

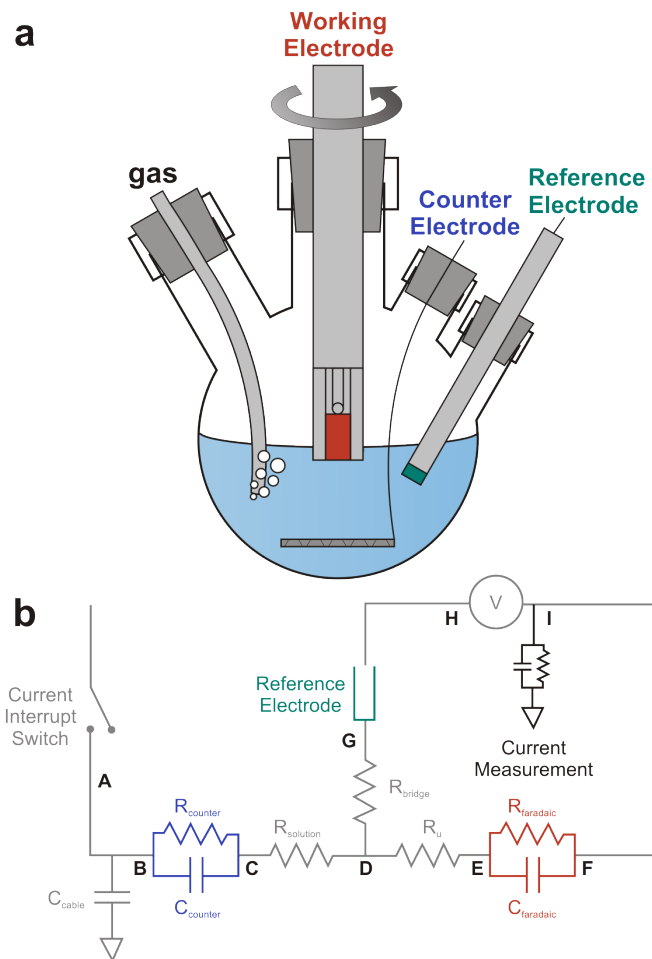
Processing of Electrocatalytic Data V1.1

Marcel Risch,
Electrochemical Energy Lab
March 2015

Feedback and discussion by Kelsey Stoerzinger, Wesley Hong and
Alex Han was greatly appreciated



Experimental setup of electrocatalytic measurements



Schematic of a three-electrode electrochemical cell. (a) Experimental setup for the three-electrode cell. (b) Circuit of a typical three-electrode cell. In these cells, the potential is measured or controlled between the working and reference electrodes (H), while the current is measured or controlled between the working and counter electrodes (I). The working electrode can be rotated to avoid limitation by transport of the analyte. An additional ring electrode offers further analytical opportunities

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<http://pubs.rsc.org/en/Content/ArticleLanding/2015/EE/C4EE03869J>

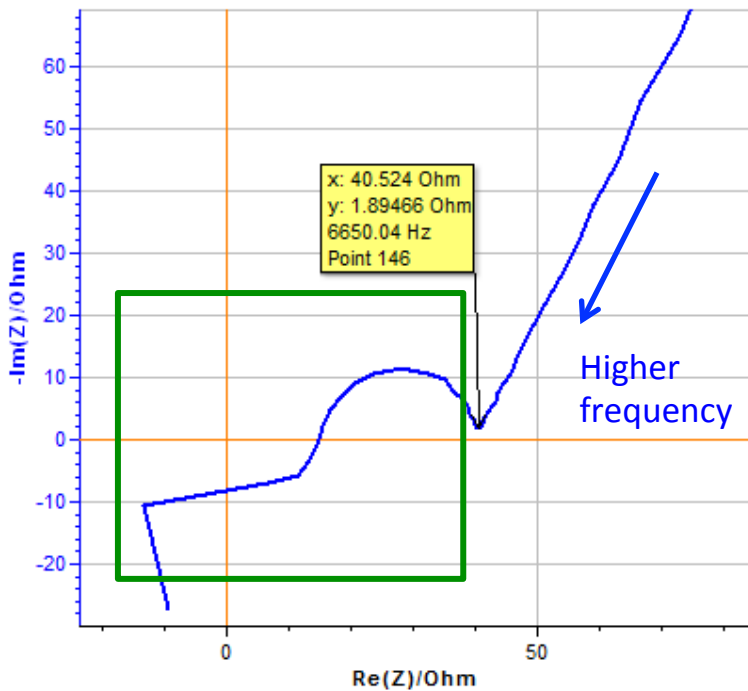
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CORRECTING MEASURED CURRENTS AND DIAGNOSTIC MEASUREMENTS

Resistance correction:

1a) Resistance measurements by impedance spectroscopy

Nyquist plot



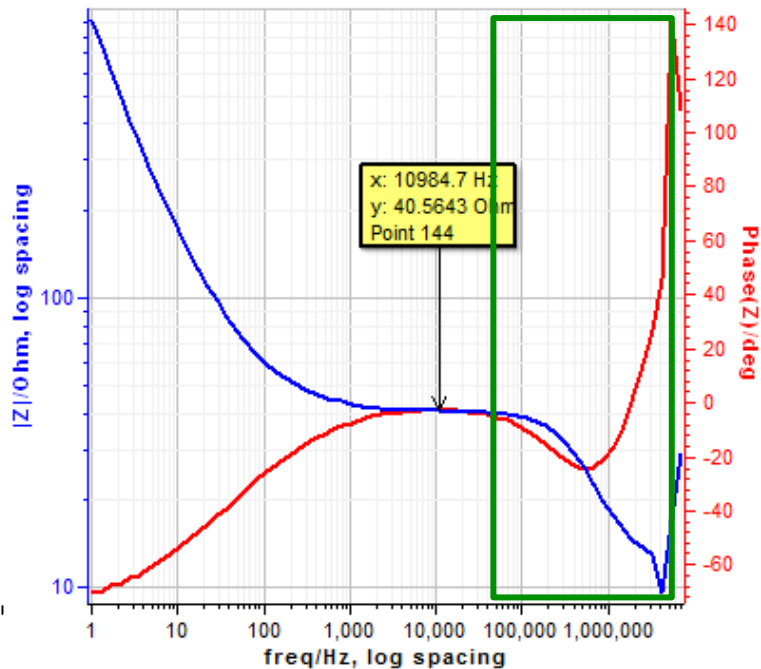
- A Nyquist plot shows the imaginary (y-axis) and real part (x-axis) of the complex resistance (also called impedance)
- We obtain the **uncompensated cell resistance** at the high frequency x-axis intercept (see yellow box)
- Caveat: we can also see impedance of components outside the electrochemical cell, e.g. the inductance of the cable (see green box).
- Marcel prefers to analyze the resistance in a Bode plot (next slide)

Experimental detail: Polished glassy carbon disk in O_2 -saturated 0.1 M KOH, open-circuit potential

Resistance correction:

1b) Resistance measurements by impedance spectroscopy

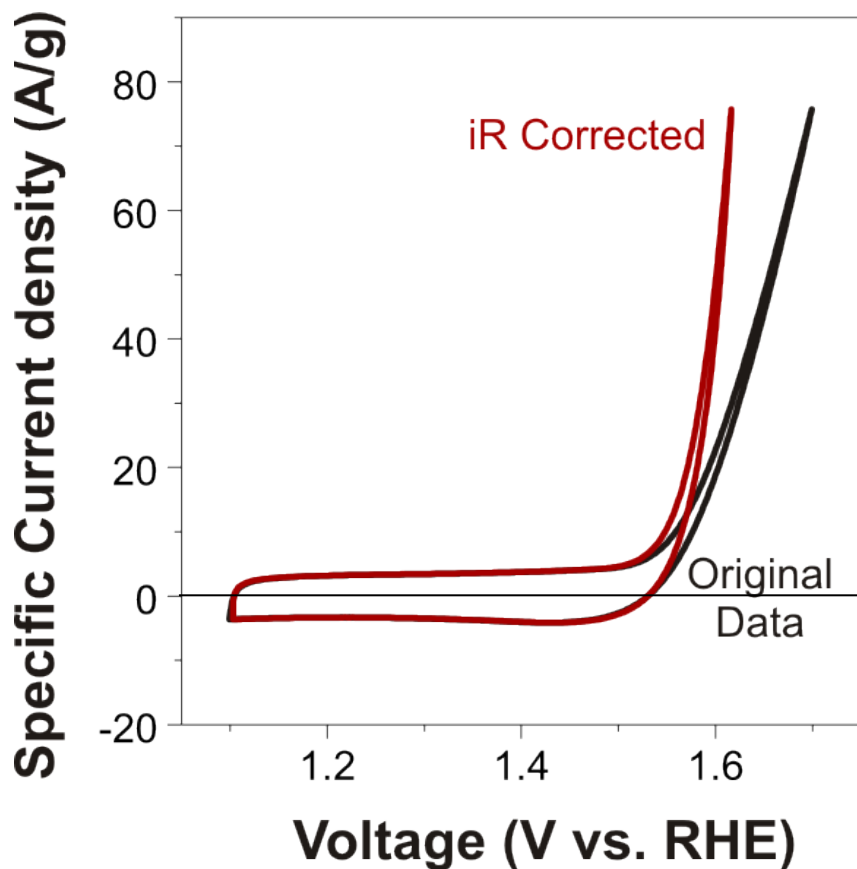
Bode plot



Experimental detail: Polished glassy carbon disk in O₂-saturated 0.1 M KOH, open-circuit potential

- A Bode plot shows both the amplitude of the impedance (y-axis 1) and the phase (y-axis 2) as function of frequency (x-axis).
- The information is equivalent to the Nyquist plot. Note a resistor has a phase angle of 0, a capacitor -90 and an inductor +90 deg.
- We obtain the **uncompensated cell resistance** at the highest frequency where the phase angle approaches 0 (see yellow box).
- We can now see that we picked up the cable capacitance and inductance at frequencies above 100 kHz. This range should be discarded in data presentation. It was recorded because we do not know before the measurement at which frequency we see the cable.

Resistance correction: 2) Applying the correction



- Using the resistance, R , obtained by impedance spectroscopy, we calculate the **corrected energy axis** using:

$$E_{\text{corrected}} = E_{\text{measured}} - iR$$

- Make sure to use current in units of A (not a current density!)
- This procedure applies to both OER and ORR

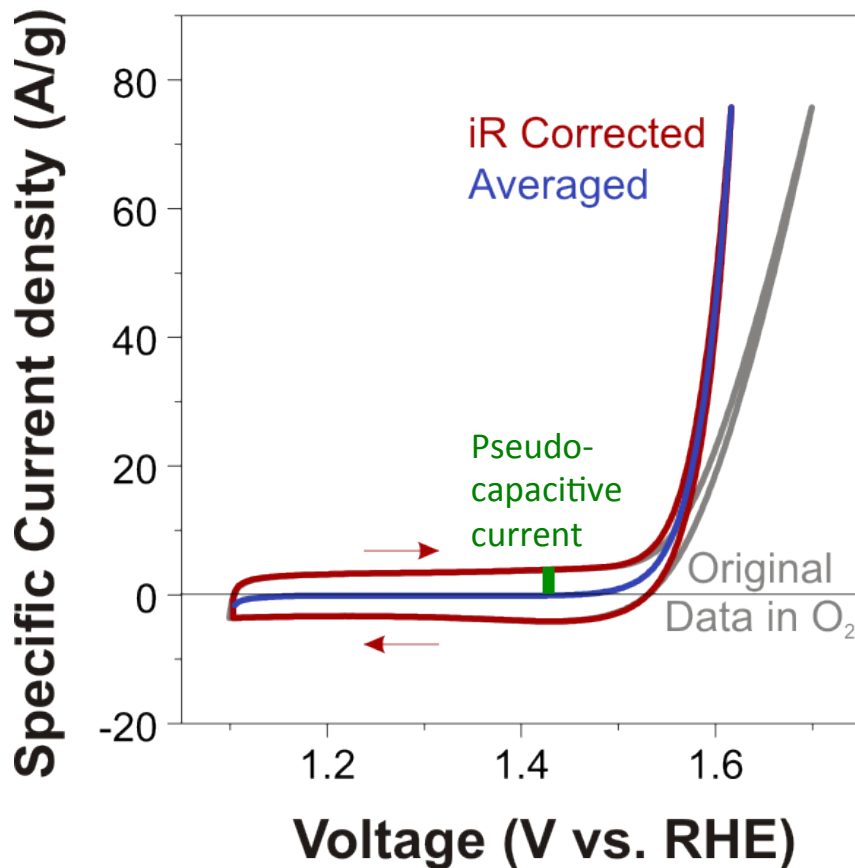
Experimental detail:

Polished glassy carbon disk in O_2 -saturated 0.1 M KOH, 10 mV/s, 1600 rpm

IrO_2 ink (Alfa-Aesar Premion, 20 μg oxide, 4 μg AB carbon, 4 μg Nafion), disk with 5 mm diameter

Capacitance correction:

1) Applying the correction for OER in CVs



- The green line indicates the amplitude of pseudo-capacitive currents; the amplitude depends on the sweep speed. We want to remove this.
- The capacitance can be corrected in some cases by the following procedure
 - a) Divide CV into two parts: current when voltage increases (arrow pointing to right) and current when voltage decreases (arrow pointing to left). The result should be a dataset with two current values for each voltage value.
 - b) At each voltage average the currents. The result is shown as the blue line
- Use this method only if the averaged currents are close to zero before OER current (as in the example)

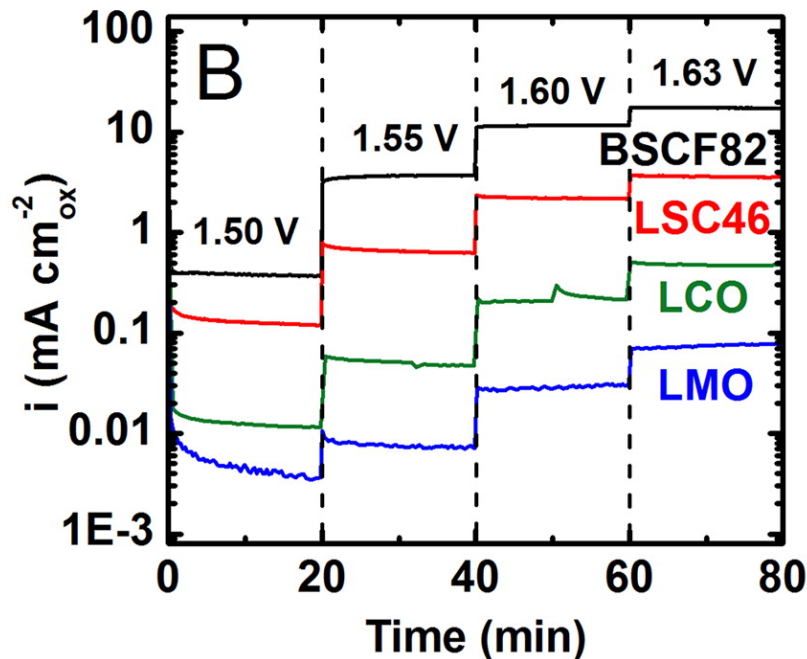
Experimental detail:

Polished glassy carbon disk in O₂-saturated 0.1 M KOH, 10 mV/s, 1600 rpm

IrO₂ ink (Alfa-Aesar Premion, 20 μg oxide, 4 μg AB carbon, 4 μg Nafion), disk with 5 mm diameter

Capacitance correction:

2a) Potentiostatic (also called amperometric) measurements



- Hold voltage in region where OER currents are suspected in CV
- Wait sufficiently long enough for steady-state and complete discharge of (pseudo) capacitive currents. The time depends on the material and applied voltage.

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<http://pubs.acs.org/doi/full/10.1021/jz301414z>

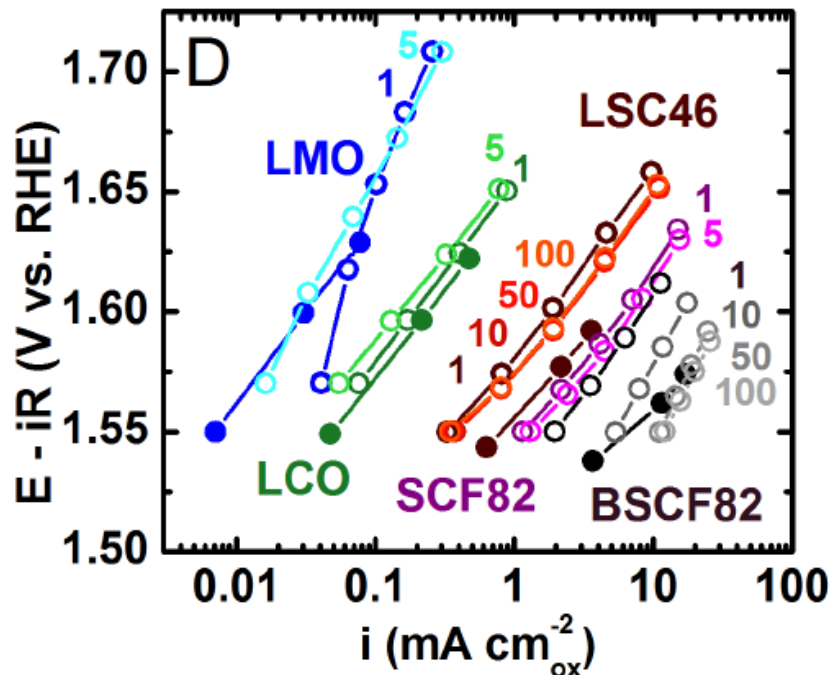
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Experimental detail:

Polished glassy carbon disk in O₂-saturated 0.1 M KOH, 10 mV/s, 1600 rpm
inks with 50 μg oxide, 10 μg AB carbon, 10 μg Nafion), disk with 5 mm diameter

Capacitance correction:

2b) Potentiostatic (also called amperometric) measurements



- Solid circles indicate Tafel slopes from potentiostatic measurements
- Open circles indicate Tafel slopes from CV measurements (please see reference below figure for CV curves)
- Tafel slopes from potentiostatic measurements are either identical to those from CV or lower because the CV measurements may contain uncorrected pseudo-capacitive currents

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<http://pubs.acs.org/doi/full/10.1021/jz301414z>

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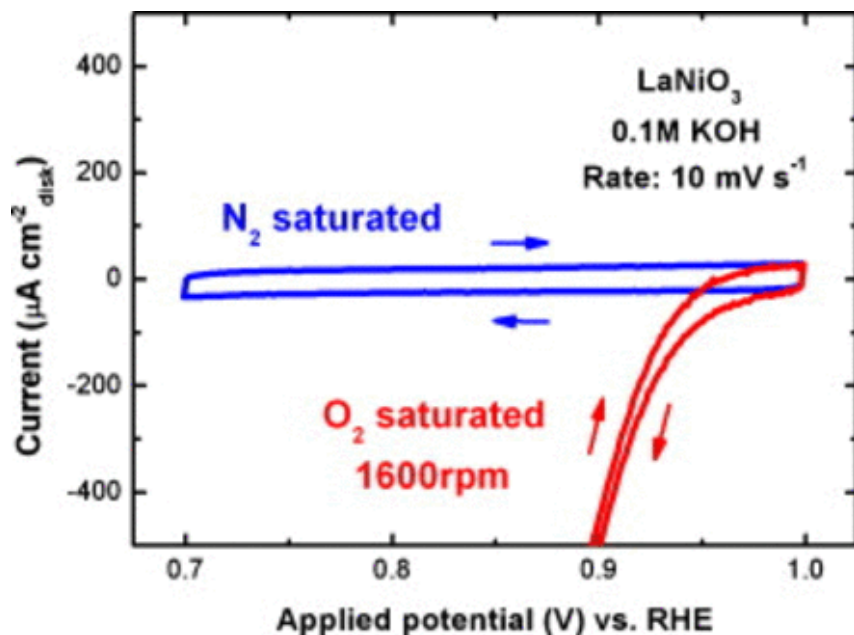
Experimental detail:

Polished glassy carbon disk in O_2 -saturated 0.1 M KOH, 10 mV/s, 1600 rpm

inks with 50 μg oxide, 10 μg AB carbon, 10 μg Nafion), disk with 5 mm diameter

Capacitance correction:

3) Applying the correction for ORR in CVs



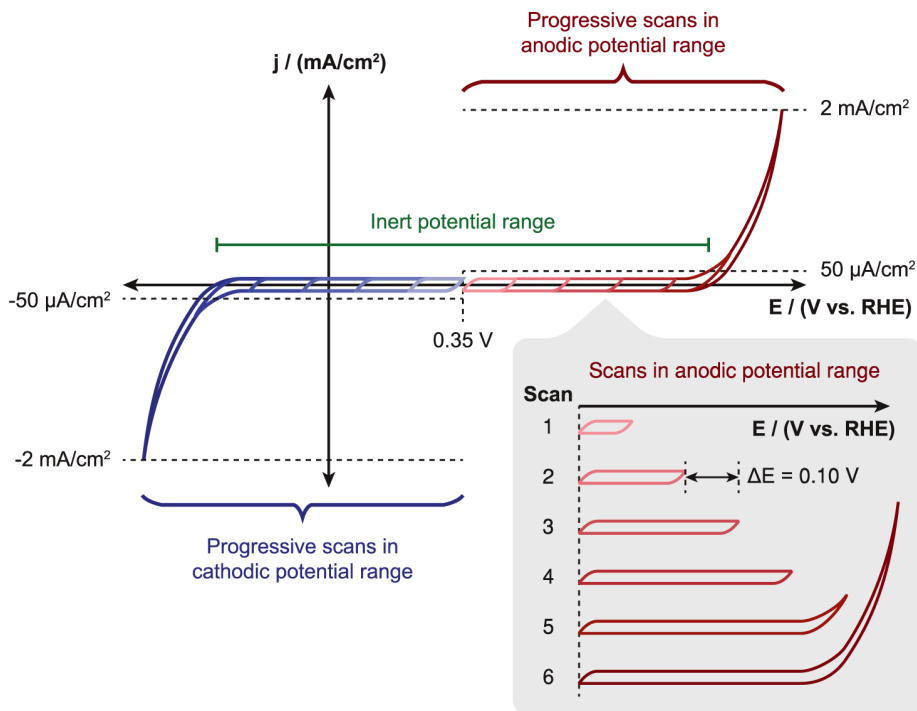
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Experimental detail:
Polished glassy carbon disk in 0.1 M KOH, 10 mV/s, 1600 rpm, LaNiO₃ ink: 50 μg oxide, 10 μg AB carbon, 10 μg Nafion, disk with 5 mm diameter

- The capacitance can be corrected in some cases by measuring a CV in Ar/N₂ and O₂-saturated electrolytes. Use the same range and sweep speed. Subtraction of the Ar/N₂ data from the O₂ data may remove the unwanted capacitive currents.
- Use this method only if the corrected currents are close to 0 at potentials above the ORR onset (as in the example).
- Potentiostatic measurements might remove the capacitance (see slides 6,7). Record appropriate potentials in Ar/N₂ and check that the currents go to 0 within the duration of each step (thus discharging the capacitance). It might be possible to subtract the currents in Ar/N₂ from those in O₂ to remove capacitance.

CV scan range:

1) Suggested protocol to determine range of stability



- Increase the range range at one end successively until the desired reaction occurs. For example, starting from a small scan range around the open-circuit potential and increasing the upper scan boundary to study OER (red curves).
- This allows to study stability. The scan range causes instability (corrosion, morphology changes etc.) if increasing the scan range produces significant changes in the shape of the CV in the OER range (or potentially before).

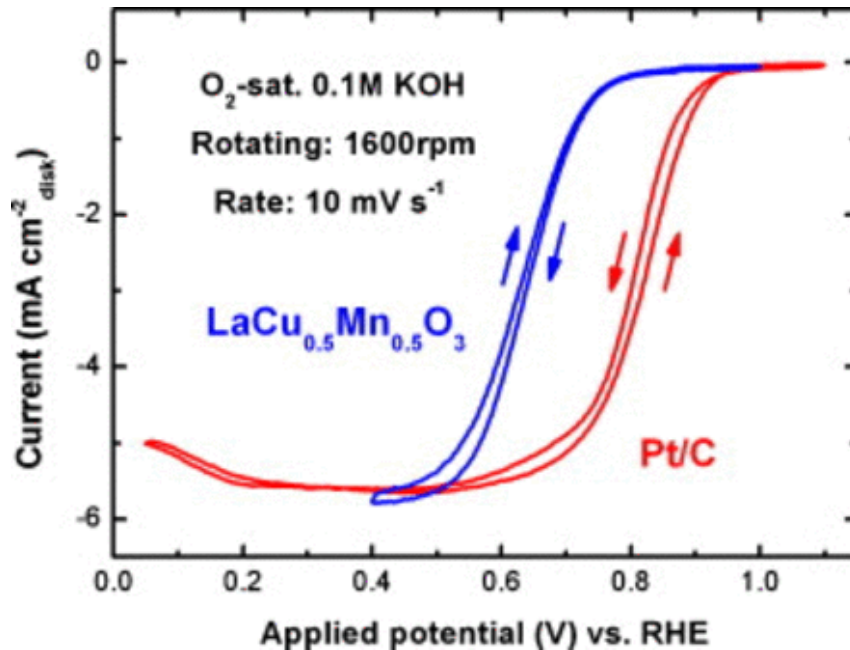
Benck et al., PLOS ONE 2014

<http://journals.plos.org/plosone/article?id=10.1371/journal.pone.0107942>

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CV scan range:

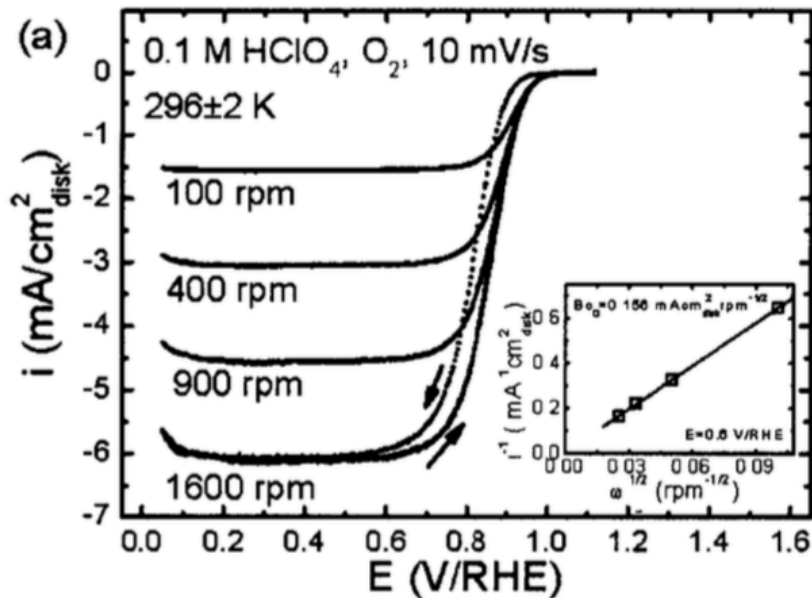
2) Some advice for ORR of oxides



- The Pt surface is stable at very reducing potentials and can be recorded until just above 0 V vs. RHE (where hydrogen evolution begins)
- Oxide surfaces are rarely stable under these reducing conditions. Often, instability occurs below ~ 0.6 V vs. RHE.
- It is recommended to identify the range of stability as described on the previous slide and then characterize the catalytic current on a freshly prepared electrode in a smaller scan range

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Limiting ORR current



Dr. Wenchao Shen, PhD thesis

<http://dspace.mit.edu/handle/1721.1/57998>

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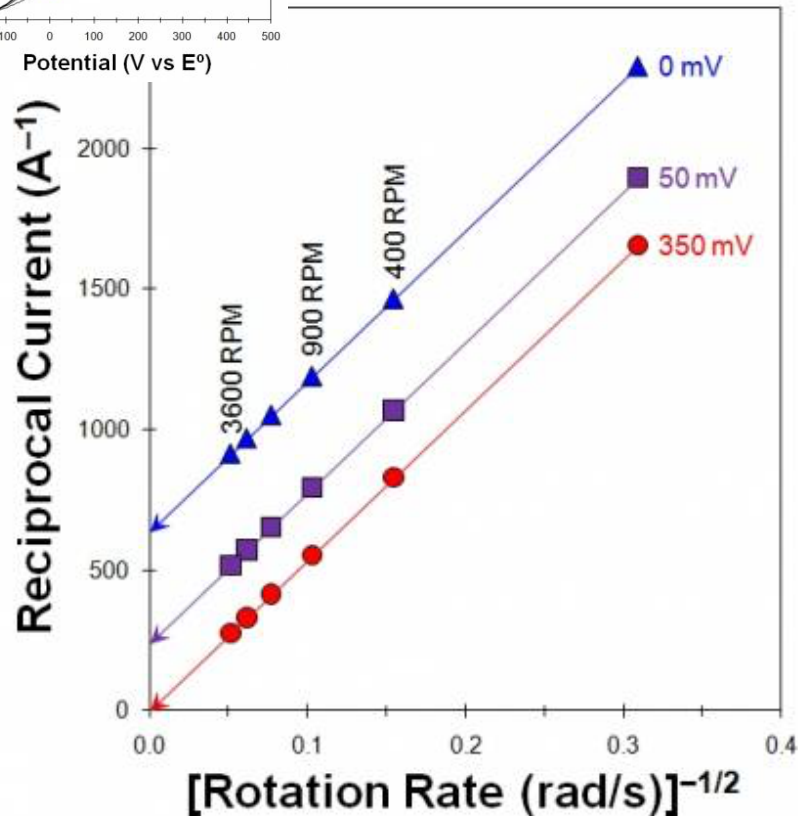
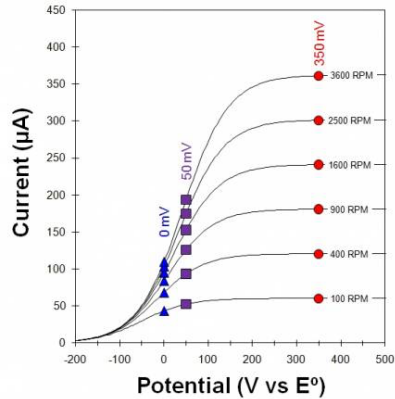
- For an ideal electrode (defined on slide x) and O₂-saturation, the limiting current only depends on the rotation rate of the disk and whether the product is water or peroxide. The limiting current density is given by:

$$j_L = x n F (D)^{2/3} \nu^{-1/6} C \omega^{1/2}$$

where $x = 0.62$ if ω in rad/s or 0.2 if ω in rpm, n is the number of transferred electrons, F is the Faraday constant, D is the diffusion coefficient, ν the kinematic viscosity, C the concentration of the reactant and ω is the rotation rate.

- The limiting current is a bad choice to compare catalysts as all catalysts that produce water will have the same limiting current at the same rotation rate.

Koutecky–Levich analysis



- The linear portion of the data on a Koutecky-Levich plot is described by the Koutecky-Levich equation:

$$\frac{1}{i} = \frac{1}{i_K} + \left(\frac{1}{0.620 n F A D^{2/3} \nu^{-1/6} C} \right) \omega^{-1/2}$$

- The axis intercept in this plot is the apparent kinetic current (further correction may be necessary, see slide 23). Use this parameter to compare the activity of catalysts

http://wiki.voltammetry.net/pine/rotating_electrode/theory#koutecky-levich_analysis

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Summary and additional recommendations

- Oxygen evolution reaction
 - Remove capacitive currents by averaging positive and negative going scans in CV
 - Analyze catalytic currents using this average
 - Alternatively, obtain the catalytic currents from potentiostatic experiments
 - The reactant is abundant (55 M H_2O), the currents should not be limited by mass transport (i.e. no rotation dependence in RDE experiments)
- Oxygen reduction reaction
 - Remove capacitive currents subtracting CVs recorded in Ar-saturated electrolyte from CVs recorded in O_2 -saturated electrolyte
 - Analyze catalytic currents using the currents with positive-going voltage (i.e. from low voltages to high voltages on the RHE scale).
 - Alternatively, obtain the catalytic currents from potentiostatic experiments in O_2 -saturated electrolyte and also record potentiostatic experiments in Ar-saturated electrolyte
 - The reactant supply is limited ($\sim 1 \text{ mM O}_2$), the currents are limited by mass transport. (defined rotation dependence)
- Catalytic currents are often shown in Tafel plots ($\log I$ vs. E) where they should give a linear trend (see slide 26).

EVALUATING CATALYTIC ACTIVITIES

Guidelines for evaluation of ORR activities

1. It is most meaningful to compare normalized currents; the normalization can be based on the loading (mass activity) or surface area (specific activity). → *slide 19* (next slide)
2. The diffusion limited current i_d of the ORR should be within 10% of the theoretical value for analysis using the Levich equation. → *slide 20*
3. The activity should be linear dependent on the loading. Otherwise the catalyst is not fully utilized → *slides 20-22*
4. The ink-casted electrode should be flat (<0.1 μm ?) for correct analysis of limiting and kinetic currents. → *slide 23-24*
5. The activity of different materials should be discussed using kinetic currents, i.e. at currents between ~10% and ~80% of the diffusion limited current, ideally below the half wave potential. → *slide 25*

Based on guidelines in: Mayrhofer et al., Electrochim. Acta 53, 3181 (2008)

<http://www.sciencedirect.com/science/article/pii/S0013468607014272>

Determining particle surface areas

- Many options all with advantages and disadvantages. Please consult the IUPAC recommendations compiled by Trasatti and Petrii (cited below).
- Common ex-situ determinations of particle surface areas are: analysis of SEM or TEM pictures or gas adsorption isotherms (BET method)
- In-situ determination of particle surface areas relies on capacitive currents of the double layer or adsorption of gas molecules (e.g. H₂ or CO)

Trasatti&Petrii, Pure Appl. Chem. 63, 711-734 (1991)

<http://www.iupac.org/publications/pac/63/5/0711/>

Finding true catalytic activities:

1) Loading dependence

- It is recommended to always check the loading dependence of the catalyst.
- The catalyst loading must be sufficiently high to ensure complete coverage of the electrode surface. This criteria is met for the data falling within about 10% of the limiting current.
- The reason for the loading dependence of the currents is that the low amount of supported catalyst is no longer capable of spreading completely over the whole surface of the glassy carbon support; therefore uncovered, inactive areas remain. The extent of this effect thus depends catalytically active area.
- Note: Too high loading makes the kinetic region very small and the diffusion limit is reached at a low overpotential, thus producing large uncertainties.

Mayrhofer et al., *Electrochim. Acta* 53, 3181 (2008)

<http://www.sciencedirect.com/science/article/pii/S0013468607014272>



2) Surface structure influences apparent onset of catalytic activity

$$\psi = \frac{A_{\text{act}}}{A_{\text{geo}}}$$

- While the diffusion limited current does not depend on the catalyst surface or catalyst loading, the kinetic current does!
- For $\psi > 1$ apparent electrocatalysis might be naively but wrongly inferred whereas for $\psi < 1$ the deduced electrochemical rate constant will be less than the actual catalytic rate constant
- We should select the measurement parameters to approximate a flat surface as good as possible

Masa et al., Nano Research 7, 71 (2013)

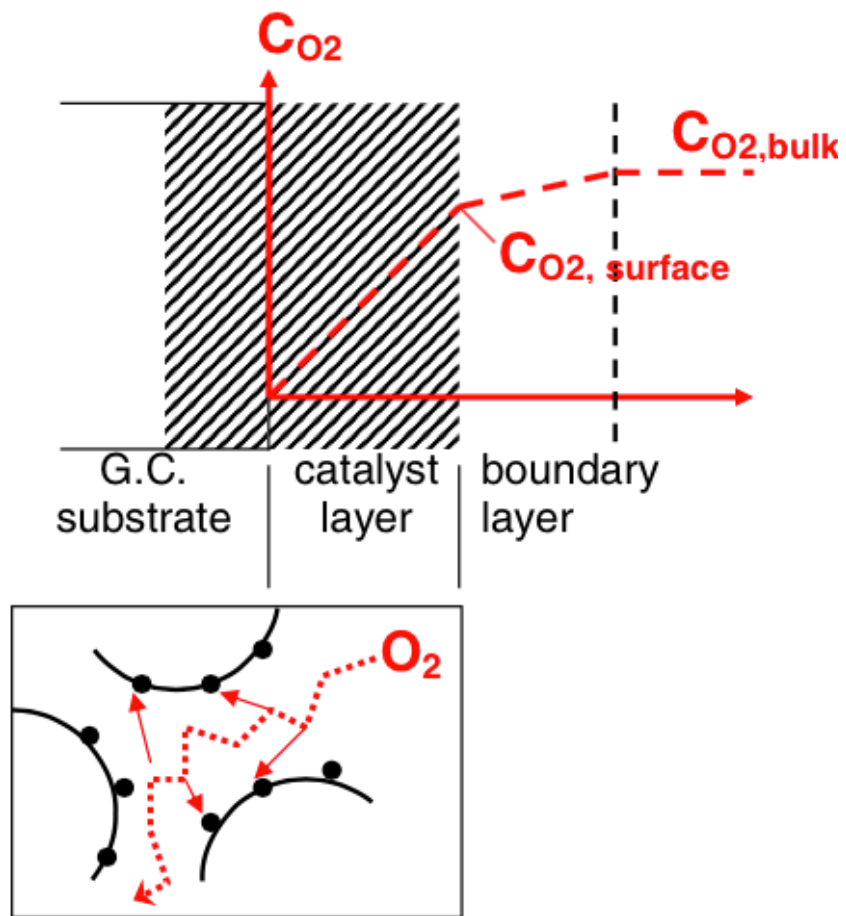
<http://link.springer.com/article/10.1007%2Fs12274-013-0372-0>

3) Distribution influences apparent onset of catalytic activity

- To make things worse, the activity also depends on agglomerate structure, particle contact and diffusion properties of oxygen in the ionomer film
- Please see Ke et al., *Electrochim Acta* 72, 120 (2012) for further discussion:
<http://www.sciencedirect.com/science/article/pii/S001346861200535X>
- Thrive for a homogenous distribution of catalyst particles

Finding true catalytic activities:

4)Explanation of loading dependence



- Two types of mass transfer limitation exist:
 - external diffusion as described by the rotating-speed-dependent Levich equation (slide 13).
 - internal diffusion within the electrode in which the electrode thickness is the governing parameter (see graphic). The electrode thickness is closely related to the catalyst loading of the electrodes.
- It is recommended to remove internal diffusion by making a layer thinner than 100 nm (calculation on next slide).
- Mathematical correction of the apparent kinetic current is possible if Fick's law is obeyed (i.e. limiting current proportional to 1/loading):
$$1/j_{k,catalyst} = 1/j_{k,apparent} - 1/j_{limiting}$$

Used with permission from Shih et al., J. Phys. Chem. C, 112, 123 (2008)

<http://pubs.acs.org/doi/abs/10.1021/jp071807h>

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Calculating the thickness of ink-casted electrodes

The thickness of ink-casted catalyst films based on Nafion is:

$$L = \psi / [(1-\theta) \rho m S \times 10^4]$$

where

ψ – Catalyst to geometric area ratio

θ – Volume fraction of Nafion

ρ – Density of the catalytic powder (in g/cm³)

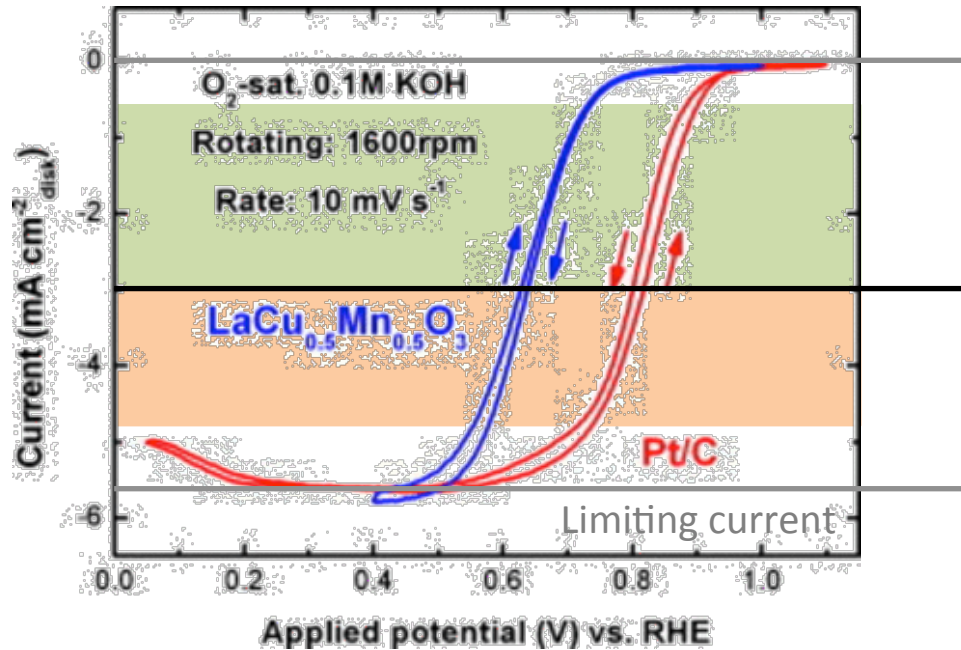
m – mass fraction of the supported catalyst

S – specific area of the catalyst (in m²/g)

Gloaguen, et al., J. Appl. Electrochem 24, 863 (1994)

<http://link.springer.com/article/10.1007%2FBF00348773>

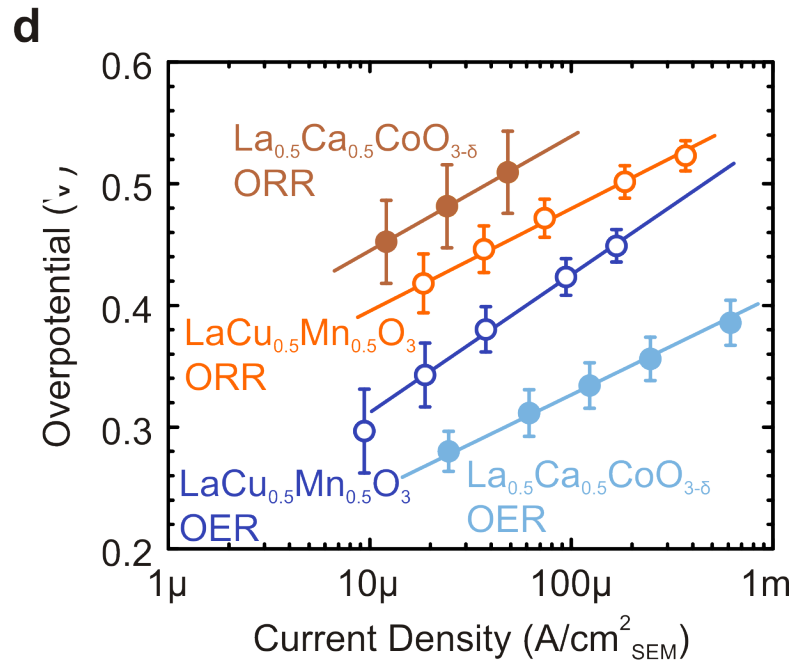
Which kinetic currents should be reported?



- Kinetic currents are highlighted between ~10% of limiting current and ~80% of limiting current.
- Preferably, catalysts should be compared in the green region, i.e. below 50% of the limiting current.
- Note that corrections may be necessary to obtain the kinetic currents of the catalyst (previous slides)
- Remember to use the positive going scan to evaluate ORR activities (arrow up)

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Reporting Tafel slopes



- In a Tafel plot, either potential (vs. RHE) or overpotential is plotted against logarithmic current (I prefer logarithmic spacing, which makes the graph easier to read)
- If the overpotential for $\text{H}_2\text{O}/\text{O}_2$ is used, OER and ORR can be compared in same plot (see figure)
- Make sure that only kinetic/catalytic currents are compared after appropriate correction for capacitance and potentially diffusion.

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<http://pubs.rsc.org/en/Content/ArticleLanding/2015/EE/C4EE03869J>

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Glossary and synonyms

Potentiostatic or amperometric measurement – control the potential and measure current

Galvanostatic or potentiometric measurement – control the current and measure potential

Voltage = potential