Errors in Electrocatalysis Measurements – Categories and Origins

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December 2024

Errors in experimental protocols, parameters, measured and derived quantities, and calculated quantities are listed in Table 1. Protocol errors apply to all measurements within a series of experiments and can be classified as systematic errors. Errors within one protocol can be detected by comparison with results obtained by an independent protocol. This is difficult to accomplish, however, since the nature of research is to probe the unknown, and therefore, the protocols themselves will always be in a state of development. In electrocatalysis, protocol errors include those in cell cleaning, electrolyte purification, electrode preparation and characterization, and uncontrolled—whether by lack of understanding or lack of capability—experimental conditions.

Experimental parameters, measured and derived quantities, and calculated quantities are three sets of information used in drafting an experiment design. Errors in these quantities can be classified as random errors. Experimental parameters establish the experiment conditions. In Table 1, the experimental parameters are species activity A_j ; temperature *T*; and reference electrode potential E_{RE} , which depends on the type, calibration, and temperature of the reference electrode. Parameter errors arise from an inability to establish the independent variables for a series of experiments with sufficient accuracy and precision.

Errors in measured quantities receive the most attention as they relate to the measurements themselves. In electrocatalysis, current *I*, potential *E*, and geometric area A_{geo} are the most significant measured quantities. Derived quantities are those directly related to measured quantities in a model-independent fashion. Derived quantities include the overpotential η and geometric current density $i_{geo} = I/A_{geo}$. Derived quantities take on the errors of the measured quantities. Calculated quantities are those derived from measured and derived quantities and are model-dependent. They carry forward the errors in measured quantities but introduce no further error other than that incurred in the approximations and assumptions used in the calculations. Examples of calculated quantities are ECSA, Tafel slopes, exchange current density, kinetic rate constants, and activation energies.

Much of electrocatalysis research is built around three main equations: the Butler-Volmer equation, the Tafel equation, and the expression for overpotential. Overpotential factors strongly into the Butler-Volmer and Tafel equations. It is the derived quantity most susceptible to parameter and measurement errors, as seen by the expression

$$\eta = E - E_r = (E_{WE} - E_{RE}) - \left\{ \left[E_o(T) - \frac{RT}{nF} \sum_j \nu_j \ln \mathcal{A}_j \right] - E_{RE} \right\}$$
(1)

where *E* is the electrode potential, measured as the potential difference between the working electrode (E_{WE}) and a reference electrode (E_{RE}); E_r is the reversible potential at reaction conditions; $E_o(T)$ is the reversible potential of the half-reaction reaction at temperature *T* and unit activity of all species; A_j is the activity of species *j*; and v_j is the stoichiometric coefficient of species *j* (positive for products, negative for reactants). The term in square brackets is the Nernst equation for E_r . Although overpotential does not depend on the nature of the reference electrode potentials. Mathematically, the reference potentials cancel each other. However, the two reference potentials might not cancel due to drift in the reference electrode as experimentation proceeds. That is, the electrode potential *E* drifts, whereas the reversible potential E_r of a calibrated reference electrode does not.

Information category	Measurement error	Protocol error	Misattribution of results
Parameters	 Species activities, A_j Temperature, T Ref. electrode, E_{RE} 	 Cell cleaning Electrolyte purity Electrode contamination 	
Measured and derived quantities	 Current, <i>I</i> Voltage, <i>E</i> Geometric area, <i>A_{geo}</i> Overpotential, η Geometric current density, <i>i_{geo}</i> 	Uncontrolled experimental conditions	
Calculated quantities	 ECSA, A_{ECSA} Current density based on ECSA, i_{ECSA} Tafel slope, b Exchange current density, i_o Kinetic rate constants and TOF, k_c, k_a Activation energies, E_{act} 		 Sample characterization Model assumptions and approximations Spectroscopy and microscopy limitations Analytical errors

Table 1. Matrix showing the relationship of types of error that compromise rigor and reproducibility and types of information needed for a well-defined experiment.

Species activities can present large problems due to errors in partial pressure, concentration, pH, and whether to invoke activity coefficients. Species concentration and activity coefficients can be affected by errors in weighing solutes, hygroscopic solutes, temperature, or other factors.¹ Control of pH can arise from errors in electrolyte preparation, CO₂ absorption, or non-ideal

solutions uncorrected by activity coefficients, as occurs for 1 M KOH.² The relevant pH at the electrode surface may differ from the bulk pH due to mass transfer effects.³ Problems relating to reference electrodes arise from improper selection, lack of calibration to account for drift, liquid junction potentials, leakage, or insufficient pH control.⁴

Specification of Electrode Area

There are two kinds of area used in electrocatalysis research –geometric area and ECSA – the choice of which depends on the application. Geometric area is an easily measurable quantity. It is best suited for device design in which the nature of the catalyst has already been specified.

In fundamental research, it is necessary to distinguish between the surface reaction kinetics of the electrocatalyst and its ECSA, the latter being controlled by the method of electrocatalyst preparation. Several methods exist to measure ECSA, among them capacitance measurements, oxidation or reduction charge, and chemical titration.⁵ None of these is a direct measurement, so estimation of ECSA depends on the physics of the method employed – it is model dependent and therefore a calculated quantity. As such, there can be considerable uncertainty in the ECSA and even which method of measurement should be used. The ECSA for an electrocatalytic reaction need not be the same as that determined by the amount of charge to oxidize an electrode, for example. There is a pressing need for a rigorous set of guidelines – especially for oxides – that can be used to validate a given method for measuring ECSA.

Advanced Characterization Methods and Misattribution Error

Interpretation of calculated quantities is subject to misattribution error, which arises from inadequate sample or electrolyte characterization; inappropriate models due to failed assumptions or coarse approximations; limitations in, or improperly conducted, spectroscopy and microscopy; and errors in analytical methods such as chromatography and mass spectrometry. A wide variety of techniques exist to characterize electrolyte, electrode, and product distributions, as listed below.

- Electrolyte characterization
 - Inductively coupled plasma-optical emission spectroscopy (ICP-OES)
 - Inductively coupled plasma-mass spectroscopy (ICP-MS)
 - Gas chromatography (GC)
 - High performance liquid chromatography (HPLC)
 - Nuclear magnetic resonance (NMR)
- Electrode characterization
 - ECSA measurements (capacitance, titration, charge)
 - Ellipsometry
 - o BET isotherms
 - X-ray methods (XRD, EDX, XPS)

- Microscopy (SEM, TEM, HRTEM, STM, AFM)
- Product identification, rates, and distributions
 - Differential electrochemical mass spectrometry (DEMS)
 - GC and HPLC
- Probing reaction mechanisms
 - o Vibrational spectroscopy (FTIR, Raman, ATR-SEIRAS, SFG)
 - o Operando X-ray methods (XAS, XAFS, XANES)
 - Electrochemical impedance spectroscopy (EIS)

It should be noted that Table 1 focusses on measurement and interpretation of electrochemical results. Every form of spectroscopy or microscopy has its own set of parameters and measured quantities, each subject to measurement and procedural error. (For clarity, these are not listed in the table.) Spectroscopic, microscopic, and analytical techniques should be applied in a redundant manner to reduce the dependence on any one method. There is no redundancy for electrochemical measurements, however.

Microkinetics, Theory, and Benchmarking

Influence of Potential Dependence in Microkinetic Modeling

A complete understanding of electrocatalysis requires a thorough integration of theory and experiment. With knowledge of reaction intermediates, product distributions, and rates, a baseline mechanism can be established. Knowledge of potential energy surfaces and vibrational modes from density functional theory (DFT) enable the mechanism to be refined. With microkinetic modeling, mechanistic insights and theoretical results can be compared with experimental results. Discrepancies identified in the comparison will call for further modeling and additional experiments to define the system better.

The situation for electrocatalysis is more complicated in that several elementary steps in the mechanism will involve charge transfer and hence a dependence on potential. The potential dependence can be expressed by multiplying the cathodic and anodic kinetic rate constants by factors of $\exp\left(\frac{-\alpha_c nFE}{RT}\right)$ and $\exp\left(\frac{\alpha_a nFE}{RT}\right)$, respectively, where α_c and α_a are the cathodic and anodic transfer coefficients with the property that $\alpha_c + \alpha_a = 1$, n is the number of electrons transferred, and F is Faraday's constant. Potential dependence on reaction rates is difficult to calculate in DFT and imposes a strong influence on elementary charge transfer kinetics, thereby compromising predictions from microkinetic modeling.

Reaction Kinetics and Mechanisms by DFT

The computational hydrogen reference electrode (CHE) is a commonly used approach in modeling electrochemical reactions and has been used to predict trends and the effect of potential on

reaction mechanisms.⁶ The CHE can predict thermodynamics of reaction paths at different potentials, is computationally affordable, and easy to apply. The CHE generally excludes solvent effects, changes in adsorbate interactions with charged surfaces or at applied potential, and kinetic barriers. Including these effects is computationally expensive though different approaches are being developed to help capture some or all these effects. A kinetic activation barrier can be estimated assuming that the potential only affects the energy of proton/electron pairs, as in the CHE, by shifting the barrier in potential while assuming a constant value of the electrochemical symmetry factor β , typically assigned to 0.5, this approach works well for systems for hydrogen evolution reaction (HER) in acid but might hard to extend to reactions with polar reactants.^{7,8}

Several studies have approximated applied potential by introducing extra electron density to the surface slab, which alters the work function of the surface. Based on the calculated work function, a corresponding equivalent applied electrode potential can be estimated. A counter-charge is included in the simulation cell to counteract the excess charge added to the slab and maintain charge neutrality of the simulation cell. There are several varieties of this approach that differ mainly by how the cell is charge neutralized. Examples include localized planar charge distribution in the form of a Gaussian profile perpendicular to the surface,^{9–14} a uniform charge background,^{15,16} and counterions within an explicitly modeled solvent.¹⁷ This approach can capture the effect of charge/potential on adsorption and the electronic structure of the slab, but it is challenging to maintain constant applied potential through electrochemical reaction steps involving charge transfer.

Constant potential calculations can be obtained in grand canonical calculations by changing the total number of electrons in a self-consistent cycle, while enforcing charge neutrality through the introduction of a jellium counter charge dispersed in an implicit solvent region above the slab.^{18,19} The homogeneous counter charge keeps the system charge neutral while the number of electrons in the cell is iteratively adjusted until the target potential is reached within a tolerance threshold.

These methods have provided a valuable mechanistic understanding, but many are computationally expensive and challenging, making routine or high throughput simulations difficult.

Benchmarking

Comprehensive benchmarking of the experimental setup is critical for distinguishing between intrinsic and extrinsic electrocatalytic phenomena.^{3,20,21} Benchmarking should consist of several steps that collectively improve the reliability of published data and the conclusions drawn therefrom. The activity and selectivity of standard electrocatalysts should be reproduced and directly compared to widely accepted benchmarks through a wide potential range. Furthermore, the stability of standard catalysts should be demonstrated by performing prolonged

chronoamperometry for several hours to detect and quantify catalyst deactivation. The accuracy and precision of reaction product quantification should be demonstrated by analyzing both the gaseous and liquid phases and closing the charge balance. Finally, the impact of mass transfer on the observed activity and selectivity should be assessed. Any activity data that is found to vary with mass transfer resistance should not be discussed as intrinsic to the material under investigation.

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