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Theory and experiments join force to characterize the electrocatalytic interface

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Electrocatalysis is gaining impetus as a key technology in fuel cells and for the medium-term energy storage in the context of intermittent, renewable energy sources such as wind and solar power. Furthermore, electrocatalysis also promises to convert rather inert molecules e.g., CO_2 and N_2 into reduced products such as CO and ammonia under relatively mild conditions (1, 2). Harnessing the full power of electrocatalysis is, however, hampered by a lack of understanding of the governing physical and chemical processes at the metal/electrolyte interface. In PNAS, Cheng et al. (3) bring key insight to the characterization of reaction intermediates during CO_2 electro-reduction via first principles molecular modelling. This reaction is timely and serves since a couple of years as the playground for advanced atomistic modelling of electro-catalysis (4–9).

The general lack of understanding is due to the inherent complexity of the electrified interface and its characterization. The characterization is difficult since most metal/liquid interfaces are amorphous. Therefore, no long-range ordering can be detected. Experimentally, the characterizations heavily rely on spectroscopy that provides average molecular orientations (Infra-Red (IR), Raman) or elemental composition and oxidation states (X-Ray Photoelectron Spectroscopy, X-Ray Absorption Near Edge Spectroscopy, etc) (10–12). Atomically resolved structures can only be obtained for rare, crystalline, interfaces such as pyridine on gold single crystal surfaces via Scanning Tunneling Microscopy imaging (13, 14). Theoretically, the simulations of electrochemical interfaces are challenging for two reasons. The first challenge originates from the structure and dynamics of the interface, i.e. its size and the relevant timescales. Just like for experiments, the amorphous nature of the interface means that, when working with periodic boundary conditions in order to well describe the metallic nature of the electrode and the liquid nature of the electrolyte, large systems need to be simulated in order to avoid spurious periodicity and thus simulation-induced crystallinity. Furthermore, the electrode surface might reconstruct in reaction conditions(15). Even in the absence of reconstructions, the dynamics at the interface tend to be orders of magnitude slower than in solution, so that the necessary simulations to reach equilibrium are computationally expensive (16–18).

The second challenge is related to the presence of an electrochemical potential. In order to accurately describe chemical bond breaking, density functional theory (DFT) computations have to be performed. However, in DFT, the positions of the electrons are optimized and cannot be chosen at will. In practice, simulating the effect of an electrochemical potential goes along with tuning the number of electrons at the metal surface, neutralized with a counter charge of either atomistic or continuous nature (19, 20). While introducing explicitly anions/cations corresponds to the operando experimental conditions, the sampling of the counterion distribution becomes very challenging. During a given simulation, the number of counterions is usually kept constant, resulting in a fluctuating electrochemical potential. Grand-canonical simulations, that keep the potential constant while varying the number of counterions, are technically feasible but would require one to two orders more time to obtain equilibrated results. On top of that, usual DFT functionals lead to self-interaction errors and associated incorrect electron localization (21). The field of electrocatalysis modelling is hence at a critical point, where simple approximations lack accuracy, but more realistic modelling is computationally very expensive. A full description from first principles of the structure, energetics and dynamics of the electrochemical interface is, therefore, extremely challenging, if not inaccessible, with today's methods.

The overarching idea of Cheng et al. in PNAS (3) is to combine experimental and theoretical IR spectroscopy in order to identify the nature of key reaction intermediates for CO_2 electro-reduction (Fig. 1). This relies on the fact that, in general, the accuracy of vibrational spectra from DFT is superior to the accuracy of thermodynamic and kinetic parameters. Hence, assigning the experimental spectra by theoretical computations can provide an insight into the species present on the electrode. Such insight is critical for catalyst design that aims at reducing overpotentials (i.e., energetic losses) and at obtaining high yield and selectivity in the targeted chemical product (e.g., ethylene).

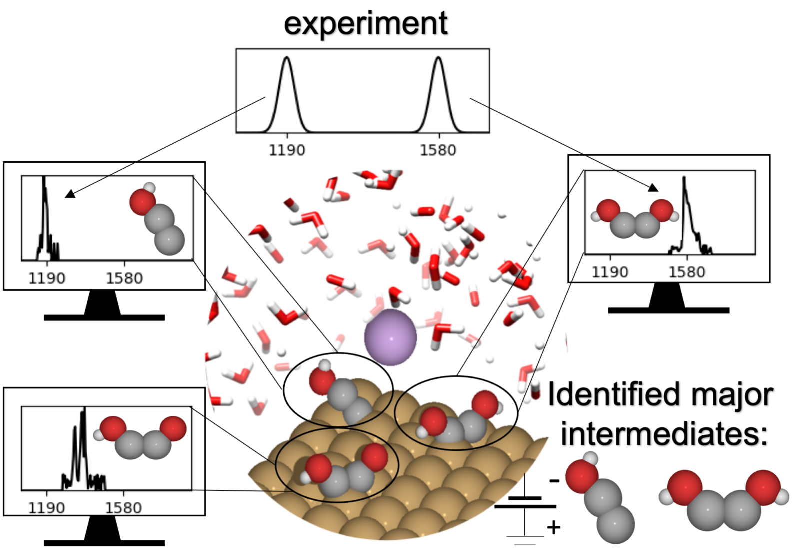

Fig. 1: Schematics of the identification procedure of surface intermediates involved in an electrocatalytic reaction by matching experimental and simulated spectra, taking into account the dynamics of the solvent and electrolyte, and the applied potential.

In electrocatalysis, the reaction is occurring at the interface between the electrode and the electrolyte. This interface is classically described by the double layer theories from Helmholtz, Gouy-Chapman, and others. These models treat the solvent and electrolyte in an averaged manner, neglecting most atomistic effects, such as finite size and preferred molecular orientations. This contrasts with the atomistic models of metal surface in contact with water, which demonstrate a partial immobilization of the solvent at the electrode interface and a high degree of structuring. This interfacial structuring has, necessarily, an influence on adsorbate geometries, energies and vibrational spectra beyond the electric field effect due to the electrochemical potential (22).

Cheng et al. in PNAS (3) adopts the confident strategy to rely on explicit, brute force, atomistic calculations of the electrode/electrolyte interface: The simulations are initialized by long molecular dynamics simulations with an approximate, but much faster, method relying on a parametrized force-field. Then, the authors switch to the DFT description for a simulation that is 100 times shorter, from which they extract the vibrational spectrum. For the local configuration, such a short simulation has previously been shown to be sufficient for retrieving thermodynamic functions and vibrational spectra for liquids. This combination of two levels of theory is highly elegant and close to the best compromise achievable today between the opposing needs of extensive configuration sampling and high accuracy in energies. Future developments of the methods and computers will certainly allow to alleviate some unavoidable present shortenings. Notably, the approach is limited today to rather small systems, in the present case only 48 water molecules have been included. For bulk water, i.e., where there are no interfaces, 64 water molecules were found necessary to converge the average structure of the liquid (23). Hence, the water structure and properties might deviate somewhat from the fully converged result. Another question relates to the water structure at the interface which might require large super cells. However, the major limitation that needs to be overcome is efficiently averaging over diverse adsorbate-electrolyte arrangements as a function of the potential and electrolyte, since a single local configuration is unlikely to be fully representative. The second bottleneck to be overcome is the parametrization of the efficient, approximate method used for system equilibration. Indeed, this method would need to be generalized to other metals, alloys, materials and electrolytes to cover the whole range of electrified solid/liquid interface that could benefit from the application of the strategy of Cheng et al. to elucidate the species and processes at the electrode/electrolyte interface. Last but not least, the accuracy of DFT for systems with separated charges (electrode/counterions) needs to be improved to confidently simulate the charge distribution at these interfaces.

With such a general method at hand, we could expect major breakthroughs in the atomistic understanding and rational design of electrified interfaces in various domains: the development of the next generation of Li, Na or Mg based batteries with a higher energy and power density. Of course, the domain of super- and pseudo-capacitors,(24) where electrical energy is stored at high rate, would also greatly benefit from an operando view on the species and reactions present at the electrode. Similarly, organic electronics could be better described if the influence of the applied voltage and the surrounding electrolyte would be included. On a more industrial level, these methods would also be ideally suited to study electroplating and corrosion (25), which is very poorly understood and, despite its economic importance (corrosion generates costs of ~3% of the GDP) (26), underrepresented in fundamental research. Last but not least, the characterization of relevant reaction intermediates during electrocatalytic reactions might accelerate catalyst design in diverse areas of electrolysis and fuel-cells: hydrogen production over (non-noble) metals from water reduction and biomass oxidation, improve the still incompletely understood oxygen reduction and evolution reaction, develop efficient nitrogen reduction catalysts that would allow to decentralize ammonia production and, of course, the CO_2 electroreduction investigated by Cheng et al.,(3) that has the potential to sustainably close the carbon cycle by converting the green-house gas CO_2 into carbon building blocks that, one day, could replace fossil resources as the basis of chemical industry.

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Figure Caption

Fig. 1: Schematics of the identification procedure of surface intermediates involved in an electrocatalytic reaction by matching experimental and simulated spectra, taking into account the dynamics of the solvent and electrolyte, and the applied potential.

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