Computational electrochemistry of oxygen 250 years after Priestley

De-en Jiang*

Department of Chemical and Biomolecular Engineering and Department of Chemistry,

Vanderbilt University, Nashville, Tennessee 37235, USA

*To whom correspondence should be addressed. E-mail: de-en.jiang@vanderbilt.edu

Standfirst: Since the first isolation of oxygen, chemists have explored oxygen reduction and evolution reactions; now, computational chemists are trying to understand and predict the best catalysts for them. Here, the importance of various considerations for such calculations, as well as their challenges and opportunities, are discussed.

Main:

First came water (H_2O), then cyanobacteria, next oxygen (O_2) on Earth via photosynthesis. Since then, oxygen redox chemistry has been intertwined with the evolution of life, culture, and technology on Earth. Now, 250 years after Joseph Priestley's heating of mercury oxide led to the discovery of "dephlogisticated air," which we now know as oxygen, scientists and engineers are working to control the oxygen redox chemistry in an electrochemical cell at scale to benefit the humanity. The high efficiency of electrochemical processes, coupled with sustainable energy production and storage, greatly motivates research into electrochemical oxygen evolution reactions and oxygen reduction reactions (OER and ORR, respectively), for both production of green hydrogen via electrolyzers and stationary and mobile power via fuel cells. The intimate chemical relations among H_2O, protons, O_2, and electrons both fascinate and challenge many researchers' minds; the goal of computational electrochemistry of oxygen redox reactions is to quantitatively describe and model such processes by conceptualizing the relations into equations and terms that can be computed by advanced hardware and software and validated by carefully designed experiments. This Comment discusses some challenges and opportunities in moving the community forward.

Aqueous electrolytes

All electrochemistry issues are an electrolyte issue. This statement, though an oversimplification it might be, focuses our attention on the main actor here–the aqueous electrolyte, which is typically 1.0 molar H^+ (acidic) or OH^- (alkaline) in water for OER and ORR (Figure 1). To date, the community has focused on the relatively easy-to-compute computational hydrogen electrode[1], gas/solid adsorption energy[2], or implicitly solvated interfaces[3]. Moving forward,

researchers will need to pivot to the much-harder-to-compute true electrolyte composition by explicitly treating the H_2O solvent and the ions in the aqueous electrolyte under an applied potential, in order to more accurately represent the experimental conditions. The hydrogen-bond network is fundamentally important to all aqueous processes, including water adsorption and dissociation, dipole orientation, formation and dynamics of the electric double layer, proton transfer[4], and proton-coupled electron transfer[5], but is missing in the popular computational approaches mentioned above. Treating these aspects explicitly at the electronic-structure level is essential for a deeper understanding of all water-related chemical processes (OER/ORR included), even for quantities as fundamental as the potential at the point of zero charge of the Pt-water interface[6].

Dynamics at the interface

Although static structures of catalyst surfaces, H^+ and OH^- adsorption energies, and volcano plots are amenable and intuitively attractive for computational electrocatalysis, the sustained electric current through a fuel cell of hydrogen oxidation and oxygen reduction reactions, or the continuous production of H_2/O_2 in an electrolyzer, is underpinned by the dynamic nature of the electrochemical interfaces where electrons, atoms, ions, and molecular groups come and go. Capturing and reproducing these dynamic processes at the functional interfaces computationally is challenging but highly valuable, as the dynamics is more difficult to measure experimentally than structure, thermodynamics, and kinetics. It would be exciting to simulate, for instance, the dynamics of an O_2 nanobubble formation at the electrode/water interface from models that integrate all the physics and chemistry ingredients from PCET to mass transport.

Kinetic modeling

Deploying OER and ORR at scale means a target current density[7] on the order of 1 $A \cdot cm^{-2}$ or 6×10^4 $e \cdot s^{-1} \cdot nm^{-2}$. Therefore, the current density, which is equivalent to a reaction rate in chemical kinetics, is an important figure-of-merit to predict from computation. Kinetic modeling is the much-needed link to the experimental observable. Similar to what is commonly practiced in heterogenous catalysis to connect elementary reaction energetics to the macroscopic reaction rates, one can use either kinetic Monte Carlo or microkinetic modeling to bridge the time scale. However, what is still needed is the integration the electron transfer processes across the electric-double layer, the explicit solvation environment, pH, and the applied potential into the computation of the elementary-step energetics. Researchers have started to address these integrations, for instance, by coupling pH (using a computational reversible hydrogen electrode together with a computational standard hydrogen electrode) and electric field (computing adsorption energies under an applied field and an implicit solvation model) into microkinetic modeling of ORR reactions[8]. Despite this, it is still challenging to make those integrations, as the involved processes span multiple time and length scales.

High-entropy catalysts

Entropy is a difficult concept to grasp, but finally its power in directing synthesis of new catalysts has been unleashed, for example, allowing mutually immiscible elements to form single-phase nanoparticles of four, five, or more elements. Now, we are facing an explosion of chemical space accessible through high-entropy materials, which is potentially nightmarish for computational scientists, because the exponentially increasing complexity demands large-scale computation and sampling. Even so, we should embrace this challenge with open arms: on one hand, we will never run out of configurations to compute; on the other hand, the use of machine learning (ML) surrogate models becomes a necessity. There are already promising studies in applying such an approach for noble-metal-based high-entropy alloys for ORR[9] and noble-metal-based high-entropy-oxide catalysts for OER[10]. Whether this computational approach can be applied to high-entropy catalysts made of only earth-abundant elements remains an open question, but discovery of a stable high-entropy-oxide OER catalyst that is platinum-group-metal-free and works in the acidic conditions with low overpotential would be revolutionary. Development of key descriptors for activity, stability, and overpotential as well as potential ML surrogate models for adsorption and elementary-step energetics would be needed to screen complex chemical compositions.

Platinum or no platinum, that is the question

Platinum remains one of the most active and effective materials for ORR, and it stays at the top of most volcano curves. However, its high cost, scarcity, and supply concentration remain as major concerns. Computational scientists can help here in two tasks: (i) design ways to increase the atomic efficiency of Pt in order to make every Pt atom count; (ii) predict new catalysts that match the performance of Pt. Single-atom/single-site non-platinum-group-metal catalysts have shown great promise in ORR reactions, especially the M-N-C type[11]. On the other hand, they leave limited innovation space to leverage the multi-element interactions. Here, ultrasmall (meaning sub-2 nanometer) high-entropy alloy nanoparticles and nanoclusters[12] present a great opportunity for computational exploration of active ORR catalysts. Both the extreme mixing (> 10 elements) and the composition fluctuation (that is, large variation of composition from particle to particle)[13] challenge computational scientists to come up with a modeling strategy to predict the ensemble-averaged activity that can be compared with the experimental measurement. Besides the computational approaches based on descriptors and ML models mentioned above, statistical theory development would be beneficial to bridge the huge gulf between experiment (easy-to-accomplish synthesis and testing) and computation (extremely difficult modeling and simulations of the structural and compositional complexity).

Catalyst stability

Reactive oxygen species are produced during OER and ORR, which reshape the catalyst surface and the electrode/electrolyte interfaces constantly. As a result, non-platinum-group-metal catalysts tend to be degraded over time. In order to develop stable ORR/OER catalysts, it would be highly valuable to be able to predict the change of the activity with time, but this would require the exploration of all possible side reaction channels, which is challenging due to the number of potential competing reactions. One strategy is to factor in the catalyst lifetime in catalyst design from the start; this requires a detailed understanding of degradation mechanisms and pathways from joint computational and experimental efforts. Once the main culprits have been found (for example, reactive oxygen species), one can then design and screen co-catalysts computationally that scavenge them[14].

Digital twin of an electrochemical cell

A water electrolyzer or a H_2/O_2 fuel cell is a device that is supposed to operate at a high-current-density for as long as possible to convert between chemical energy and electric energy. Catalyst-loaded electrodes, electrolytes, membranes, and gas inlet/outlets are parts of the device. It is many computational researchers' dream to build and run such a device in a computer which mirrors a real device in operation. We hope to use such a digital twin to exchange information with the real device so that we can understand the OER/ORR chemistry in the context of the whole device, including the hydrogen evolution and oxidation chemistry, the degradation or dissolution of the electrocatalyst, the impurities in the electrolytes, and many other important factors. To build such a digital twin would require the collaboration of computational chemists, chemical engineers, materials scientists, and mechanical engineers to integrate electrolyte/interfacial/surface chemistry, electronic and mechanical properties of the electrodes, electron/ion/mass transport, and heat transfer and management. It is not only a multiscale modeling challenge, but also a multidisciplinary-collaboration challenge.

Accelerated computation

From the closed shell and large gap of a water molecule to the triplet ground state of the O_2 molecule, spin states are intrinsically inherited in electrochemistry of oxygen. To accurately compute the adsorption and reaction energetics of such open-shell states on a catalyst and also fully take into the explicit aqueous solvation environment and the applied potential would be extremely demanding for the standard density functional theory (DFT) approach. However, we do need the *ab initio* predictive power of such method grounded on sound physics and capable of describing bond formation and breaking from first principles. Wherever we look, accelerated computation at the electronic-structure (for instance, DFT) level[15] is needed to sample as much

as chemical space and potential-energy-surface as possible, to create the data needed to train ML models and to run future digital twins involving OER/ORR reactions.

Summary and outlook

Electrochemical oxygen redox reactions are crucial for sustainable chemicals and energy; computational research aims to understand and predict how they can be catalyzed efficiently. The importance of accurately modeling aqueous electrolytes, capturing dynamic processes at electrochemical interfaces, and integrating various factors in kinetic modeling to predict current density is emphasized. Given the need for efficient alternatives to Pt, computational researchers should pursue the opportunities and challenges presented by high-entropy materials as well as address the stability issue of non-platinum-group-metal catalysts. Accelerated computation is needed to handle the complexities of such catalyst development for oxygen electrochemistry and to train ML models. A digital twin for electrochemical cells can help understand and optimize system performance for water splitting and hydrogen-fuel cells but require interdisciplinary collaboration. Still, there is a long way to go toward accurately predicting the performance and evolution of ORR/OER catalysts in the aqueous electrolytes, but the great advances in computing hardware and ML give us great hope, as electrons/electricity and their coupling with water/oxygen chemistry have become central to the transition to a sustainable society.

Acknowledgements

This work was sponsored by the National Science Foundation (Award number: CHE-2245564).

Competing interests

The author declares no competing interests.

References

[1] Nørskov, J. K. et al. *J. Phys. Chem. B* **108**, 17886-17892 (2004).
[2] Zhang, J., Yang, H. B., Zhou, D., Liu, B. *Chem. Rev.* **122**, 17028-17072 (2022).
[3] Ringe, S., Hörmann, N. G., Oberhofer, H., Reuter, K. *Chem. Rev.* **122**, 10777-10820 (2022).
[4] Sun, Y. et al. *ACS Appl. Mater. Interfaces* **12**, 763-770 (2020).
[5] Zhong, J., Reinhardt, C. R., Hammes-Schiffer, S. *J. Am. Chem. Soc.* **144**, 7208-7214 (2022).
[6] Xu, P., von Rueden, A.D., Schimmenti, R. *et al*. *Nat. Mater.* **22**, 503–510 (2023).
[7] Luo, Y., Zhang, Z., Chhowalla, M., Liu, B. *Adv. Mater.* **34**, 2108133.
[8] Zhang, D. et al. *Chem. Sci.* **15**, 5123-5132 (2024).
[9] Xu, W., Diesen, E., He, T., Reuter, K., Margraf, J. T. *J. Am. Chem. Soc.* **146**, 7698-7707 (2024).

[10] Mints, V. A., Svane, K. L., Rossmeisl, J., Arenz, M. *ACS Catal.* **14**, 6936-6944 (2024).
[11] Zeng, Y. et al. *Nat. Catal.* **6**, 1215–1227 (2023)
[12] Chen, T. et al. *J. Am. Chem. Soc.* **146**, 1174–1184 (2024).
[13] Minamihara, H. et al. *J. Am. Chem. Soc.* **145**, 17136-17142 (2023).
[14] Xie, H. *et al*. *Nat. Energy* **7**, 281–289 (2022).
[15] Gavini, V. *et al*. *Modelling Simul. Mater. Sci. Eng.* **31**, 063301 (2023).

Figure legends

Figure 1. Electrochemical oxygen evolution reactions (OER) and oxygen reduction reactions (ORR) in acidic and alkaline electrolytes and typical catalysts employed. M-N-C refers to metal-nitrogen-carbon catalysts, especially those of Fe or Co as the metal center coordinated with nitrogen dopants in a carbon matrix.

Twitter info:

De-en Jiang: @DeenJiang

VU Engineering: @VUEngineering

Vanderbilt Chemistry: @VanderbiltChem