Proton relays in molecular electrocatalysis: specifications for efficiency and insights into their relevance for reversible behavior

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Hydrogen is now confirmed as a key component of a CO_2-neutral economy, we need to transition towards. The production of large quantities of hydrogen now requires breakthroughs in finding new catalysts that are efficient, stable and cheap, i.e. based on abundant elements. Indeed fuel formation involves multi-electron multi-proton reactions that are inherently kinetically sluggish. Efficient catalysts can be found in living micro-organisms producing or metabolizing hydrogen thanks to hydrogenases. Catalysis in these enzymes only requires Earth-abundant metal centers, the reactivity of which is enhanced thanks to the presence of basic sites acting as proton relays[1] at their vicinity. We will show how such active sites can be used as an inspiration to design new synthetic catalysts for H_2 evolution[2-4] and oxidation[5-6] and how the introduction of proton relays significantly impacts the catalytic properties of such catalytic platforms, opening in some cases the possibility for bidirectional and even reversible catalysis.[7]

References

1. Saveant, J. M., Angew. Chem. Int. Ed. 2019, 58 (7), 2125-2128.
2. Sun, D.; Harshan, A. K.; Pecaut, J.; Hammes-Schiffer, S.; Costentin, C.; Artero, V. Chemelectrochem 2021, 8 (14), 2671-2679.
3. Queyriaux, N.; Sun, D.; Fize, J.; Pecaut, J.; Field, M. J.; Chavarot-Kerlidou, M.; Artero, V. J. Am. Chem. Soc. 2019.
4. Li, C.-B.; Bagnall, A. J.; Sun, D.; Rendon, J.; Koepf, M.; Gambarelli, S.; Mouesca, J.-M.; Chavarot-Kerlidou, M.; Artero, V. Sustainable Energy & Fuels 2022.
5. DuBois, M. R.; DuBois, D. L. Chem. Soc. Rev. 2009, 38 (1), 62-72.
6. Schild, J.; Reuillard, B.; Morozan, A.; Chenevier, P.; Gravel, E.; Doris, E.; Artero, V. J. Am. Chem. Soc. 2021, 143 (43), 18150-18158.
7. Ahmed, M. E.; Nayek, A.; Križan, A.; Coutard, N.; Morozan, A.; Ghosh Dey, S.; Lomoth, R.; Hammarström, L.; Artero, V.; Dey, A. J. Am. Chem. Soc. 2022, 144 (8), 3614-3625.