

The role of protons in water oxidation: a study of the kinetic isotope effect on a Co-based model catalyst

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The mechanism of water oxidation in oxygenic photosynthesis is very interesting for various reasons. It is of fundamental importance for life on earth as we know it and it serves as an inspiration in the development of artificial photosynthesis. However, we still lack a good knowledge at atomic scale of the water oxidation process in natural and in synthetic catalyst. Different artificial catalysts have been studied, which have a very strong structural similarity with the oxygen-evolving complex in photosystem II. Herein an amorphous oxide catalyst (CoCat) is investigated [1], where Co takes over the role that Mn has in the natural system. The CoCat has several advantages: efficiency at neutral pH, self-assembly from low cost materials and a self-repair mechanism. X-ray absorption spectroscopy (XAS) reveals a cluster of interconnected complete or incomplete CoIII-oxo cubanes [2]. Recent experiments indicate that the catalytic rate is strongly dependent on the protonation state of the buffer electrolyte, which works as a proton acceptor [3]. However, the protonation state of the Co clusters and the details of the proton transfer mechanism are still unclear. A proton-coupled electron transfer, similar to what might happen in PSII, has been proposed.

To have a better understanding of the role of protons, we have investigated the electrochemical properties of the CoCat using deuterated water (D₂O). Cyclic voltammetry and Tafel plot experiments have been performed in water and deuterated water solutions. We observed a strong kinetic isotope effect in both the oxygen formation and the Co oxidation process. Further analysis performed at different pH gives more insight in the reaction mechanism.

References:

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