

## CHAPTER

## 1

## THEORY-EXPERIMENT GAP

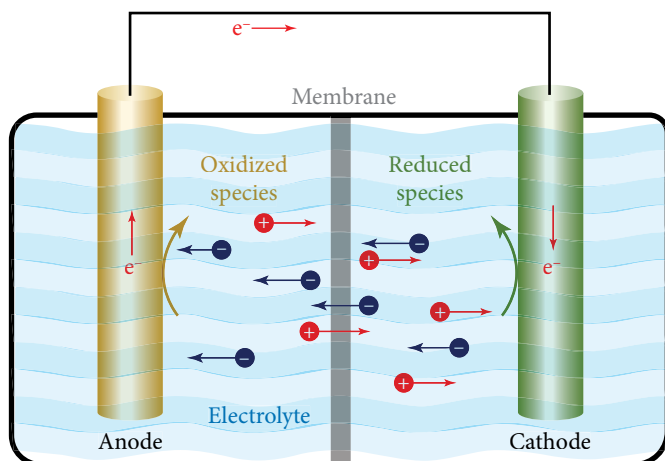
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## 1.1 INTRODUCTION

In spite of its importance, modern industry is associated with severe energy shortages and environmental pollution. In response to these global crises, numerous scientists are devoted to the study of green chemistry. Electrochemistry is one of the most promising green technologies because it focuses on sustainable energy conversion and storage, providing clean solutions for reducing pollutant generation and utilizing environmentally friendly reagents and solvents. More generally, electrochemistry is a branch of physical chemistry involving the conversion between chemical energy and electrical energy. In a two-electrode galvanic cell, electrical energy is generated through spontaneous reduction-oxidation (redox) reactions. In a three-electrode voltammetric cell, the electric current is governed by the applied bias potential to realize the desired redox reactions.

The overall energy conversion processes in electrochemical cells involve both mass transport and charge transfer (Bard and Faulkner, 2001). In general, three types of mass transport occur in an electrolyte solution: diffusion, migration, and convection. Diffusion is caused by the concentration gradients of the ions. The direction of migration is determined by the direction of the electric field. Convection is driven by mechanical forces, such as stirring. There are also three charge transfer processes: (1) the electrical flow in the external circuit, (2) the transport of ions as charge carriers in the solution, and (3) the charge transfer across the interfaces between the electrodes and electrolyte solution. The last process is directly related to the redox reaction at the interface and the Faradaic efficiency of the energy conversion. The simple galvanic cell depicted in Fig. 1.1 is used as an example to illustrate the mass transport and charge transfer processes. In this cell, two electrodes are immersed in an electrolyte solution and connected by an external circuit. Two half reactions occur at the two electrodes, with oxidation at the anode and reduction at the cathode. An electric current is generated as a result of electron transfer from and to the reactants participating in the redox reactions. In this case, a species in solution must become oxidized (lose electrons) at the anode when another species becomes reduced (gains electrons) at the cathode.



**FIG. 1.1**

Illustration of a simple galvanic cell.

of electrode surfaces through instrumental characterization. Although some state-of-the-art experimental techniques, such as scanning tunneling microscopy (STM) and annular dark-field transmission electron microscopy (ADF-TEM), can reveal atomic-scale information, the application of these characterization methods is limited by the operating environment in electrochemical cells. Therefore, theoretical studies have become an indispensable tool for comprehensively understanding electrochemical processes owing to the increased availability of unprecedented computational resources and novel algorithms.

## 1.2 ELECTRODE

In general, most electrochemical studies focus on the electronic properties of the electrode surfaces and the nature of the corresponding surface reactions because these aspects determine the intrinsic structure–performance relationships of the electrocatalysts. Numerical modeling techniques have also been developed for this purpose. For example, the computational hydrogen electrode (CHE) method developed by Nørskov and co-workers is the most commonly used approach for identifying the active sites of electrocatalysts and exploring the reaction mechanisms (Nørskov *et al.*, 2004). However, as the CHE method is based on the relatively expensive density functional theory (DFT) technique, the simulation scales are limited in terms of both size and time and cannot comprehensively reflect the complexity and dynamic nature of electrochemical systems. To this end, classical force-field-based molecular dynamics (MD) simulations have also been adopted to model the solid–liquid interface,

Owing to the importance of electrochemistry, numerous studies have been conducted to optimize the overall performance of electrochemical cells in terms of energy conversion efficiency, lifetime, and cost. An electrochemical reaction is a relatively complex process. In general, the overall electrochemical reaction rate is predominantly determined by the properties of the electrodes and reactants. As such, the design and discovery of electrode materials plays a central role in these studies because their structural and electronic properties largely govern the reactivity and selectivity of the electrochemical reactions.

However, it is challenging to obtain direct information regarding atomic-scale properties such as the nature

albeit with lower computational accuracy (Selvan *et al.*, 2010 and Pezeshki and Lin, 2015). As such, simulation results can be used to explain experimental observations of electrochemical systems at the atomic level.

Electrocatalysts facilitate the electron transport between the electrodes and reactants and promote the formation of intermediates involved in the overall electrochemical reaction through decreased activation barriers, thus playing a key role in electrochemical processes. As mentioned above, Nørskov and co-workers proposed the CHE approach to model electrochemical processes, which can be implemented in first-principles calculations (Nørskov *et al.*, 2004). They also first demonstrated the Brønsted–Evans–Polanyi principle in electrochemical reactions, in which the reaction energy barriers are proportional to the Gibbs free energy change associated with the adsorption of the intermediates. Therefore, the electrocatalytic process can be evaluated solely on the basis of the thermodynamic properties of the system, which can greatly simplify the computations and reduce the computational cost.

The CHE approach has been extensively applied to identify the active sites of electrocatalysts, elucidate reaction mechanisms, and assist with the design of high-performance electrocatalysts. As the active sites of a particular electrocatalyst determine the binding energies of the reaction intermediates, their identification provides an insight into the reaction pathways. Active sites are typically related to the exposed surfaces, defects, and modifiers of electrocatalysts. It is well known that electrocatalytic performance is closely connected with the atomic arrangements and coordination numbers of the exposed surfaces. Zhao *et al.* identified the active site of NiCo ultrathin metal–organic framework nanosheets (NiCo-UMOFNs), which are a promising electrocatalyst for the oxygen evolution reaction (OER) under alkaline conditions (Zhao *et al.*, 2016). DFT calculations revealed that coordinatively unsaturated metal atoms were the dominant active centers for the electrocatalytic OER. The high performance of the NiCo-UMOFN electrocatalysts was ascribed to the electronic coupling effect between Co and Ni cations. One of our recent studies indicated that the electrocatalytic hydrogen evolution reaction (HER) performance of one-dimensional (1D) dithiolene metal–organic frameworks (MOFs) can be significantly influenced by altering the nature of the metal node (Liu *et al.*, 2019). Dong *et al.* used the CHE method to investigate the active sites of pristine and partially oxidized Ni(111) surfaces in the HER, with the results indicating that only slightly oxidized Ni atoms with relatively low oxygen coverage gave rise to superior HER performance (Dong *et al.*, 2018). Furthermore, Al-Mamun *et al.* theoretically designed a novel surface-sulfur-doped Co(111) electrocatalyst that displayed significantly improved OER performance (Al-Mamun *et al.*, 2016). The Gibbs free energy diagram revealed that the theoretical overpotential of the Co(111) surface decreased from 2.20 to 0.86 V upon sulfur doping.

### 1.3 OPERATING ENVIRONMENT

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In addition to the electrode, a series of external factors must be carefully optimized to maximize the performance of an electrocatalyst, e.g., temperature, pH, electrolyte, solvent, conductive support, and applied bias potential.

### 1.3.1 Solvent

The solvent plays a fundamental role in electrochemical reactions owing to its direct interactions with the catalysts, substrates, and products, which can either increase or decrease the reaction rate and/or selectivity. The solvent properties, such as polarity, hydrogen-bond donating ability, and hydrogen-bond accepting ability, can strongly affect the catalyst performance, balance of chemical reactions, activation energy, and reaction rate. For instance, it has been reported that MoO<sub>2</sub> microparticles can serve as an active catalyst for the electrochemical reduction of CO<sub>2</sub> in organic solvents such as acetonitrile and dimethylformamide, where the catalytic activity and product selectivity were dependent on the temperature and water content of the solvent (Oh *et al.*, 2014). Recent experiments have also revealed that the solvation of the electrolyte can significantly affect the diffusion behavior of lithium ions therein and their deintercalation behavior on the electrode surface, which can change the formation mechanism of the interface between the positive/negative electrodes and the electrolyte (Zhang, 2006).

In most of the CHE calculations for the free energies of reaction intermediates, the solvent was not considered owing to the approximation of these systems as potential-free neutral systems, in which solvent effects are expected to only slightly influence the energetics of surface reactions (Oberhofer, 2020). However, recent studies have demonstrated that solvent effects are not trivial for some electrocatalytic reactions. To this end, despite the difficulty, it is necessary to take into account the solvent effects in computational simulations.

At present, there are three distinct approaches for dealing with solvent effects, namely, implicit, explicit, and hybrid methods. In the first model, the solvent is treated implicitly as a polarizable continuum. This theory can be traced back to the works of Kirkwood (1934) and Onsager (1936), which seeded the development of several variants. By assuming that the solvent displays isotropy, homogeneity, and a linear response to electrostatic perturbations, it is possible to determine the total electrostatic potential  $\phi(\mathbf{r})$  of a solute with charge distribution  $\rho_{sol}(\mathbf{r})$  embedded in a dielectric continuum from the generalized Poisson equation given in Eq. (1.1) (Tomasi *et al.*, 2005):

$$\nabla\epsilon(\mathbf{r})\nabla\phi(\mathbf{r}) = -4\pi\rho_{sol}(\mathbf{r}), \quad (1.1)$$

where  $\epsilon(\mathbf{r})$  is the dielectric function (a constant) of the system. In brief, the implicit model places a quantum-mechanical solute in a cavity surrounded by a dielectric continuum description of the solvent. Then, implicit solvation models for plane wave DFT codes were pioneered by Fattestberg and Gygi (2003), independently developed and placed into the rigorous framework of joint density functional theory (JDFT) by Arias and co-workers (Petrosyan *et al.*, 2005), and extended by Marzari and co-workers (Andreussi *et al.*, 2012) to include a model for cavitation and dispersion. These methods provide a more computationally tractable way to model the solvent, which assumes that all interactions between the solute and solvent are considered in appropriate detail. Owing to the widespread use of the Vienna Ab initio Software Package (VASP) for DFT-based calculations,

Hennig and co-workers further placed this theory into the self-consistent field (SCF) framework within the VASP code (Mathew *et al.*, 2014). This implementation in VASP (VASPsol) provides an efficient approach for determining the solvation energies of molecular and extended systems. For example, Hörmann *et al.* compared standard electrode potentials in water calculated using VASPsol with experimental values and found good agreement between the two sets of results (Hörmann *et al.*, 2015). However, the applicability of the implicit solvent model has been controversial. For the oxygen reduction reaction (ORR) on N-doped graphene, it was found that the implicit solvent model underestimates the adsorption energies of  $O^*$  and  $O_2^*$  (Reda *et al.*, 2018). As the implicit solvent model neglects granular structures of the solvent, it cannot describe all of the solvent–adsorbate interactions during the ORR, which indicates that it is not particularly suitable for modeling the ORR on N-doped graphene.

An alternative approach is to treat all solvent molecules explicitly, which affords a more realistic picture of direct solvent interactions compared with implicit models. Water layers near the surfaces of metal electrocatalysts tend to possess relatively ordered structures, referred to as ice-like solvent, as a result of strong surface–solvent interactions (Ogasawara *et al.*, 2002 and Skúlason *et al.*, 2010). In addition to using the ice-like solvent structure to consider the solvent effects on metal catalysts, solvent effects on oxide electrocatalysts can also be examined by adding a number of ice-like solvent layers to the surface. The water oxidation reaction on the  $IrO_2(110)$  surface, for instance, can be significantly affected by explicit non-dissociated water molecules; in particular, these influence the geometries and stabilities of the adsorbed intermediates  $OH^*$  and  $OOH^*$  because of the interaction of these species with the water bilayer (Gauthier *et al.*, 2017). Although ice-like solvent models have shown very good results at affordable computing cost, they are not applicable to some systems where the solvent near the electrode surface displays a preference for more liquid behavior with a disordered nature. Therefore, the above-mentioned ice-like models are not appropriate and full sampling of the solvent degrees of freedom is necessary. The realization of such models is usually achieved by performing molecular mechanics (MM) or molecular dynamics (MD) simulations. Mattioli and co-workers used DFT molecular dynamics (DFT-MD) simulations with explicit solvent degrees of freedom to investigate the reaction pathways for the OER on a cobalt-based catalyst (Mattioli *et al.*, 2013). Although MD simulations for explicit solvent models can provide a spatially detailed description of the solvent, they are often less computationally economical.

Hybrid models, as the name suggests, are a compromise between implicit and explicit models. In other words, part of the solvent is treated explicitly, while bulk effects are taken into account effectively by a surrounding dielectric continuum. In this way, not only is the computational cost caused by numerous solvent degrees of freedom greatly reduced but also the interaction between the solvent and electrode is retained. The quantum mechanics/molecular mechanics (QM/MM) approach can be applied in this case, which represents an optimal compromise between accuracy and efficiency (Tomasi *et al.*, 2005). In general, however, a large number of calculations are still required in QM/MM simulations, and other methods have also been explored. For example, in the reference interaction site

model (RISM) molecular dynamics is replaced by the integral equation theory of molecular liquids, which is substantially less time consuming (Kovalenko and Hirata, 1999).

### 1.3.2 pH and electrolyte

The nature of the electrolyte and the pH value have been experimentally demonstrated to govern the rates of some reactions by mediating changes at an interface. A well-known example is the hydrogen evolution reaction (HER), the cathodic half reaction of electrolytic water splitting. The performance of the HER on Pt electrocatalysts may vary by approximately 2 to 3 orders of magnitude depending on the pH value (Selvan *et al.*, 2010 and Sheng *et al.*, 2010). Zheng *et al.* found that there exists a common linear correlation between the hydrogen binding energy (HBE) and pH for four supported platinum-group metal catalysts (Pt/C, Ir/C, Pd/C, and Rh/C) over a broad pH range (0 to 13) (Zheng *et al.*, 2016). Furthermore, changes in pH can also alter the speciation of reactants and products as well as the reaction mechanisms. Similarly, the electrolyte has been experimentally demonstrated to influence the performance of electrocatalysts (Subbaraman *et al.*, 2011). Therefore, the pH and electrolyte must be optimized to achieve the best performance of an electrocatalyst.

The electrical double layer (EDL) refers to a region of the electrolyte in the vicinity of an electrode surface that plays a critical role in electrochemical processes. In the 1850s, Helmholtz first observed that a charged electrode attracts oppositely charged ions from the electrolyte, resulting in a capacitor-like arrangement. Subsequently, the well-known Gouy–Chapman (GC) and Gouy–Chapman–Stern (GCS) models were developed. The properties of the interface formed by a charged electrode surface immersed in an electrolyte govern the charge transfer processes through the interface itself, thus influencing the electrochemical responses of the electrode/electrolyte system. Comprehensive investigation of the EDL structure and associated charge transfer processes constitutes an essential step toward a better understanding and further improvement of a variety of electrochemical processes, such as electrocatalysis, electrochemical energy storage, ion transport through biological membranes, and corrosion (Favaro *et al.*, 2016).

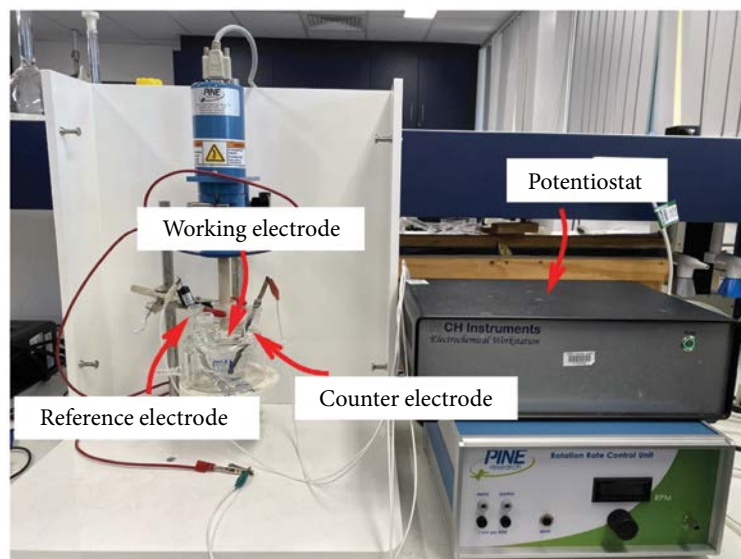
In realistic electrocatalytic systems, electrolytes are required to increase the conductivity of the solution. Thus, an understanding of the effects of electrolytes at the atomic level is essential for obtaining insights into and enhancing electrochemical performance. Within the CHE method, the influence of the pH is corrected by the concentration dependence of the entropy:  $G_{\text{pH}} = -kT \ln[\text{H}^+] = kT \cdot \text{pH} \ln 10$  (Nørskov *et al.*, 2004). In addition, the effect of electrolyte cations has been investigated in recent years. We studied the influence of electrolyte cations on the HER performance of one-dimensional (1D) cobalt–dithiolene metal–organic frameworks (MOF) by adding various alkali metal cations (Wang *et al.*, 2018). DFT calculation results revealed that the electrolyte played an essential role in improving the electrocatalytic performance of the 1D cobalt–dithiolene MOFs, and the effect of the electrolyte was highly dependent on the electron affinity of the cation. In another example, Ringe *et al.* developed a multiscale continuum/*ab initio* modeling approach to explore the influence of electrolyte

cations on CO<sub>2</sub> reduction (CO<sub>2</sub>R) (Ringe *et al.*, 2019). This method applies a continuum electrolyte model and the size-modified Poisson–Boltzmann approach to describe the variation of surface charge density as a function of cation type and applied electrode potential. It was predicted that cations with a smaller hydration shell such as Cs<sup>+</sup> are more concentrated at the electrode compared to larger cations such as Li<sup>+</sup>. The resulting higher concentrations of Cs<sup>+</sup> cations lead to greater surface charge density and a stronger interfacial electric field, which drives the adsorption of CO<sub>2</sub>.

Furthermore, the electrochemical interface structures including the liquid electrolyte in the near-surface region are required because these can veritably describe actual electrochemical systems. Continuous improvements in simulations and first-principles theory based on EDL models are being made. From the theoretical perspective, proper modeling of electrode–electrolyte interfaces must take into account the liquid nature of the electrolyte by averaging over multiple molecular dynamics simulations and demands appropriate electronic structure calculations that can reliably reproduce electronic polarization effects at the same time. This can be implemented by performing *ab initio* molecular dynamics (AIMD) simulations (Magnussen and Gross, 2019). Although the AIMD approach is well established and justified, these calculations usually require substantial computing resources, making them only applicable to small systems and a limited number of reactions. In a recent work, Melander and co-workers extended multicomponent canonical electronic and nuclear DFT to the grand canonical ensemble to provide a detailed route from a fully quantum mechanical description to coarse-grained classical and continuum grand canonical DFT (GC-DFT) models of electronic systems in contact with an electrolyte (Melander *et al.*, 2019). This method enables the properties of solid–liquid interfaces at fixed electrode and electrolyte chemical potentials to be explored by combining nuclear and electronic DFT within the grand canonical ensemble.

### 1.3.3 Applied bias potential

Because electrochemical reactions usually occur far from equilibrium, an external force is needed to drive the entire process. Figure 1.2 shows a three-electrode voltammetric cell. The potentiostat is used to provide the electrical energy that drives the chemical reactions on the electrode surfaces. By applying a bias potential, the energies of the molecular orbitals of the adsorbates and the activation barriers of the reactions can be altered, thereby changing the kinetic parameters (Che *et al.*, 2018). Moreover, the applied bias potential can also affect the electrode–electrolyte interface. For example, in an examination of the intrinsic OER electrocatalytic activity of Ru, Ir, and Pt metals, perchloric acid was used as the electrolyte for Pt and Ru, whereas sulfuric acid was used as the electrolyte for Ir (Reier *et al.*, 2012). The reason for this was that the applied bias potential required for Ir is 0.8 V, while perchloric acid is unstable below 1.0 V owing to the reduction of perchlorate ions to chloride ions, which have a tendency to bind strongly to Ir metal surfaces and thereby contaminate the surface and reduce the catalytic activity. The applied bias potential, therefore, is of paramount importance for controlling and understanding the electrochemical properties at the interface.

**FIG. 1.2**

Photograph of a three-electrode voltammetric cell.

To consider the electrochemical reactions at the interface, it is necessary to take into account the influence of the applied bias potential that governs the charge transfer reactions. To date, several theoretical methods representing different levels of approximation have been proposed, and considerable progress has been made in recent years. The CHE model is the simplest way to account for the free energy of intermediates as a function of the electrode potential because it is based on thermodynamics without considering the effect of the activation energy of each elementary step on the kinetics (Nørskov *et al.*, 2004). Within the CHE method, the influence of the electrode potential  $U$  in an

electrochemical step is indirectly included by setting the total energy of the electron in the electrode to  $-eU$ . The free energy change of each elementary step can thus be adjusted by shifting the energy of each step using  $-neU$ , where  $n$  is the number of electrons transferred. This approach was first applied to the ORR on Pt(111) surfaces, in which the overpotential was estimated and found to be in close agreement with the experimental value (Nørskov *et al.*, 2004). The CHE model provides a practical method to explore reaction energetics without explicit treatment of the electrons and ions in solution. However, it is necessary to include the solvent, excess charge, and electrode potential in the model system when analyzing the kinetic barriers to charge transfer (Haruyama *et al.*, 2018). To this end, numerous methods have been proposed to treat charged electrochemical interfaces. For example, a metal slab can be charged by adding a predetermined number of electrons to the system, and a compensating background charge is subsequently distributed homogeneously over the unit cell to maintain overall charge neutrality (Filhol and Neurock, 2006). Lozovoi *et al.* presented a method to calculate the charged slabs at a constant electron potential  $\mu$ , rather than a constant number of electrons, within standard *ab initio* supercell calculations (Lozovoi *et al.*, 2001). Another example that uses the electrode potential is Marcus–Hush–Chidsey (MHC) theory, where the reductive rate constant reaches a limiting value. MHC theory has been widely adopted to parameterize the redox reactions of surface-bound species and has proved reasonably successful in this regard (Henstridge



*et al.*, 2012). Furthermore, by introducing an extended system as a reservoir of electrons, a potentiostat scheme that realizes the constant chemical potential of electrons ( $\mu_e$ ) condition for performing DFT-MD simulations within the effective screening medium (ESM) scheme was developed (Bonnet *et al.*, 2012). This method reproduces thermal fluctuations of the charge with the correct statistics, implying a realistic treatment of the potential as a control variable. Furthermore, DFT calculations combined with the ESM technique and the RISM model, referred to as ESM-RISM, have been applied to electrode–solution interfaces (Haruyama *et al.*, 2018). These electronic structure calculations include additional self-consistent interactions with implicit solvent molecules and ions in solution.

### 1.3.4 Temperature

According to the Arrhenius equation, increasing the temperature exponentially enhances the rate constant of a chemical reaction, which is also the case for electrochemical reactions. For example, Marković *et al.* studied the hydrogen oxidation reaction (HOR) on the (100), (110), and (111) crystal facets of platinum in sulfuric acid solution over the temperature range of 274–333 K (Marković *et al.*, 1997). It was found that each crystal facet afforded a unique and temperature-dependent Tafel slope for the HOR. Furthermore, the viscosity and conductivity of an electrolyte are both dependent on the temperature, which leads to strong effects on the rate of mass transport within the solution during electrochemical processes (Buzzeo *et al.*, 2004). Therefore, the temperature needs to be carefully controlled when attempting to improve the efficiency of electrochemical processes.

### 1.3.5 Conductive support

In heterogeneous electrochemical processes, the reactions typically occur at the surface atoms of heterogeneous catalysts. However, the finite surface area of these catalysts limits the electrocatalytic activity. Consequently, great efforts have been devoted to maximizing the surface area of catalysts. One of the most common methods is to disperse the catalyst on a conductive support. Although the catalytic activity of the underlying carrier or substrate is generally poor, strong electronic interactions can occur between the catalyst and support that significantly improve the overall catalytic performance. For example, conductive carbon materials are among the most widely used support materials in electrochemistry owing to their large surface area, high electrical conductivity, tunable graphitization, and porous structure (Dicks, 2006). Furthermore, changing the underlying support can greatly influence the associated electronic properties of surface catalysts, which in turn can significantly affect the catalytic activity. The role of the support has been extensively investigated for electrocatalytic water splitting in an effort to improve the electrocatalytic performance by optimizing the bonding properties of intermediates (Zhang *et al.*, 2019). For instance, a NiCeO<sub>x</sub>–Au catalyst, where the Au layer acted as the support, exhibited high oxygen evolution reaction (OER) activity in alkaline media, which exceeded that of NiCeO<sub>x</sub> supported on glassy carbon (Ng *et al.*, 2016).

## 1.4 THEORY–EXPERIMENT GAP

A good model of electrochemical systems should afford consistency between experiment and theory, such that experimental data and computational results can be directly compared. In recent decades, the application of modern *in situ* experimental methods has allowed electrochemical processes to be probed in great detail. Furthermore, the developed theoretical approaches based on quantum mechanics provide deep insights into these processes at the atomic level. However, substantial gaps remain between the theoretical and experimental studies, as demonstrated by the few studies on the influence of the operating environment, which have been hampered by the complexity of these systems.

In addition, there are two main theory–experiment gaps with respect to the atomistic modeling of holistic electrochemical processes, which must be narrowed to achieve even closer agreement with experiments. First, the mass transfer occurring during electrochemical processes must be elucidated to understand the electrochemical kinetics. During actual electrochemical processes, multiple mass transport mechanisms including diffusion, migration, and convection exert considerable effects on electrochemical reactions. For example, one of the major limiting factors in industrial electrochemical systems is the slow mass transfer of reactants toward the active surface areas of the electrodes, which is often caused by the low solubility of reactants in the electrolyte solution. By the middle of the 20th century, theoretical models for describing transfer processes in electrochemical systems had been developed, e.g., the Poisson–Nernst–Planck (PNP) model, which is based on a mean-field approximation of ion interactions and continuum descriptions of the concentration and electrostatic potential (Zheng and Wei, 2011). This model provides a qualitative explanation and increasingly quantitative predictions of experimental measurements for ion transport problems. However, for a complex system containing multiple ionic species, the PNP model can be computationally expensive and parametrically demanding, as experimental measurements of diffusion coefficient profiles are generally quite limited for most confined regions such as ion channels, nanostructures, and nanopores (Zheng and Wei, 2011). At present, accurate and comprehensive models for understanding the mass transfer process remain scarce.

The second gap between theoretical and experimental investigations is the limited simulation scales in terms of both size and time. In principle, we know that AIMD simulations are advanced methods for exploring the structure and dynamics at electrochemical interfaces. Nevertheless, AIMD simulations are still rather computationally expensive. The severe limitation on the total simulation time in atomistic modeling arises from the intrinsic time scale of atomic dynamics, which is typically of the order of femtoseconds. In numerical simulations using finite time steps, the step size must be sufficiently small to keep the simulation stable. However, to fully simulate experimental observations, it is necessary to follow the dynamic evolution of a system over a realistic experimental time scale to accurately describe microstructure evolution mechanisms. These experimental time scales are

very long (nanoseconds or greater) compared with atomic time scales, such that over a billion time steps are required for such simulations. Moreover, the number of atomic degrees of freedom in a typical material system is extremely large, and the equations of motion for a few billion atoms must be numerically solved to model a cubic micron of the material. Furthermore, the atomic scale of AIMD simulations is limited to the nanoscale. Hence, for large-scale simulations of structures and processes at electrochemical interfaces, other simulations at different levels are crucial.

## 1.5 CONCLUSIONS AND OUTLOOK

The brief review presented in this chapter illustrates that a thorough description and understanding of electrochemical processes at the atomic scale is gradually being developed. First-principles theory has enabled the complexity of these processes to be captured with increasing success and consideration of the presence of liquid electrolytes, explicit electrode–solvent interfaces, and the applied potential. Nevertheless, further progress in this field is still essential and major challenges remain, both of which will require novel approaches.

One of the main outstanding challenges is to establish more reliable modeling of electrochemical processes to bridge the microscopic and macroscopic domains. On the one hand, modern calculation methods based on quantum mechanics provide a means to uncover the atomic details of electrochemical systems. On the other hand, the concepts of statistical mechanics are essential for extending the results of these molecular-scale models to a macroscopic description of electrochemical processes. As such, multiscale simulation of electrochemical processes is required, extending from the atomic details of quantum states to a description of the electrochemical phenomena observed in macroscopic systems. In general, there are two categories of multiscale simulation, namely, concurrent multiscale modeling techniques and sequential multiscale modeling techniques. The former represent an incorporated approach in which a single simulation directly applies various levels of theory and explicitly describes phenomena taking place over a range of time and length scales. A common example of concurrent coupling in electrochemistry is QM/MM modeling (Pezeshki and Lin, 2015), in which the electronic structure method is used to describe a small portion of reactions, while the dynamical part is described using molecular force fields. The latter techniques utilize the results from modeling at one level as the input for modeling at another level, which is referred to as parameter passing. Thus, the subsequent simulations are not constrained by the time and length scale limitations of the parent model. Of course, there is a price to be paid for these gains in computational efficiency.

With the continued increase in computing power, it is difficult to predict how much the computational cost associated with multiscale simulations will become less of a restriction in the coming years. However, it is reasonable to expect that increased computing capacity will facilitate the development of more accurate and effective methods. We thus anticipate that the development of multiscale simulations describing the entire electrochemical process will become more efficient.

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