

Proton-Coupled Electron Transfer: From Molecular Models to Catalytic Systems

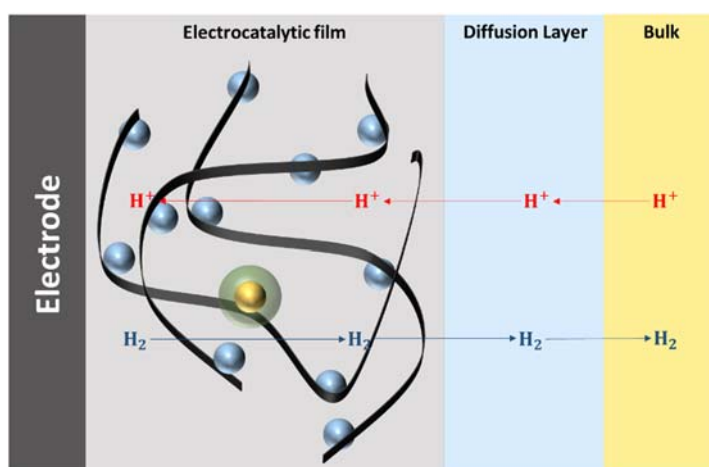
Cédric Tard

Ecole Polytechnique, IP Paris

cedric.tard@polytechnique.edu

Electrochemical water splitting is one of the clean technologies for the production on a large scale of highly pure dihydrogen H_2 , a potential major energy vector for the near future. Benchmarking protocols for evaluating the electrocatalytic water splitting have been proposed over the years in order to rationalize the assessment of the activity and stability of heterogeneous hydrogen and oxygen evolution reaction (HER and OER) electrocatalysts. Nevertheless it is still difficult to have access to reliable electrochemical measurements to get a direct insight into the mechanism for the HER and OER due to the complexity of these multiple electron/proton transfer reactions.

In-depth cyclic voltammetry (CV) analysis has been shown to be a very powerful tool to address intricate reaction mechanisms involving proton-coupled electron transfer (PCET) reactions.^[1] We demonstrated that we could use this analytical technique to study intramolecular PCET reactions,^[2] molecular bond breaking coupled with PCET reactions,^[3] molecular catalytic reactions coupled with PCET,^[4] and recently heterogeneous electrocatalyst mechanisms involving PCET.^[5] Those fundamental reactions are illustrated with theoretical analysis and experimental examples.



- [1] a) Bonin, J.; Costentin, C.; Robert, M.; Savéant, J.-M.; Tard, C., Hydrogen-bond relays in concerted proton–electron transfers. *Acc. Chem. Res.* **2012**, *45* (3), 372-381; b) Costentin, C.; Robert, M.; Savéant, J.-M.; Tard, C., Breaking bonds with electrons and protons. Models and examples. *Acc. Chem. Res.* **2014**, *47* (1), 271-280.
- [2] Costentin, C.; Robert, M.; Savéant, J.-M.; Tard, C., Inserting a hydrogen-bond relay between proton exchanging sites in proton-coupled electron transfers. *Angew. Chem. Int. Ed.* **2010**, *49* (22), 3803-3806.
- [3] a) Costentin, C.; Hajj, V.; Robert, M.; Savéant, J.-M.; Tard, C., Concerted heavy-atom bond cleavage and proton and electron transfers illustrated by proton-assisted reductive cleavage of an O–O bond. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108* (21), 8559-8564; b) Savéant, J.-M.; Tard, C., Proton-coupled electron transfer in azobenzene-hydrazobenzene couples with pending acid-base functions. Hydrogen-bonding and structural effects. *J. Am. Chem. Soc.* **2014**, *136* (25), 8907-8910.
- [4] a) Savéant, J.-M.; Tard, C., Attempts to catalyze the electrochemical CO_2 -to-methanol conversion by biomimetic $2e^-+2H^+$ transferring molecules. *J. Am. Chem. Soc.* **2016**, *138* (3), 1017-1021; b) Costentin, C.; Savéant, J.-M.; Tard, C., Catalysis of CO_2 electrochemical reduction by protonated pyridine and similar molecules. Useful lessons from a methodological misadventure. *ACS Energy Letters* **2018**, *3* (3), 695-703.
- [5] Costentin, C.; Di Giovanni, C.; Giraud, M.; Savéant, J.-M.; Tard, C., Nanodiffusion in electrocatalytic films. *Nat. Mat.* **2017**, *16* (10), 1016-1021.