

Emerging Electrochemical Techniques for Probing Site Behavior in Single-Atom Electrocatalysts

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Conspectus: Single-atom catalysts (SACs) have aroused tremendous interest over the last decade, particularly in the community of energy and environment-related electrocatalysis. A rapidly growing number of recent publications have recognized it as a promising candidate with maximum atomic utilization, distinct activity, and selectivity in comparison to bulk catalysts and nanocatalysts. However, the complexity of localized coordination environments as well as dispersion of isolated sites lead to significant difficulties when it comes to gaining insights into the intrinsic behavior of electrocatalytic reactions. Furthermore, the low metal loadings of most SACs make conventional ensemble measurements less likely to be accurate at the sub-nanoscale.

Thus, it remains challenging to probe the activity and properties of individual atomic sites by available commercial instruments and analytical methods. In spite of this, continuing efforts have been lately focusing on the development of advanced measurement methodologies, which are highly useful for a fundamental understanding of SACs. There have been recently a number of in situ/operando techniques applied to SACs, such as electron microscopy, spectroscopy, and other analysis methods, which support relevant functions to identify the active sites and reaction intermediates, as well as investigate the dynamic behaviors of localized structures of the catalytic sites.

This Account aims to present recent electrochemical probing techniques which can be used to identify single-atomic catalytic sites within solid supports. First, we describe the basic principles of molecular probe methods for the study and analysis of electrocatalytic site behavior. In particular, the in-situ probing technique enabled by surface interrogation scanning electrochemical microscopy (SI-SECM) can measure active site density and kinetic rate with high resolution. An alternative electrochemical probing technique is further demonstrated on the basis of single-entity electrochemistry, which allows the unique electrochemical imaging of the size and catalytic rate of single atoms, molecules and clusters. The merits and limitations of different electrochemical techniques are then discussed, along with perspectives about future prospects. Apart from this, we further showcase the powerful capability of emerging electrochemical probing techniques for determining significant effects and properties of SACs for various electrocatalytic reactions, including oxygen reduction and evolution, hydrogen evolution, nitrate reduction. Overall, electrochemical techniques with atomic resolution have greatly increased opportunities for observing, measuring, and understanding the surface and interface chemistry during energy conversion. In the future, it is anticipated that the development of electrochemical probing

techniques will be advanced with innovative perspectives on the behavior and features of SACs. We thereby hope this Account can contribute in several ways to promote the fundamental knowledge and technical progress of emerging electrochemical measurements for studying SACs.

KEY REFERENCES

- Jin, Z.; Li, P.; Meng, Y.; Fang, Z.; Xiao, D.; Yu, G., Understanding the inter-site distance effect in single-atom catalysts for oxygen electroreduction. *Nat. Catal.* **2021**, *4*, 615-622.¹ Using the in situ electrochemical probing technique can determine the relationship between the inter-site distance of single-atomic Fe sites and kinetic rates for oxygen reduction.
- Li, P.; Jin, Z.; Fang, Z.; Yu, G., A single-site iron catalyst with preoccupied active centers that achieves selective ammonia electrosynthesis from nitrate. *Energy Environ. Sci.* **2021**, *14*, 3522-3531.² Competitive nitrate/water reduction reactions over single-atom and nanoparticle catalysts were interrogated by in situ electrochemical probing technique, where a preoccupied mechanism was revealed in isolated Fe-N₄ moieties with specific selectivity toward ammonia formation.
- Li, P.; Jin, Z.; Qian, Y.; Fang, Z.; Xiao, D.; Yu, G., Supramolecular confinement of single Cu atoms in hydrogel frameworks for oxygen reduction electrocatalysis with high atom utilization. *Mater. Today* **2020**, *35*, 78-86.³ Electrochemically probing the number of active sites that truly evolve in catalytic reactions was reported to estimate the atomic utilization of single-atom electrocatalysts.

- Jin, Z.; Bard, A. J., Atom-by-atom electrodeposition of single isolated cobalt oxide molecules and clusters for studying the oxygen evolution reaction. *Proc. Natl. Acad. Sci.* **2020**, *117*, 12651-12656.⁴ The size and catalytic kinetic rate of single isolated metal oxide deposits were measured with an alternative molecular probing technique, which offers a strategy to gain insights into the size effect of oxygen-evolving catalysts.

1. INTRODUCTION

Developing renewable energy technologies remains profoundly important in our modern society given the urgency of our energy crisis and the threat of climate change. Single-atom catalysts have been of tremendous interest over the past decade, particularly to the energy and environment communities.⁵⁻⁷ SACs, defined as atomically dispersed metal catalysts on solid supports, e.g. carbon and metal oxides, combine the merits of heterogeneous and homogeneous catalysts.⁸⁻⁹ Specifically, metal sites normally exist in well-defined coordination environments composed of heteroatom ligands, of which structures can be molecularly designed for achieving high activity and selectivity. On the other hand, SACs exhibit relatively high robustness even under harsh conditions and are readily separated from reactors. Compared to bulk catalysts, using single atomic sites has shown promising features, such as maximum atom utilization, distinct activity, and selectivity.¹⁰⁻¹¹ However, when attempts are made to gain insights into intrinsic behavior toward a variety of electrocatalytic reactions, the complexity of the distribution of isolated sites and electrode/electrolyte interfaces poses significant challenges. Since metal loadings on most SACs are low, conventional ensemble measurements are unlikely to provide a quantitative level of

resolution. To this end, the development of advanced measurement methodologies has become increasingly important to better understanding fundamental properties of SACs.¹²⁻¹³

Operando/in situ spectroelectrochemistry has been widely applied as powerful tools for exploring catalytic mechanisms, such as X-ray absorption spectroscopy, ambient pressure X-ray photoelectron spectroscopy, Fourier-transform infrared spectroscopy, surface-enhanced Raman spectroscopy, etc.¹⁴⁻¹⁷ These techniques are generally valid for obtaining structural information of interactions between metal sites and reactants/intermediates, as well as the valence transition under operating potentials. As a result of the limitation of sensitivity and resolution, most spectroscopes are unlikely to provide quantitative analysis over catalytic site behavior, especially measurements of kinetic rate remain unresolved. Nonetheless, electrochemical probing techniques by using redox mediators that generally react through outer-sphere electron-transfer reactions have been demonstrated for measuring the number of active sites that participate in catalytic reactions, thus increasing the accuracy in specific activity determination, e.g. turnover frequency (TOF).¹⁸

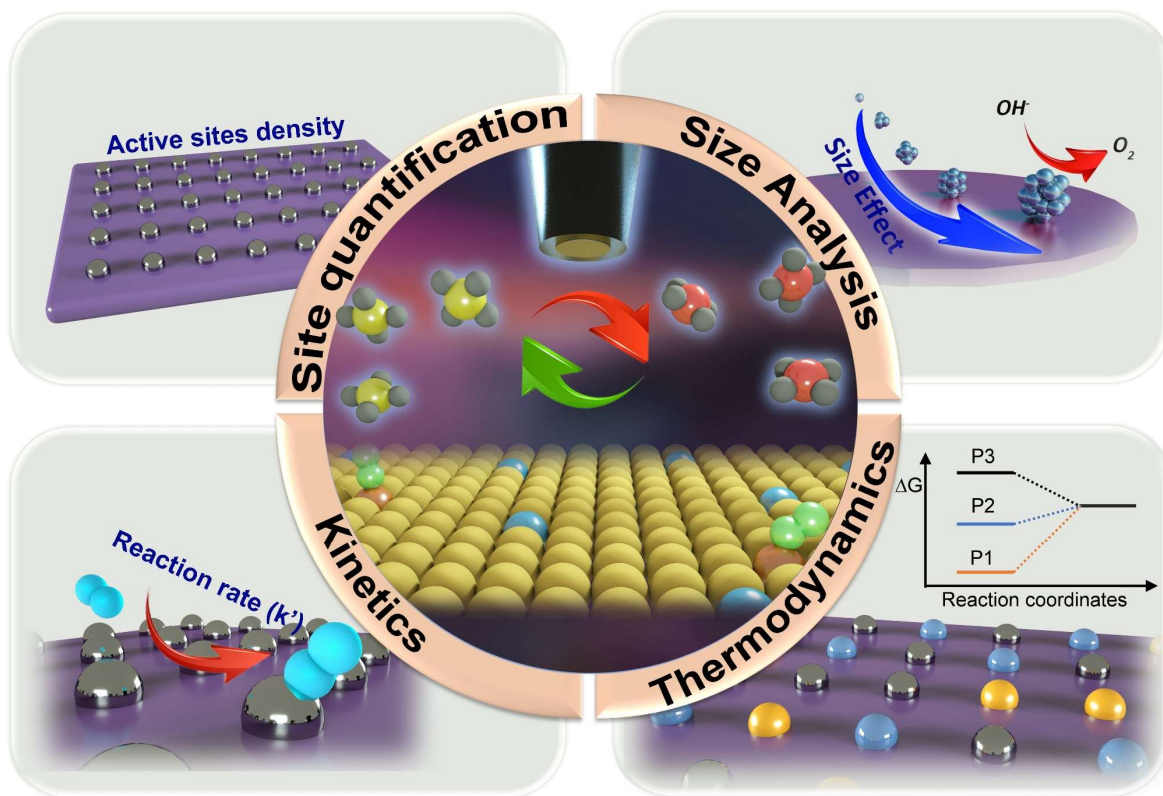


Figure 1. Overview of electrochemical probing techniques for studying fundamental behavior of single-atom electrocatalysts.

This Account presents the electrochemical probing techniques that our group and others have recently developed, which can be used to provide important insights into single-atom catalysts (Figure 1). We particularly highlight the high-resolution in situ electrochemical probe enabled by surface interrogation scanning electrochemical microscopy, as well as an alternative probing technique combining the single-entity electrochemistry. Additionally, the proposed electrochemical probing techniques, which offer complementary approaches to measuring significant effects and properties of SACs, are demonstrated in several key works that show their feasibility and capability. These techniques with atomic resolution have vastly increased the ability to observe and measure electrochemical reactions at catalytic surfaces and interfaces during energy

conversion. Innovations in emerging perspectives are thus expected to lead to the advancement of next-generation electrochemical probing techniques and deepen our understanding of intrinsic behaviors of SACs.

2. OPERATING PRINCIPLES

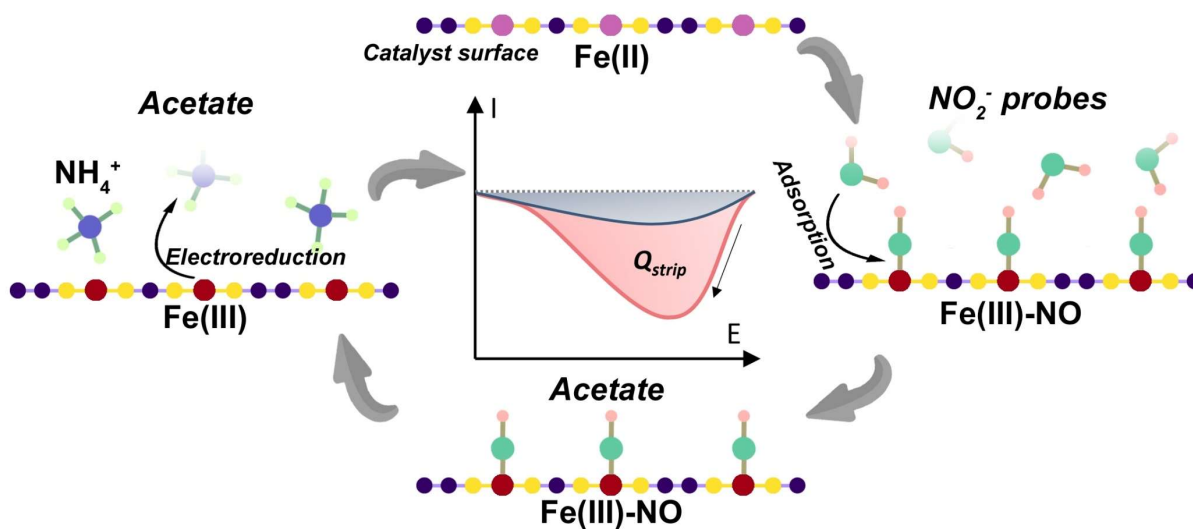


Figure 2. Schematic of conventional ex-situ probing (NO_2^-) technique for determining active site number (Fe-NC) related to the ORR.

Probe ions, such as halide ions (Cl^- , F^- , and Br^-) and low valence state sulfur-containing species, have been used to identify active centers that are responsible for electrocatalysis.¹⁹⁻²¹ This method is particularly helpful for investigating Fe-NC-based SACs, where the probe ions can bind to Fe sites and inhibit catalytic reactions, e.g. the oxygen reduction reaction (ORR). As such, one can provide insights into the nature of active sites, while little quantitative information is permitted. Malko et al. reported an electrochemically active probe for determining the number of active sites in Fe-NC catalysts.²²⁻²³ In the process as shown in Figure 2, nitrite ions (NO_2^-) first interact

strongly with metal centers to selectively poison the catalytic sites of Fe atoms instead of supporting materials in Fe-NC SACs. The nitrite is then electrochemically stripped with the recovered activity of the catalyst, thus enabling a measurable signal of charge transfer, which can be used to estimate the number of adsorbed anions and therefore calculate how many active sites there are. Catalysts without metals are not affected by the process since the nitrite cannot chemically adsorb on carbon or nitrogen atoms. The reaction rate per metal site, TOF, can be determined in this way, permitting a rationalization of trends in performance and the promotion of catalyst design. It is further highlighted that only standard electrochemical characterization equipment is required, and the method is thereby relatively facile and economic to implement.

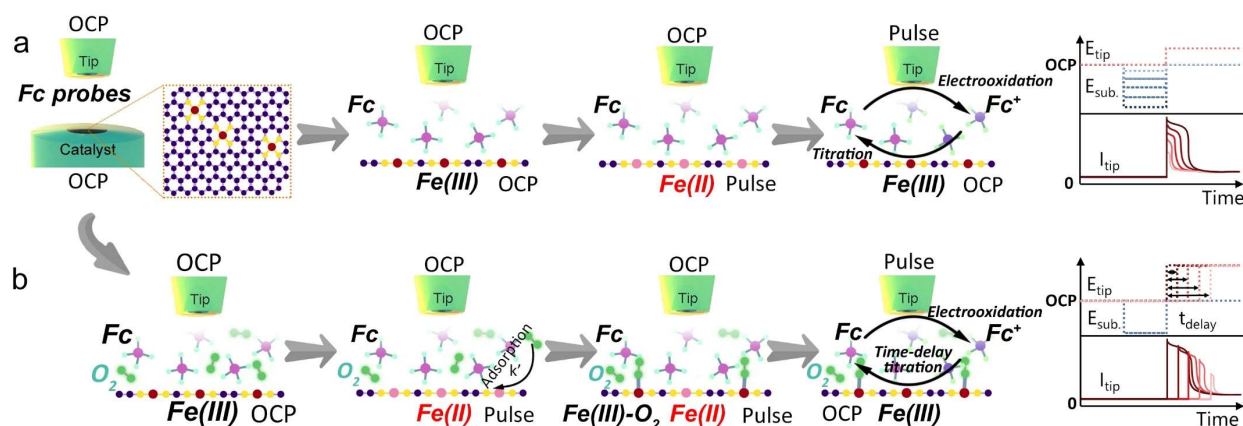


Figure 3. In situ electrochemical probing technique based on the SECM with ferrocene derivatives (Fc) as molecular probes. **a)** Investigation of site density at varying potentials. **b)** Kinetics study with time-delay titration of residue active sites that have not proceeded adsorption.

We recently introduced the in situ electrochemical probing technique enabled by SECM with surface interrogation mode.¹ As illustrated in Figure 3a, the schematic of Fe-NC SACs for the ORR demonstrates how the measurement is conducted. Here, the technique involves molecular probes, e.g. ferrocenium (Fc⁺), electro-generated from ferrocenemethanol (Fc) at the tip

ultramicroelectrode (UME), after which active species formed on catalyst layers (immobilized on substrate UME) at given pre-pulsed potentials are titrated by the Fc^+ . Positive feedback on the tip current is observed as the result of the regeneration of Fc reduced by Fe(II) in the catalyst. The tip current originated by the Fc oxidation reaches a steady state until all reactive Fe(II) sites are consumed. The number of active sites can be then determined by integrating the net charges (Q_{tip}) produced by the probes that react with the catalyst. The site density (n_s) is further obtained by normalizing the active site number with the electrochemical active surface area of catalysts loaded on UME (ECSA_{UME}).

$$n_s = Q_{\text{tip}} / (F \times N_A \times \text{ECSA}_{\text{UME}}) \quad (1)$$

where F is faraday constant and N_A is Avogadro constant. Namely, this purely electrochemical approach allows precise coulometric measurements to be made that shows the amount of charge passed to a starting catalyst layer.

Another important function of the technique is the time-delay titration, making it possible to measure the kinetic rate of catalytic sites interacting with reactants, like O_2 , H_2O , N_2 , and NO_3^- .²⁴⁻²⁸ Figure 3b shows a typical procedure of the measurement, where specific delay time (t_{delay}) is applied between the potential pulse over the substrate and tip. By involving the time-of-flight method with a rapid analog switch,²⁹ the resolution for the delay time control can achieve $\sim 1 \mu\text{s}$. The precise time-delay titration then allows the quantification of residual Fe(II) active sites that have yet to react with O_2 at a given t_{delay} . The kinetic rate of Fe(II) binding with O_2 (k'_{O_2}) can be calculated by plotting the number of residual Fe(II) sites and t_{delay} through Equation 2. Generally, pseudo-first-order reaction behavior is found because of the rate mostly determined by the active site concentration over the catalyst.

$$-\frac{d[\text{Fe(II)}]}{dt_{\text{delay}}} = k'_{\text{O}_2} [\text{Fe(II)}] \quad (2a)$$

$$\ln[\text{Fe(II)}]_{t_{\text{delay}}} = -k'_{\text{O}_2} \times t_{\text{delay}} + \ln[\text{Fe(II)}]_0 \quad (2b)$$

The above analytical protocol can also be applied to other transition metal-based SACs such as Cu and Co sites and a variety of reactions beyond ORR.

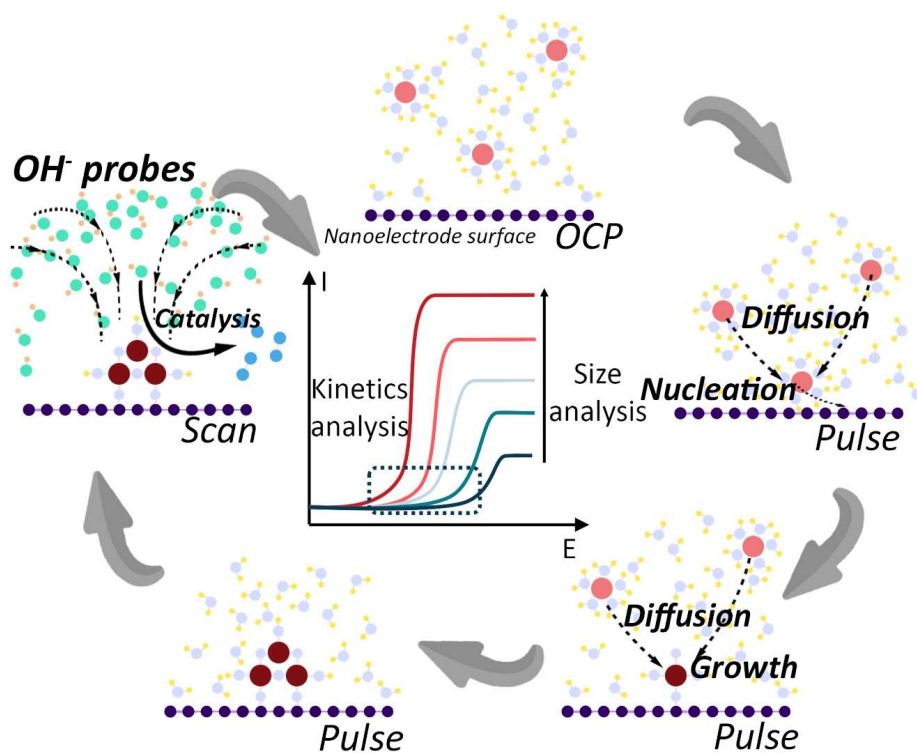


Figure 4. Schematic of alternative electrochemical probing technique for measuring the size and kinetic rate of isolated single atoms, molecules, and clusters.

An alternative electrochemical probing technique was reported by several recent publications, which combines single-entity electrochemistry for characterizing the size effect of catalytic materials.^{4, 30-32} The measurement is conducted with nanoelectrodes that show sluggishness in electrocatalytic reactions of interest. Figure 4 displays an example of a carbon fiber nanoelectrode

with electrodeposited cobalt oxide single molecules and clusters for studying the oxygen evolution reaction (OER). Briefly, the protocol proceeds in two steps. First, cobalt oxide single molecules or clusters are electrodeposited on carbon nanoelectrodes from solutions with femtomolar Co^{2+} precursors. Deposition on sub-100-nm-radius carbon fiber UMEs generally results in only one nucleation site.³³⁻³⁵ When such conditions are present, precursor ions reach the electrode surface from bulk solution and nucleate governed by the diffusion of Co^{2+} . Hence, the deposition frequency is about 0.1 Hz, corresponding to average one Co^{2+} ion every 10 seconds. In this way, the number of cobalt ions colliding with the electrode surface can be estimated and controlled. Second, electrochemical probes, such as hydroxide ions, are used to characterize the catalyst and estimate the size of the deposit. With a known concentration of OH^- in the electrolyte solution, sufficiently large OER currents in steady state can be observed even though the catalytic entity is a single atom/molecule. The voltammetric response allows the precise analysis of the size and kinetic rate assuming the deposits with hemispherical geometry.

3. ELECTROCHEMICALLY PROBES FUNDAMENTAL BEHAVIORS OF SAC_5

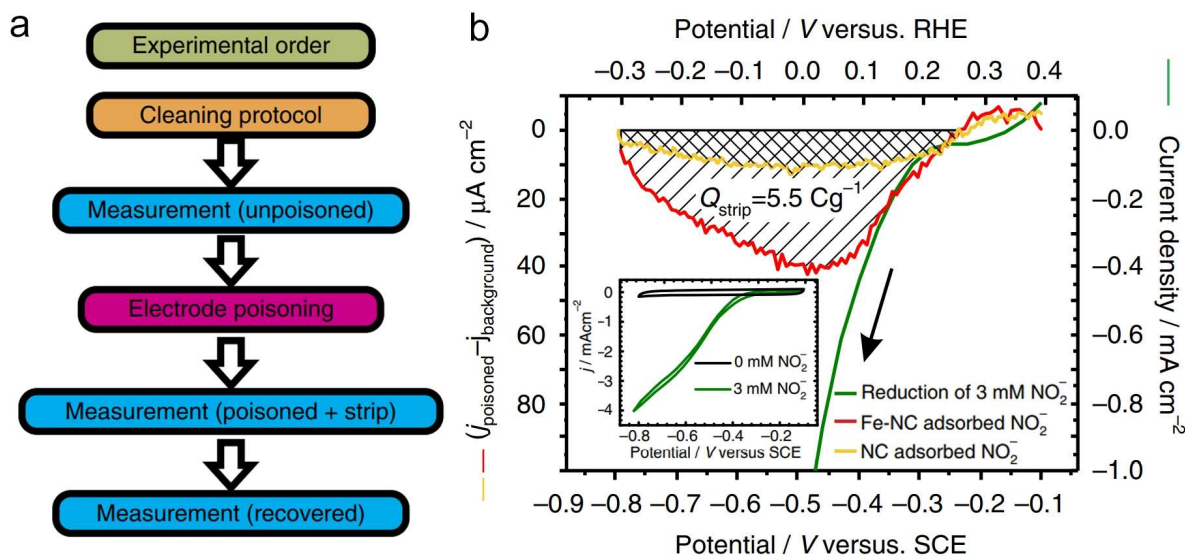


Figure 5. a) Protocol to determine active site density with the nitrite probe. **b)** Voltammetric study of nitrite electroreduction in homogeneous aqueous solution (green curve, 3mM NaNO₂ in acetate buffer) and reductive stripping of intermediate adsorbed on Fe-NC (red curve) or NC (yellow curve) catalysts. Reproduced with permission from ref 22. Copyright 2016 Springer Nature.

Important catalytic descriptors and scaling relationships can be determined with advanced electrochemical probing techniques. To assess the intrinsic activity of a catalyst, it is best to provide its TOF, which is the ratio between the amount of product produced per unit time and the number of active sites involved. While TOF represents a straightforward intrinsic activity metric, its calculations in electrocatalytic studies have been largely inaccurate due to the difficulties in identifying how many active sites participate in the reaction. Additionally, the use of geometrical area normalized current density further reduces the accuracy of the TOF determination. For SACs, the inhomogeneity of site distribution on supporting materials causes greater challenges in measuring the exact number of active sites by conventional techniques. To this end, using nitrite adsorption followed by reductive stripping, Malko et al. demonstrated a method that could quantify

active centers in Fe-NC SACs operating under acidic conditions, which established a direct correlation with their catalytic activity.²³ A flow diagram described how reversible nitrite poisoning is used to determine catalyst site density is shown in Figure 5a. Figure 5b then exhibits the stripping peak current and background current for the Fe-NC and NC (with iron-free) catalysts. The nitrite stripping charge calculated from the voltammogram can allow an estimation of Fe active sites regardless of the NC substrate. The TOF at 0.8V versus RHE is about $1.6 \pm 0.2 \text{ s}^{-1}$, which agrees well with the value for Fe-NC SACs as measured with the Mossbauer/chemisorption study.³⁶ This strategy offers a chance to unveil the intrinsic activity of Fe-NC with distinct local structures. For example, Primbs et al. developed an analytical tool based on the NO_2^- probing technique to deconvolute ORR reactivities of Fe-NC catalysts prepared with different approaches.³⁷ Combining with spectroscopy, the analysis can well support the conclusions of relationships among macrostructures, electronic states, and reactivity.

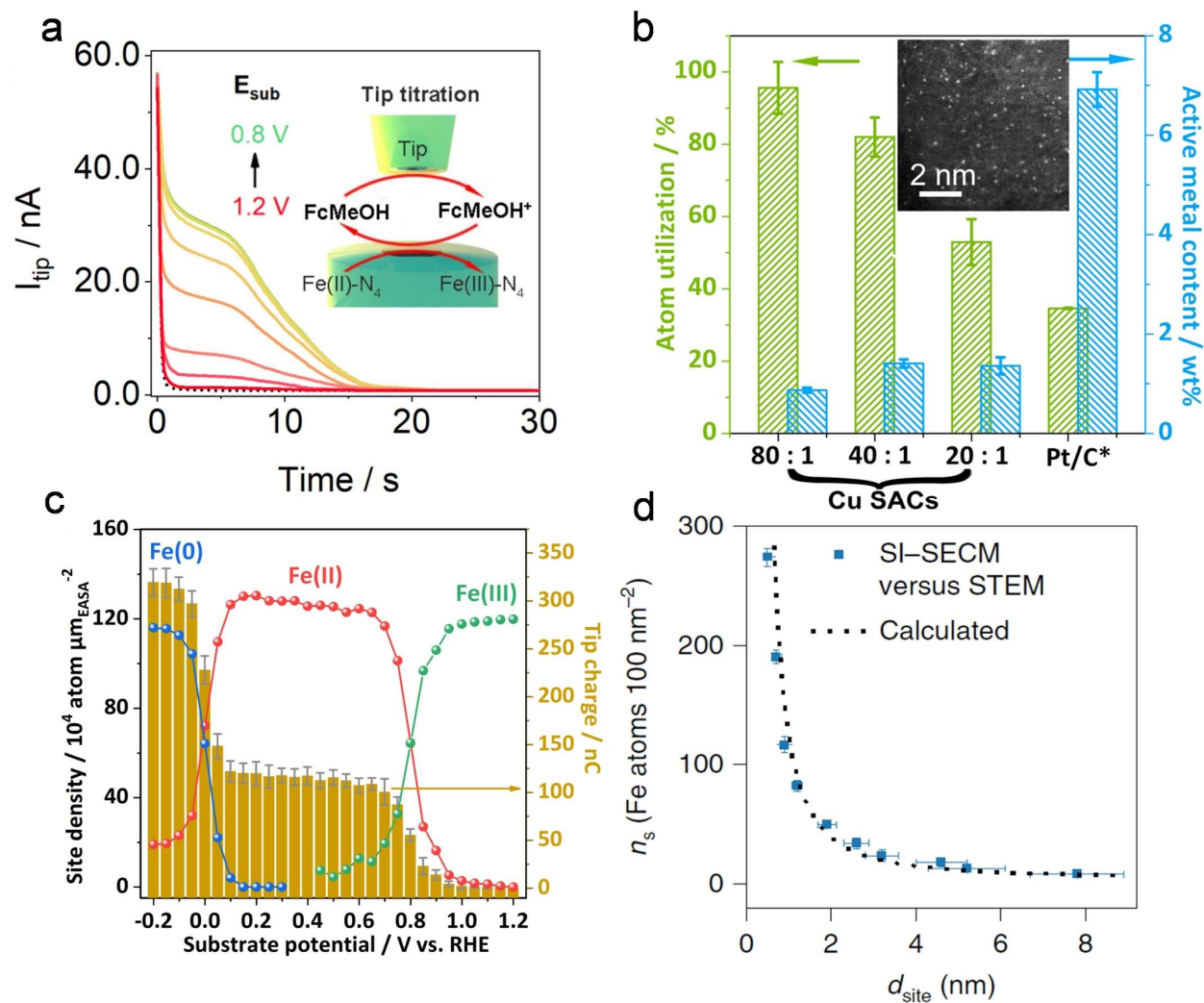


Figure 6. **a)** Tip currents of the FcMeOH probe oxidation associated with different potential biases on the Fe-N₄ catalyst. The oxidation state transition of atomic Fe sites results in varying tip currents. **b)** Atomic utilization determined with in situ electrochemical probes, which is related to the active Cu sites during the ORR. Reproduced with permission from ref 3. Copyright 2020 Elsevier. **c)** Potential-dependent active site density of Fe with oxidation state analysis. Reproduced with permission from ref 2. Copyright 2021 Royal Society of Chemistry. **d)** Comparison between the determined site density with the in situ electrochemical probe and statistical analysis of

scanning transmission electron microscopy. (a) and (d) are reproduced with permission from ref 1. Copyright 2021 Springer Nature.

Although nitrite ions can selectively probe Fe active sites associated with the ORR, its universality to other SACs for various reactions has not been validated yet. In addition, the analysis is assumed all active sites remain unchanged at varying potentials. The dynamic atom states, in fact, raise further concerns upon the interrogation of intrinsic activity. In situ electrochemical probing technique by using SECM offers direct measurements of site behaviors under exact same conditions as electrocatalysis. As demonstrated in the above section, the active site density of SACs can be determined by the tip electrode, which collects current from the redox reaction of molecular probes after reacting with active species in catalysts. Figure 6a presents typical $i_{\text{tip-t}}$ curves at different substrate potentials through surface interrogation mode of SECM, where Fe(III) reducing to Fe(II) can be recorded with the corresponding transformation potential. The thermodynamic property of Fe SACs is thus revealed, and the measured redox behavior of active centers is relevant to catalytic performance. Our recent work successfully extended the technique to studying Cu SACs. The ratio between titrated active site density during the ORR and total metal content represents the atomic utilization of SACs. Figure 6b shows the measured values for Cu SACs, where decreased atomic utilization is observed with metal loading increasing. The technique we developed to study SACs for the first time obtained the atomic utilization experimentally, providing an important criterion for synthetic SAC benchmarking.

In addition to site density analysis, in situ electrochemical probing technique can be also used to characterize the oxidation state transition at given potentials. The function is based on the titrated charge as displayed in Figure 6c. Two plateaus of tip charge are found when studying Fe SACs for the nitrate electroreduction, assigning to $\text{Fe(III)} \rightarrow \text{Fe(II)}$ and $\text{Fe(II)} \rightarrow \text{Fe(0)}$ reduction,

respectively. As such, it demonstrates one can quantify the site density with oxidation state information, which allows insights into fundamental properties of active centers. Furthermore, the site density can estimate the average inter-site distance of neighboring atoms according to the model we reported in a recent publication. The results appear high consistency with those obtained by electron microscopy (Figure 6d). Thus, the developed in-situ electrochemical probing technique offers comprehensive information regarding thermodynamic properties of active single-atomic sites during electrocatalysis.

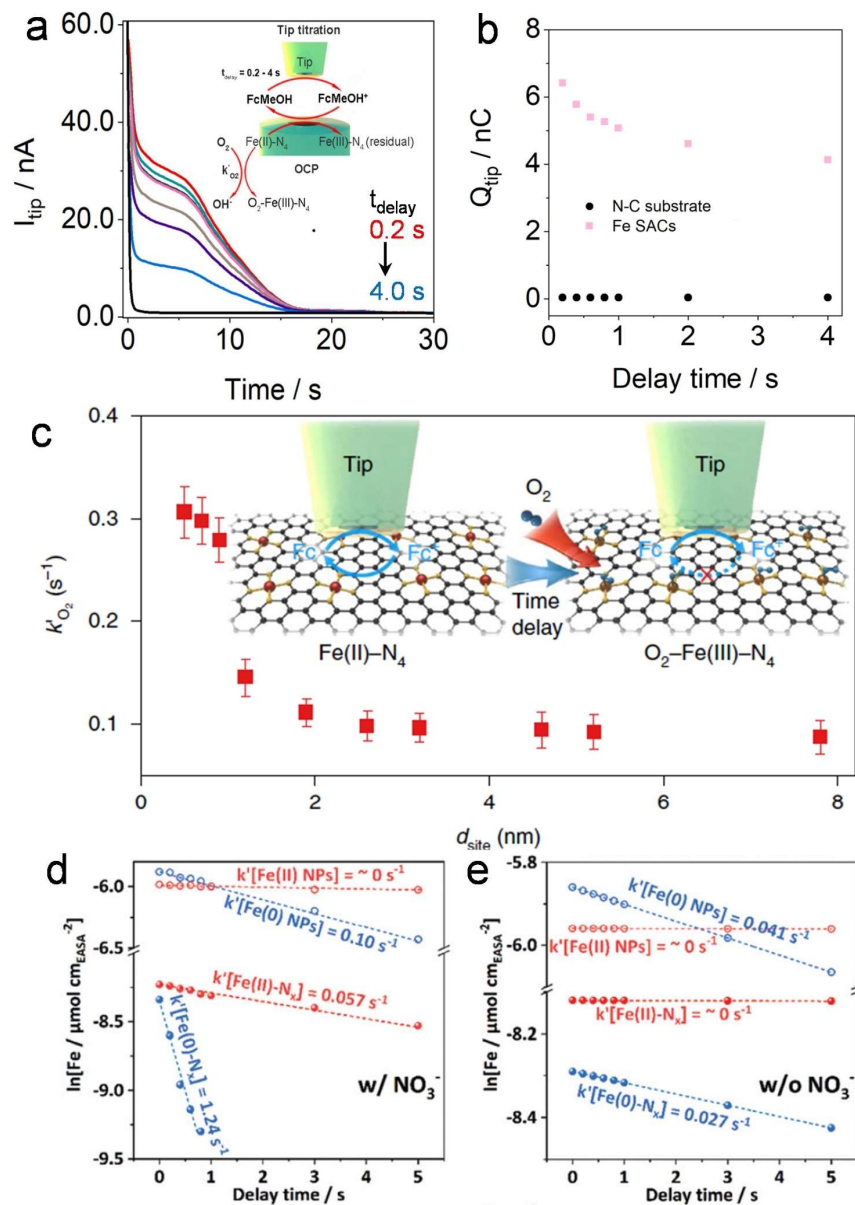


Figure 7. **a)** Tip currents of the in situ electrochemical probe oxidation with time-delay titration. **b)** Integrated charges against delay time related to the active site number of Fe atoms loaded on NC substrate. **c)** Kinetic rate constants of dioxygen adsorbed on Fe sites with varying inter-site distance. Reproduced with permission from ref 1. Copyright 2021 Springer Nature. A comparison between the decay of Fe(II) and Fe(0) active site concentrations in solutions **d)** with and **e)** without nitrate; Both hydrogen evolution reaction (HER) and NO_3RR follow the pseudo-first-order

reaction rate equation. Reproduced with permission from ref 2. Copyright 2021 Royal Society of Chemistry.

Another important feature of in situ electrochemical probing technique is the capability of high time-resolution surface interrogation of catalytically active sites. As discussed earlier, the so-called time-delay titration permits the measurement of kinetic rate between sites and reactants. The parameter is of importance for understanding the intrinsic activity of SACs. Figure 7a exhibits titration *i-t* curves for studying the ORR rate over Fe(II)-N₄ sites. With the precise control of delay time, decayed tip currents are shown because of the chemisorption of O₂ on Fe(II) before being titrated by molecular probes. The carbon support (NC) with iron-free shows no such feedback on the tip current compared with that of Fe SACs (Figure 7b), which can be used to selectively identify site behavior regardless of the substrate. The technique was further utilized to interrogate the rate constant of O₂ adsorption on isolated Fe atoms with varying inter-site distances. The effect on the ORR resulted from the proximity of adjacent active Fe-N₄ sites has been experimentally validated and measured. Specifically, when the inter-site distance is less than 1.2 nm, strong interactions between Fe-N₄ moieties alter their electronic structures, leading to increased intrinsic ORR activity. Besides, as close as 0.7 nm away from neighboring Fe atoms, site performance continues to improve significantly, below which the intrinsic activity tends to diminish. By using the in situ electrochemical probing technique, this work further highlights the importance of understanding the density and local dynamics of iron atoms in SACs, which would unlock a previously unattainable level of efficiency for fuel cells.

Additional attempts were made to extend this powerful tool to other prominent electrocatalytic reactions, e.g. ammonia electrosynthesis, which has been receiving tremendous attention as it aims to decentralize the industrial Haber-Bosch process that relies heavily upon fossil fuels.³⁸⁻⁴⁴ In our

preceding report, the molecular probe was successfully applied to measure the kinetic rate of nitrogen reduction reaction (N₂RR) over lattice Ti³⁺ sites in TiO₂.²⁵ The competing reaction, HER, generally occupies most available active sites at the potential of N₂RR, which brings considerable troubles upon the determination of reactivity. Thus, we developed two-step titrations to analyze the kinetic rate of the HER and N₂RR independently, assuming all active sites are available for two reactions. According to the protocol, the electrocatalytic nitrate reduction reaction (NO₃RR) on Fe SACs was studied, and important insights into the mechanism were uncovered. Figure 7d demonstrates the relationship between the surface concentration of Fe sites, [Fe], on Fe SACs and Fe nanoparticles and the delay time. It was observed that single-atom Fe(II)-N_x and Fe(0)-N_x were both able to adsorb NO₃⁻ with rate constants of 0.057 and 1.24 s⁻¹, respectively. In comparison, the transition state of Fe(II) in Fe NPs does not display such catalytic activity. NO₃⁻ is, thus, supposed to occupy the majority of Fe sites in SACs at Fe(II) transition state before the formation of Fe(0), the HER active center. Although the nitrate-preoccupied Fe(II)-N_x would undergo further reduction to Fe(0)-N_x, there would be no or very few adsorption sites available for water molecules in this case, so the HER would not be triggered. Accordingly, SACs can be effectively regulated their electronic structures of transition-metal atoms, which greatly enhances their activity and selectivity in a way that would be less possible for bulk metals.⁴⁵⁻⁴⁷

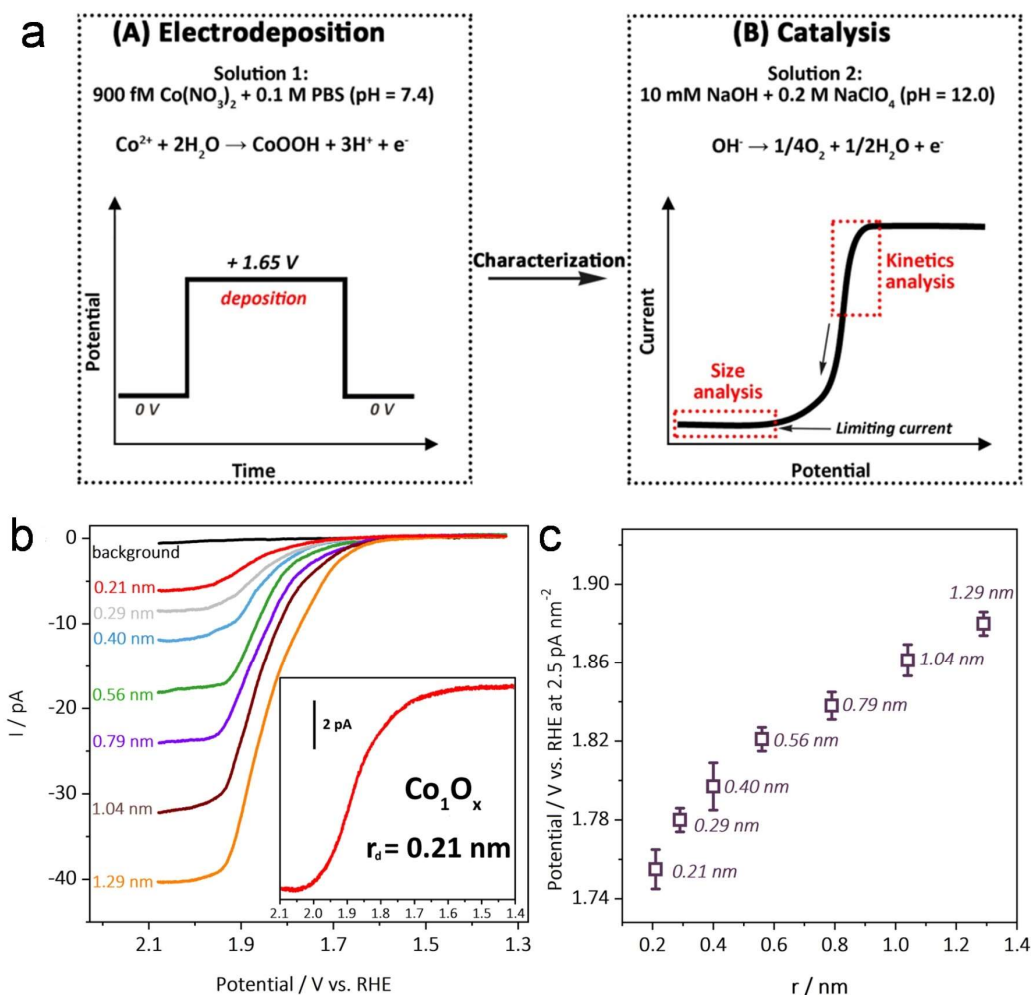


Figure 8. a) Protocol of the alternative electrochemical probing technique for studying the OER. b) Voltammograms of the hydroxide ion probe oxidation over different size cobalt oxide clusters. c) Potential at given OER current density normalized by the geometric surface area of hemispherical clusters with different effective radii. Reproduced with permission from ref 4. Copyright 2020 National Academy of Sciences.

The alternative electrochemical probing technique was introduced to measure the size and reactivity of isolated single atoms, clusters, and nanoparticles.^{4, 30, 34, 48} We recently reported a protocol (Figure 8a) based on this technique to unveil the size-dependent OER behavior over cobalt oxides, e.g. Co_1O_x single molecules, and Co_nO_y single clusters. The voltammogram as

shown in Figure 8b provides an estimate of the size of deposits based on the limiting current of hydroxide ion probes oxidation. On the assumption of the hemisphere on a planar inert surface, equivalent radii ranging from 0.21 to 1.29 nm were determined for catalytically active entities. By the electrochemical probing strategy, the smallest size was ~ 0.2 nm, which is comparable to the reported distance between Co-O atoms in CoO_6 octahedra (1.89 nm) as measured by X-ray absorption spectroscopy.⁴⁹ In addition, from the relative potential of isolated Co_nO_y clusters at a given low current density, the relative catalytic activity for the OER can be estimated. In Figure 8c, the potential at 2.5 pA nm^{-2} is plotted against effective radii of clusters, in which it shifts in a positive direction with increasing cluster size. This suggests the lowest overpotential for the OER is shown by a single molecule with one cobalt ion while larger cluster sizes deliver a slower OER rate. This work for the first time estimates the ultrafast reaction rate ($\sim 1.5 \times 10^7 \text{ e}^- \text{ s}^{-1}$) of heterogeneous single molecules by using the unique electrochemical probes, thereby supplying relevant information on single-molecule electrochemistry.⁵⁰⁻⁵² These results also provide crucial guidance for the design of highly active catalysts for water oxidation, a reaction that is ubiquitous in many energy systems.⁵³⁻⁵⁶

4. CONCLUSIONS AND OUTLOOK

Electrochemical probing techniques have emerged as powerful tools in studying fundamental properties of SACs. In this Account, we present operating principles and recent progress of several molecular probing methods that can obtain quantitative information of single-atomic active sites associated with electrocatalysis. In situ electrochemical probe enabled by SECM with surface interrogation mode has been particularly highlighted because of its high universality and precision.

Site density and kinetic rate can be measured, offering great opportunities to look at critical effects and mechanisms in catalytic reactions over SACs. We further discuss an alternative electrochemical probing technique, which permits simultaneously determining the size and catalytic kinetics of OER on single atoms and clusters.

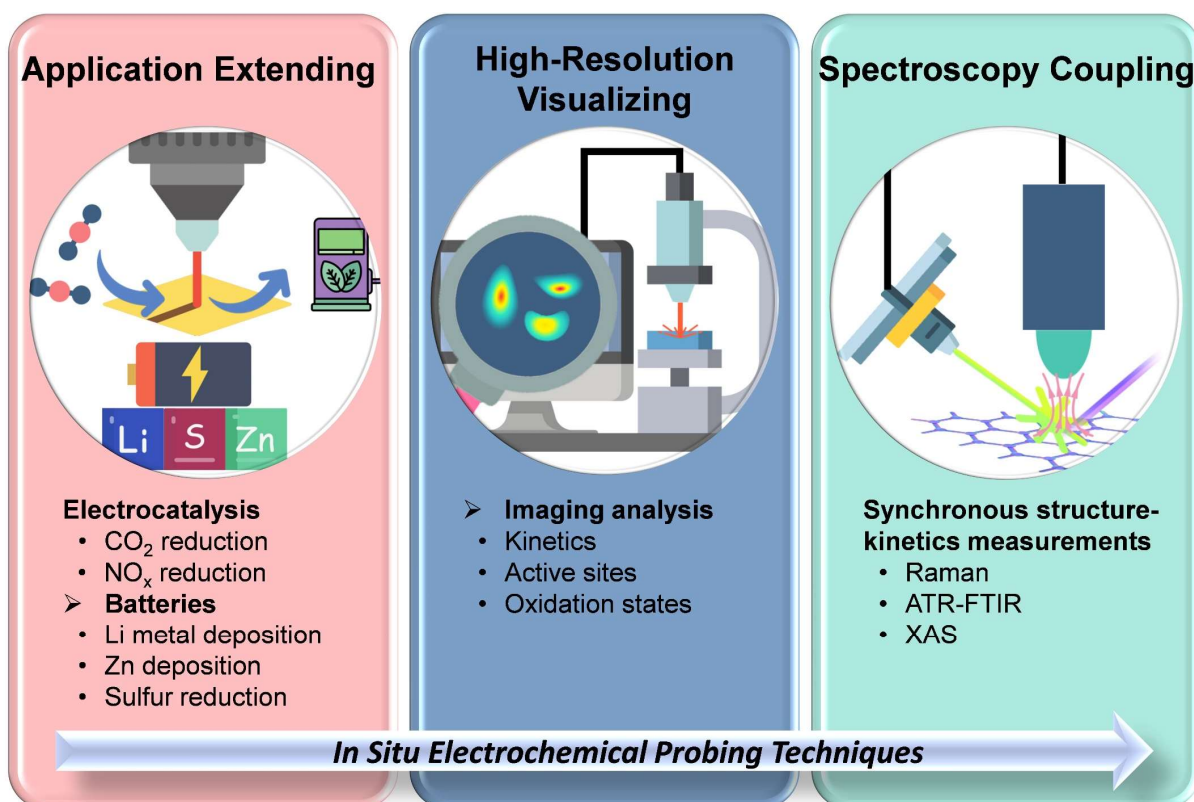


Figure 9. Perspectives of in situ electrochemical probing techniques.

Electrochemical probing techniques are expected to be developed in the future to reveal new perspectives on the behavior and features of SACs as displayed in Figure 9. To start with, it is anticipated that the introduced approaches will be extended to other reactions, such as CO₂ electroreduction and battery reactions. This may involve more complicated protocols, customized electrochemical cells, and compatible molecular/ion probes.⁵⁷ Moreover, the reported techniques are currently limited to measurements of single-dimensional analysis of ensemble catalyst

specimens loaded on UMEs. Further efforts may be focused on establishing the local-area analysis by electrochemical probes for obtaining high-resolution images related to kinetics, active sites, and oxidation states. Moreover, current electrochemical strategies discussed here are unlikely to resolve localized structures of active sites during reactions. It would be greatly advantageous to combine spectroscopy with in situ electrochemical probing techniques to synchronously investigate dynamic coordination environments, chemical bonding, and reactivity. For example, Raman spectroscopy and SECM have been combined to simultaneously probe material structure and reactivity during electrochemical reactions.⁵⁸⁻⁵⁹ Moreover, other powerful spectroscopy when coupled with the electrochemical probing techniques, including Fourier transform infrared spectroscopy-attenuated total reflectance (ATR-FTIR) and X-ray absorption spectroscopy (XAS), may have potential to provide comprehensive information relevant to intrinsic properties of SACs. Hence, we hope that this Account will contribute in several ways to the advancement of fundamental understanding and instrumental development in emerging electrochemical measurements for studying SACs.

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synthesis and self-assembly of nanoarchitected polymeric materials and hybrid organic–inorganic nanomaterials, fundamental understanding of their chemical and physical properties, and exploration of their technologically important applications in energy, environment, and sustainability.

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