

iR Compensation for Electrocatalysis Studies: Considerations and Recommendations

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Careless adoption of electrochemical methods/concepts without evaluating their applicability can lead to misleading and contradictory results. This problem is particularly apparent in recent electrocatalytic benchmarking studies such as water electrolysis and carbon dioxide reduction. As electrochemists and journal editors have repeatedly criticized, performance indicators can be exaggerated or manipulated due to overlooked preconditions, inappropriate data treatments, and misunderstood concepts.^{1,2} In this Viewpoint (Scheme 1), we highlight the use of *iR* compensation,

Scheme 1. Questions Asked and Answered in This Viewpoint Regarding *iR* Compensation

E- <i>iR</i>	Applicability
	- What is the target of <i>iR</i> compensation?
	- Should all studies use <i>iR</i> compensation?
	Resistance
- What is the meaning of <i>R</i> ?	
- Which <i>R</i> needs to be compensated?	
- How to measure <i>R</i> (as precisely as possible)?	
Current	
- What is the meaning of <i>i</i> ?	
- Which <i>i</i> should be used?	
Problems and Recommendations	
- Why should partial compensation be avoided?	
- How to do <i>iR</i> compensation in electrocatalysis?	

a technique widely used in electrochemical data treatment but rarely discussed for its applicability. Brief considerations of its technical background and practical limitations in electrocatalysis research are presented, followed by operational recommendations.

Technical Background. *iR* compensation is developed to correct for the voltage loss (i.e., *iR* drop) caused by the electrolyte solution between the working electrode and the reference electrode, where *R* stands for the resistance of the electrolyte solution.^{3,4} Assuming a simplified three-electrode configuration (Figure 1) with a voltage ($\Delta\phi_{1,3}$) applied between the working electrode (point 1 with the potential of ϕ_1) and the reference electrode (point 3 with the potential of ϕ_3), the potential drop between 1 and 3 can be resolved into $\Delta\phi_{1,2}$ (between 1 and 2) and $\Delta\phi_{2,3}$ (between 2 and 3). $\Delta\phi_{1,2}$ represents the potential drop across the electrical double layer (EDL, $\Delta\phi_{EDL}$), and $\Delta\phi_{2,3}$ is the potential drop across the bulk

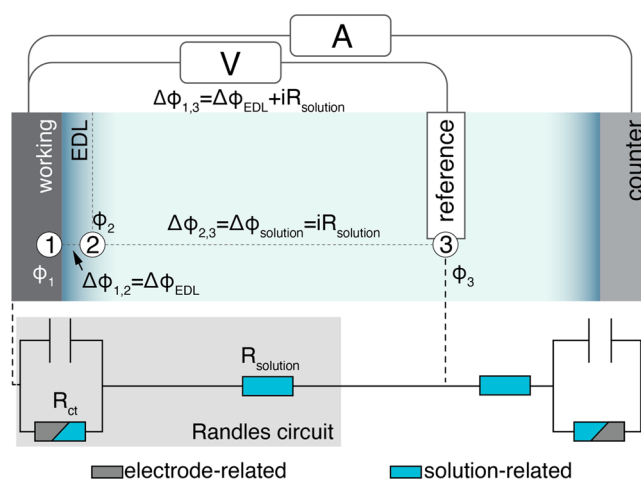


Figure 1. Schematic representation of potential drop across a simplified three-electrode system and the corresponding equivalent circuit diagram: (1) surface of the working electrode; (2) outer boundary of the diffuse layer; (3) junction of the reference electrode. The term “simplified” indicates that all electrodes’ geometric/structural/configuration differences are ignored, and all surfaces are equipotential. The dimensions are not to scale.

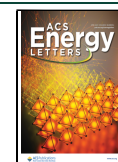
electrolyte ($\Delta\phi_{solution}$). Operationally, the working electrode’s potential is controlled by adjusting the charge on the EDL. According to Ohm’s law, $\Delta\phi_{solution} = iR_{solution}$ (*i*, current flowing through the electrolyte; $R_{solution}$, ohmic electrolyte solution resistance between 2 and 3, related to the volume of solution containing current paths between the working electrode and reference electrode). The EDL potential ($\Delta\phi_{EDL} = \Delta\phi_{1,3} - iR_{solution}$) can be calculated, namely, *iR* compensation.⁴ Traditionally, the *R* needed to be compensated is called R_u (uncompensated resistance). In this simplified case, $R_u = R_{solution}$.

Current Practice. In the literature, *iR* compensation is conducted by two methods. The most popular one is after-the-scan compensation: the experimental data points are manually

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corrected with a predetermined resistance. The resistance is obtained by fitting the high-frequency region (HFR) of the electrochemical impedance spectroscopy (EIS) data with an equivalent circuit (often the Randles circuit), denoted as R_{HFR} . Another method is on-the-fly correction: the points are automatically corrected by instruments with built-in *iR* compensation, including “positive feedback (PF)” and “current interruption (CI)” modes.^{4,5} After-the-scan compensation assumes a constant R_{HFR} can be used as R_{w} , while on-the-fly correction frequently interrupts the experiments to measure R_{u} (an initial input is still required).

A factor is often applied to the measured R_{w} , where 100% means full compensation. Partial compensation (often between 85% and 95%) is typically configured to avoid potentiostat oscillations (in on-the-fly correction) and “overcorrected” results (e.g., “bend back” polarization curves in after-the-scan correction⁶). However, the choice of the percentage is highly empirical and lacks theoretical support. For example, Jaramillo et al. used 85% for oxygen evolution reaction (OER) studies,⁷ while Cao et al. engaged 90% for overall water electrolysis.⁸ Some researchers have suggested a standard factor. For instance, Ren et al. suggested an 85% *iR* compensation for all water electrolysis studies,⁹ while Marshall et al.¹⁰ and Anantharaj et al.⁶ recommended a 100% compensation for CO₂ reduction studies and water electrolysis studies.

Performing *iR* compensation with different factors dramatically affects the benchmarking indicators. As shown in Figure 2,

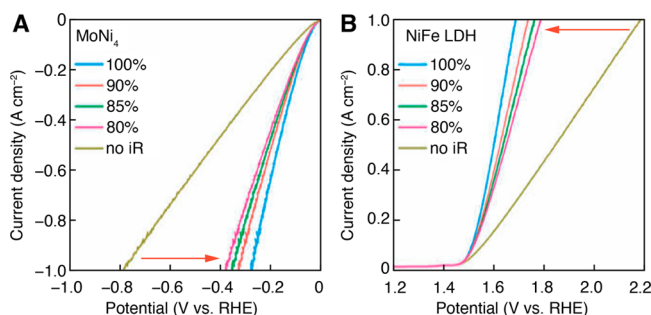


Figure 2. Examples showing the experimental data without and with after-the-scan *iR* compensation with different factors. (A) HER polarization curves of lab-developed MoNi₄ catalyst. (B) OER polarization curves of lab-developed NiFe LDH catalyst. Red arrows indicate the decrease of overpotential after *iR* compensation. Adapted with permission from ref 9. Copyright Elsevier, 2020.

at 100 mA cm⁻², 100% *iR* compensation reduces the overpotential of lab-developed HER and OER catalysts by 60–70 mV. It becomes even more dramatic at higher currents (1 A cm⁻²), reaching 500–600 mV, enough to change the rating of the catalyst from “mediocre” to “promising”. *iR* compensation also alters the Tafel slope. Chen et al. demonstrated that the Tafel slope of polycrystalline Pt in 0.05 M H₂SO₄ decreases from

31 to 23 mV dec⁻¹ when the factor rises from 90% to 95%.¹¹ These differences can affect the outcome of microkinetic modeling and mechanistic studies of electrocatalysis.

However, since such empirical practice shows significant impacts, is it reasonable to use *iR* compensation in all electrocatalytic studies, and how can it be done accurately? In

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the following content, after a few considerations of the technical assumption made in *iR* compensation about both resistance and current, together with the practical issues in electrocatalysis, we suggest a standard protocol for performing *iR* compensation.

Resistance: The Measured R_{HFR} is Not Always the R That Needs to Be Compensated. To start with *iR* compensation, it is critical to know the physical meaning of R that should be compensated. Depending on the region of interest, the definition of R_{u} is different, even for the same electrocatalytic system, where the measured R_{HFR} cannot be used in all cases. In Figure 1, the assumption of using R_{HFR} as the R_{u} is that the potential drop between the working and reference electrodes includes only $\Delta\phi_{\text{EDL}}$ and $\Delta\phi_{\text{solution}}$, meaning the resistance to be compensated is R_{solution} only. This can be true for

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well-defined homogeneous planar electrodes, such as Pt plates, where the electrodes act as the catalytic surface. But the meaning of R_{u} can be different for modified electrodes composited of multiple layers.

Modified electrodes have at least two composites: a catalyst layer and a conductive substrate that is catalytically inactive (or current collector, e.g., glassy carbon, graphite paper, etc.). They can be prepared by either *in situ* growth (e.g., hydrothermal reaction, chemical/physical deposition) or drop-cast. In the following discussion, we use a simplified layer-by-layer configuration of a dense catalyst film-modified electrode as an example (Figure 3A). Operationally for modified electrodes, the substrate, not the catalyst, is connected through wires to the potentiostat. Compared to Figure 1, two major resistors are added, namely, the contact resistance at the substrate/catalyst interface (R_{contact}) and the material resistance of the catalyst (R_{catalyst}). Minor contact resistors, such as the cable and connection junctions, are ignored for clarity. As a result, the potential drop between the working electrode (point 1) and the reference electrode (point 5) ($\Delta\phi_{1,5}$) is distributed not only in the EDL ($\Delta\phi_{3,4}$ or $\Delta\phi_{\text{EDL}}$) and electrolyte solution ($\Delta\phi_{4,5}$ or $\Delta\phi_{\text{solution}}$) but also at the substrate/catalyst interface ($\Delta\phi_{\text{contact}}$) and in the catalyst ($\Delta\phi_{\text{catalyst}}$): $\Delta\phi_{1,5} = \Delta\phi_{\text{contact}} + \Delta\phi_{\text{catalyst}} + \Delta\phi_{\text{EDL}} + \Delta\phi_{\text{solution}} = \Delta\phi_{\text{EDL}} + i(R_{\text{contact}} + R_{\text{catalyst}} + R_{\text{solution}})$. When researchers measure the R_{u} via EIS, the value obtained (R_{HFR}) is a sum of subresistances ($R_{\text{u}} = R_{\text{HFR}} = R_{\text{contact}} + R_{\text{catalyst}} + R_{\text{solution}}$), as observed by many research groups.^{12,13} Therefore, in

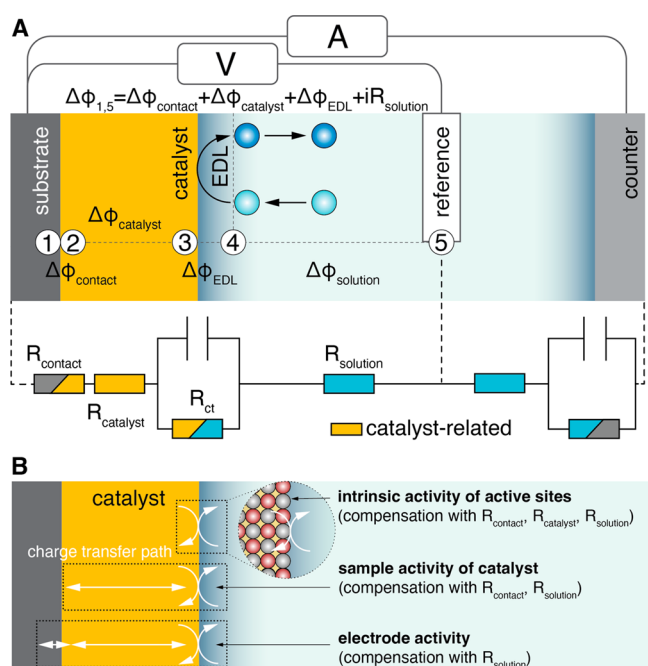


Figure 3. (A) Schematic representation of potential drop across a simplified three-electrode system with a modified working electrode and the corresponding equivalent circuit diagram: (1) surface of the substrate; (2) surface of the catalyst contacting the substrate; (3) surface of the catalyst contacting the electrolyte solution; (4) outer boundary of the diffuse layer; (5) junction of the reference electrode. (B) Schematic representation of a modified electrode and the region of interest (dotted box) with different definitions of activity. White arrows represent the charge transfer path. The dimensions are not to scale.

cases where only R_{solution} should be compensated, using R_{HFR} will result in overcompensation. This is probably one of the reasons for the partial compensation because only part of the R_{HFR} should be compensated in some studies.

Before further analysis, we must clarify the term “activity” in the literature. The *intrinsic activity* of a catalyst refers to the activity of specific active sites on the surface (i.e., the interfacial electron/ion transfer rate at the site), regardless of the material or cell parameters, and is determined only by the structural configurations of the sites.¹⁴ It is helpful for mechanism analysis (e.g., modeling with theoretical calculations) but useless for benchmarking catalysts for industry, where the *sample activity* of catalysts is more meaningful. *Sample activity* means the overall activity of the specific catalyst, related to the particle size, junction type, etc., but not the coating process and cell configuration. After the coating process, the modified electrode is produced, and the *electrode activity* is related to both the catalyst and the substrate. Finally, when the modified electrode is used in an industrial device (e.g., fuel cell stacks¹⁵), the *industrial activity* is decided by both the electrode activity and the cell configuration.

Depending on the region of interest, as summarized in Figure 3B, the concept of R_u is different. When studying *intrinsic activity* for fundamental understanding, it is desirable to eliminate the interference from the contact resistance (related to the way the catalyst is coated on the substrate, substrate properties, etc.), the material resistance (associated with the thickness of the catalyst layer, particle size, binder concentrations, etc.), and the electrolyte solution resistance (related to the cell parameters, the electrolyte type, concentration, interelectrode distance,

etc.),¹⁶ as suggested by Boettcher et al. in their work on metal (oxy)hydroxides.¹⁷ In this case, the iR compensation with R_{HFR} (i.e., $R_{\text{contact}} + R_{\text{catalyst}} + R_{\text{solution}}$) is adequate. However, only $R_{\text{contact}} + R_{\text{solution}}$ should be used as R_u when studying *sample activity*. The reason for this is that R_{catalyst} is characteristic of the catalyst.¹⁸ For *electrode activity*, only R_{solution} needs to be compensated, because R_{contact} needs to be addressed by the electrode design other than being “compensated”.¹⁹ An excellent example is shown in the analysis of IrO_x conductivity on a porous substrate for water electrolysis by Gasteiger et al.²⁰ For *industrial activity* evaluation, no iR compensation should be performed. Because the cell configuration is part of the analysis, which allows the assessment of energy efficiency.¹⁵

In current practice, most researchers use R_{HFR} measured with modified electrodes (denoted as $R_{\text{HFR},M}$) by either pre-experimental EIS or on-the-fly approaches as the R_u for iR compensation. It makes the studies of *sample activity* and *electrode activity* most problematic. Performing iR compensation with detected $R_{\text{HFR},M}$, other than R_{solution} , will mask possible conductivity issues of the electrode and suggest some “highly active” electrocatalysts with poor conductivity,²¹ which is unsuitable for industrial use. An example is FeO_xH_y , which exhibits highly active Fe sites but limited sample activity due to the large R_{catalyst} .²² With this in mind, we suggest using $R_{\text{HFR},M}$ for *intrinsic activity* study only and using R_{HFR} measured with the bare substrate (denoted as $R_{\text{HFR},S} \approx R_{\text{solution}}$) as the R_u for *electrode activity* and *sample activity* (only if a small R_{contact} is proven/achieved) evaluation. An excellent example of using $R_{\text{HFR},S}$ (measured on FTO), other than $R_{\text{HFR},M}$, was demonstrated by Nocera and co-workers, where the catalytic activity of the sample (electrochemically deposited NiB) was evaluated.²³

R_{contact} and R_{catalyst} can be measured in many ways, and two preferred methods are Kelvin four-terminal sensing and measurement *via* an interdigitated array electrode.^{22,24} For modified electrodes prepared *via in situ* growth, the R_{contact} is typically within a few $\text{m}\Omega \text{ cm}^{-2}$. But those prepared by drop-casting catalyst ink on the substrate typically show higher R_{contact} which can be reduced by adding conductive binders, improving the coating procedure, surface modification of the substance (e.g., removing the surface oxidation layer before coating, introducing a conductive layer), etc.^{25,26} Also, the R_{contact} is proportional to the contact area between the substrate and the sample, and a small substrate can reduce the R_{contact} .

The above discussion is based on a dense catalyst layer. Sometimes, if the catalyst layer film is porous or electrolyte-permeated (which is very common in the literature), one may expect identical R_{HFR} detected using both substrate and the modified electrode (i.e., $R_{\text{HFR},S} \approx R_{\text{HFR},M}$).²⁷ This is because the substrate is in direct contact with the electrolyte (see the Supporting Information for analysis). The same suggestion about *sample* and *electrode activity* studies still applies. However, one may find it challenging to analyze the *intrinsic activity* because R_{catalyst} is not reflected in the detected $R_{\text{HFR},M}$. In such cases, the resistance components need to be analyzed individually. An example involving the analysis of spherical particles on the substrate is provided by Mallouka and co-workers.²⁸

Resistance: R_u May Depend on the Reaction Conditions (Potential and Time), so a Predetermined Value May Not Be Accurate. For after-the-scan compensation, the R_u is assumed to be constant, and the value is often measured at open-circuit potential (OCP) where no current flows and no catalytic reaction occurs. Such an assumption may not be

accurate for modified electrodes under different reaction conditions, where R_{contact} , R_{catalyst} , and R_{solution} can be dynamic.

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For modified electrodes, space charge layers can form when electrical contact is made between the catalyst particles, catalyst/catalyst support (e.g., conductive carbon), and particle/substrate.²⁹ Such layers can quickly form in poorly conducting catalysts, especially with large particle sizes, or when the conductive support forms passivating oxide layers (e.g., TiO_2 on Ti). Under applied potential, these space charge layers exhibit potential-dependent resistance, affecting both R_{catalyst} and R_{contact} .³⁰ In addition, catalysts typically undergo structural and morphological changes during electrocatalysis, including material transformation (phase change, redox reaction, etc.), particle migration and agglomeration, active site dissolution, and catalyst detachment (Figure 4A).³¹ These changes result in dynamic R_{catalyst} and R_{contact} over time. For example, we measured the $R_{\text{HFR,M}}$ of an anodically treated Co planar electrode (i.e., $\text{Co}(\text{OH})_2$ -coated Co electrode) at different potentials during OER (Figure 4B). The resistance value is potential-dependent, and those at reaction potentials are lower than that at OCP (except the one before OER, time = 0 s). Moreover, as the OER

continues, the R_u increases, indicating possible structural changes. R_{solution} can also change during reactions, especially for gas evolution reactions like water electrolysis. As pointed out by Ren et al. and Luo et al., the produced gas bubbles will block the surface of the catalyst and alter the ionic conduction path in the electrolyte solution.^{9,32} We also found that, at 1.0 V where bubbles are generated rapidly on the electrode, the R_u is higher than at other potentials (Figure 4B).

Therefore, when performing after-the-scan compensation, measuring the R_{HFR} at the potential/current/time of interest rather than at the often-used OCP is recommended. For electrocatalysis studies, one common choice is to do the iR measurement while the electrode is quasi-stable (at or below the exchange current density) after conditioning at the reaction condition for some time. This allows the activation/reconstruction to finish before measuring R_{HFR} . For cases where the R_{HFR} depends significantly on the conditions (e.g., the formation of gas bubbles alters the R_{HFR} significantly), on-the-fly compensation (use PF mode, because CI mode still measures R_{HFR} at OCP) is more accurate, as demonstrated in Figure 4C where after-the-scan method results in overcorrection.

Resistance: R_u is Uneven for Individual Sites. An overall assumption made during iR compensation is that R_u values are the same at all individual active sites on the surface, regardless of the geometric/structural features of the working electrodes. This may be true for homogeneous ultramicroelectrodes, but not for modified electrodes with complicated nanoarchitecture.

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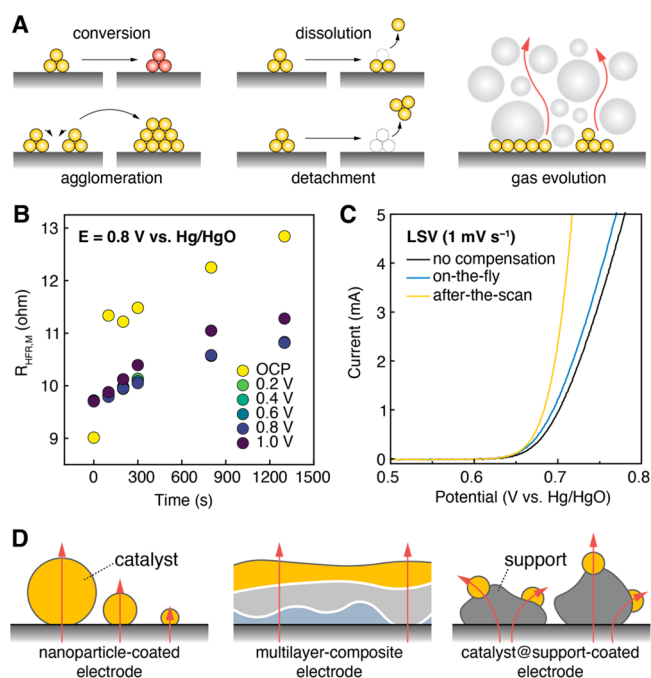


Figure 4. (A) Schematic representation of material transformation and gas evolution during electrocatalysis. (B) Measured $R_{\text{HFR,M}}$ of anodically treated Co planar electrode at different potentials during OER. (C) LSV curves of anodically treated Co planar electrode for OER, comparing on-the-fly and after-the-scan (PF) correction methods ($R_u = 10.5 \text{ ohm}$ is used/input). Experimental details are provided in the Supporting Information. (D) Illustration of charge transfer paths (red arrows) at modified electrodes with complicated nanoarchitecture.

In Figure 3, we assumed a modified electrode where the catalyst is evenly coated on the substrate. However, most modified electrodes are different from this, often having porous structures and rough surfaces. For such electrodes, it is well-known that the potential distribution on the surface is not homogeneous. The local electric field and R_{catalyst} at the individual active sites depend on the morphology and structure, as many scanning electrochemical microscopy studies demonstrated.^{33,34} It becomes more complicated when there are multiple compounds and structural features in the catalyst. Figure 4D shows three representative examples: the nanoparticle-coated electrode, the multilayer composite-coated electrode, and the catalyst@support-coated electrode. The charge transfer paths to different catalytic sites are different, which implies a different R_{catalyst} (and possibly a different R_{contact} too). In this regard, for a more accurate analysis of the *intrinsic activity* of specific sites, it may be necessary to measure the R_u locally instead of using an overall value.

Of course, obtaining the localized R_u for individual sites is challenging and requires *in situ* probe technology. Regarding this consideration, we suggest that, if the R_{catalyst} (which can be determined by Kelvin four-terminal sensing) is not overwhelmingly higher than the $R_{\text{contact}} + R_{\text{solution}}$, the measured R_{HFR} ($R_{\text{catalyst}} + R_{\text{contact}} + R_{\text{solution}}$) can still be used to evaluate the *intrinsic activity*. As to *sample activity* and *electrode activity*, no

special precautions need to be taken since R_{catalyst} should not be compensated for.

Current: Not All i Can Be Used for iR Compensation.

Principally, the current used for iR compensation should be the current flowing between points 1 and 5 (Figure 3A). For stationary studies with fixed potential, the measured current can be used directly for iR compensation. But if a dynamic potential is involved (e.g., in linear sweep voltammetry (LSV) or polarization analysis), the current is always contributed by both Faradaic and non-Faradaic currents. Because the non-Faradaic part is associated with the dynamic evolution of EDL, which does not flow across the bulk electrolyte solution, it cannot be used for iR compensation (i.e., only the Faradaic part of the measured current should be used). This is most likely another reason for using partial compensation because only a portion of the i should be used for iR compensation.

For most polarization tests in the literature, LSV is used, and the potential scan rate is between 1 and 10 mV s^{-1} . In these cases, the non-Faradaic current is inevitable, especially for nanomaterial-coated electrodes with large electrochemical surface areas (ECSAs). To minimize the impact, it is suggested that the iR compensation should only be performed with data collected at a low scan rate (5 mV s^{-1} or below). The larger the ECSA is, the slower the scan rate should be. It should also be noted that the iR compensation needs to be done with raw current data, not the normalized current density.⁶

Furthermore, instead of LSV, we suggest researchers use another electrochemical technique, staircase linear sweep voltammetry (S-LSV), to do the polarization tests. In short, the potential changes in large steps, and the non-Faradaic current decreases rapidly within a few seconds when reaching a new step. After the initial spike, the Faradaic current dominates and can be used for more precise iR compensation.

Conclusion and Recommendations. Overall, iR compensation is a powerful electrochemical technique to determine and control potential. However, as discussed above, some considerations about the current and resistance must be taken into account when performing iR compensation in electrocatalytic studies. This is due to the increased complexity of the working electrode structure. Most of the catalysts reported today are studied in the form of modified electrodes, in contrast to the last century when homogeneous metal planar electrodes were the focus. Consequently, some assumptions for iR compensation must be revisited and clarified to suit general use, including the resistance to be compensated and the current that should be used.

Recently, a few experimental studies on performing iR compensation have been conducted.^{6,9,10} Combining the experimental evidence and our considerations, the following “best practices” are suggested, as arranged in Figure 5 as a workflow chart. It is hoped that these suggestions can increase general awareness and benefit researchers in the field for more accurate analysis.

- R_{HFR} measurement.** Measure the R_{HFR} value at the reaction potential with low current ($<0.1 \text{ mA cm}^{-2}$, this value is chosen because most reactions have exchange current density lower than 0.1 mA cm^{-2}), rather than the often-used OCP. The steady-state condition should also avoid vigorous gas bubble formation. A small substrate is recommended to limit the total current and contact resistance. If more than one modified electrode is studied, measure R_{HFR} for every electrode every time.

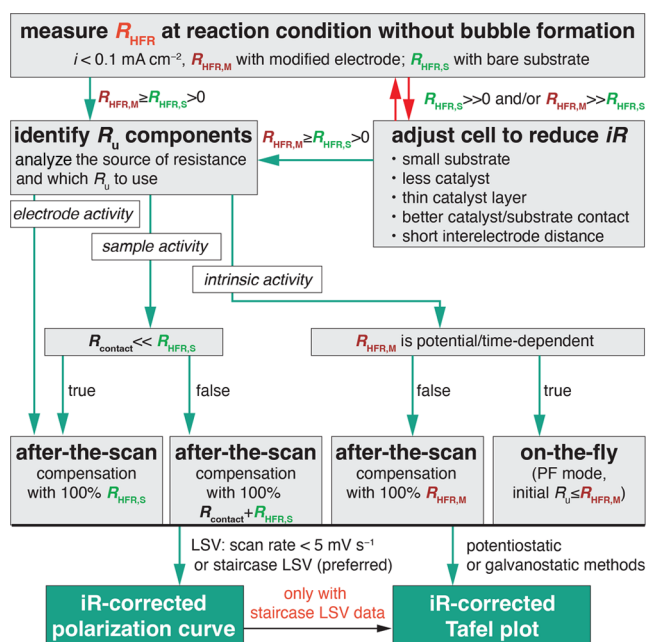


Figure 5. Suggested workflow chart for performing iR compensation in electrocatalysis studies.

- Experimental efforts.** After setting up the experiment, measure the R_{HFR} values with the modified electrode ($R_{\text{HFR},M}$) and the bare substrate ($R_{\text{HFR},S}$, $\approx R_{\text{solution}}$), respectively. Typically, $R_{\text{HFR},M} > R_{\text{HFR},S} > 0$. If $R_{\text{HFR},S} \gg 0$, use experimental methods to reduce $R_{\text{HFR},M}$ and $R_{\text{HFR},S}$. To reduce R_{solution} , reduce the interelectrode distance between the reference and working electrode [e.g., via Luggin capillary, but not too close ($>2d$, where d is the diameter of the tip of reference electrode,^{4,5} the interelectrode distance should be the same when studying a series of samples)] and increase the concentration of the supporting electrolyte (e.g., KClO_4 in HClO_4 , KCl in HCl). If $R_{\text{HFR},M} \gg R_{\text{HFR},S}$, improve the coating process to reduce the R_{contact} . For intrinsic activity analysis, use a thin catalyst coating layer to reduce the R_{catalyst} as suggested by Boettcher et al.^{17,27} If $R_{\text{HFR},M} \approx R_{\text{HFR},S}$, the catalyst layer is most likely porous, and one should be aware that R_{catalyst} is not reflected by $R_{\text{HFR},M}$.
- Identifying the components of R_u and selecting compensation methods.** After-the-scan compensation using $R_{\text{HFR},S}$ is suggested for electrode activity and sample activity studies (for sample activity: only if the R_{contact} is negligible in comparison to R_{solution} ; otherwise, use $R_{\text{HFR},S} + R_{\text{contact}}$). The R_{contact} can be measured by Kelvin four-terminal sensing. For intrinsic activity analysis, if the difference between $R_{\text{HFR},M}$ values detected at the studied potential range is negligible, the after-the-scan method can also be used. Otherwise, on-the-fly compensation using detected $R_{\text{HFR},M}$ (i.e., $R_{\text{contact}} + R_{\text{catalyst}} + R_{\text{solution}}$) is preferred.
- Polarization curve and Tafel plot correction.** Only perform iR compensation on polarization data collected at a low scan rate (for LSV, 5 mV s^{-1} or below; the slower, the better) or on S-LSV data (preferred). The Tafel plot is suggested to be collected from iR -corrected potentiostatic or galvanostatic responses (e.g., S-LSV), not converted

from a dynamic LSV polarization curve (error appears even at an extremely slow rate like 0.1 mA cm^{-2}).⁵⁵

- 5. Large current.** *iR* compensation (especially after-the-scan method) on data points with large current (not current density! Ren et al.⁹ suggested a normalized value of $>50 \text{ mA cm}^{-2}$) should be avoided since it may involve gas production on the electrode and thus a dynamic R_u . The error introduced by inaccurate R_u will be enlarged at a higher current density.
- 6. 100% *iR* compensation.** Full compensation is recommended, as suggested by Marshall et al.¹⁰ and Anantharaj et al.⁶ The frequently used partial compensation is an empirical attempt to correct the error caused by careless adoption of overall R_{HFR} and current. With a full understanding of the R_u to be compensated and the suitable current, there is no need to use an empirical factor. However, one should be cautious about possible potentiostat oscillations in the on-the-fly method, where a smaller initial input may be needed. This is due to the dynamic resistance during electrocatalysis, where the detected R_u may be lower than the initial input, causing instrumental damage.
- 7. Data presentation.** Always present uncompensated data alongside compensated data with the details of *iR* compensation (e.g., after-the-scan or on-the-fly method, R_u value, mode, factor, etc.).

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■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsenerylett.3c00366>.

Case analysis of an electrolyte-permeated electrode and experimental details related to B,C (PDF)

■ AUTHOR INFORMATION

Complete contact information is available at:

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Notes

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■ REFERENCES

- (1) Christopher, P.; Jin, S.; Sivula, K.; Kamat, P. V. Why Seeing is Not Always Believing: Common Pitfalls in Photocatalysis and Electrocatalysis. *ACS Energy Lett.* **2021**, *6* (2), 707–709.
- (2) Akbashev, A. R. Electrocatalysis Goes Nuts. *ACS Catal.* **2022**, *12* (8), 4296–4301.
- (3) Britz, D. *iR* Elimination in Electrochemical Cells. *J. Electroanal. Chem. Interfacial Electrochem.* **1978**, *88* (3), 309–352.
- (4) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; John Wiley & Sons, Inc., 2001.
- (5) Gamry Instruments. Application Note: Understanding *iR* Compensation. <https://www.gamry.com/application-notes/instrumentation/understanding-ir-compensation/>.

(6) Anantharaj, S.; Noda, S. *iR* Drop Correction in Electrocatalysis: Everything One Needs to Know! *J. Mater. Chem. A* **2022**, *10* (17), 9348–9354.

(7) McCrory, C. C.; Jung, S.; Peters, J. C.; Jaramillo, T. F. Benchmarking Heterogeneous Electrocatalysts for the Oxygen Evolution Reaction. *J. Am. Chem. Soc.* **2013**, *135* (45), 16977–87.

(8) Wang, H.; Chen, Z. N.; Wu, D.; Cao, M.; Sun, F.; Zhang, H.; You, H.; Zhuang, W.; Cao, R. Significantly Enhanced Overall Water Splitting Performance by Partial Oxidation of Ir through Au Modification in Core-Shell Alloy Structure. *J. Am. Chem. Soc.* **2021**, *143* (12), 4639–4645.

(9) Yu, L.; Ren, Z. Systematic Study of the Influence of *iR* Compensation on Water Electrolysis. *Mater. Today Phys.* **2020**, *14*, 100253.

(10) Heenan, A. R.; Hamonnet, J.; Marshall, A. T. Why Careful *iR* Compensation and Reporting of Electrode Potentials are Critical for the CO₂ Reduction Reaction. *ACS Energy Lett.* **2022**, *7* (7), 2357–2361.

(11) Chen, J.; Ye, X.-X.; Liao, L.-W.; Wei, Z.; Xu, M.-L.; Chen, Y.-X. Ohmic Drop Compensation in Electrochemical Measurement. *J. Electrochem.* **2021**, *27*, 291–300.

(12) Schuler, T.; Schmidt, T. J.; Büchi, F. N. Polymer Electrolyte Water Electrolysis: Correlating Performance and Porous Transport Layer Structure: Part II. Electrochemical Performance Analysis. *J. Electrochem. Soc.* **2019**, *166* (10), F555–F565.

(13) Ito, H.; Maeda, T.; Nakano, A.; Kato, A.; Yoshida, T. Influence of Pore Structural Properties of Current Collectors on the Performance of Proton Exchange Membrane Electrolyzer. *Electrochim. Acta* **2013**, *100*, 242–248.

(14) Dionigi, F.; Zhu, J.; Zeng, Z.; Merzdorf, T.; Sarodnik, H.; Gliche, M.; Pan, L.; Li, W. X.; Greeley, J.; Strasser, P. Intrinsic Electrocatalytic Activity for Oxygen Evolution of Crystalline 3d-Transition Metal Layered Double Hydroxides. *Angew. Chem., Int. Ed.* **2021**, *60* (26), 14446–14457.

(15) Kennouche, D.; Fang, Q.; Blum, L.; Stolten, D. Analysis of the Cathode Electrical Contact in SOFC Stacks. *J. Electrochem. Soc.* **2018**, *165* (9), F677–F683.

(16) Anantharaj, S.; Kundu, S. Do the Evaluation Parameters Reflect Intrinsic Activity of Electrocatalysts in Electrochemical Water Splitting? *ACS Energy Lett.* **2019**, *4* (6), 1260–1264.

(17) Burke, M. S.; Zou, S.; Enman, L. J.; Kellon, J. E.; Gabor, C. A.; Pledger, E.; Boettcher, S. W. Revised Oxygen Evolution Reaction Activity Trends for First-Row Transition-Metal (Oxy)hydroxides in Alkaline Media. *J. Phys. Chem. Lett.* **2015**, *6* (18), 3737–42.

(18) Bohn, L.; von Holst, M.; Ortiz, E. C.; Breitwieser, M.; Vierrath, S.; Klose, C. Methods—A Simple Method to Measure In-Plane Electrical Resistance of PEM Fuel Cell and Electrolyzer Catalyst Layers. *J. Electrochem. Soc.* **2022**, *169* (5), No. 054518.

(19) Pham, C. V.; Escalera-Lopez, D.; Mayrhofer, K.; Cherevko, S.; Thiele, S. Essentials of High Performance Water Electrolyzers - From Catalyst Layer Materials to Electrode Engineering. *Adv. Energy Mater.* **2021**, *11* (44), 2101998.

(20) Bernt, M.; Schramm, C.; Schröter, J.; Gebauer, C.; Byrknes, J.; Eickes, C.; Gasteiger, H. A. Effect of the IrO_x Conductivity on the Anode Electrode/Porous Transport Layer Interfacial Resistance in PEM Water Electrolyzers. *J. Electrochem. Soc.* **2021**, *168* (8), No. 084513.

(21) Chung, D. Y.; Park, S.; Lopes, P. P.; Stamenkovic, V. R.; Sung, Y. E.; Markovic, N. M.; Strmcnik, D. Electrokinetic Analysis of Poorly Conductive Electrocatalytic Materials. *ACS Catal.* **2020**, *10* (9), 4990–4996.

(22) Burke, M. S.; Enman, L. J.; Batchellor, A. S.; Zou, S.; Boettcher, S. W. Oxygen Evolution Reaction Electrocatalysis on Transition Metal Oxides and (Oxy)hydroxides: Activity Trends and Design Principles. *Chem. Mater.* **2015**, *27* (22), 7549–7558.

(23) Bediako, D. K.; Surendranath, Y.; Nocera, D. G. Mechanistic studies of the oxygen evolution reaction mediated by a nickel-borate thin film electrocatalyst. *J. Am. Chem. Soc.* **2013**, *135* (9), 3662–74.

- (24) Kuo, J. J.; Kang, S. D.; Chueh, W. C. Contact Resistance of Carbon–Li_x(Ni,Mn,Co)O₂ Interfaces. *Adv. Energy Mater.* **2022**, *12* (31), 2201114.
- (25) Nara, H.; Mukoyama, D.; Shimizu, R.; Momma, T.; Osaka, T. Systematic analysis of interfacial resistance between the cathode layer and the current collector in lithium-ion batteries by electrochemical impedance spectroscopy. *J. Power Sources* **2019**, *409*, 139–147.
- (26) Chen, S.-K.; Chiu, K.-F.; Su, S.-H.; Liu, S.-H.; Hou, K. H.; Leu, H.-J.; Hsiao, C.-C. Low contact resistance carbon thin film modified current collectors for lithium ion batteries. *Thin Solid Films* **2014**, *572*, 56–60.
- (27) Stevens, M. B.; Enman, L. J.; Batchellor, A. S.; Cosby, M. R.; Vise, A. E.; Trang, C. D. M.; Boettcher, S. W. Measurement Techniques for the Study of Thin Film Heterogeneous Water Oxidation Electrocatalysts. *Chem. Mater.* **2017**, *29* (1), 120–140.
- (28) Chen, G.; Waraksa, C. C.; Cho, H.; Macdonald, D. D.; Mallouka, T. E. EIS Studies of Porous Oxygen Electrodes with Discrete Particles. *J. Electrochem. Soc.* **2003**, *150* (9), E423.
- (29) de Klerk, N. J. J.; Wagemaker, M. Space-Charge Layers in All-Solid-State Batteries: Important or Negligible? *ACS Appl. Energy Mater.* **2018**, *1* (10), 5609–5618.
- (30) Heymann, L.; Weber, M. L.; Wohlgemuth, M.; Risch, M.; Dittmann, R.; Baeumer, C.; Gunkel, F. Separating the Effects of Band Bending and Covalency in Hybrid Perovskite Oxide Electrocatalyst Bilayers for Water Electrolysis. *ACS Appl. Mater. Interfaces* **2022**, *14* (12), 14129–14136.
- (31) Liu, L. C.; Corma, A. Structural Transformations of Solid Electrocatalysts and Photocatalysts. *Nat. Rev. Chem.* **2021**, *5* (4), 256–276.
- (32) Zhao, X.; Ren, H.; Luo, L. Gas Bubbles in Electrochemical Gas Evolution Reactions. *Langmuir* **2019**, *35* (16), 5392–5408.
- (33) Laskowski, F. A. L.; Oener, S. Z.; Nellist, M. R.; Gordon, A. M.; Bain, D. C.; Fehrs, J. L.; Boettcher, S. W. Nanoscale Semiconductor/Catalyst Interfaces in Photoelectrochemistry. *Nat. Mater.* **2020**, *19* (1), 69–76.
- (34) Wahab, O. J.; Kang, M.; Daviddi, E.; Walker, M.; Unwin, P. R. Screening Surface Structure-Electrochemical Activity Relationships of Copper Electrodes under CO₂ Electroreduction Conditions. *ACS Catal.* **2022**, *12* (11), 6578–6588.
- (35) Anantharaj, S.; Noda, S.; Driess, M.; Menezes, P. W. The Pitfalls of Using Potentiodynamic Polarization Curves for Tafel Analysis in Electrocatalytic Water Splitting. *ACS Energy Lett.* **2021**, *6* (4), 1607–1611.