Ecat-RR Breakout Questions Survey Responses

July 3, 2025

Yellow highlight = Questions voted most important

1(a) Identify key protocols necessary for validating electrolyte purity in acidic and alkaline media.

Pt(111) CV response, Conductiviy, pH, ICP-MS

ICP-MS should be used to identify electrolyte purity.

For alkaline electrolytes, PTFE cells should be used instead of glass cells. Electrolytes should be pretreated/electrolyzed to reduce concentration of Fe impurities. Analytical techniques should be used when possible to validate impurity concentration (e.g. ICP-MS).
For acidic electrolytes, impurities are somewhat less of a concern. Researchers should take care that the electrolyte chosen does not itself have unintended consequences on activity (e.g. anion specific adsorption). Researchers should ensure the catalyst is at least thermodynamically stable from a Pourbaix diagram before use in a specific electrolyte.

I'm a theorist - I'd only embarrass myself with an answer....

Depends on the reaction... ICP-MS (metals), TOC (organics), blank measurement in the absence of reactant for e.g. urea production, N2 oxidation (to assess for N impurities)

Using 18.2 MOhm*cm water, de-aerating CO2 and measuring pH, using pre-electrolysis of a sacrificial electrode to remove transition metal impurities prior to measurements, checking electrode surfaces with XPS after reaction

Should include certificate of analysis in SI, should analyze electrolyte with ICP-MS, should record activity of standard catalysts and compare the results to reputable reports published in the literature.

useful although manufacturers can hopefully provide analysis

- pretreatment methods are necessary (such as pre-electrolysis to remove trace heavy metals)
- ICP is a gold standard, though not available to everyone easily

**also in non-aqueous media --> ppm's of water is a contaminant and dramatically changes the results (use Karl Fischer Coulometric Titration)

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1(b) Identify the attributes of a well-defined electrode and the measurements necessary to validate the electrode.

Most interested in this. Long range order/well-characterized/controlled defects Diffraction (LEED/SXRD), Microscopy (STM/AFM), Finger print CVs

The electrode should be a foil or a deposited film, but not consiste of nanoparticles.

A well defined electrode need not be a single crystal. As long as a catalyst can produce repeatable results across research groups and is not corrupted by artifacts associated with impurities, catalyst instability, mass or charge transport limitations, or active site density, then it can be used as a well defined standard.

Of course, researchers should keep in mind that certain sites on a catalyst surface may be more responsible than others for observed activity. This is also the case for single crystal studies. A small offset during single crystal preparation can easily lead to a step or defect density than can entirely dominate measured results.

Uniform sample thickness. spray-coating/screen printing/electrodeposition offer a higher degree of uniformity in thickness of sample deposited, and through masking, a higher degree of certainty in the area of the sample for determining metal/area concentrations.

spatial resolved measurements may be able to identify variations in sample thickness/uniformity.

Identical characterization before and after use to identify changes that can occur during use.

Known surface area and density of "active sites" with a given motif. This is not always tractable. For some reactions, planar electrode (to rule out cascade processes). Good electrical conductivity, ion transport, well-defined pH/local concentration of reactant/product species.

Active-site density quantified with a reproducible method under conditions that closely resemble those of the catalytic reaction. For example, CO stripping on Pt. For a single-crystalline electrode, CV features are also reproducible.

well-defined can mean many things. Hard to prescribe a single set of attributes. However, well-defined electrodes should be characterized using a variety of techniques like SEM/TEM, XRD, XPS, etc. I think it is also important to report cyclic voltammograms. However, the voltage range will depend on the material in question.

important but vague, will be very system dependent

- a metal that does not reconstruct easily (Cu highly unlikely to ever be a well-defined electrode)
- CVs to observe the structured effects on Pt. How do we go beyond Pt well?

Yellow highlight = Questions voted most important

1(c) Identify and compare pitfalls in characterizing electrode/electrolyte combinations consisting of platinum group metal (PGM) or non-PGM electrodes in contact with acidic or alkaline electrolytes.

Surface oxidation and roughening transitions, carbonyl contamination, hydride formation, corrosion.

The purity of the electrode material is not known, the ECASA is not known, contimination of the electrode by impurites from the counter electrode are not known.

Platinum should not be used as a counter electrode when studying reduction reactions (e.g. HER, CO2R). Platinum will oxidize and dissolve at the anode and can plate onto the working electrode, significantly influencing measured activity. This is also an issue during spectroscopy measurements, where undivided cells are commonly used. Spectroscopic artifacts can be introduced from the Pt which have nothing to do with the catalyst under investigation.

"ECSA" is just capacitance, and should not be over interpreted or used to e.g. compare catalysts of different chemistry or in different electrolyte. Hupd may not quantify the type of sites you care about (e.g. if reaction takes place at a different potential).

yes

Counter electrode decomposition is a concern, e.g. with carbon it can produce organic species and/or CO2, and with a Pt counter electrode, you must be wary of Pt dissolution and deposition on the working electrode if the WE is not Pt.

I think that the counter electrode chemistry should always be considered. Especially when the material of interest is a cathode or when CVs are performed. Anodes often corrode and this is exacerbated when the material is put through oxidation and reduction cycling. I think authors should demonstrate that activity and selectivity are not a function of counter electrode identity.

- non-PGMs do not have the characteristic HUPD regions to characterize the areas. Often left to BET or capacitance measurements to go beyond geometric surface areas
- stability of the analytical systems in the very high or very low pH's (ex. stability of the FTIR crystals, the in situ cells, etc.)

1(d) Develop a set of measurements that can be used as a benchmark to verify reproducibility among different laboratories.

This is important but there is a risk of stifling innovation or stopping interesting work from outsiders being published.

When reporting on the activity of a new catalyst, this should ALWAYS be accompanied by an appropriate comparison with a well-defined standard material. Appropriate comparisons involve active site normalized (or surface area normalized) activity comparisons under conditions where mass transport limitations are explicitly excluded. The standard or benchmark material should have identical (within reason) performance to well accepted standards in the literature. For well studied reactions (HER, OER, ORR, HOR, CO2R), these are readily available. The most serious issues in electrocatalysis stem from inappropriate reporting or comparisons of catalytic activity.

This is very reaction dependent. I don't think the biggest problem is that lab A and lab B can't get the same results, but rather that lab A and lab B might do different things in preparation/characterization/treatment that make their results incomparable. I have been most passionate about this lately for NO3RR (a minefield) where mass transport, electrode preparation, and electrolyte composition can give wildly different results, and have written up a set of standard electrolytes and variables to report (on arxiv and still dealing with reviews).

Yes

Turnover rates at a standard potential normalized to a reproducible active-site density, and variation of those turnover rates with potential and/or fluid-phase concentrations of reacting species.

I think this can be done. In fact, we did something similar in the best practices manuscript I published with Alex Bell. However, very few studies have followed our recommendation. Thus, I think it is important to make these recommendations brief so that performing them isn't too time consuming. Otherwise, people might just skip it entirely!

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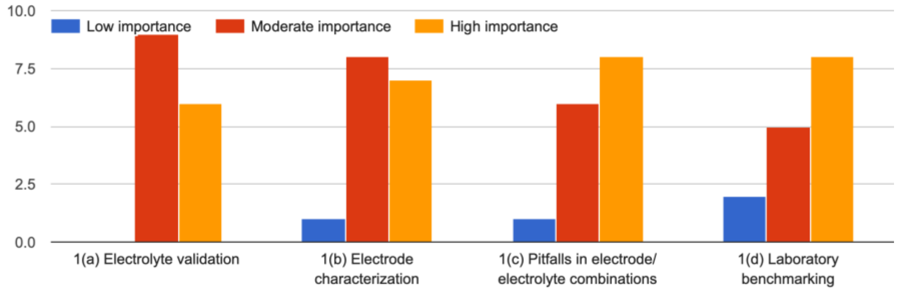
Rank the order of importance of items 1(a)-(d)



Yellow highlight = Questions voted most important

2(a) List guidelines for ECSA measurements and their suitability for typical electrocatalytic reactions; consider the effects of reaction potential, pH, type of electrode, and other characteristics.

Seems quite important

ECSA measurements should be conducted under conditions where there are no faradaic processes and in which the electrode is stable. ECSA requires an assumption about the specific capacitance of a flat material, which may not be available. There may be certain electrolytes that facilitate ECSA measurements. Researchers should ensure ECSA measured is coming from the active material rather than a high surface area support.

Despite these limitations, ECSA is a simple and relatively universal technique for measuring surface area. It is much more common that electrocatalysis studies arrive at a questionable conclusion based on a lack of active site normalization than inaccuracies in the site normalization technique itself.

I am far from convinced there are ECSA techniques that provide the level of certainty in normalizing electrokinetics that are comparable to "thermal catalysis" surface area and chemisorption measurements. I'd enjoy a discussion to learn more about this topic, including the best practice in noting the uncertainty in the measurement (and how much that uncertainty might vary among different catalyst compositions and structures).

I mentioned this in the previous section -- this is just capacitance (we shouldn't call it ECSA). It depends on everything. We should invest more time as a community understanding how and why if we want to use it further. That being said of course we should measure it and consider it a tool in our toolbox, but taken for what it is (yet another way to assess surface area, just like BET/surface area analysis/Hupd/Pb or Cu stripping is one to measure in another way)

yes

ECSA measurements should be done under conditions as similar to catalysis as possible using specifically adsorbing titrants. Assumptions should be carefully considered including that surface saturation coverage is reached, the binding stoichiometry of the titrant and/or the electron stoichiometry of the stripping reaction, if stripping is used for quantification. ECSA measurements via capacitance should be regarded with skepticism.

I think it would be very good to summarize the different techniques out there, their pros and cons, and their compatibility with different materials. A few that come to mind: capacitive cycling (not ideal when using carbon supports), CO stripping (does not work for all metals 0 must be less noble than Cu), H under potential deposition (must bind H strongly), post-transition metal UPD (does not work for early or post transition metals), surface limited oxidation (for example exposing Cu to N2O). There is a huge need to methods that can quantify the surface area of oxides.

2(b) Identify the features of cell design and the measurements required to define electrochemical reactor hydrodynamics and/or minimize mass transfer limitations at the electrode.

Well-defined hydrodanmics are perferred; mass transfer and buffer reactions must be taken into account in the analysis of product partial current demsoties.

If researchers are interested in understanding the intrinsic behavior of the catalyst, experimental demonstrations should be provided that transport limitations are not controlling rates. Therefore, reactors should be designed such that in some way they are able to controllably modify the hydrodynamics in the cell. This could be through the use of a rotating disk electrode or simply through agitation of the cell (e.g. stirring, gas sparging). If this is available, very simple measurements can be done to demonstrate whether (external) mass transport limitations are present (e.g. does activity change with rotation rate? stir speed? gas sparging flow rate? If so, transport limitations are significant).

For XAS:
1. minimal attenuation through the electrolyte (back-side illumination) - works for low-z, thin substrates and deposited NPs and thin films (ideally 10 nm max)
2. for batch cells - some sort of mixing to minimize bubble formation
3. for flow cells - a high face velocity to help sweep bubbles away as quickly as possible.

for in-situ measurements one should test how pump speed/mixing influence the EC performance. Often best done off-line to minimize down time at the beamline.

I think (1) having consistent and reproducible mass transport for an individual investigation, (2) being able to share/reproduce this, and (3) being able to assess whether it is limiting measured rates are all important.

yes

Mass transfer should be considered early in reactor design and experiments should be carried out to verify the absence of mass transport effects on measured currents. The convection rate to the electrode surface should be systematically varied and the current should be shown to be independent of the convection rate. For porous electrodes, the Thiele modulus should be considered and ideally, the rate should be shown to be invariant to the thickness of the porous electrode layer.

I think it is important to report the average hydrodynamic boundary layer thickness of your reactor. This can easily be done using ferricyanide reduction. It is also important to demonstrate that activity measurements are not significantly influenced by hydrodynamics. Partial currents should increase exponentially with potential. If they do not, mass transfer could be a likely reason why.

- flow systems are preferrable unless doing R(R)DE
- reduce volume:electrode area
- gas sparging can increase mixing just as well as stirring (or better) in a (semi-)batch cell
- electric fields and current distributions influence the reaction performance as well

2(c) Explain how the reaction of study, working electrode, and electrolyte affect the choice of reference and counter electrodes.

Many reference electrodes have a specific pH range for which they are stable. For instance, Hg/HgO reference electrodes can be used in alkaline conditions but not acid, whereas Hg/HgSO4 electrodes should be used in acid rather than base. Reversible hydrogen electrodes can be easily constructed in a laboratory or purchased commercially which avoid these issues.

Pt should not be used as a counter electrode for reduction reactions as it will introduce Pt impurities onto the working electrode.

Reference: involving proton transport and having uniform pH in the reaction media: RHE.
Counter: ideal to isolate (frit/membrane). If not possible, need to consider impact of products/dissolution (e.g. beware of Pt as an oxidative counter in acid).

REs should be calibrated to a stable standard reference (not by equation but actually measurements), i.e., the RHE in aqueous media or Fc/Fc+ in organic media. Counter electrodes should allow sufficient current density as not to limit the reaction rate and not introduce the potential for convoluting phenomena like dissolution into the electrolyte.

I see a lot of people using these micro Ag/AgCl reference electrodes. They do not have very stable potentials. I also see a lot of people using Ag/AgCl REs in alkaline conditions, which can also be problematic. It would be good to provide a list a viable counter electrodes in different pHs. If the counter is a cathode then Pt can be used in almost any pH. However, some care must be taken if CVs are performed, since the Pt will oxidize and could release some contamination. If the counter is an anode then IrO2 can be used in acid and Ni can be used in based. Sacrificial C electrodes can also be used if they are of high purity (graphite usually isn't).

- Is OER or HER possible in the electrolyte?
- Will the counter or reference contaminate the system?
- Can we get away from need of Hg/HgO in alkaline media? I see folks use Ag/AgCl but usually the frits dissolve in base (and people don't notice)
- Cell resistance and overall potential of the cell also become challenging and result in voltage compliance issues with potentiostats

2(d) Explain how total current, faradaic efficiency, partial reaction products, and ECSA affect reporting of electrocatalyst activity.

Faradaic efficiency should not be used to describe the activity of a catalyst. This is a very common error. Increases in FE may or may not be accompanied by an increase in rate for forming a certain product (depending on the total current). Therefore partial current densities to forming a specific product should always be provided.

Similarly, geometric activity should never be used to compare activity between catalysts. It may be useful for situations where the catalyst is not changing (e.g. the effect of pH over a fixed polycrystalline metal) but otherwise should be avoided in favor of site normalized activity metrics. If a site counting technique is available, a turnover frequency is the preferred metric. If not, ECSA normalized activity is the next best option. Many misconceptions exist in electrocatalysis (e.g. about the activity of oxide derived Cu catalysts in CO2R) due to these two errors.

Turnover frequencies should always be calculated using a site counting technique. Dividing by the total number of metal atoms gives a mass normalized activity, not a turnover rate.

Usually rates of individual product formation and selectivity to different products is most valuable (in the absence of appreciable e.g. corrosion that decreases FE). Surface area needs to be assessed if a rate is claimed; capacitance (called ECSA here) may enable this, or not.

FEs need to be compared at similar extents of reaction (analogy to comparing thermal catalyst selectivity at the same conversion level) so that comparisons are not convoluted by different reaction progress along series pathways. ECSA is essential to convert current densities to turnover rates and compare catalysts with one another on a per-site basis.

In general I think partial currents and Faradaic efficiencies should always be reported side by side. If only 1 will be shown then I think it should be partial current densities, which are harder to misinterpret. I see a lot of misinterpretation in the literature that is derived from too heavily focusing on the FE trends. FE can be misleading since selectivity can be impacted by the rate of reaction.

- Tafel slopes that use total currents are unreasonable in multi-reaction systems. Should use partial current densities (and therefore CVs don't work for this analysis anymore)
- In fundamental studies, normalizing by ECSA (or another catalyst feature) is important; in applied studies, geometric area is still most important as the reactor performance is what makes it viable or not

2(e) Identify and compare different methods for measuring multiple reaction products.

GC should be used for gaseous proucts and NMR for liquid-phae products. Attention should be given to product crossover - ethanol produced at the cathode crosses over and is oxidized to acetate at the anode during CO2R. The carbon balance should include carbon-containing products that leave from the cathode compartment as well as carbon-containing products produced in the anode compartment.

For gas phase products, gas chromatography or mass spectrometry can be used. GC is quite simple but suffers from a lack of time resolution. This makes data slow to acquire and may miss transient behaviors. MS is experimentally more challenging to set up and requires some thought for electrochemical applications.

For liquid phase products, HPLC, NMR, or GC-MS can be used.

Close the mass balance by measuring all reaction products, do not assume the remainder is a product that was not measured.

Depends on the reaction... direct methods (e.g. MS) are better over indirect (e.g. spectrophotometric, chromatography), but sometimes indirect are fine if no interferents.

GC, NMR, DEMS/EC-MS are all possible depending on the reaction, reactor, etc.

- NMR vs. chromatography --> need bulk electrolysis for this
- R(R)DE techniques for more simple systems --> faster screening possible

2(f) Identify examples where experiment and theory were successfully compared and those where they were not.

This is most interesting.

The disconnects between theory and experiment can be summarized as follows:
(1) The parameter being calculated is not actually what is measured. For instance, DFT will have no ability to explain rate data if it is controlled by mass transport and is not normalized by the number of sites.
(2) Experimentalists are often not providing parameters that the DFT can simulate. Electrocatalysis researchers often only measure rates (that are corrupted by transport, surface area artifacts, etc.). But measurements of activation energies, kinetic isotope effects, reaction orders, and spectroscopic signatures can all be used as additional validation tools for modeling.
(3) The model of the active site has little or no relationship with the real catalyst. There are many complications with simulating active site structure. Even simple metals have a variety of surface terminations and structures, certain sites on the catalyst may be responsible for all measured activity, the catalyst structure and composition can change under reaction conditions, etc. In addition to the composition and structure of the active site being appropriately represented, the environment around the active site may have a critical influence on rates. Simulating a bare K+ ion on top of a metal single crystal in vacuum may have no connection to an electrochemical interface.
(4) The agreement may be in direction only. Measuring a 2x difference in activity at room temperature between two catalysts and calculating a 1 eV difference in barrier heights is not agreement. The theory would predict a change in rate of many orders of magnitude.

Generally, the best examples of combining these find multiple points of qualitative validation, and use the two tools for what they are most useful in answering research questions rather than striving for quantitative agreement. An example of our work that I am most proud of stems from the collaborations between Ian McCrum and Marc Koper, looking at how pH effects voltammetry features in the "hydrogen region" on Pt. In general, Ian's work is a great example of integrating information from experiment and theory to make conclusions, balancing and recognizing the challenges in precision in both tools - this has continued (arguably, further improved) in his post-doctoral time with Marc and his independent career.

Virtually all publications show agreement but not all of them calculate what is experimentally present (e.g. calculations of Co_3O_4 surfaces to compare with something at -0.3 V vs RHE, where the surface is reduced).

Usually when they are not, the issue is that the theory is "decorative." The models do not accurately describe the real state of the surface and electrochemical double layer, and the direct connection with experimental observables is weak. Many theoretical studies on atomically dispersed metals in N-doped

carbon invent active-site structures that have no experimental support, especially so-called "dual-atom" catalysts.
DFT should not be used the explain FE trends unless the barriers for producing all of the various products are being considered.

Not: Many of the Cu CO2ER works where the copper reconstructs under reaction conditions

2(g) Identify challenges in estimating electrocatalytic kinetics with DFT.

DFT methods are insuffieicently benchmarked to provide reliable predition of reaction kinetics for electrochemical systyems.

It is difficult to simulate a real electrochemical interface. The presence of a solvent, dissolved ions, an interfacial field, and a constant applied potential during reactions are all very challenging to simulate accurately with DFT. Furthermore, simulating the solvent side requires significant sampling timescales to equilibrate the solvent that are computationally infeasible.

Beyond this, I believe DFT is often receiving poor experimental information. They may start with a false assumption (e.g. why is CuO more active than Cu for CO2R?) and try to find differences between the two in computed parameters. Giving computational researchers more extensive high fidelity kinetic data will make comparisons between theory and experiment easier.

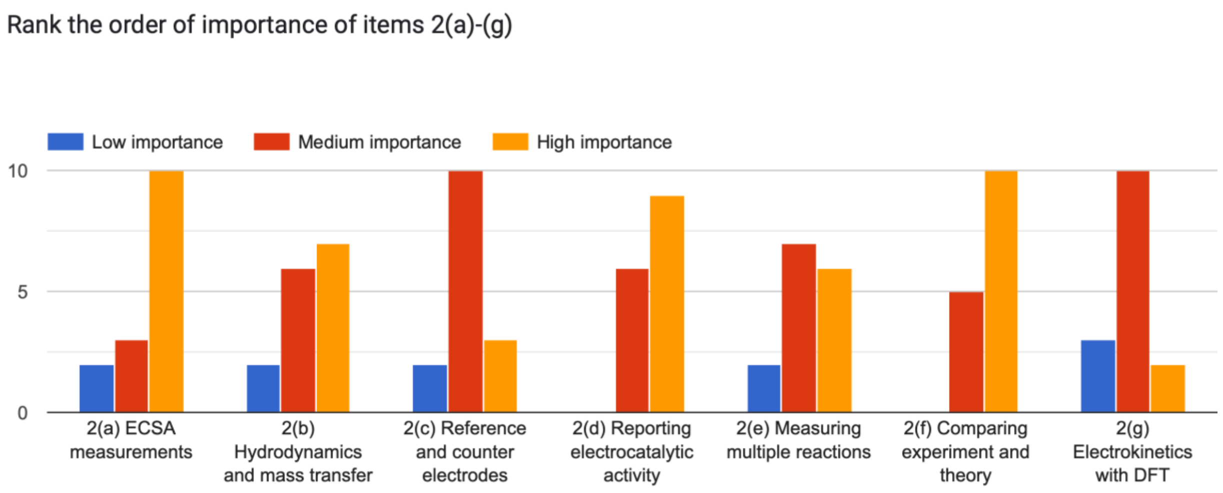
These are numerous - I like categorizing them generally as "method" and "model" challenges. DFT has underlying theoretical challenges, summed up as the undetermined proper XC functional, and this brings at least ~0.2 eV of concern for even the most direct experiment and theory comparisons. Trends (ie, differences between similar materials) will be more reliable. But for electrocatalysis, model accuracy is even more challenging, with the complex environment that electrocatalytic processes occur within. In absolute energy terms, surface intermediates interactions with the solvent/electrolyte are worth at least 0.5 eV for pretty much all adsorbates beyond a simple H atom, and often much more. As adsorbates become more complex, differences in these interactions between adsorbates, catalysts, and electrolytes can also be on the order of 0.5 eV - ie, we can get reaction energies or barriers off by 0.5 eV due to not well representing differences in interaction energy within the EDL. The trend towards fully continuum approaches to these interactions worries me further, as these tools embed parameters we don't know about the EDL for a given catalyst/electrolyte pair, and remove the ability to probe atomistic interactions in the EDL.

Activation barriers and site utilization seem challenging to capture, but I'm not an expert.

DFT struggles to accurately account for the complexities of the double layer, charge, etc. Depending on the catalyst, assumptions will also have to be made about its structure. On the experimental side, lack of data that can be directly compared with DFT causes challenges. Current densities are not a fundamental quantity that can be calculated without a reactor model, site density, full microkinetic model, etc. Experimental attempts to measure more detailed kinetic data can help connect to theory better. For example, rate constants (through mechanism-derived rate equation analysis), apparent activation barriers, KIEs, reaction orders, Tafel slopes, can all provide deeper information that theory can try to explain (usually in conjunction with a microkinetic model).

Many!

Complexity of systems with bigger molecules; interfacial effects



3(a) Identify guidelines and tests to assure that use of a thin layer cell adequately represents the electrochemistry of the system of study.

2nd preference

The cell used to obtain IR or XAS data should have the same geometry and hydrodynamics as the cell used to obtain electrochemical data.

The thickness of the sample should not be altered for the spectroscopic measurement (XAS) as adding/removing material may alter the chemistry/catalytic performance.

For in-situ electro chemical measurements, being able to test if the cell/sample functions prior to exposure to the beam is paramount. This may require better designed cells as electrical hook ups/contact is a leading delay in making a measurement. Testing the cell off-line may speed this process up.

Synthesis/deposition methods should be geared toward applying the most uniform layer of catalyst down on the substate.

Need very low rates of reaction to ensure no gas generation, no reactant depletion, no product accumulation. This is hard if the thin layer cell is closed/stagnant. If its flowing, or if gases are extracted, this is easier to ensure.

yes

Hydrodynamics and benchmarking of turnover rates and other kinetic parameters to match those measured in a standard cell with well-controlled hydrodynamics.
Best case: quantitative electrocatalytic activity comparison. However, I think that comparative CVs are a bare minimum. If the CVs vary considerably, then I imagine the electrocatalytic activity will as well.

- I'm not an expert in this

3(b) List control experiments necessary to validate operando techniques such as ATR-SEIRAS and XAS.

Most interesting

Researchers should be aware of how translating from a RDE to a vertical stationary phase change their electrocatalytic performance. It should not be expected that operando echem cells to have the same performance as a EC testing capability in the lab unless it is designed to specifically do that. This is due to operando measurements often having to make compromises in terms of wetting one instead of both sides, having a mass transport limitations due to a static sample.

It would be good to understand at what potentials bubbles start to form (in an operando electrochemical cell) as these potentials may be slightly different than a cell designed specifically for an EC measurement.

it is often good to test how stable the deposited samples is on the substrate as the substrate may not be the same as the one used in the lab (e.g. using glassy carbon instead of carbon paper). This may limit how much can be deposited, or at what potential the catalyst starts to delaminate from the substrate.

Need same echem as in system where the mass transport etc. is well controlled.

yes

ATR-SEIRAS needs an initial validation of the extent of surface enhancement with a standard benchmarking adsorbate, for example, acetate on gold, CO on Pt. To claim "operando," turnover rates and other kinetic parameters must match those measured in a standard cell with well-controlled hydrodynamics.

I am very interested to see what we come up with here. I think this is kind of the Wild West right now. Very little, if any, validation being done on these operando techniques.

3(c) Describe pitfalls in pre- and post-characterization of electrodes with ex-situ techniques.

Ex-situ XPS cannot be used to obtain meaningful information about oxidation state of catalysts, such a Cu which are highly oxophilic.

I believe it is well established now that the i) as-prepared dry sample, ii) the sample in the electrolyte, iii) the sample at OCP, iv) the sample under various potentials, v) the sample in electrolyte post echem (no electrode), and vi) the sample removed from the electrolyte (and dried) are all different as the potential changes drive phase changes. fresh and spent samples may give insights into long term cycling changes (e.g. forming a core-shell or phase segregation structure) but they are not directly representative of the sample under those conditions.

This is to say, the pre and spent samples likely do not represent the working material, and in-situ measurements are likely the only way to gain insights into the structure-activity relationship of echem experiments.

hard to get surface chemistry information by e.g. XPS due to adventitious carbon. Can't get oxidation state.

Return to open-circuit potential and exposure to atmosphere can radically change structures or adsorbates.

Near-surface alloy compositions and constituent oxidation states can change considerably upon air exposure.

3(d) Following an electrochemical experiment, explain the processes that may occur on an electrode once it is brought to OCP and removed from the electrolyte for ex-situ characterization.

Oxidation

Change in oxidation state, reactions with electrolyte/reactants/air...

yes

Changes can also occur in air. You should never rely on post-reaction XPS to tell you anything about the working state of the catalyst.

3(e) Describe the relative detection sensitivities of various ex-situ characterization techniques.

Given the relative low mass loadings of thin films/deposited electrocatalysts, XAS is almost always a FY measurement, sometimes requiring the use of an energy discretizing detector. The best detectors are sensitive down to 50-100 ppm (wt), with the trade-off of a longer collection time for S/N. Transmission measurements can be made on ex-situ samples through stacking to build up an appropriate absorption length, however, ex-situ samples should be avoided as they do not represent the working material.

For XAS measurements, it is rather challenging to translate mg/cm^2 into a way to assess potential signal strength. Being able to convert the value to a weight # of metal with X mg deposited (in a specific area) would allow for easy determination limits and guidance on measurement geometry.

This is further complicated with the addition of electrolyte and crystalline substrates.

https://pubs.aip.org/aip/cpr/article-abstract/4/2/021309/2892912/Surface-transformations-of-electrocatalysts-during?redirectedFrom=fulltext see fig 3 for info re: sampling depth, where sensitivity depends on if something is uniformly distributed in the sample or at it's surface.

I think we should caution the use of post reaction XPS to validate experiment purity. Open circuit corrosion of contaminants can easily occur, making them undetectable. I would like to see more post-reaction CV.

XPS is often inappropriately used to prove that a compound is not present in a catalyst - detection limits ~0.5 atomic%. Definitely can be catalytic well below that limit. Need to use ICP or AAS for proof of absence.

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Rank order of importance of items 3(a)-(e)