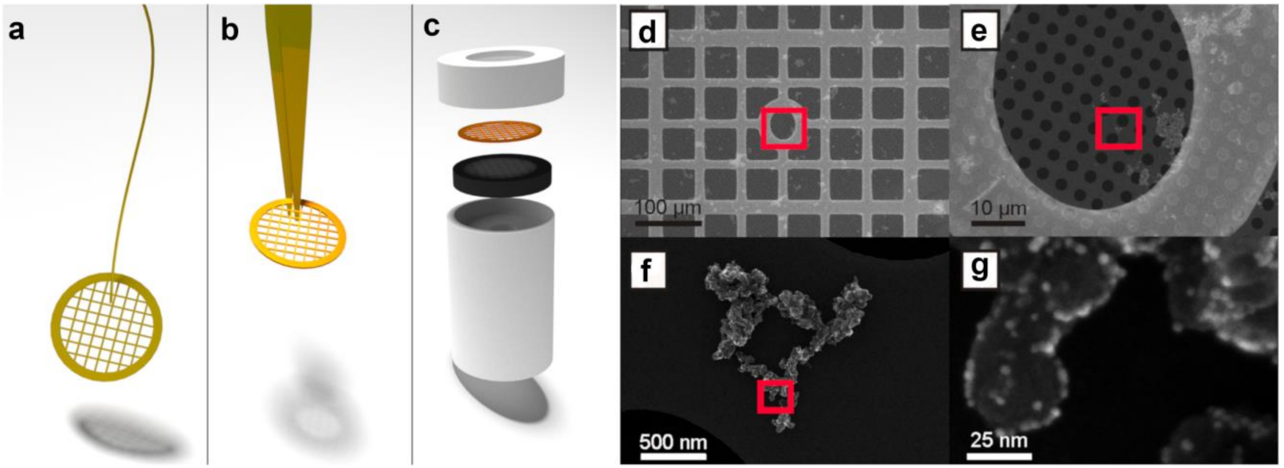
Electrolyte:
- UV-Vis
- ICP-OES
- ICP-MS



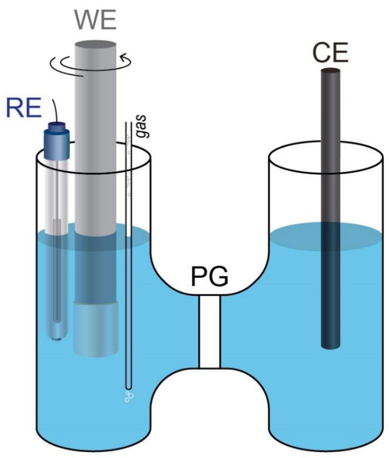
Pros:
- Complementary data

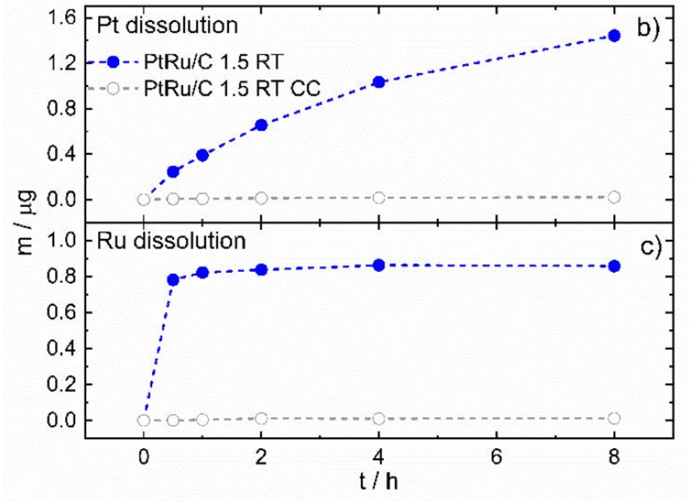
Cons:
- integrated signal

IL-TEM



H-cell + ex-situ ICP-MS

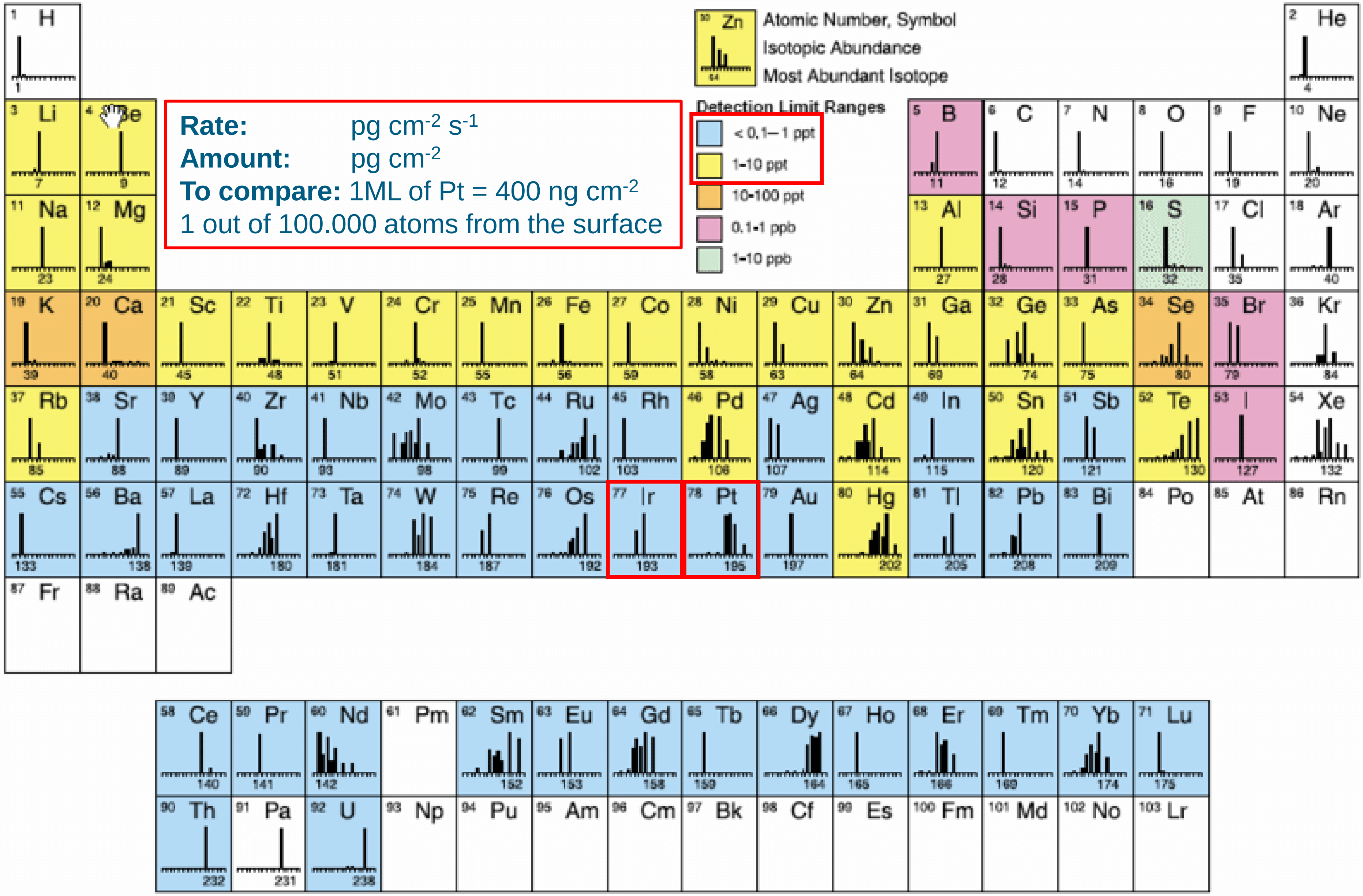




[1] N. Hodnik and S. Cherevko Current Opinion in Electrochemistry 15 (2019) 73-82
[2] M. Minichova et al. Electrochimica Acta (2024) in Press

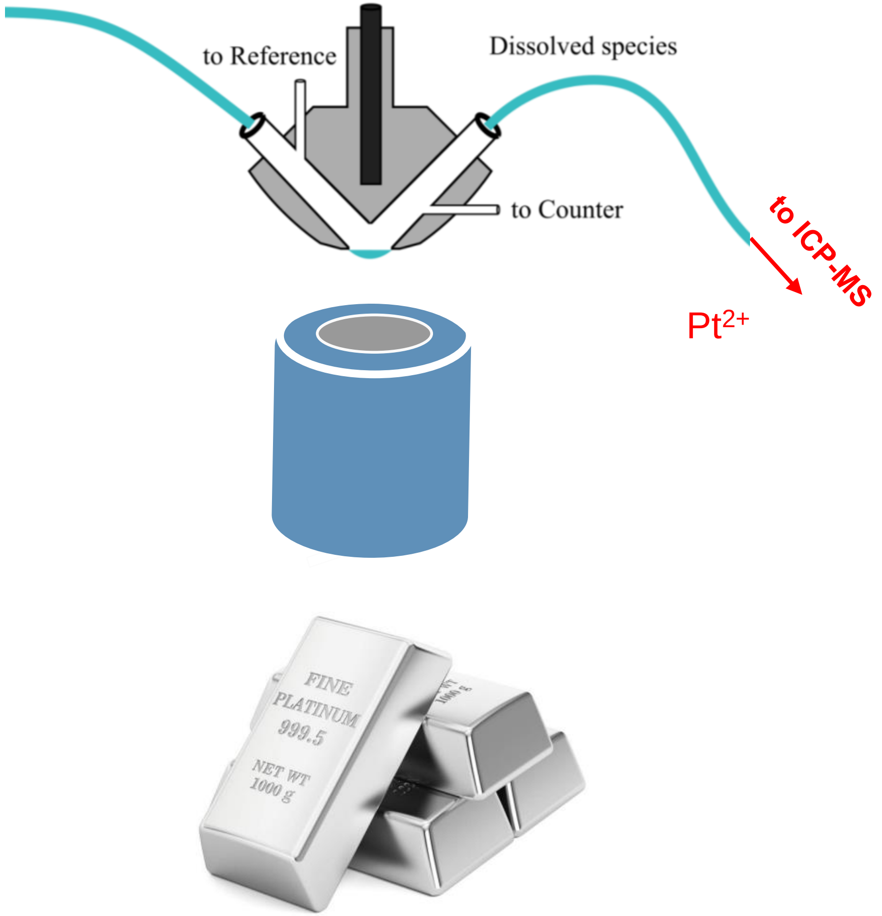
Measured elements

Rate: pg cm^{-2} s^{-1}
Amount: pg cm^{-2}
To compare: 1ML of Pt = 400 ng cm^{-2}
1 out of 100.000 atoms from the surface

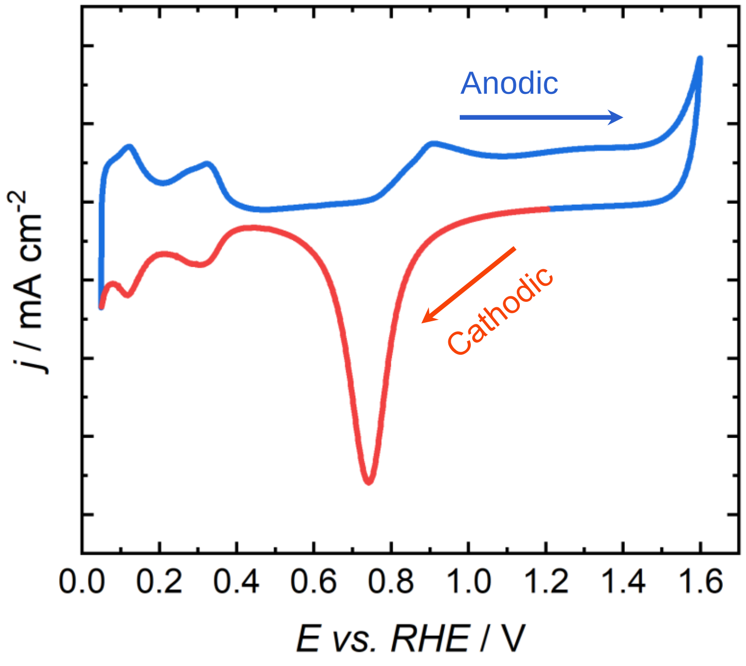


Quantifying Pt dissolution

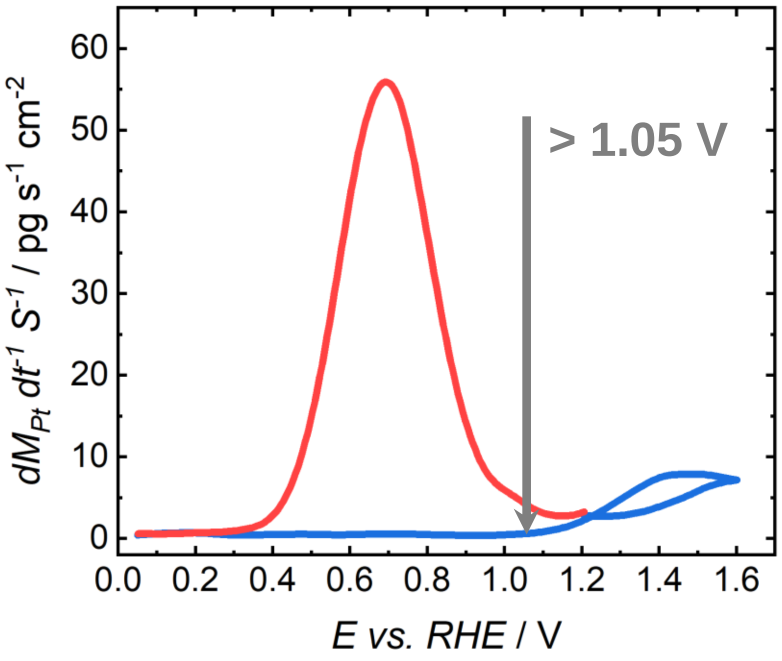
In-situ ICP-MS



Electrochemistry



Dissolution



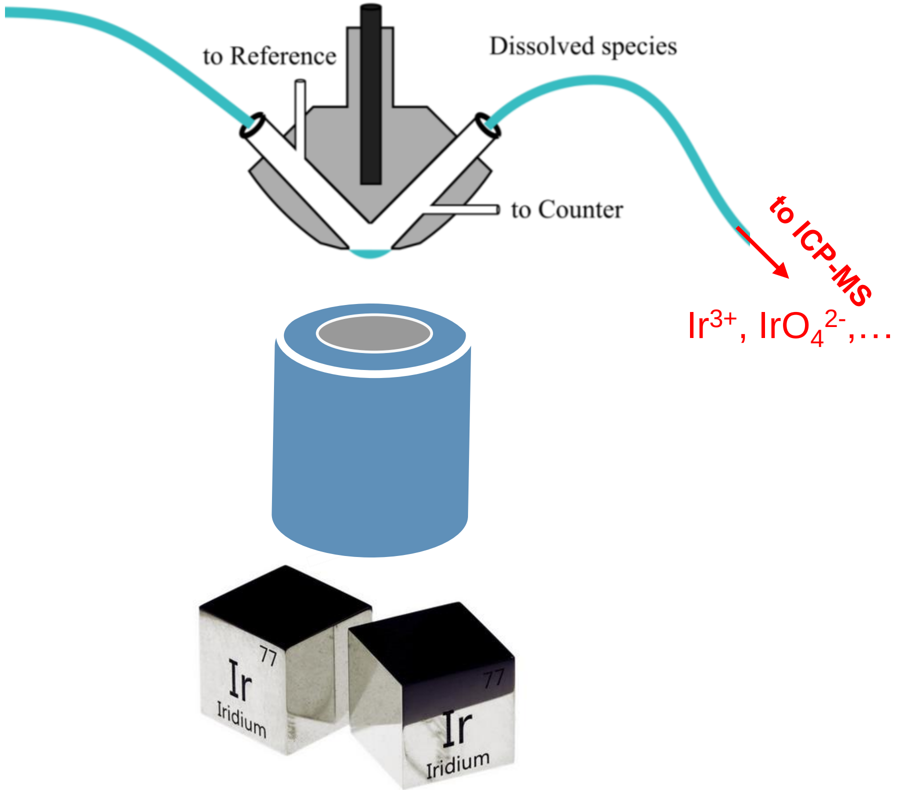
We can quantify!

In liquid electrolyte…

[1] S. Cherevko et al. Journal of The Electrochemical Society 161 (2014) H822-H830
[2] S. Cherevko et al. Nano Energy 29 (2016) 275-298 (Review paper)

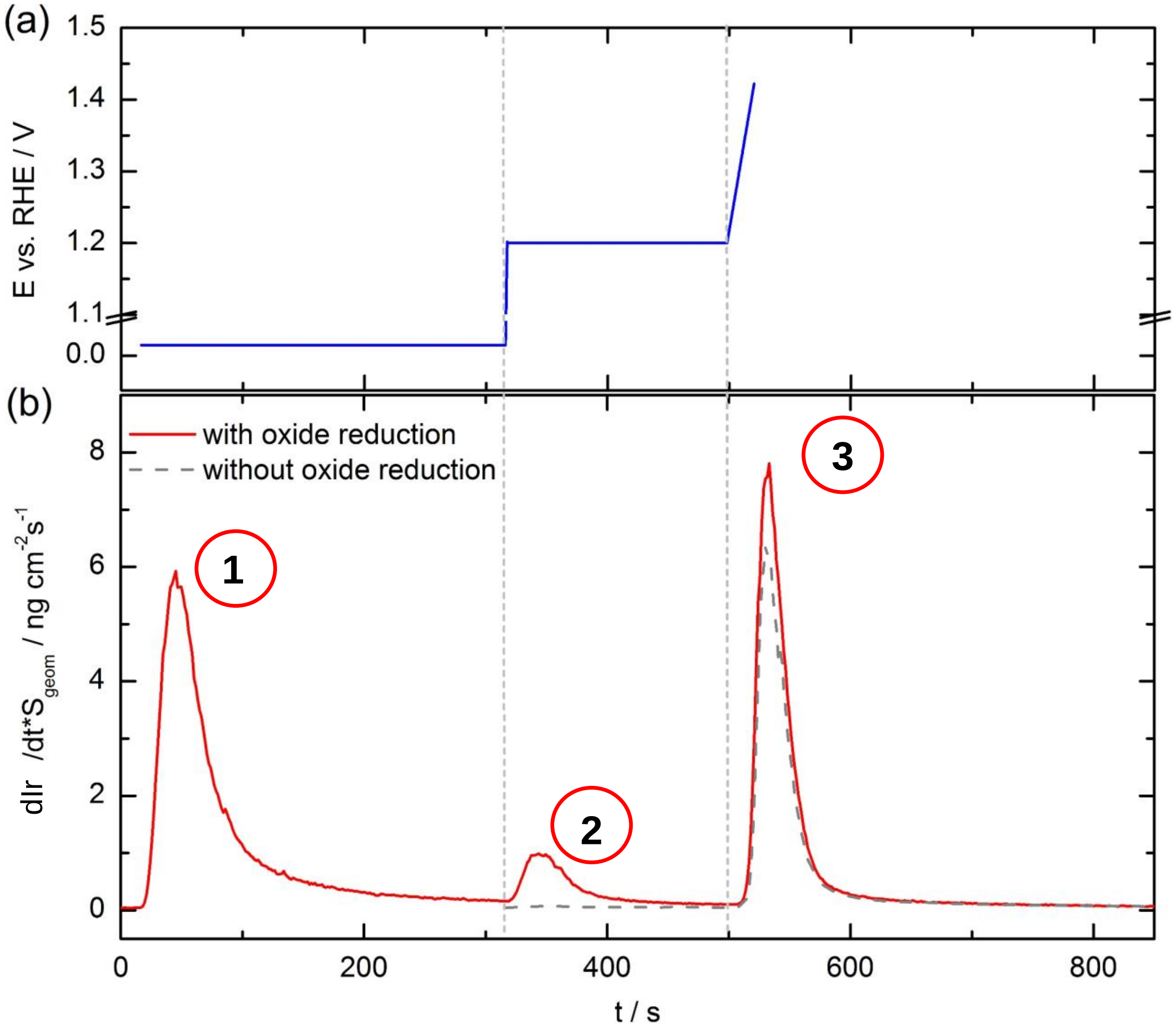
Ir dissolution (PEMWE)

on-line ICP-MS



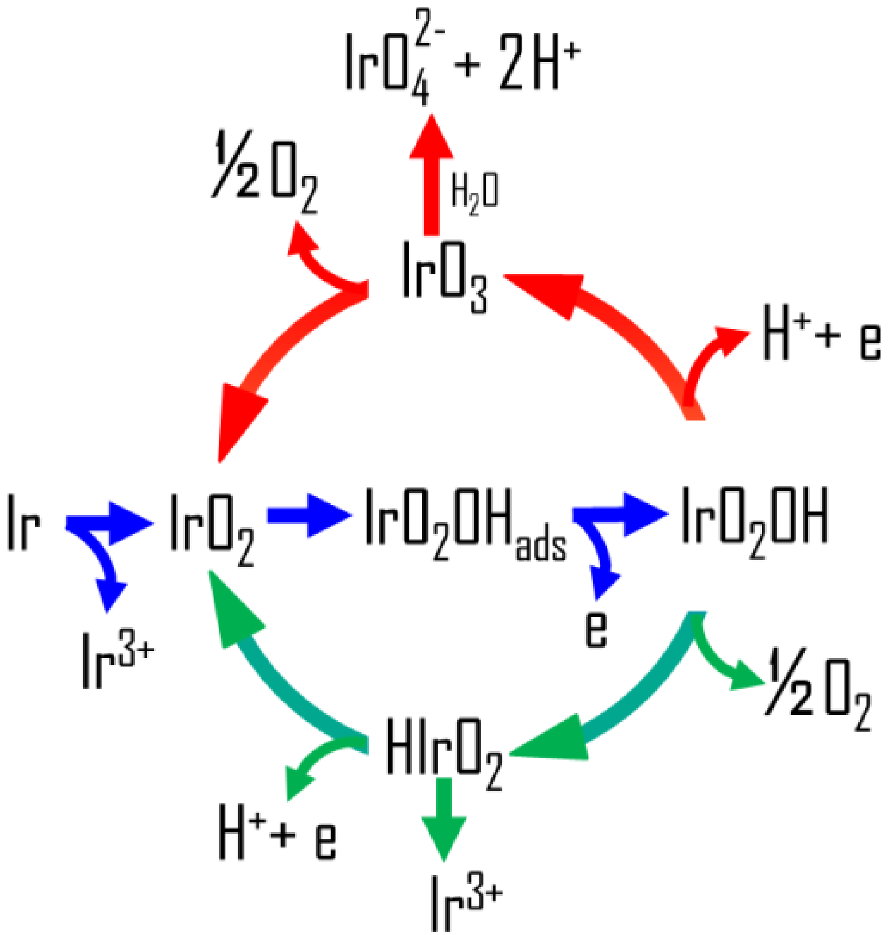
1. **Reduction (cathodic)** — IrO_x to Ir metal
2. **Oxidation (anodic)** — Ir metal to IrO_x
3. **OER** — IrO_x to O_2 and Ir…

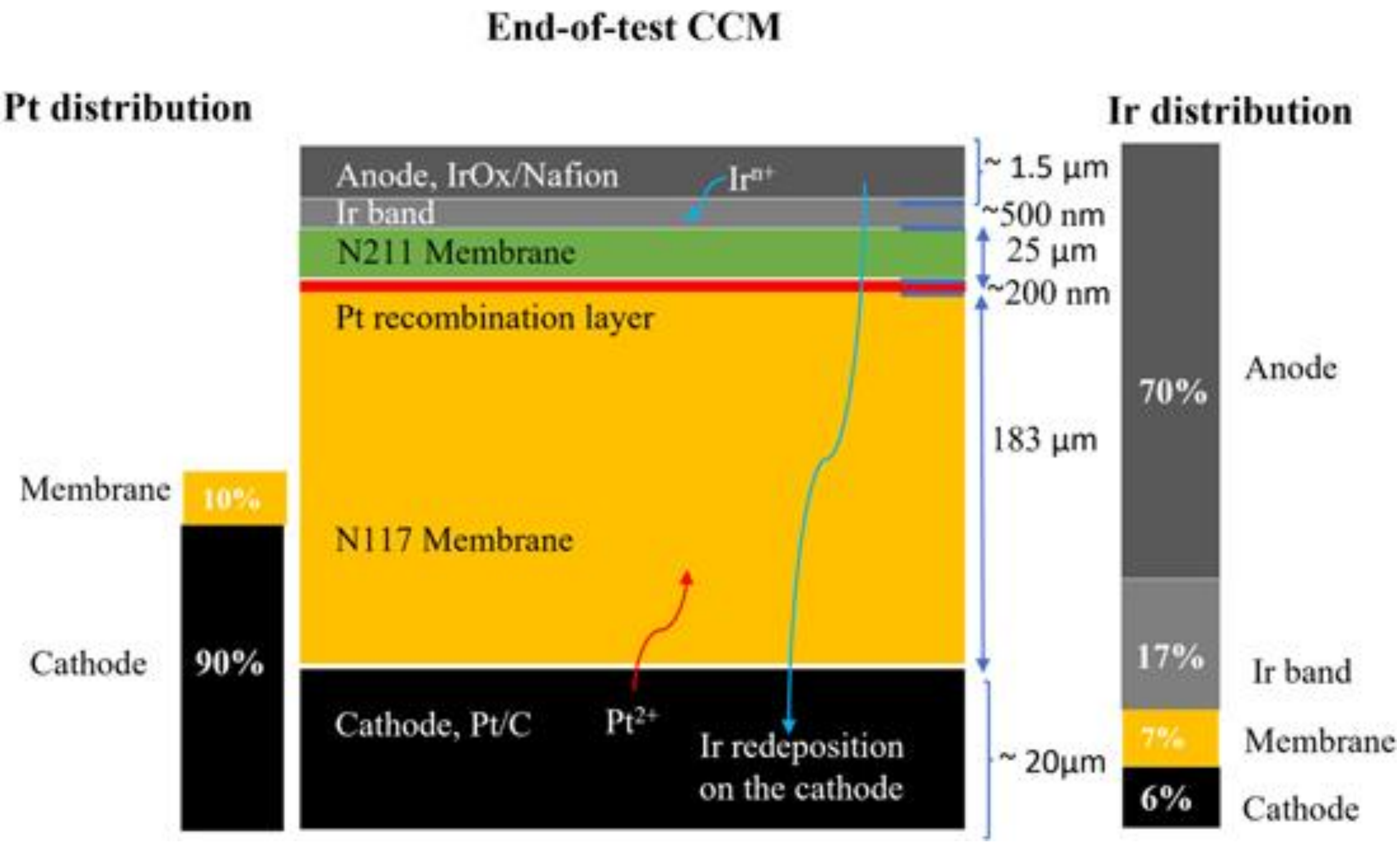
Dissolution rate



[1] S. Cherevko et al. *Catalysis Today 262 (2016) 170-180*

Ir dissolution (PEMWE): Consequences



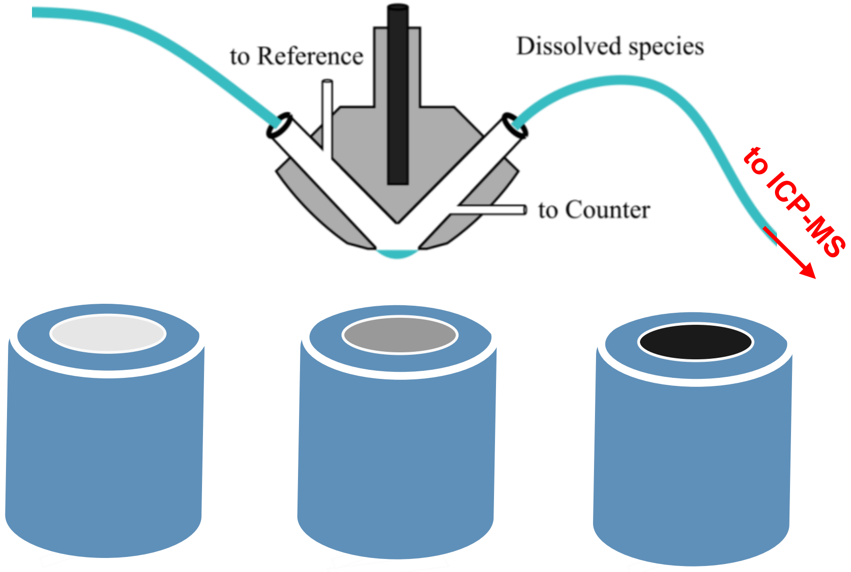


Loading: 0.2-0.3 mg_{Ir} cm^{-2}

After 5000h at constant operation: 30% lost

[1] O. Kasian et al. Angewandte Chemie 57(9) (2018) 2488–2491
[2] S. Geiger et al. Nature Catalysis 1 (2018) 508-515
[3] S. Czioska, …, J.-D. Grunwaldt ACS Catalysis 11(15) (2021) 10043-10057
[4] Z. Zeng et al. JES 169 (2022) 054536

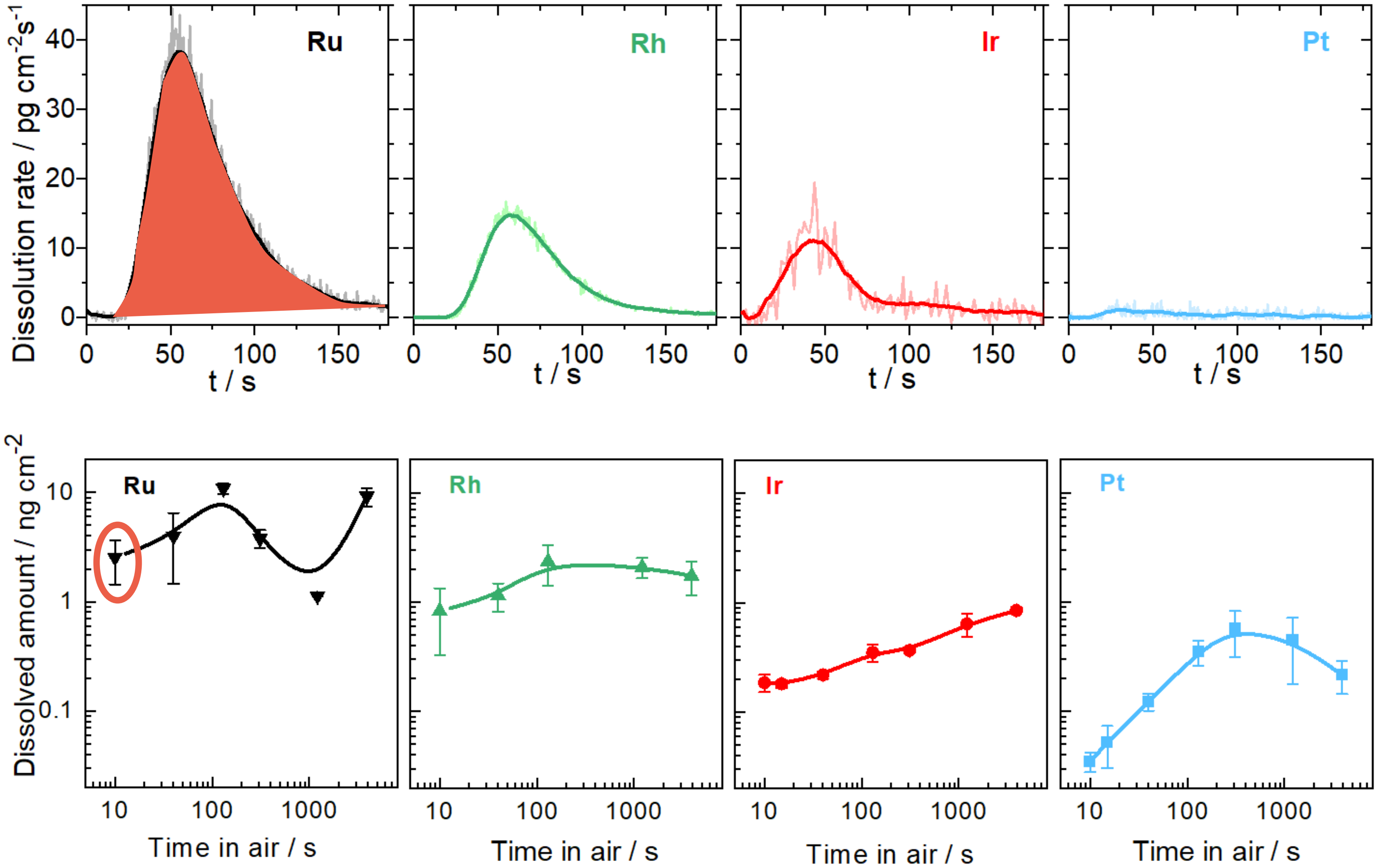
All noble metal oxides dissolve



Amount of native oxide formed in air

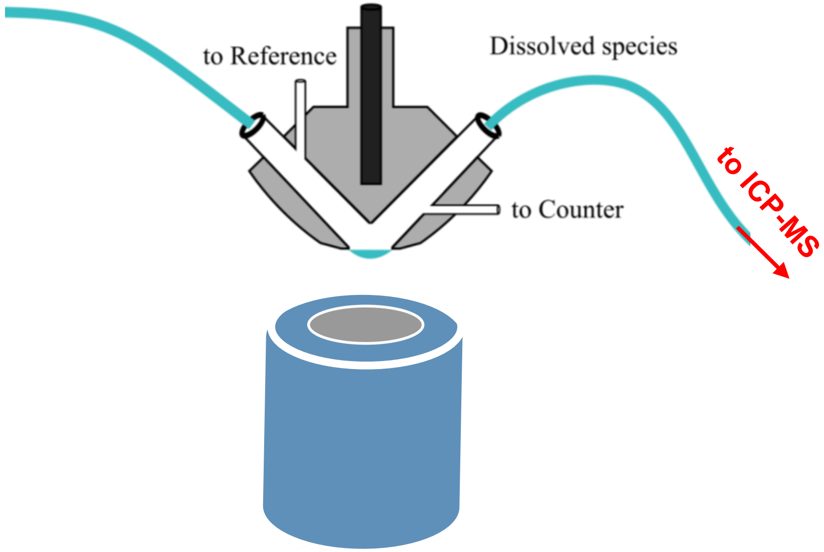
$$W_i = \int_{t=t_1}^{t=t_2} v_{S,i}(t)$$

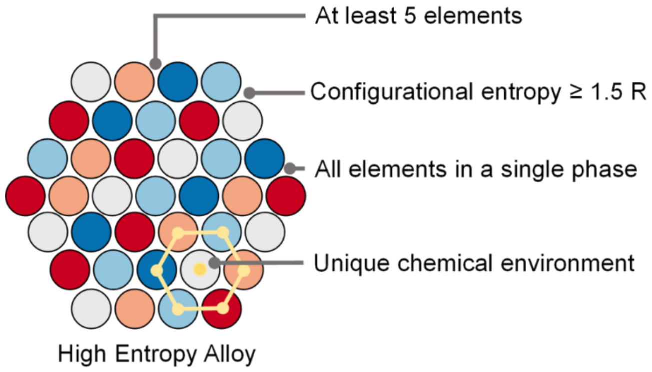
Dissolution of native oxides



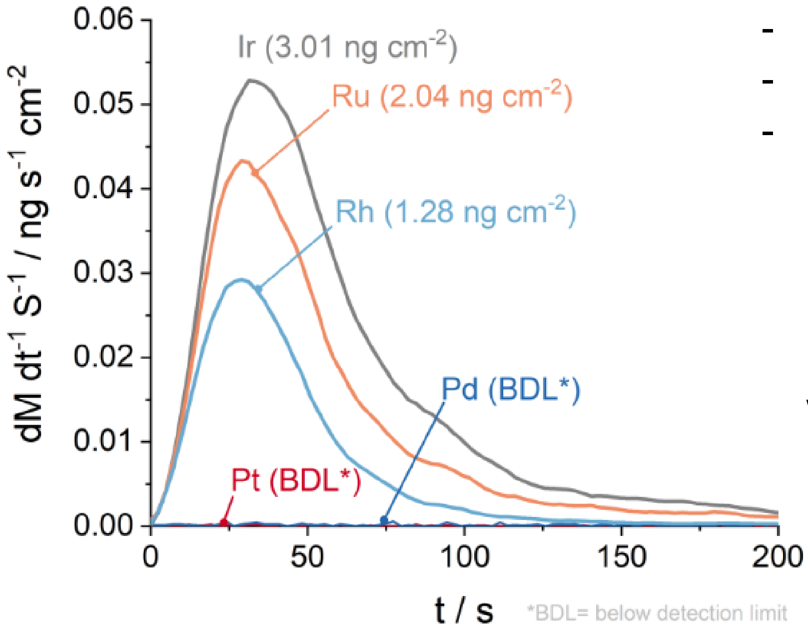
[1] Cherevko et al. *Journal of Electroanalytical Chemistry 787 (2017) 11–13.*

High entropy alloys dissolution





Contact with electrolyte



Observations

- Dissolution trend as Ir < Ru < Rh
- Dissolution almost stops after 3 min
- No dissolution for Pt and Pd

Assume you study activity/selectivity

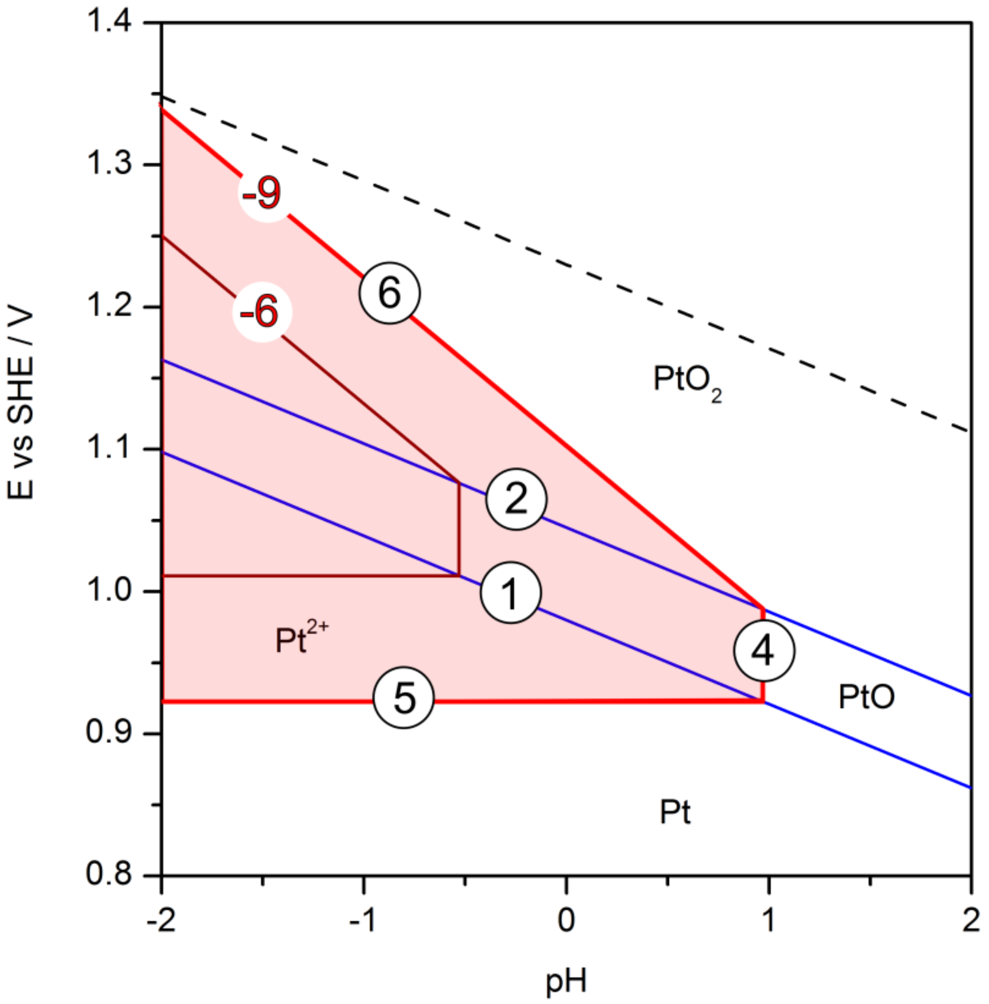
Which composition to take?

What do we learn from this?

Thermodynamics
Kinetics
Mass Transport
Mechanism

[1] T. Priamushko et al. Current Opinion in Chemical Engineering 44 (2024) 101020
[2] A. Kormányos et al. iScience 26(10) (2023) 107775

Pt dissolution thermodynamics – Pourbaix diagram



Oxidation/reduction:

(1) $Pt + H_2O = PtO + 2H^+ + 2e^-$ $E^0(Pt^0/PtO) = 0.98 – 0.0591pH$

(2) $PtO + H_2O = PtO_2 + 2H^+ + 2e^-$ $E^0(Pt^0/PtO) = 1.045 – 0.0591pH$

Dissolution/deposition:

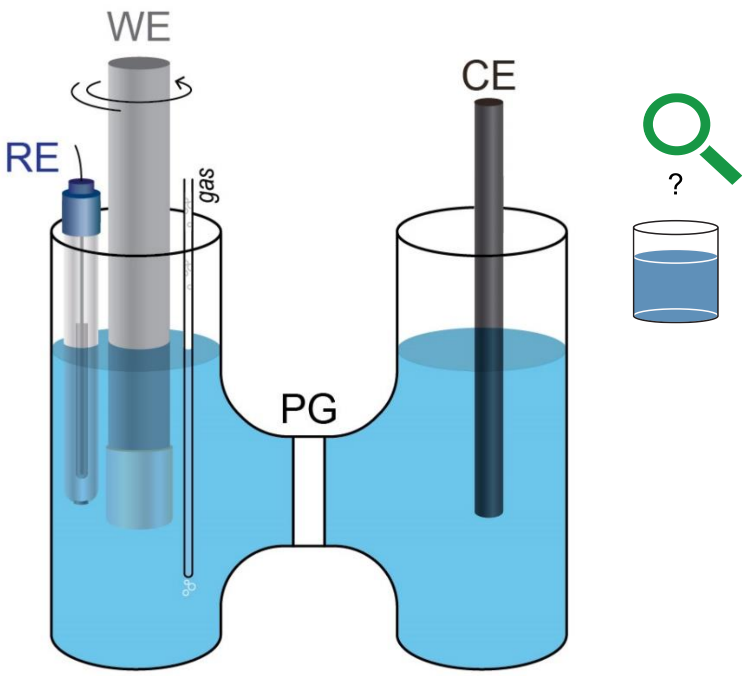
(4) $PtO + 2H^+ = Pt^{2+} + H_2O$ $\log(Pt^{2+}) = –7.06 – 2pH$

(5) $Pt = Pt^{2+} + 2e^-$ $E^0(Pt/Pt^{2+}) = 1.188 + 0.0295 \log(Pt^{2+})$

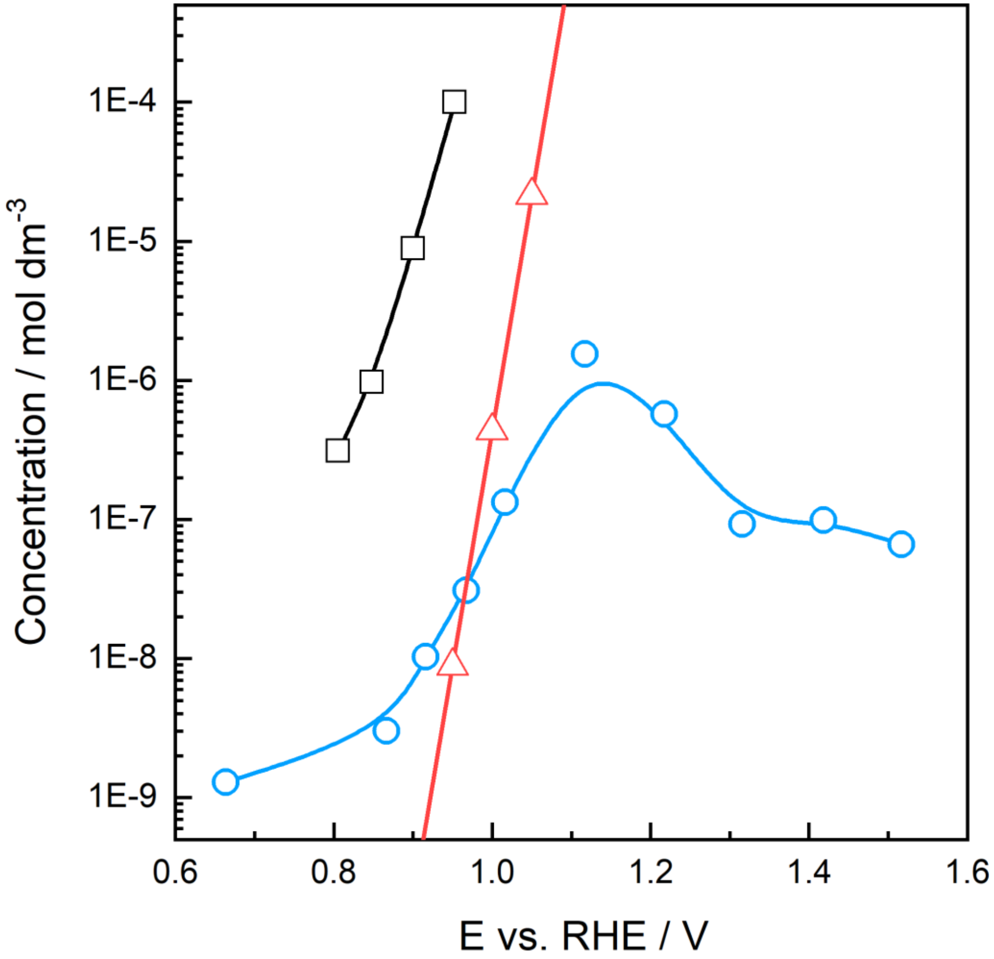
(6) $PtO_2 + 4H^+ +2e^- = Pt^{2+} + 2H_2O$ $E^0(PtO_2/Pt^{2+}) = 0.837 – 0.1182pH – 0.0295\log(Pt^{2+})$

Pt dissolution thermodynamics: measurements

$Pt = Pt^{2+} + 2e^-$ $E^0(Pt/Pt^{2+}) = 1.188 + 0.0295 \log(Pt^{2+})$



$t \rightarrow \infty$



Nernst equation

$$E_e = E_e^{\ominus\prime} - \frac{RT}{zF}\sum_i \nu_i \ln c_i$$

Limited amount of experimental data

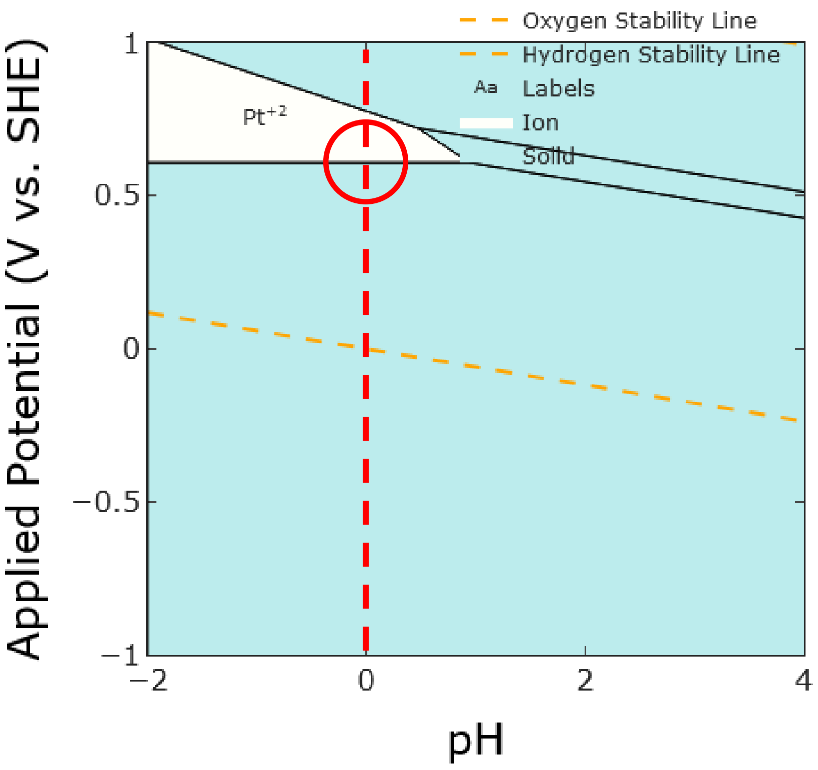
[1] S. Cherevko et al. Nano Energy 29 (2016) 275-298 (

From: X. Wang et al. Electrochem. Solid-State Lett. 9 (2006) A225–A227

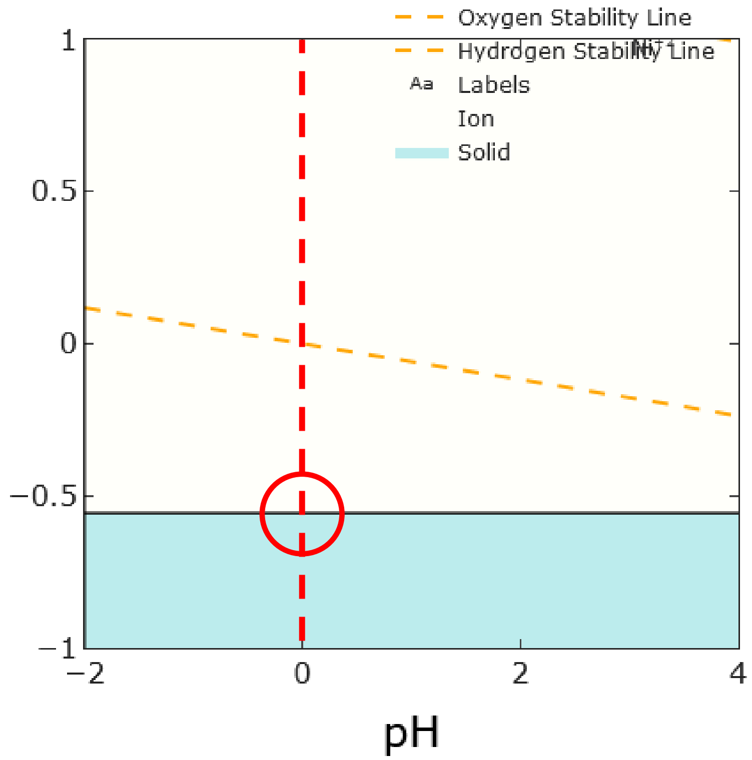
From: P. Bindra et al. Journal of The Electrochemical Society.126 (1979)1631–1632

Using Materials Project: Pt alloys

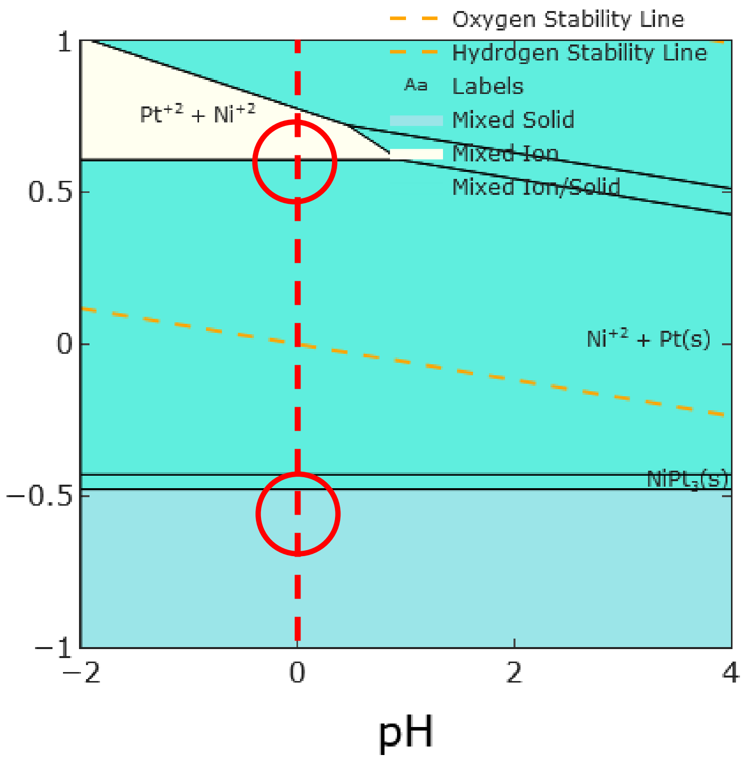
Platinum



Nickel



Platinum (0.5) + Nickel (0.5)

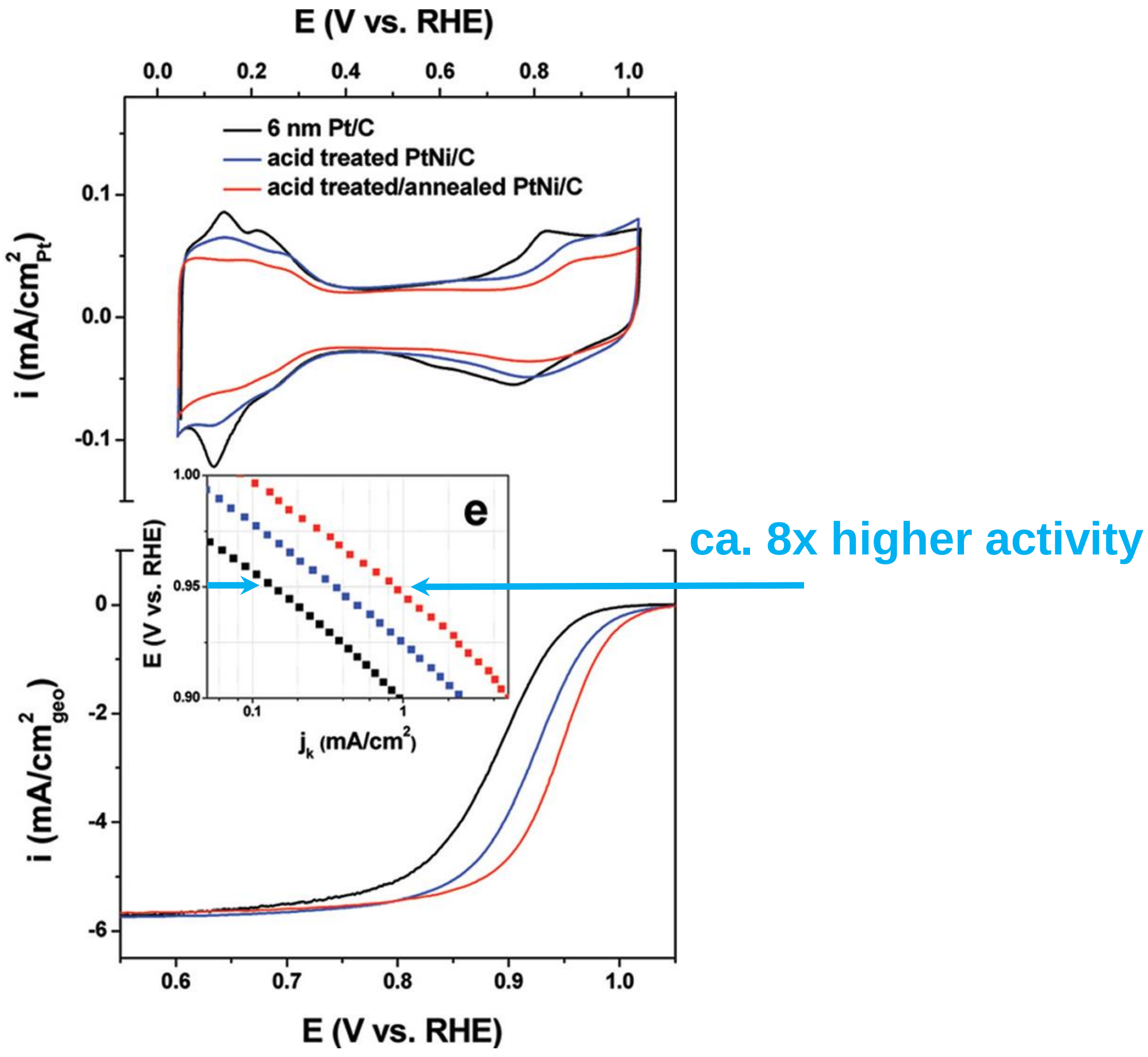


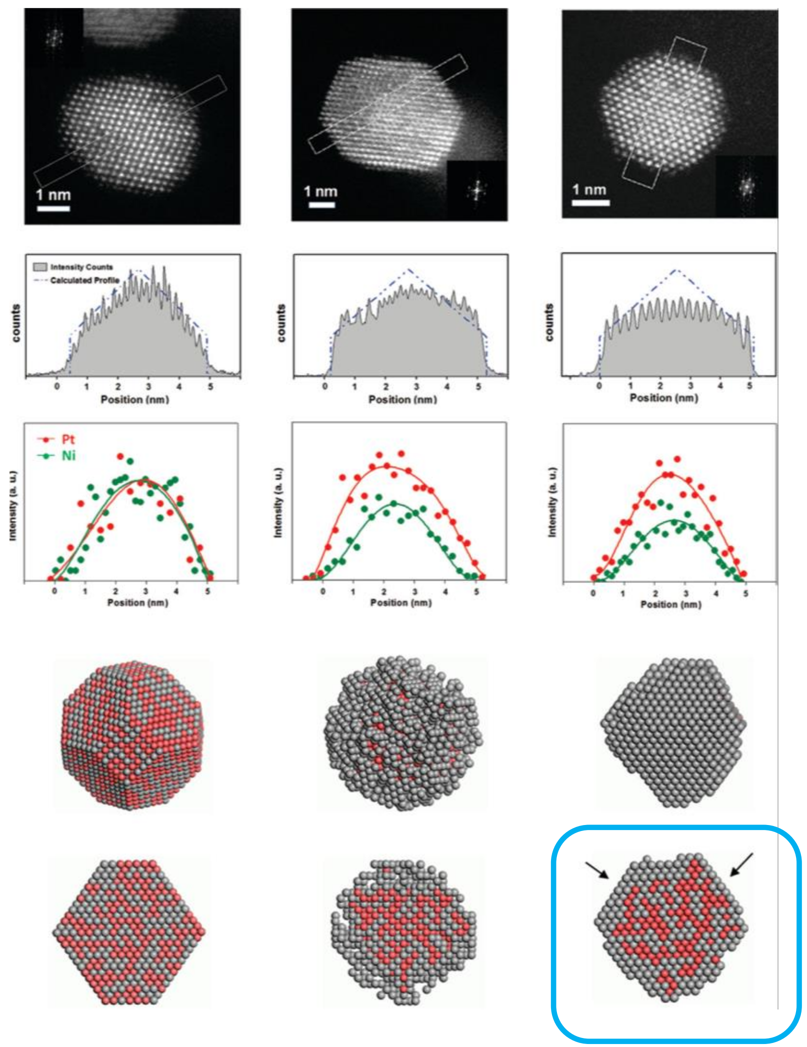
$[M^{x+}] = 10^{-12}$ M

https://next-gen.materialsproject.org/pourbaix

Why and how PtCo in this car  **?**

No Co or Ni on the surface



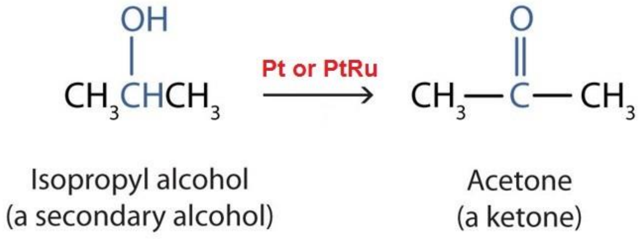


Pt “skin” electrocatalysts

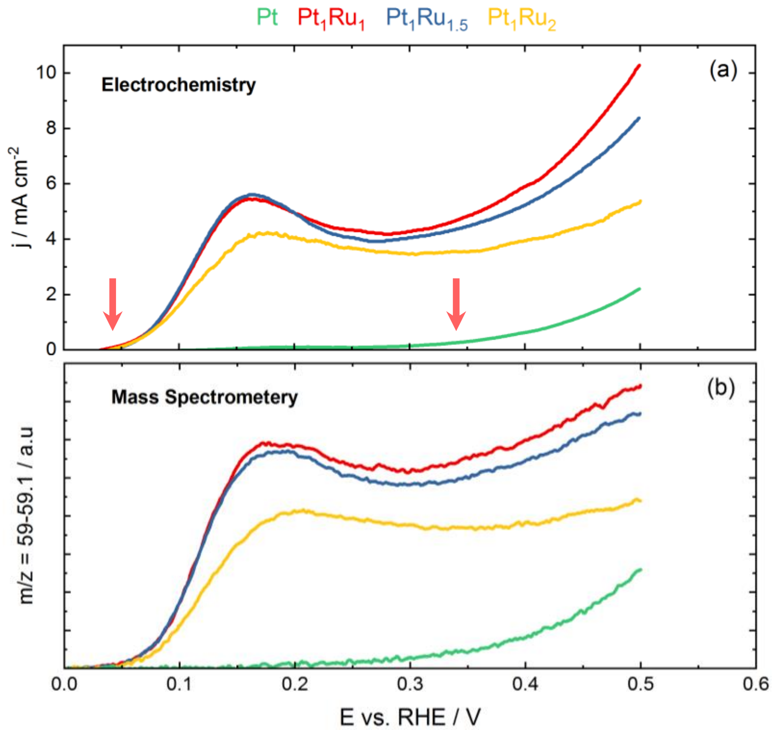
From: C. Want et al., JACS 133(36) (2011) 14396–14403

Bifunctional PtRu electrocatalysts for LOHCs

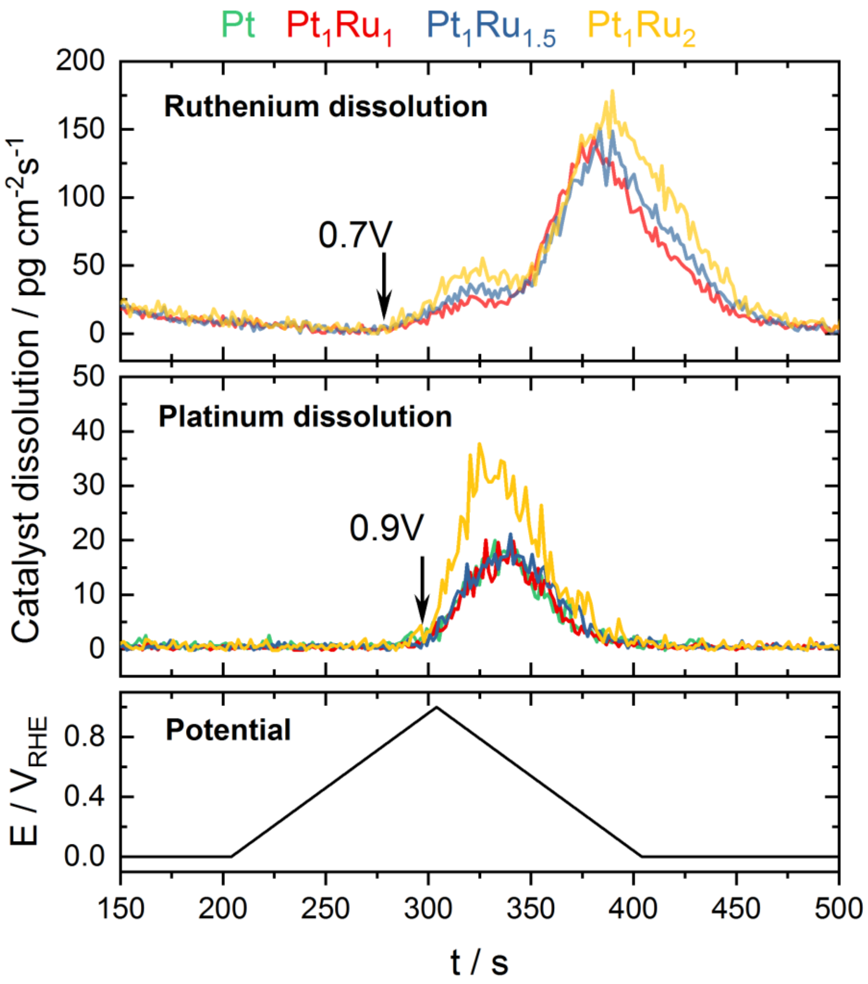
LOHC concept with IPA fuel cell



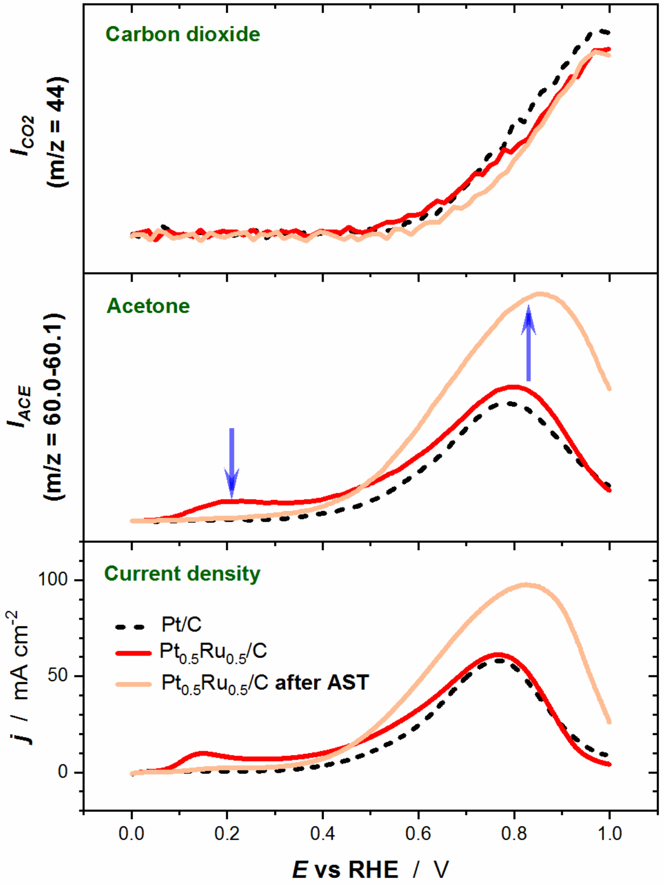
Activity and Selectivity



Dissolution of Pt and Ru

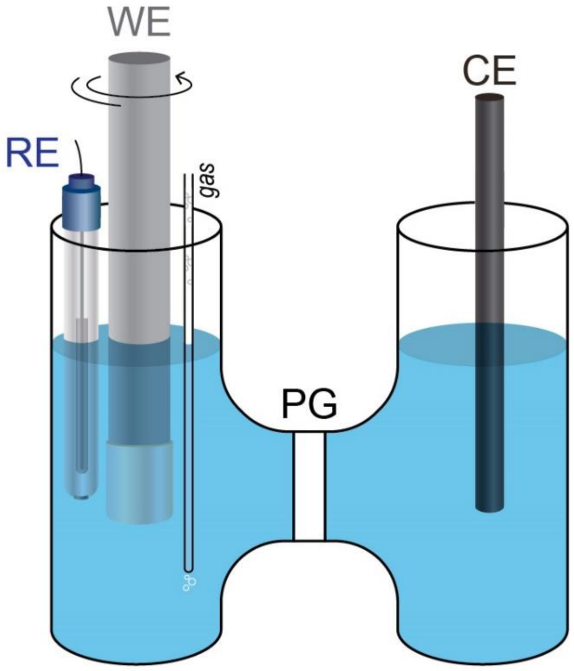


Consequences



[1] P. Khanipour, …, I. Katsounaros ACS Applied Materials & Interfaces 12(30) (2020) 33670-33678
[2] M. Minichova et al. Electrochimica Acta (2024) in Press

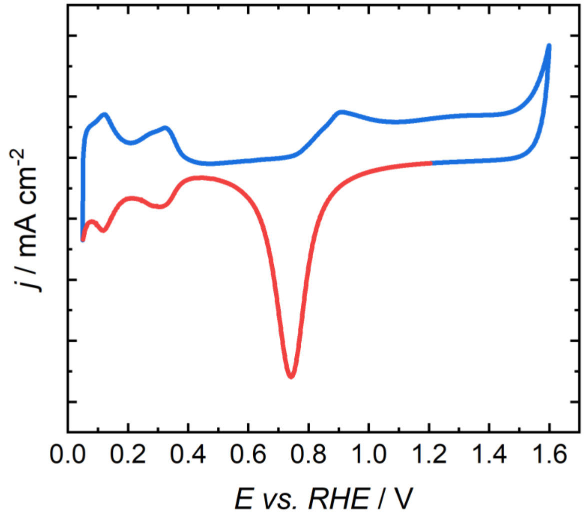
Pt dissolution kinetics



$$\frac{d[Pt^{2+}]}{dt} = f(E,t)$$

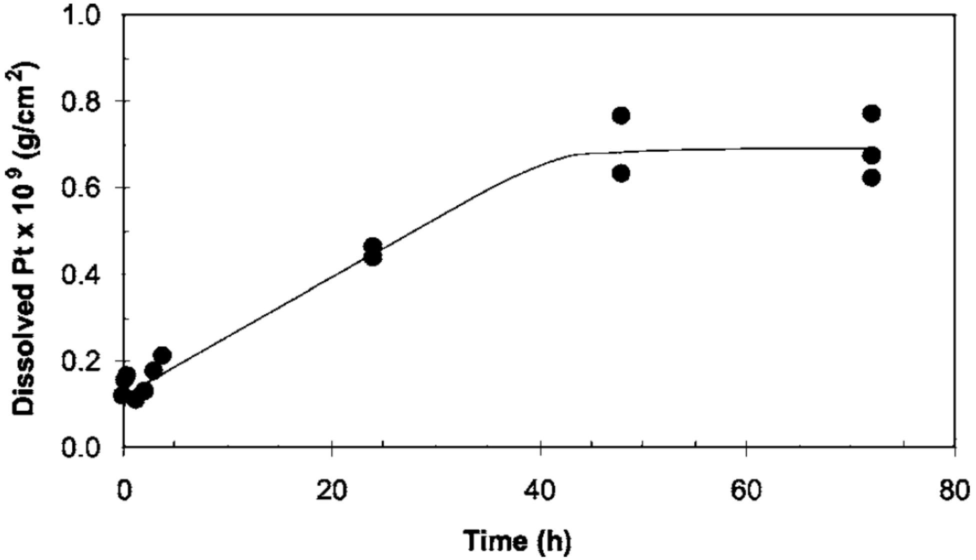
Tafel equation

$$i_a = i_0 \exp(\frac{\alpha z F \eta}{RT})$$



1 Monolayer 400 ng cm^{-2} (nA cm^{-2})
Dissolution selectivity < 0.01%

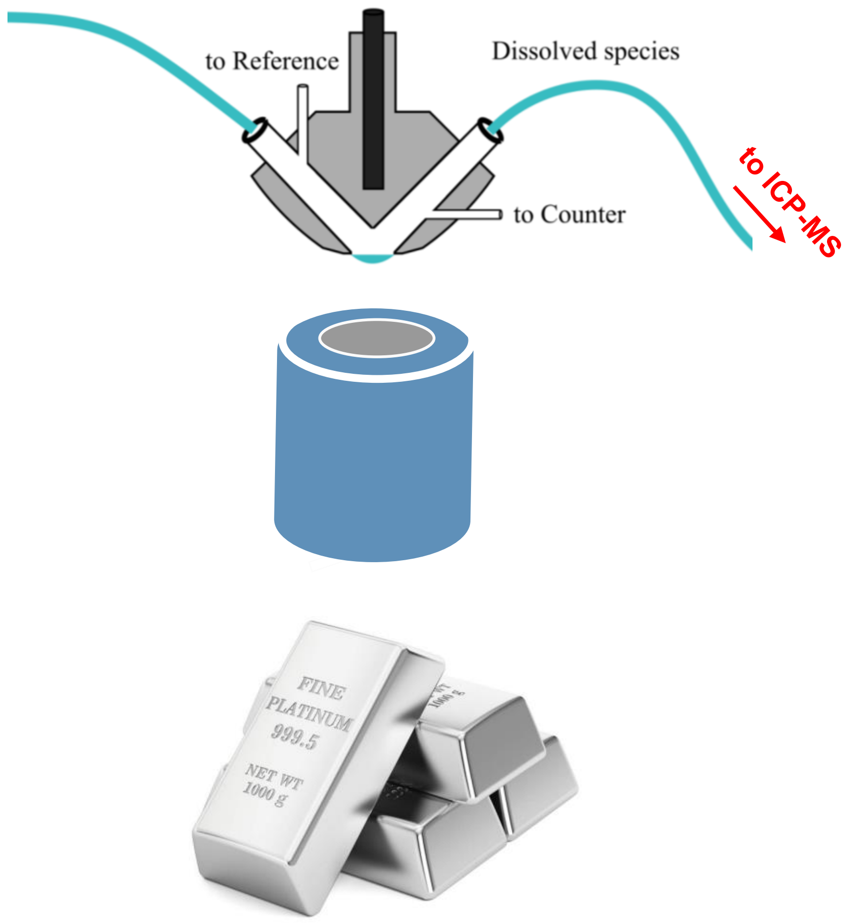
Bulk concentration (ex-situ)



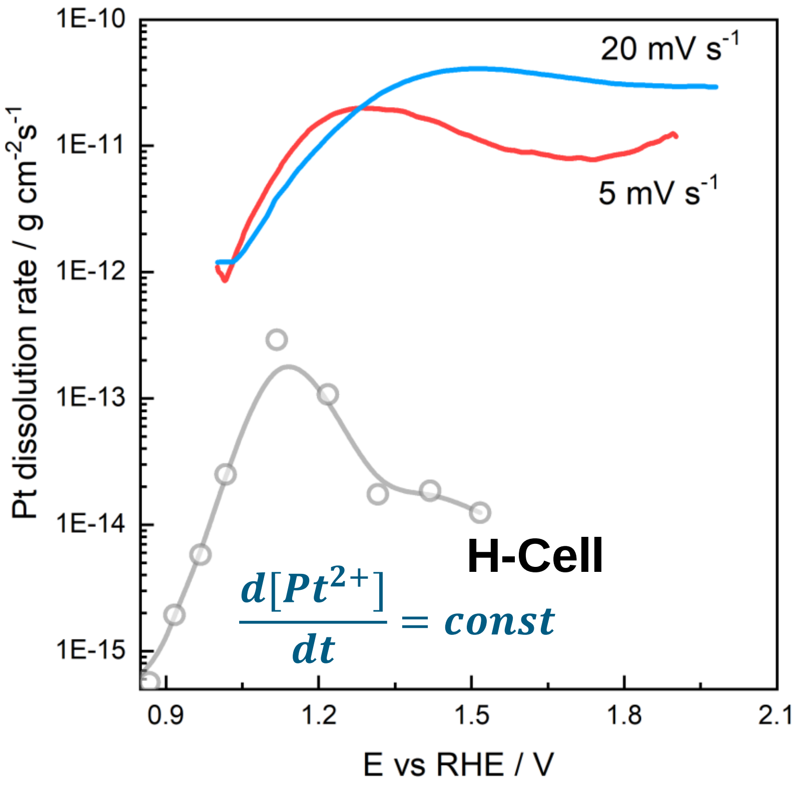
$$\frac{d[Pt^{2+}]}{dt} = const$$

[1] S. Cherevko et al. *Nano Energy 29 (2016) 275-298 (Review paper)*
From: X. Wang et al. *Electrochem. Solid-State Lett. 9 (2006) A225–A227*

Pt dissolution (kinetics?)



Time effect

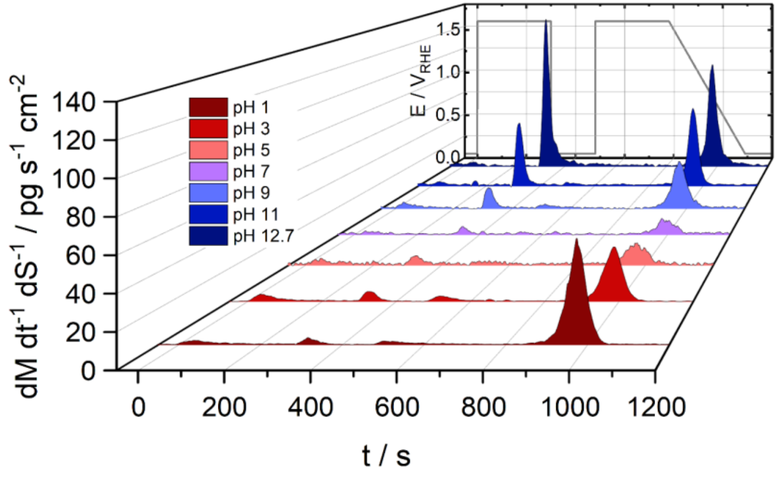


$$\frac{d[Pt^{2+}]}{dt} = const$$

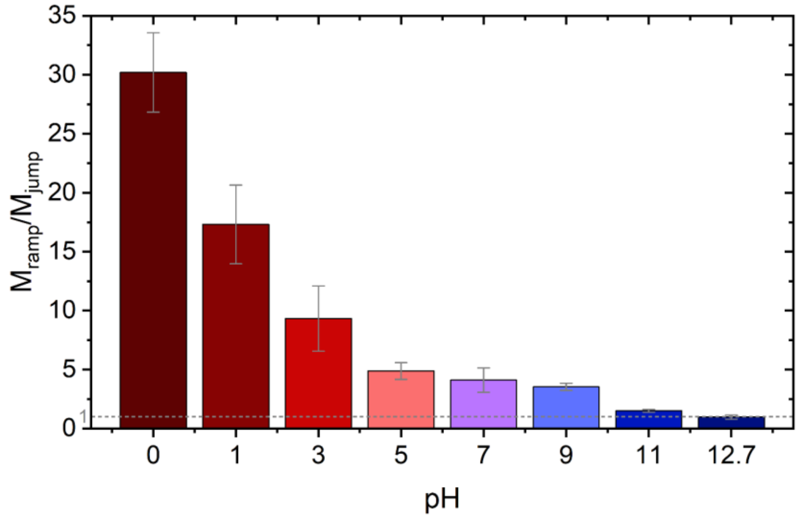
Mass transport effects

Redeposition?

A) Potential jump vs. ramp, UPL = 1.6 V_{RHE}

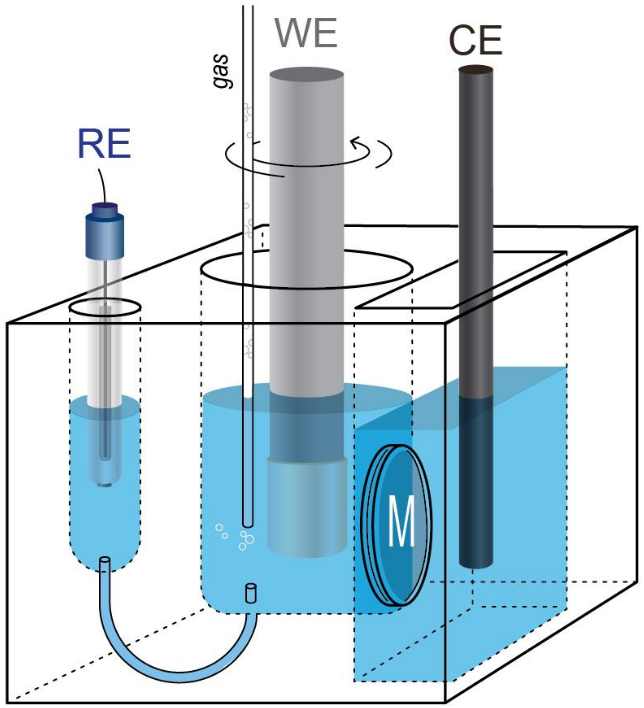


B) Dissolved amounts ratio (ramp:jump)

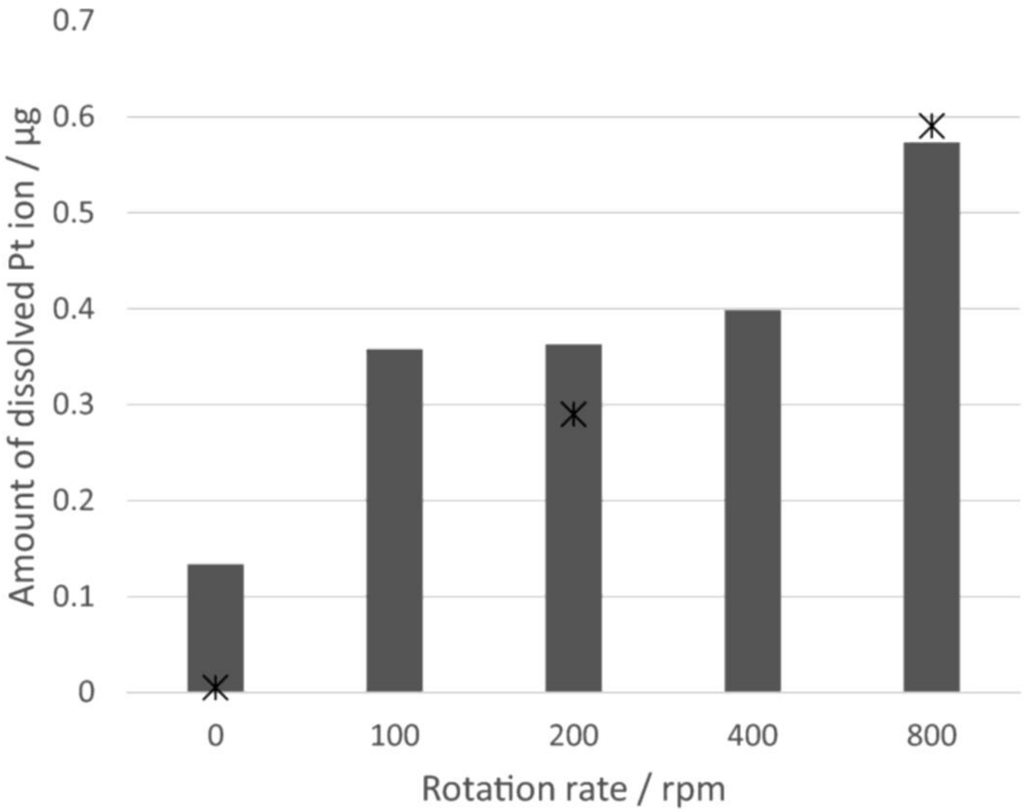


[1] S. Cherevko et al. Nano Energy 29 (2016) 275-298 (Review paper)
[2] V. Briega-Martos et al. Electrochimica Acta (2024) In Press
From: X. Wang et al. Electrochem. Solid-State Lett. 9 (2006) A225–A227

Pt dissolution mass transport



$$\frac{d[Pt^{2+}]}{dt} = f(\omega)$$



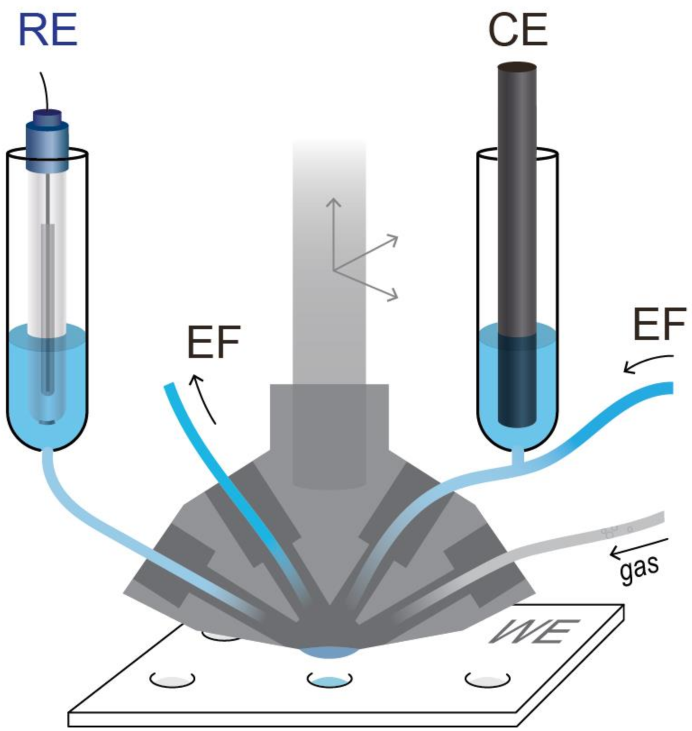
Nernst-Planck equation

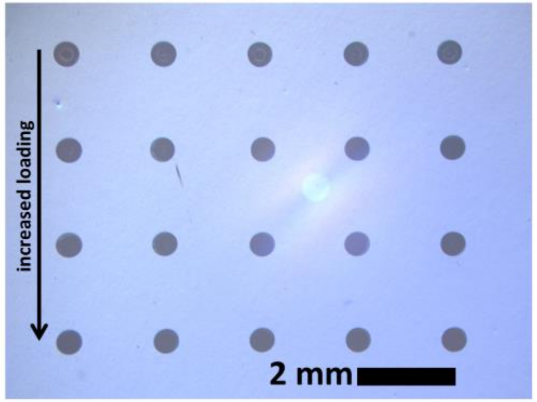
$$J = cv - D\nabla c - Dc\frac{zF}{RT}\nabla\varphi$$

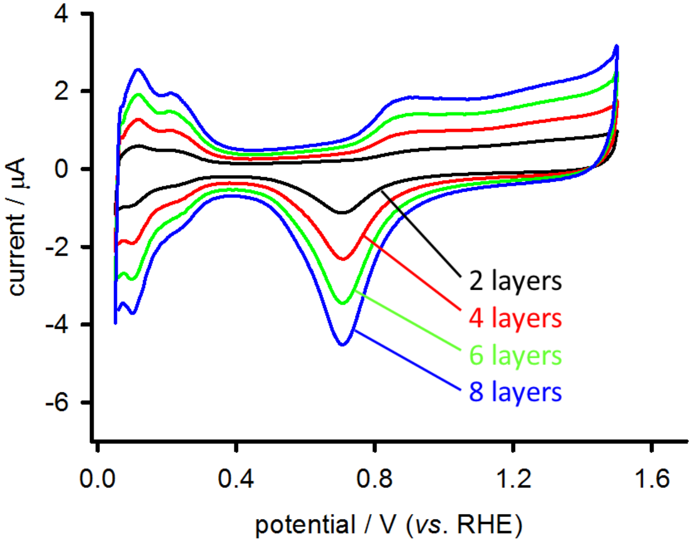
No clear trends
Dissolution/redeposition

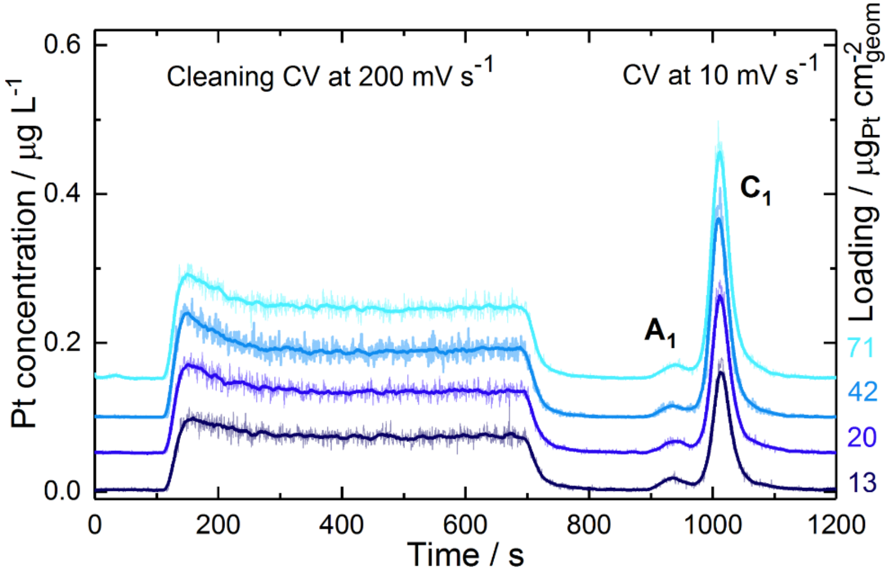
From: T. Nagai et al. J. Electrochem. Soc. 161 (2014) F789

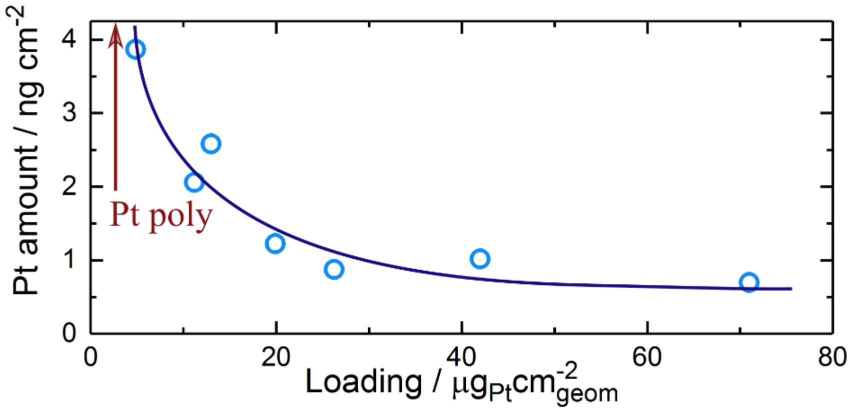
Pt dissolution from Pt/C thin film catalyst layers







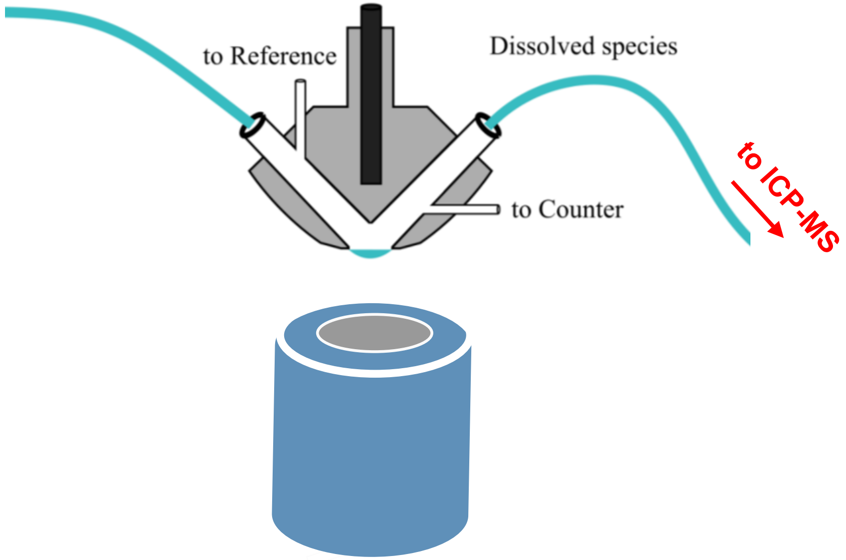




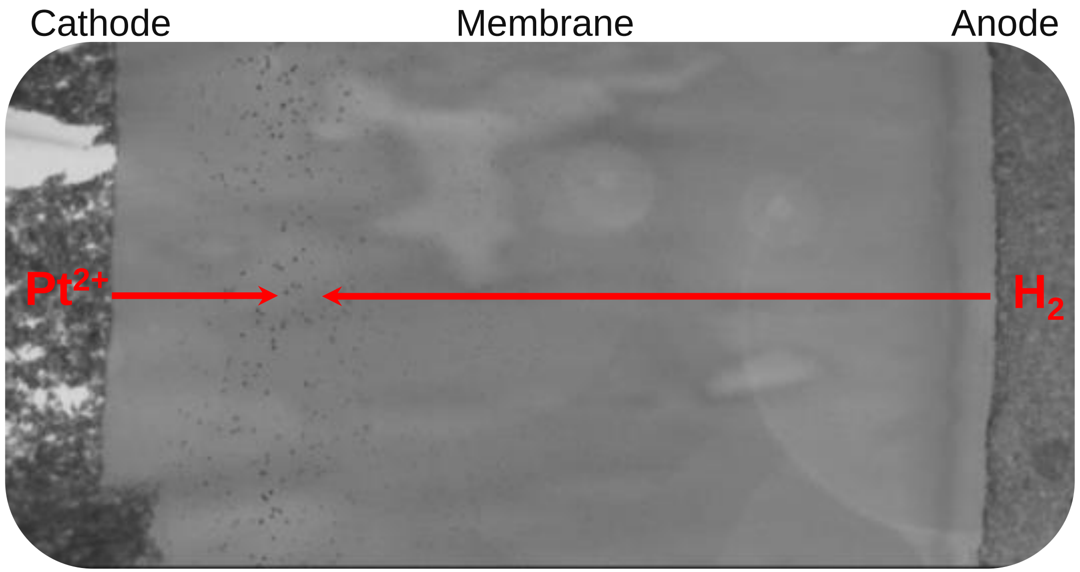
Specific Pt dissolution is increasing with loading decrease

[1] G. Keeley et al. ChemElectroChem 3 (2016) 51
[2] D.J.S. Sandbeck, .. , J. Kibsgaard, … ACS Catalysis 10(11) (2020) 6281-6290

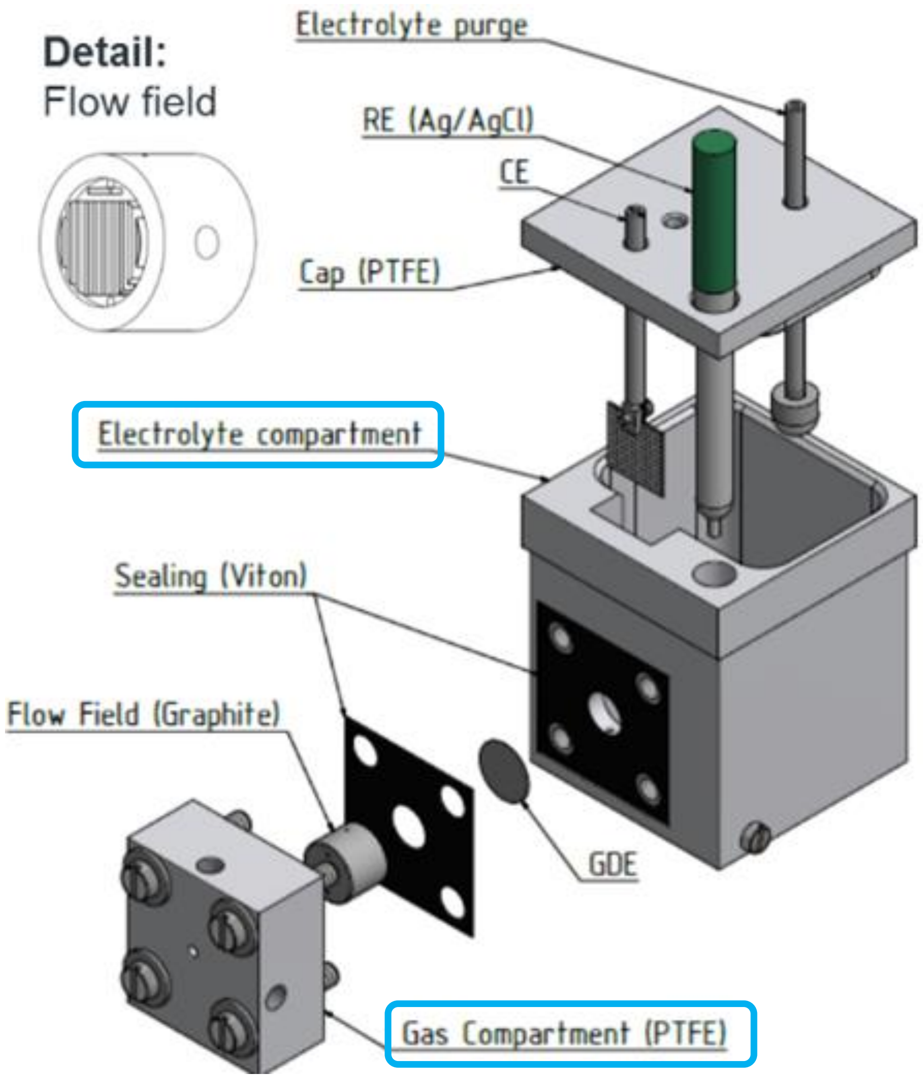
Pt dissolution in real systems

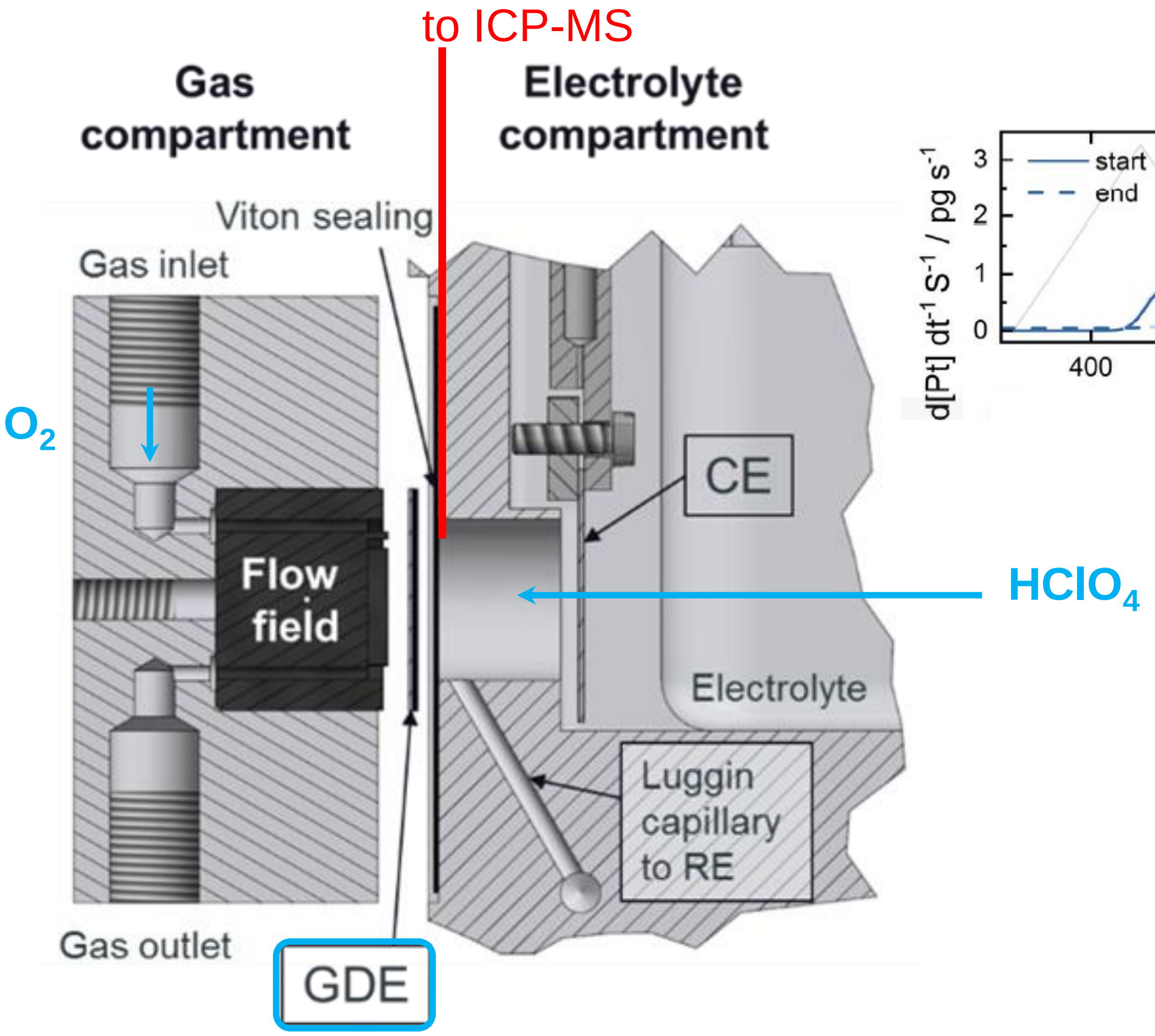


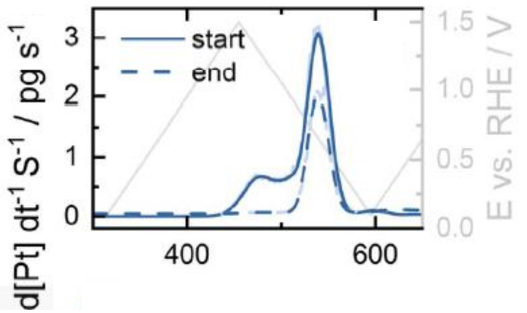
VS.



Pt dissolution from “breathing” catalyst layers





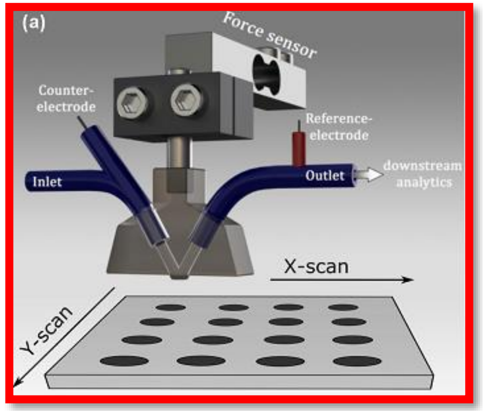


[1] K. Ehelebe et al. *JES 166 (2019) F1259-F1268.*
[2] K. Ehelebe, T. Ashraf et al. *Electrochemistry Communications 116 (2020) 106761.*

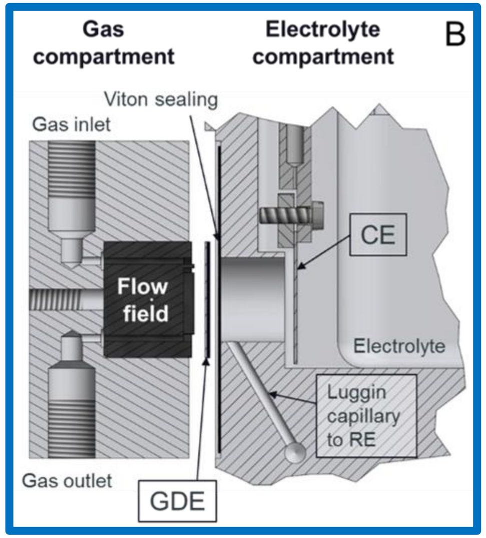
Check also:
B. A. Pinaud et al. JES 164(4) (2017) F321.

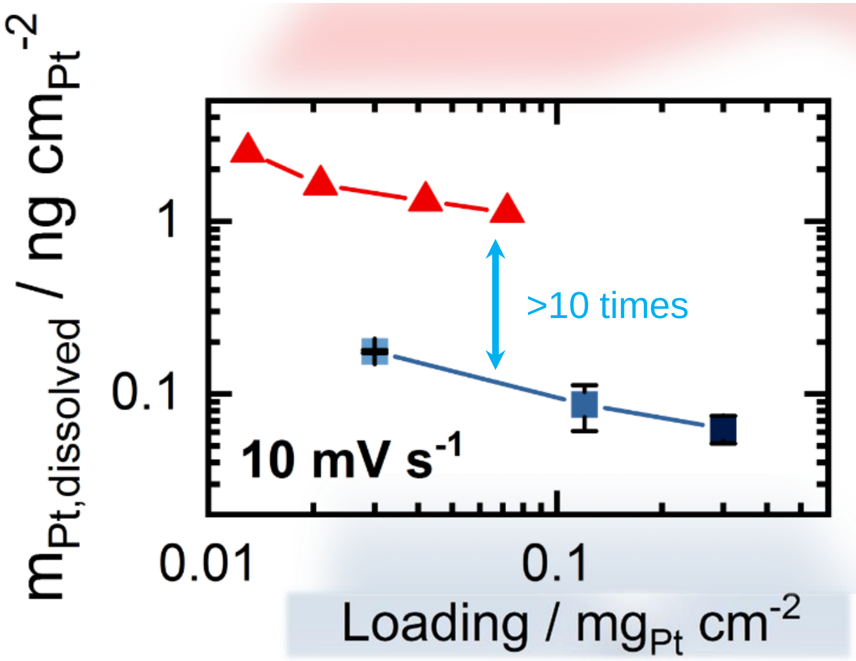
Pt dissolution: liquid vs solid electrolyte

Pt dissolution in aqueous electrolyte and MEA

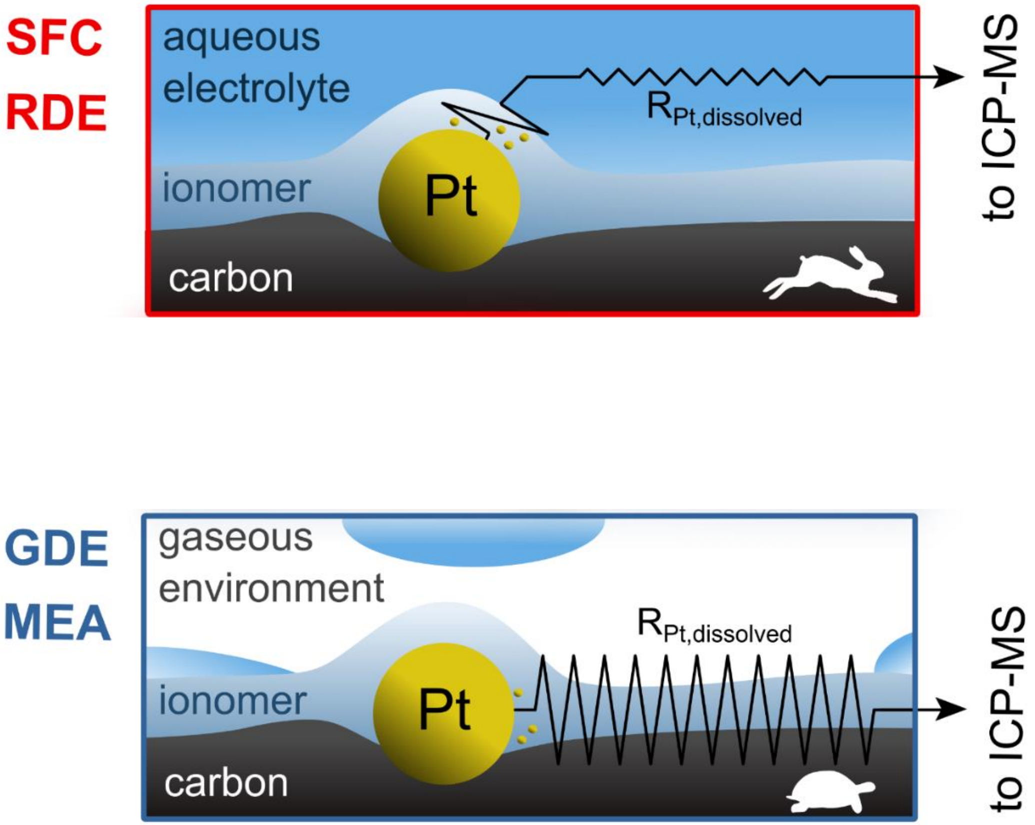


VS





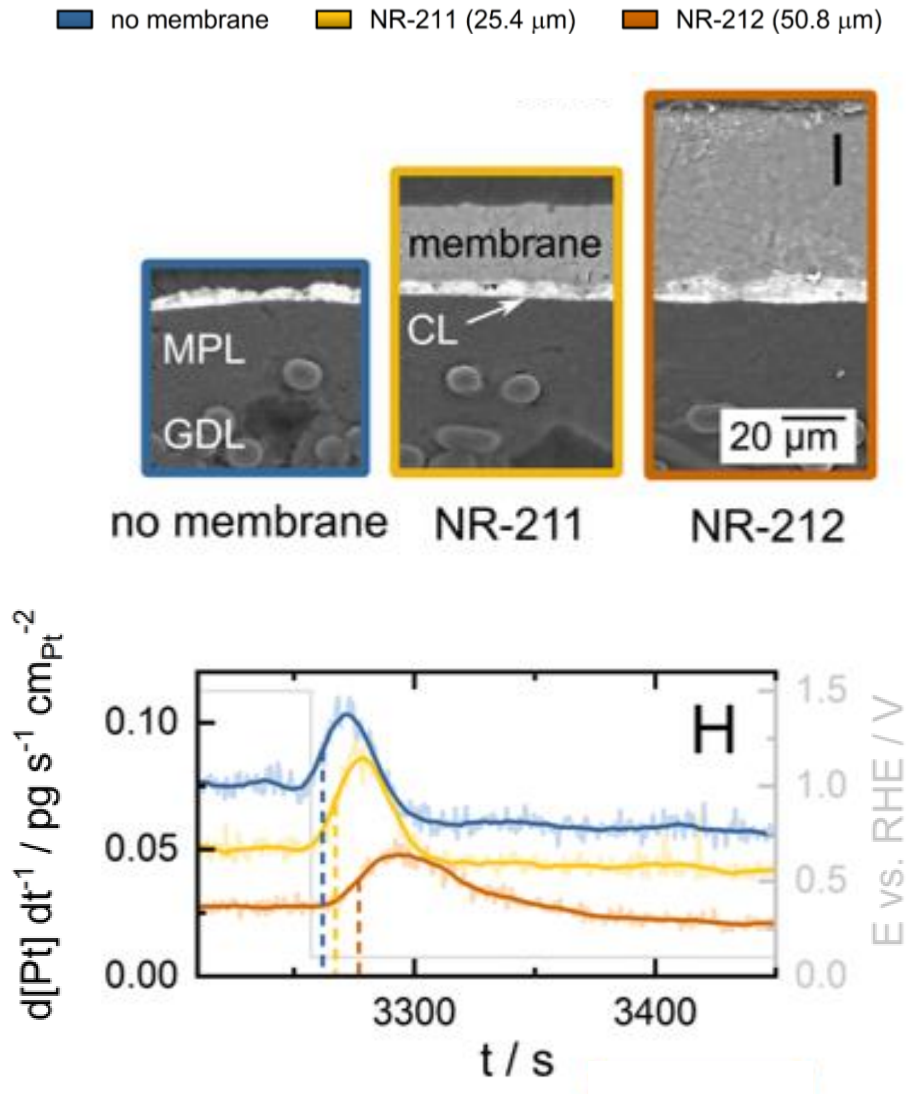
Mechanism – effect of mass transport

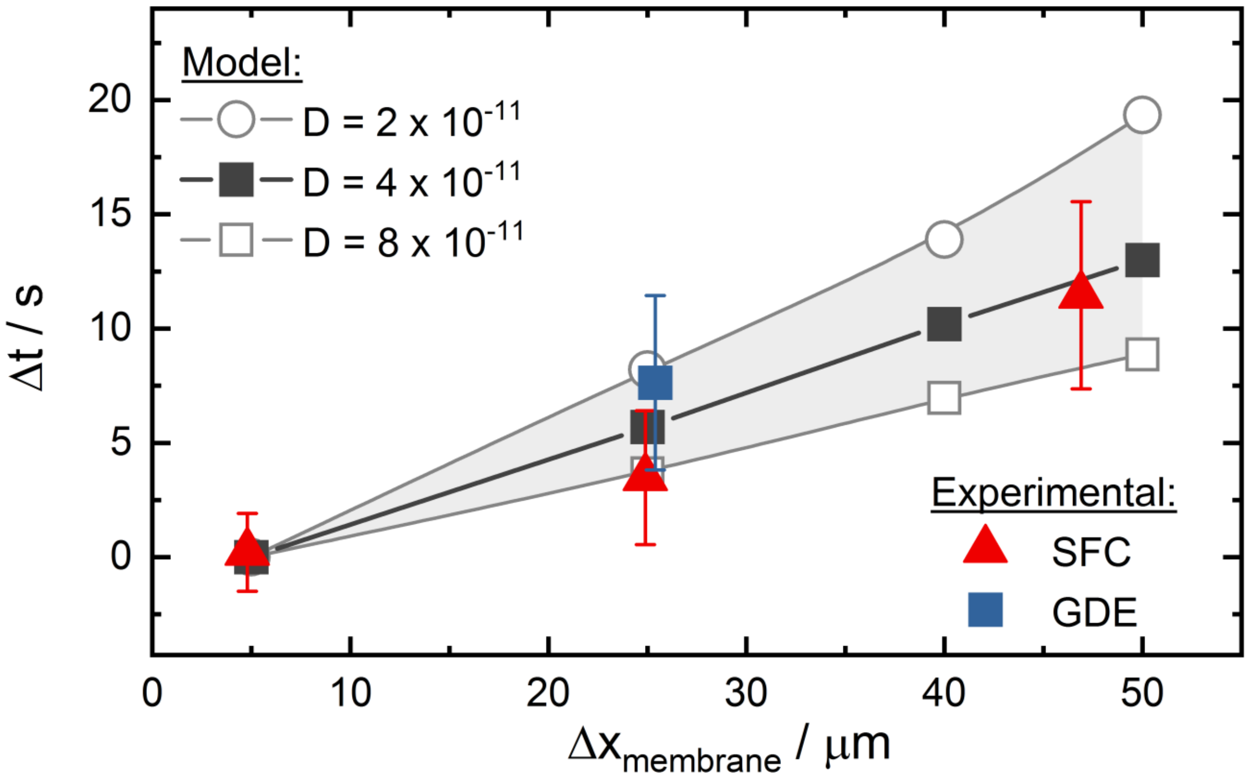


[1] K. Ehelebe et al. *Journal of The Electrochemical Society 166 (2019) F1259-F1268.*
[2] K. Ehelebe et al. *Angewandte Chemie 60 (2021) 8882-8888.*

Diffusion coefficient of Pt ions in Nafion

Experimental estimation of Ptx+ diffusion coefficient



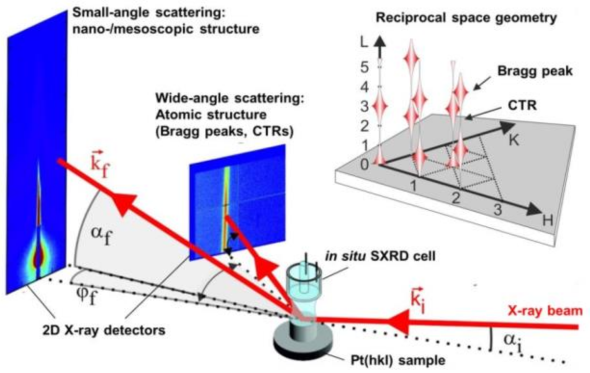


$D_{Pt/Nafion} \sim 4\text{x}10^{-11}\ m^2\ s^{-1} \ll D_{Pt/water} \sim 1\text{x}10^{-9}\ m^2\ s^{-1}$

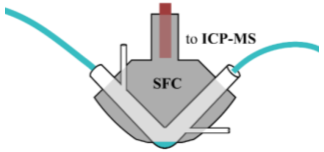
[1] K. Ehelebe et al. *Angewandte Chemie 60 (2021) 8882-8888.*

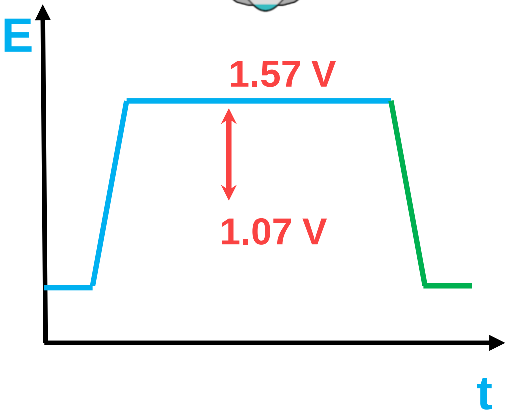
Pt dissolution mechanism

Surface XRD

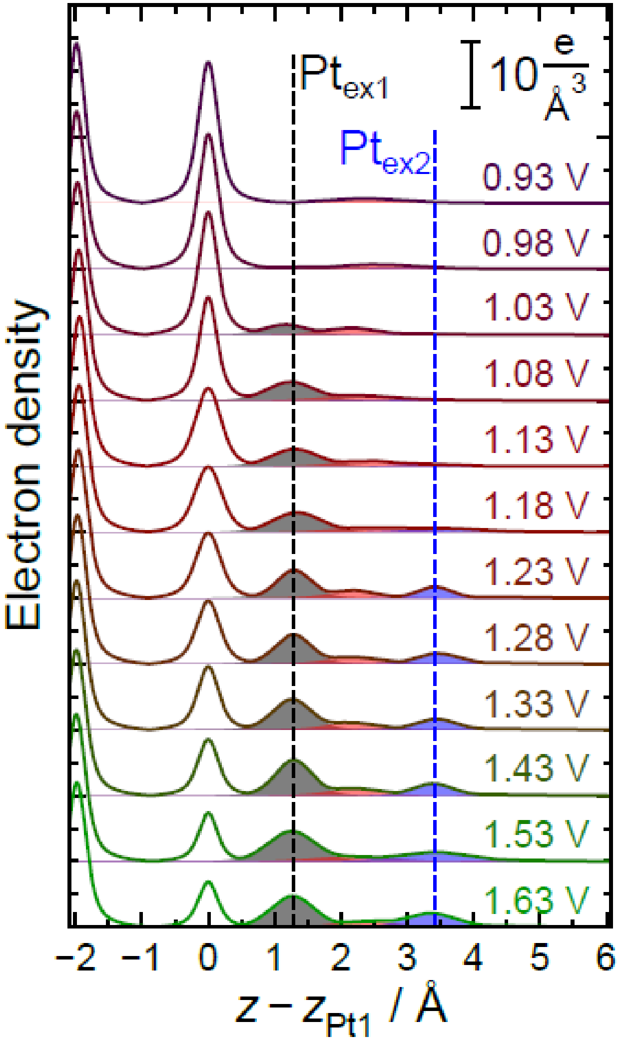


On-line ICP-MS

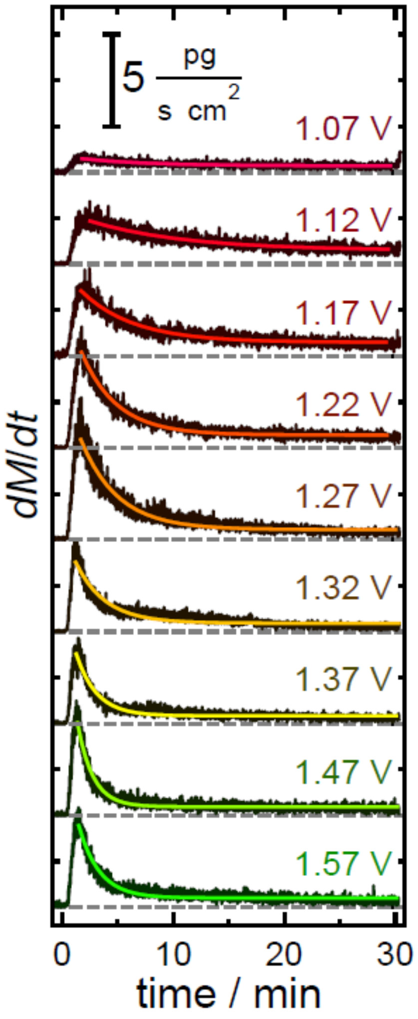




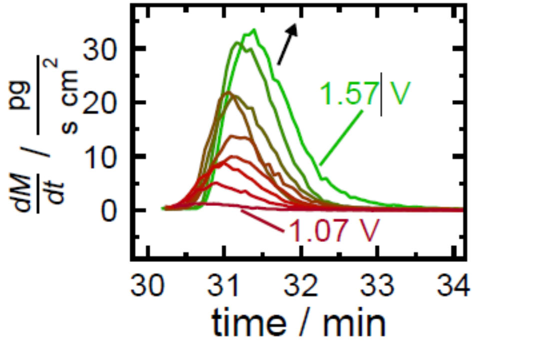
Electron density profiles



Anodic dissolution



Cathodic dissolution



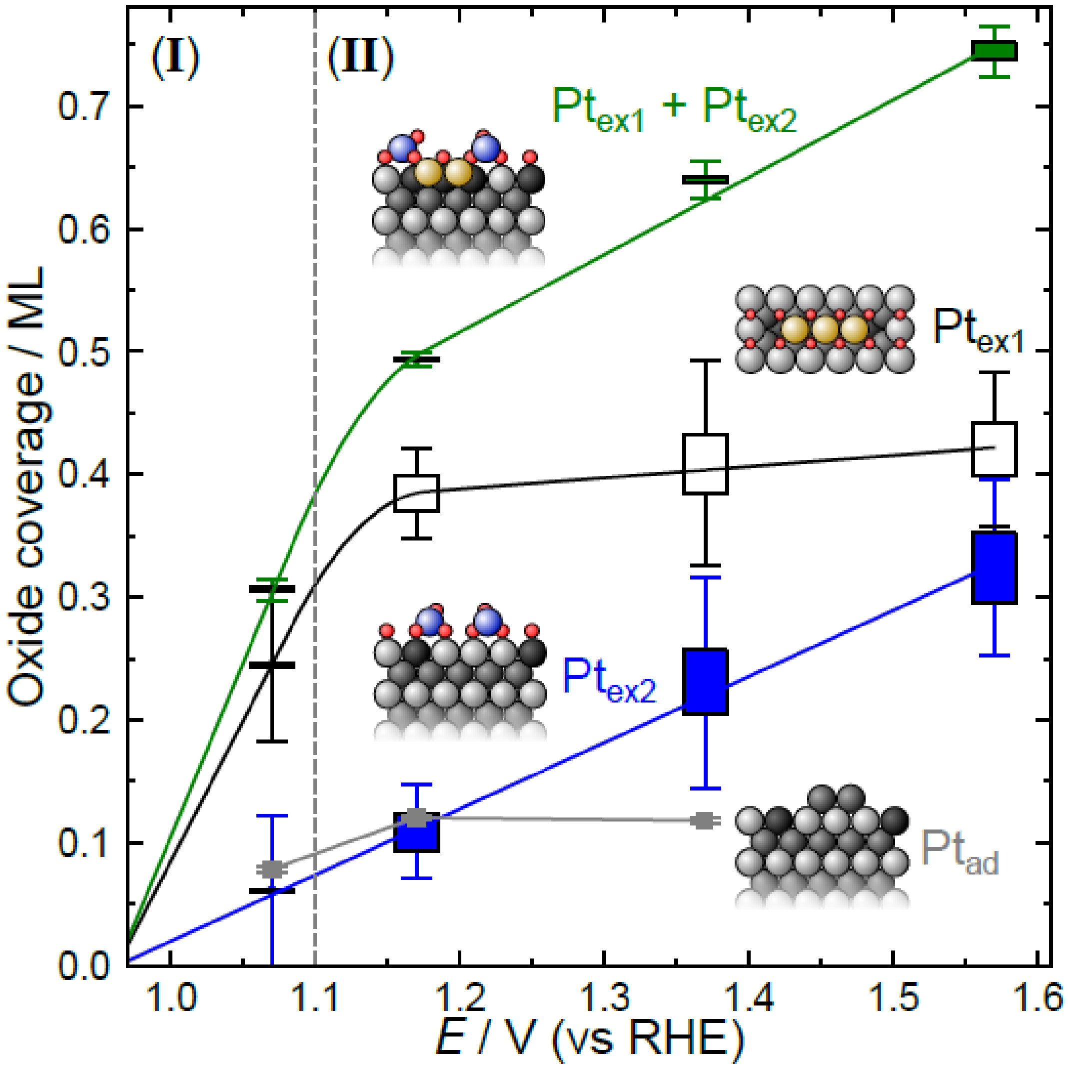
$$W_i = \int_{t=t_1}^{t=t_2} v_{S,i}(t)$$

Olaf Magnussen (Uni. Kiel, Germany)
Jakub Drnec (ESRF, France)
Federico Calle-Vallejo (UPV/EHU, Spain)

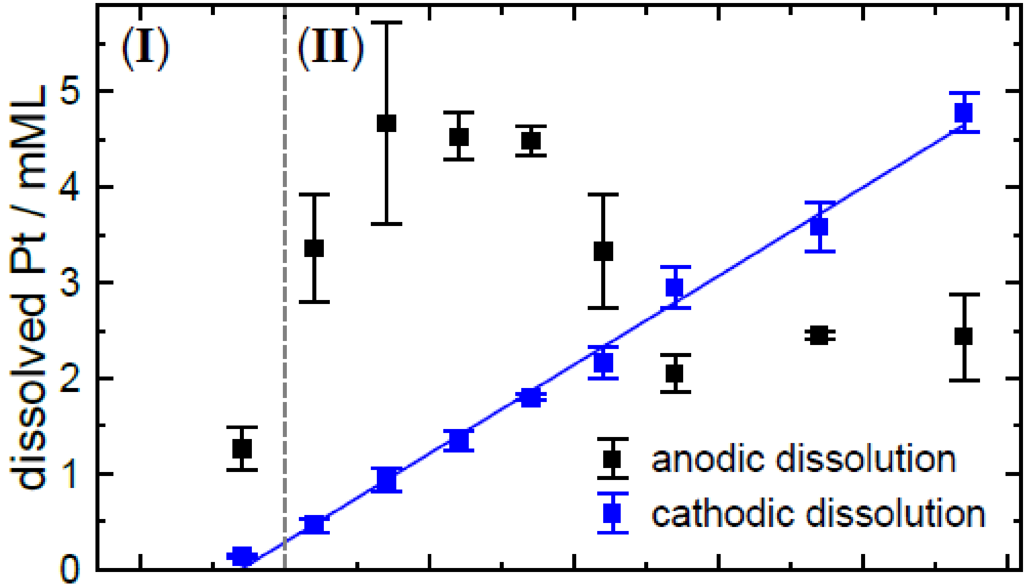
[1] T. Fuchs, … and O. Magnussen *Angewandte Chemie 62 (2023) e202304293*

Pt dissolution mechanism

SXRD: different oxides



ICP-MS: dissolution amounts



$Pt = Pt^{2+} + 2e^-$

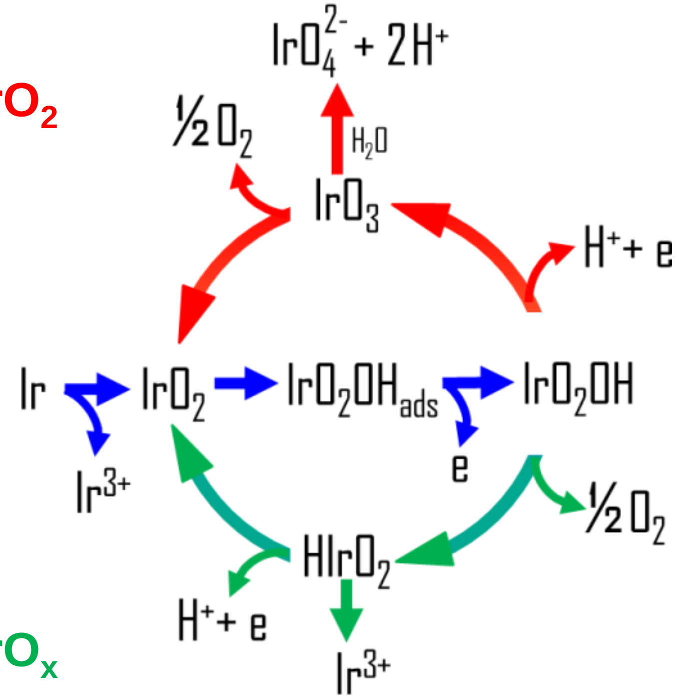
$PtO_2 + 4H^+ + 2e^- = Pt^{2+} + 2H_2O$

[1] T. Fuchs, … and O. Magnussen Angewandte Chemie 62 (2023) e202304293

Outlook: destructive reactions

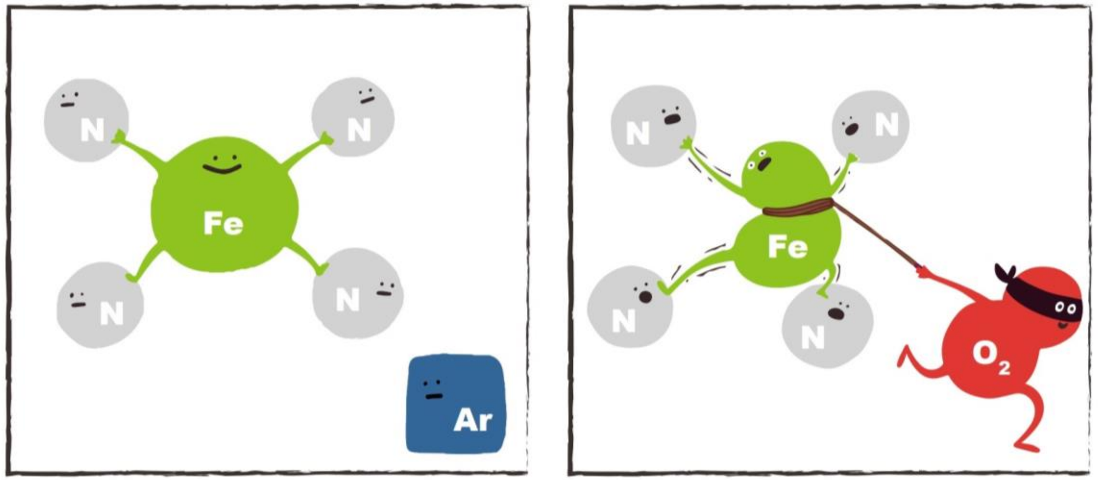
OER:

IrO_2

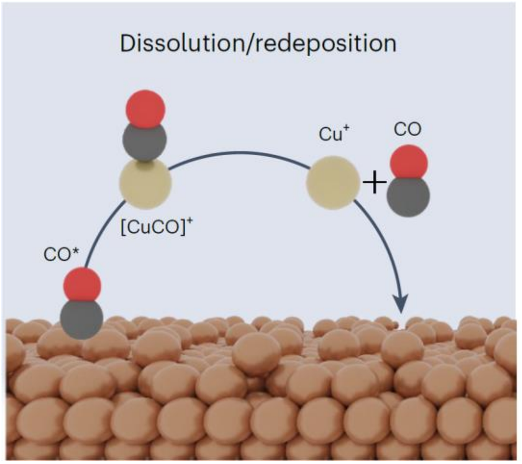


IrO_x

ORR:



CO2RR:



[1] O. Kasian et al. *Angewandte Chemie 57(9) (2018) 2488–2491*
[2] S. Geiger et al. *Nature Catalysis 1 (2018) 508-515*
[3] Y.-P. Ku et al. *JACS 144(22) (2022) 9753–9763*
[4] J. Vavra, …, R. Buonsanti *Nature Catalysis 7 (2024) 89-97*

Summary

- (Almost?) All electrocatalysts dissolve
- Dissolution can be quantified using ex-situ and in-situ ICP-MS
- Pourbaix diagrams is a good starting point to understand dissolution tendencies
- Material loss in real devices is often governed by mass transport processes
- Reactions like OER or ORR can be destructive to electrocatalysts

Team - Electrochemical Energy Conversion

From MPIE: Simon Geiger, Olga Kasian, Marc Ledendecker, Karl Mayrhofer

Posters!

Joanna Przybysz

Carolin Igel

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And many more…

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