

How pH affects electrochemical processes

Three mechanisms underlie the impact of pH on the activity of electrochemical reactions

By **Nitish Govindarajan, Aoni Xu, Karen Chan**

A promising approach to the sustainable and fossil-free production of fuels and chemicals is the electrochemical conversion of atmospherically available gases such as H_2O , CO_2 , O_2 , and N_2 to fuels and chemicals with renewable electricity (1). Electrocatalysts are essential for practical processes because they increase the reaction rate, efficiency, and selectivity toward desired products. Unfortunately, state-of-the-art electrocatalysts have drawbacks such as the use of precious metals that limit widespread adoption and large overpotentials that lead to very low efficiency. The outstanding challenge is to design and discover active and selective electrocatalysts that are based on earth-abundant materials. It has been understood for decades that the electrolyte pH affects the activity of electrochemical processes. However, the origins of this effect are still under debate.

Interfacial proton-electron transfer reactions are central to electrochemical conversion schemes and include H_2 and O_2 redox reactions and CO reduction (COR), as well as alcohol oxidation reactions (AORs). The reaction thermodynamics of these multistep reactions depend both on pH and the absolute electrode potential, which are captured by the potential U [here, all U values and voltages are versus the reversible hydrogen electrode (RHE)]. However, the reaction kinetics, given by the current density J , do not generally follow the same dependence on U .

We define “pH effects” as such deviations in J from a dependence on U . The relative increase in J with a change in pH (ΔpH) for several proton-electron transfer reactions for a given U (see the figure, top) can be several orders of magnitude. Three possible sources of pH effects in electrochemical systems are changes in the proton donor or acceptor with the electrolyte pH, adsorbate dipole-

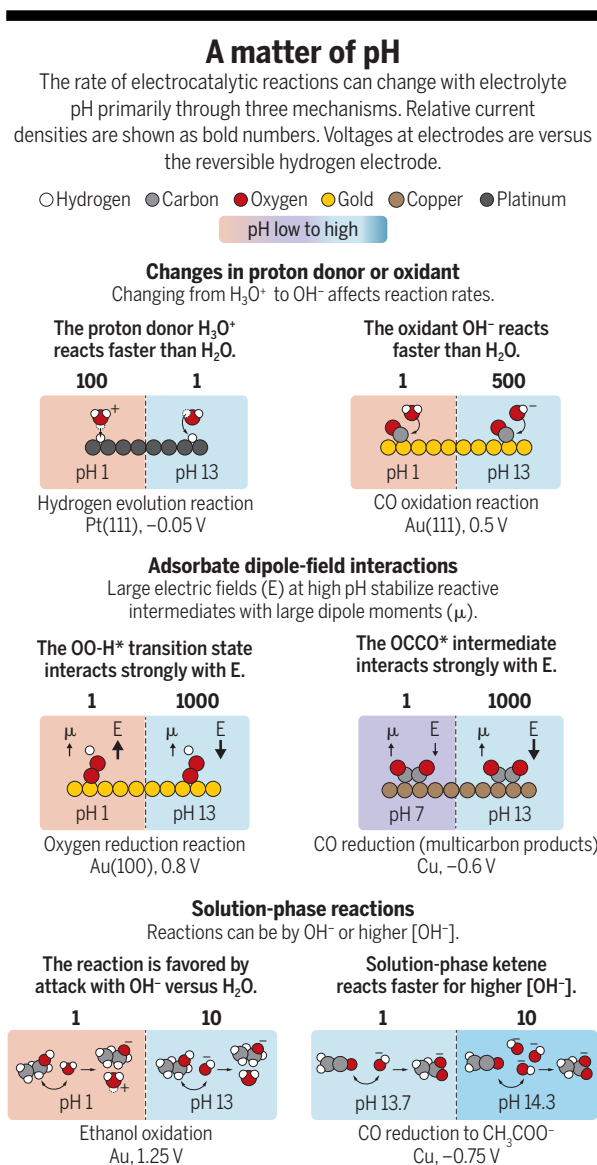
field interactions, and solution-phase reactions. These mechanisms are illustrated in the figure for relevant intermediates in the rate- or selectivity-determining steps of the reactions shown.

The change in the proton donor, such as H_3O^+ to H_2O , or oxidant, such as OH^- to H_2O , with pH can affect the rates of electrochemical reaction steps by orders of magnitude. The magnitude of this effect is analogous to that in the variation in acid (K_a) and base (K_b) dissociation constants for bulk acid-base reactions. The potential impact of changes

in proton donor and oxidant on electrocatalytic activity are exemplified by the hydrogen evolution (HER) and CO-electrooxidation (COOR) reactions, respectively.

In the HER, the proton donor changes from H_3O^+ in acidic solution to H_2O in alkaline solution. The proton-electron transfer barriers for the elementary steps are much lower with H_3O^+ as the proton donor than with H_2O —that is, $K_a(\text{H}_3\text{O}^+) \ll K_a(\text{H}_2\text{O})$ (2). Thus, the activity at pH 1 is about two orders of magnitude higher than at pH 13 at -0.05 V on Pt(111) electrodes (3). Similarly, the strong pH dependence of COOR on Au(111) surfaces has also been proposed to likely originate from a change in the oxidant from OH^- to H_2O with a decrease in electrolyte pH (4). Because OH^- is a more facile oxidant than H_2O as $K_b(\text{OH}^-) \gg K_b(\text{H}_2\text{O})$, there is a ~ 2.5 orders of magnitude increase in the COOR current density at 0.5 V in base versus acid (5).

A second mechanism behind pH effects is the adsorbate dipole-field interaction (see the figure, middle). Electrochemical interfaces are in general highly charged, and these charges give rise to large interfacial electric fields at the electrode-electrolyte interface. These fields drive the electron transfer to and from the adsorbates involved in the reaction. The electric field also interacts strongly with adsorbates that have a large dipole moment (μ), polarizability (α), or both, which results in changes in their adsorption energies. Because the interfacial field strength depends only on the absolute electrode potential, for a given U versus RHE, different pH conditions create different interfacial fields and corresponding stabilizations of the polar adsorbates. This mechanism gives rise to the pH-dependent activity in COR on Cu (6) and oxygen reduction (ORR) on Au(100) (7). In the former process, the critical reaction intermediate $^*\text{OCCO}$ has a large dipole moment (8), and its stabilization by the interfacial field gives rise to more than three orders of magnitude increase in activity toward multicarbon products such as ethylene or ethanol under alkaline conditions



compared with neutral conditions at -0.6 V. For ORR on Au(100) electrodes, adsorbate dipole-field interactions result in up to three orders of magnitude increase in activity from acidic to alkaline conditions at 0.8 V (7) through strong-field stabilization of the *OOH transition state (9).

The electrolyte pH can also affect electrocatalytic activity through solution-phase reactions with OH^- without any involvement of the electrode (see the figure, bottom). The pH dependence then arises from the first-order dependence of the corresponding elementary step on OH^- concentration. For several AORs on Au, the first deprotonation step was proposed to be catalyzed by OH^- ions in alkaline solutions, which react with the alcohol to form a reactive alkoxide species that promotes the overall reaction rate (10). For the specific case of ethanol oxidation on Au electrodes, a ~ 10 -fold increase in the peak current density was observed at pH 13 relative to pH 1 (11). More recently, a 10-fold increase in acetate production from COR was observed at -0.75 V on Cu nanosheets with increasing pH (12). This effect was attributed to the solution-phase reaction of a highly reactive ketene intermediate (*CH_2CO) with OH^- ions (13).

Other complex pH effects deserve further attention. Buffering anions used to regulate electrolyte pH can act as proton donors and can promote reactions such as CO_2 electroreduction to methane on Cu electrodes (14). The dependence of interfacial solvent dynamics and reorganization effects on pH may play a role in hydrogen electrocatalysis (15). Together, pH effects provide additional descriptors beyond conventional adsorption energies that can open new avenues for catalyst design and enable large-scale adaptation of electrochemical conversion schemes. ■

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Fossil pollen from dipterocarps show shared floristic heritage between Asia and Africa

By Carina Hoorn¹ and Jun Ying Lim²

With more than 400 species in the tropical lowlands and hill forests of Asia, dipterocarps are among the most abundant, diverse, and economically important trees on the planet (1). Many Asian dipterocarp species, belonging to the subfamily Dipterocarpoideae, are renowned for their stature and have long been valued for their timber. These trees dominate the canopy of the tropical Asian forests and are among the tallest trees on the planet (2). Yet, the biogeographic origin of Asian dipterocarps has been a puzzle because of the lack of fossils that capture the early history of the group. On page 455 of this issue, Bansal *et al.* (3) report filling this critical gap in dipterocarp evolutionary history by presenting fossil pollen from Sudan and India that is far older than any dipterocarp fossils described previously and by characterizing dipterocarp resin from sediments collected in India.

Using the pollen fossils and published molecular data (4), the authors generated a revised time-calibrated phylogenetic tree of dipterocarps. Along with paleogeographic and climatic reconstructions, they propose that these trees originated

in tropical Africa in the Late Cretaceous, 100 million years ago (Ma), and expanded into India between 72 and 66 Ma, during a window of geographic connectivity that coincided with a warming climate, the rise of the angiosperms (5), and the formation of the Deccan Traps in western India—one of the largest volcanic features in the world. The final stage of the dipterocarp journey took place between 50 and 40 Ma, when India and Asia collided, bringing the stowaway plants and animals closer to the tropical habitats of Asia (see the figure). Among these, dipterocarp lineages expanded and diversified, resulting in the integration of ancestrally African elements into the Asian biota.

The flora of tropical Asia is increasingly recognized by biogeographers as a melting pot that has been shaped by multiple exchanges (6). Scientists have long suspected that Asian dipterocarps originate from India, and the out-of-India pattern of dispersal has been documented for a wide variety of plant and animal groups (7). However, several fundamental questions remain: How and when did the dipterocarps colonize India, and where did they migrate from?

Palynology, the study of pollen and spores, is a powerful tool in paleobiogeography and can provide information not only on past plant composition and diversity, but also on former climatic conditions and topography. When combined with paleobotany, these disciplines provide an even higher accuracy in landscape and vegetation reconstructions.

¹Institute for Biodiversity and Ecosystem Dynamics, University of Amsterdam, Amsterdam, Netherlands.

²Department of Biological Sciences, National University of Singapore, Singapore. Email: m.c.hoorn@uva.nl; junyinglim@gmail.com