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Viewpoint

Single-Crystal Metals and Oxides as Atomically Precise Energy Materials Platforms for Fundamental Electrocatalysis

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INTRODUCTION

Electrocatalytic reactions involve a specific interaction between the electrode surface and certain adsorbed species. Therefore, the reaction rate and mechanism strongly depend on the surface composition and atomic structure. The use of well-defined model surfaces of single-crystal electrodes is necessary to understand the influence of surface structure on electrocatalytic reaction kinetics and elucidate their reaction mechanisms. In addition, the simplicity of single-crystal surfaces permits the direct comparison of the experiments with the theoretical calculations. Measurements with well-defined surfaces require strict control of the experimental conditions to be achieved so that the observed differences are a consequence of the different surface structures, and all the possible species involved in the reaction mechanism should be taken into account in the analysis of the experimental results and included in the theoretical modeling. In this Viewpoint, we review the most recent advances in single-crystal electrochemistry and propose future possibilities for expanding the fundamental knowledge, together with the precautions that should be taken to implement the new analytical methods. Moreover, not only the use of noble metal single-crystal surfaces is considered, but also new possibilities are explored for using single-crystal samples of non-noble metal oxides, which are becoming more relevant for substituting the expensive and scarce noble metals that are typically used for a wide range of energy-related electrocatalytic reactions. One of the key challenges facing electrocatalysis is that catalyst surfaces are evolving and experience dynamic reconstruction under operating reaction conditions, which calls for developing surface-sensitive *operando* methods. The use of single-crystal metals and oxides greatly simplifies the complexity of establishing structure-(re)activity relationships. Combining single-crystal electrochemistry with theoretical simulations and *operando* methods has the potential to profoundly shape our fundamental understanding of electrocatalysis at solid—liquid interfaces.

RECENT ADVANCES AND FUTURE CHALLENGES IN NOBLE METAL SINGLE-CRYSTAL ELECTROCHEMISTRY

In recent years, the influence of various experimental parameters on the activity and mechanism of electrocatalytic reactions on noble metal surfaces has been investigated, such as the surface structure and composition, electrolyte composition, concentration of the reagents, pH, temperature, etc.[1] However, other experimental techniques have not yet been explored widely. For example, one tool not often employed for probing the electrocatalytic reaction mechanisms is the measurement of kinetic isotope effects (KIE) by substituting the protons in the electrolyte with deuterons. The H/D KIE number is the ratio of the kinetic current in H_2O to that in D_2O, and an inverse KIE corresponds to the case in which H/D KIE is lower than 1. One of the problems of the previously reported studies of the KIE on the oxygen reduction reaction (ORR) on Pt is that they were carried out in unpurified D_2O. Therefore, the results could be influenced by the presence of contaminants. We recently developed a D_2O purification method based on using a home-built glass ion-exchange resin column followed by distillation in the presence of KOH and $KMnO_4$.[2] The D_2O purified by this method was used to study the ORR on a single-crystal Pt(111) electrode in 0.1 M $HClO_4$ and the results were presented in Figure 1a.[2] It can be observed that the OD* adsorption/desorption peak for the cyclic voltammetry in the absence of oxygen is shifted by 32 mV toward more positive potentials than the OH* feature. Regarding the ORR, the half-wave potential is shifted by 46 mV toward more positive potentials in the purified D_2O, indicating an inverse KIE of ca. 0.25 at 0.85 V vs RHE. The inverse KIE can be explained in terms of more available Pt sites for O_2 adsorption in the case of the D_2O electrolyte.

Another relevant aspect of the measurements with single-crystal surfaces is the application of *operando*/*in situ* characterization techniques, such as vibrational spectroscopic methods, to obtain direct molecular information about the nature of the reaction intermediates. In the case of single-crystals, the in situ electrochemical shell-isolated nanoparticles enhanced Raman spectroscopy technique (EC-SHINERS), developed by Tian et al., was ground-breaking for the mechanistic studies on well-defined electrode surfaces.[3] The EC-SHINERS technique was applied to the study of the ORR on Pt single-crystals in acidic media, and it was experimentally evidenced, for the first time,

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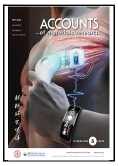

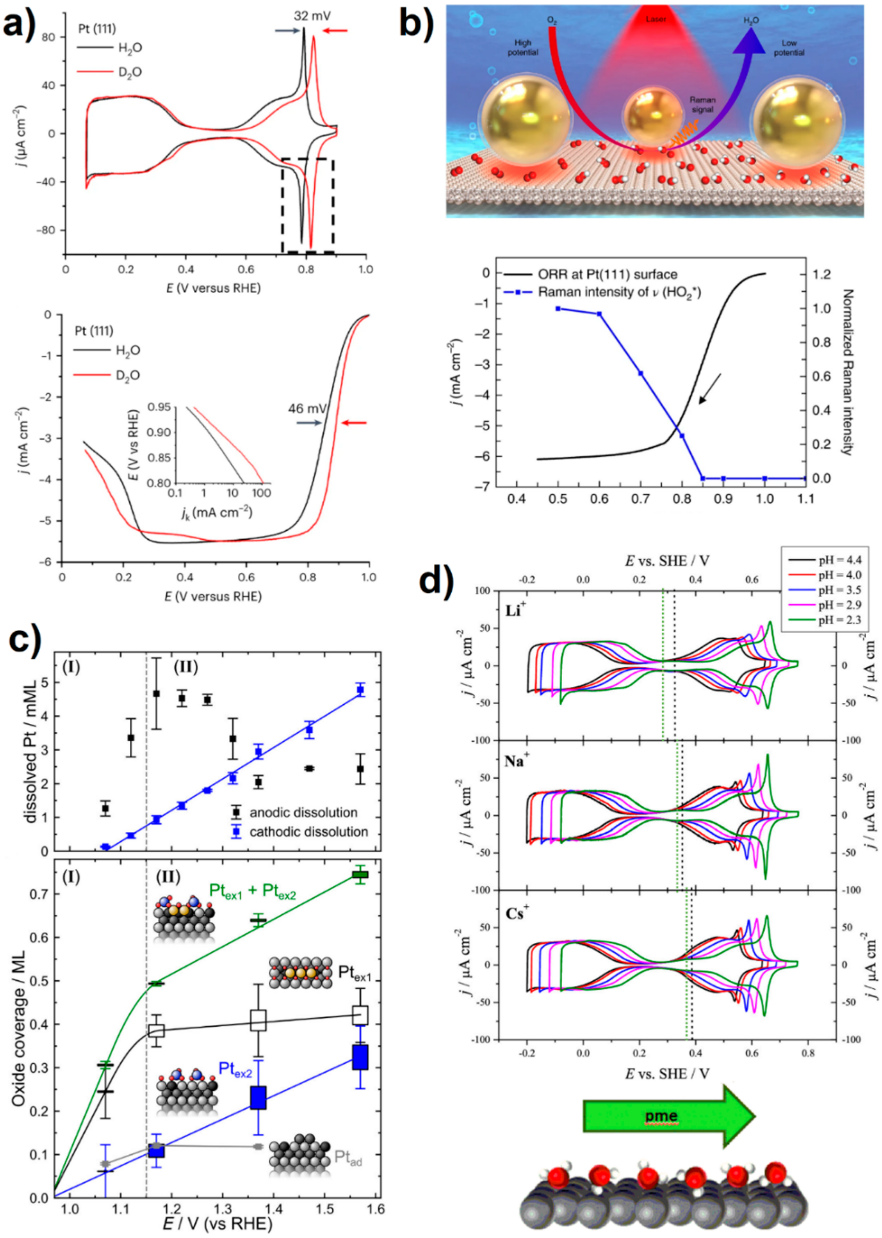

Figure 1. (a) Cyclic voltammetry profiles of Pt(111) in Ar-saturated 0.1 M $HClO_4$ in H_2O and D_2O (top). ORR polarization curves for Pt(111) in O_2-saturated 0.1 M $HClO_4$ in H_2O and D_2O at 1600 rpm. Adapted with permission from ref 2. Copyright 2023 Springer Nature by the authors. (b) Schematic illustration of Au@SiO_2 SHINs on a Pt(111) surface and the mechanism of the ORR revealed by EC-SHINERS technique (top). Normalized EC-SHINERS intensities of O−OH stretching mode around 732 cm^{-1} at different potentials and ORR polarization curve on Pt(111) in O_2-saturated 0.1 M $HClO_4$ solution at 1600 rpm (bottom). Adapted with permission from ref 4. Copyright 2019 Springer Nature by the authors. (c) Total amount of dissolved Pt during anodic and cathodic dissolution (top). Coverage of the two Pt surface oxide species Pt_{ex1} and Pt_{ex2} obtained from HEXRD measurements (bottom). Adapted with permission from ref 5. Copyright 2023 John Wiley & Sons by the authors. (d) Cyclic voltammograms for Pt(111) in Ar-saturated MeF/$HClO_4$ mixtures (Me^+ = Li^+ (top), Na^+ (center), Cs^+ (bottom)) for pH 4.4 (black), 4.0 (red), 3.5 (blue), 2.9 (magenta), and 2.3 (green). The vertical black dashed lines indicate the maximum of the reversible broad peak in the double-layer region, and the vertical green dashed lines indicate the value of the pme for each cation measured by the LITJ technique. Adapted with permission from ref 7. Copyright 2021 American Chemical Society by the authors.

the participation of the OOH* intermediate on Pt(111), as shown in Figure 1b.[4] It is of vital importance to examine the absence of pinholes in the SiO_2 layer of the shell-isolated nanoparticles (SHINs) to avoid interferences from Au signals and to perform a correct cleaning procedure for the SHINs to provide reliable results when using the EC-SHINERS method.

Surface oxidation, restructuring and dissolution processes are crucial since they can affect the activity and stability of electrocatalysts. High-energy surface X-ray diffraction (HESXRD) and online inductively coupled plasma mass spectrometry (ICP-MS) measurements are useful tools for getting information about the mechanism of oxidation and restructuring of the surface of the electrocatalyst and its dissolution behavior, respectively. These techniques were combined to understand these processes on the Pt(100) surface in acidic media. The results suggested that the anodic dissolution is related to a stripe-like surface oxide (Pt_{ex1}), while the cathodic dissolution originates from a more disordered

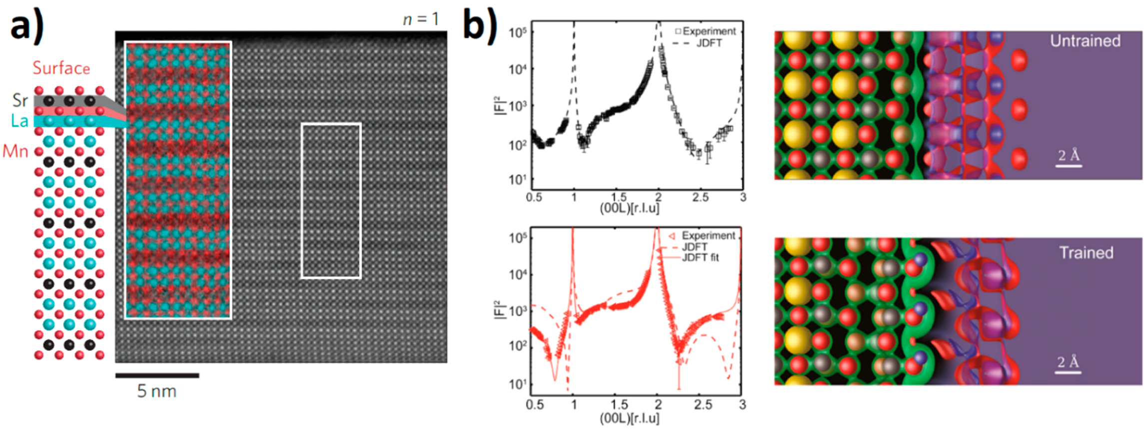

Figure 2. (a) Atomic-scale STEM images and EELS elemental maps of $(LaMnO_3)_{2n}/(SrMnO_3)_n$ oxide superlattices (n = 1). Adapted with permission from ref 9. Copyright 2012 Springer Nature. (b) *Operando* X-ray studies with the structure factor of 00L CTR of untrained $SrTiO_3$ in 0.1 M NaOH and JDFT structure for the untrained $SrTiO_3$ surface. Black squares are experimental data. Black dashed line is the structure factor calculated from the JDFT structure, with no adjustable parameters (top). Structure factor of 00L CTR of trained $SrTiO_3$ in 0.1 M NaOH. JDFT structure for the trained $SrTiO_3$ surface before fitting. Red triangles are experimental data. Red dashed line is from the JDFT structure with no adjustable parameters. Red solid line is a guided fit constrained to the JDFT structure with a penalty function (bottom). Yellow spheres are strontium, red are oxygen, blue are hydrogen, and silver are titanium atoms. Green, red, and blue density contours represent electron, oxygen, and hydrogen density, respectively. Adapted with permission from ref 11. Copyright 2016 American Chemical Society.

(hydr)oxide phase (Pt_{ex2}, Figure 1c).[5] The HESXRD and online ICP-MS measurements require more sophisticated experimental setups, which must be adapted to the strict cleanliness requirements of working with well-defined surfaces.[6]

The interfacial water structure is another fundamental property that can be correlated with the electrocatalyst activity. One descriptor is the potential of maximum entropy (pme), which is close to the potential of zero free charge (pzfc) and can be measured using the laser-induced temperature jump (LITJ) technique. The pme corresponds to the potential in which the water molecules in the interface are randomly oriented. Measurements of the pme on Pt(111) in solutions with pH ranging from 2 to 5 in the absence of anion-specific adsorption showed that it is dependent on the cation present in the solution, shifting to more positive values as the size of the cation increases (Figure 1d).[7]

We have shown that there are several novel techniques, such as D_2O purification for studying KIE, EC-SHINERS, HESXRD, online ICP-MS, and LITJ, when combined and complemented with theoretical studies, can serve as powerful tools for obtaining new information about the activity, stability and mechanisms of electrocatalytic reactions of interest.

PAVING THE WAY TO FUNDAMENTAL STUDIES ON SINGLE-CRYSTAL NON-NOBLE METAL OXIDE SURFACES

The use of noble metals in electrocatalysis presents the drawbacks of being expensive and scarce, which could limit their commercial deployments, such as Pt-based catalysts in fuel cells and Ru/Ir-based catalysts in water electrolyzers. Working on alkaline media offers the advantage of using low-cost materials, especially non-noble metal oxides, which present competitive activities and stabilities compared to their noble metal counterparts in acidic media technologies.[8] However, the methods for preparing single-crystalline samples of non-noble metal oxides are not as well established as for the noble metal electrodes. One of the possibilities is to use a combination of molecular-beam epitaxy (MBE) oxide growth and angle-resolved photoemission spectroscopy (ARPES) that allows the synthesis and measurement in the same ultrahigh vacuum manifold, preventing surface contamination. This methodology was used to prepare and investigate the electronic structure of oxide superlattices composed of $LaMnO_3$ and $SrMnO_3$, as illustrated in Figure 2a.[9] The physicochemical properties of these superlattices depend on the separation between interfaces in $(LaMnO_3)_{2n}/(SrMnO_3)_n$, which can be characterized by atomic-scale aberration-corrected scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS). Another way of characterizing the atomic sharpness and precise control of the stacking periodicity of these superlattices is using *operando* synchrotron-based high-resolution X-ray diffraction (XRD) and X-ray reflectivity (XRR).[10] The latter was successfully employed for tracking the dynamic structural evolution of an n-$SrTiO_3$ electrode in *operando* conditions during water splitting (Figure 2b). Combining the experimental results with first-principles joint density functional theory (JDFT) simulations allowed the identification of an anatase-like structure (TiO_x) as the more active surface after dissolution of the surface Sr layer.[11] These previous studies show the potential of non-noble metal oxides as atomically precise platforms to combine electrochemical measurements, theoretical simulations and *operando* methods to characterize the surface structure and dynamic reconstruction to form true active sites responsible for electrocatalysis.

CONCLUSION AND OUTLOOK

We have shown that the use of new experimental approaches for studying electrocatalytic reactions on single-crystal surfaces can still be expanded or should be revisited. For example, we believe that the D_2O purification method presented in ref 2 can be used to investigate KIE for a wide range of electrocatalytic reactions on well-defined surfaces in a reliable way. This approach could be used, for example, for studying CO_2 electroreduction on single-crystal electrodes, which in combination with other *operando* characterization techniques such as surface-sensitive electrochemical scanning tunneling microscope (EC-STM) and online electrochemical mass spectrometry (OLEMS),[12] has a great potential to provide new information about the mechanism of this relevant reaction. The obtained results can be combined with LITJ experiments and theoretical simulations to disentangle the key proton-coupled electron transfer (PCET) events and the interfacial water structure during this reaction. On the other side, the combination of MBE oxide and *operando* X-ray techniques provides the possibility of preparing and characterizing both the pristine and operating structures of well-defined non-noble metal oxide surfaces in an atomically precise way, paving the way for fundamental studies of electrocatalytic reactions on these promising materials.[13] In conclusion, we propose using single-crystal metals and oxides as atomically precise platforms for fundamental investigations of electrocatalytic reactions. Moving forward, we anticipate that the use of single-crystal metals and oxides will advance our fundamental understanding of the following electrochemical solid–liquid interfaces related to renewable energy technologies.

(1) **Single-crystal electrode/electrolyte interfaces.** The combination of atomically precise single-crystal electrodes, theoretical simulations and *operando* surface-sensitive vibrational spectroscopy and synchrotron X-ray methods will identify the real-time activity descriptors and establish a structure-(re)activity relationship under operating conditions. Insights gained here will help advance our understanding of interfacial electrocatalysis, electron transfer as well as ionic and potential gradients at charged interfaces, and eventually tackle one of the fundamental challenges in physical chemistry, resolving the electrochemical double layer (EDL).

(2) **Well-defined nanocatalyst/electrolyte interfaces.** Shape-controlled nanocrystals (1–100 nm) exclusively expose certain facets at the catalyst surfaces to achieve tunable catalyst activity/selectivity. The use of shape-controlled nanocrystals could bridge the knowledge gap between bulk single crystals in the electrochemistry community and practical nanoparticles widely used in the nanomaterials community. *Operando* electrochemical scanning transmission electron microscopy (EC-STEM), powered by the latest development in four-dimensional (4D) STEM and machine learning-based data analysis,[14] shows great potential to interrogate complex structural evolution of realistic polycrystalline active sites of nanocatalysts at atomic-to-nm scale.

(3) **Practical energy material interfaces.** The methodologies, developed based on bulk single crystals and shape-controlled nanocrystals, can be applied to tackle complex and realistic energy material interfaces. For instance, the polymer/ionomer/catalyst interfaces have been widely proposed but poorly understood due to the lack of necessary nm-scale time-resolved *operando* methods to probe gas–solid–liquid triphase interfaces.[8] Another important example is the formation of the solid-electrolyte interphase (SEI) in lithium batteries, which determines the cycle life, charge rate, and safety of batteries.[15]

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Notes

The authors declare no competing financial interest.

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Valentín Briega-Martos is a postdoctoral researcher at Cornell University starting in Fall 2024, before which he was a postdoctoral researcher at Forschungszentrum Jülich, Germany. He received his PhD in Electrochemistry at the University of Alicante, Spain (2019). His research interests comprise single-crystal electrochemistry and electrocatalysis with a deep understanding of the electrochemical interface considering both activity and stability.

Yao Yang is an assistant professor of chemistry at Cornell University starting in Fall 2024. He received his PhD at Cornell University (2021) and the Miller postdoctoral fellowship at UC Berkeley (2021-2024). His group focuses on developing *operando* electrochemical liquid-cell scanning transmission electron microscopy (EC-STEM) and correlative synchrotron-based X-ray methods to probe electrochemical dynamics of energy materials at solid–liquid interfaces across multiple spatiotemporal scales.

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