

# Electron migration mechanisms within covalently immobilised Co porphyrin-based catalysts for oxygen reduction reaction

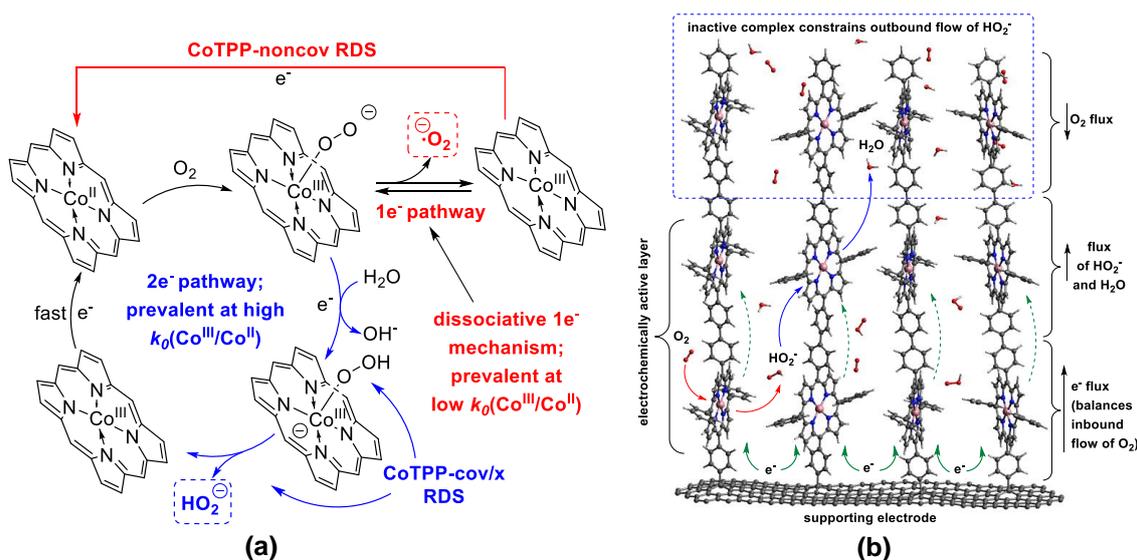
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Electrocatalytic oxygen reduction reaction (ORR) is a multielectron, multiproton reaction taking place on the cathode of proton exchange membrane (PEM) fuel cells. Carbon-supported Co tetraphenylporphyrin (CoTPP) is an excellent ORR catalyst, however the reaction almost exclusively follows an undesirable  $2e^-$  reduction pathway.<sup>1</sup> Hence, a method enabling  $4e^-$  reduction mechanism on an otherwise efficient, but  $H_2O_2$ -selective catalyst would be of high value for the renewable energy industry.

In this work we demonstrate that the selectivity of the porphyrin-based catalysts could be controlled via covalent immobilization of the complex on the electrode surface. Covalent grafting of the CoTPP was performed using potentiostatic electroreduction of the corresponding diazonium salt.<sup>2-3</sup> The resulting **CoTPP-cov/10** electrode (where 10 is the electrografting time in min) demonstrates a selectivity to  $4e^-$  reduction of 55 % in contrast to 0 % observed on noncovalent counterpart **CoTPP-noncov**. The  $H_2O_2$  reduction also proceeds  $\sim 2.9$  times faster on **CoTPP-cov/10**. The direct imaging of the surface redox kinetics using variable-frequency square wave voltammetry (VF-SWV) shows a strong outbound propagation of electrons across covalently grafted layer which results in  $\sim 9$  times higher abundance of active sites compared to **CoTPP-noncov**. The improved charge transfer rate in turn increases the probability of multielectron reaction events (Figure 1a). Thus, the porphyrin-to-porphyrin bonds turn a simple molecular catalyst into an extended conductive macromolecular framework (Figure 1b). Such a structure provides a strong electron flux matching the inbound flow of  $O_2$  and gives a longer residence time for the intermediates via a diffusion-mediated mechanism.



**Figure 1:** (a) Molecular and (b) macromolecular mechanisms of ORR on Co porphyrins.

## References

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