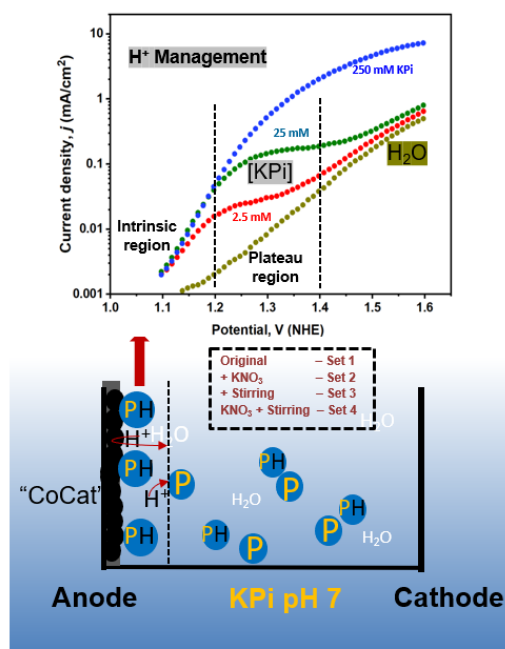


Systematically experimental evidence on proton management from phosphate buffer at neutral pH based on CoCat water oxidation catalyst

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Water oxidation reaction (OER) is a significant energy storage and conversion process directly or indirectly in natural and artificial photosynthesis. The neutral reaction environment especially facilitates the CO₂ reduction reactions (CO₂RR) with coupling proton from water oxidation reaction. For achieving technologically relevant current densities, it is important to understand the regulating factor on catalytic current. Not only intrinsic catalytic activity is crucial, but also proton transfer efficiency is needed to be considered seriously to prevent local pH gradient effect on water oxidation dynamics.

Amorphous CoCat catalyst acts as a model catalyst to study different phosphate buffer concentration sets (set 1-4) on determining catalytic current density. Our earlier work reported current density at high potential depending on the pK_a-value of the buffering groups rather than obeying a classical, 'thermodynamic' pH dependence.^[1] A simplified first-order model predicted the major trends of catalytic OER currents determined by the proton activity at catalyst-electrolyte interface.^[2] Herein, the extended current-potential curves (Tafel plot) at steady state were collected from 1.1 V to 1.6 V vs NHE at different phosphate buffer (KPi) concentration at neutral pH. Interestingly, it is found that the catalytic current at three different potential regions show different trend with buffer concentration. At low potential region, catalytic current is not dependent on buffer concentration. However, at middle current range, the j -V curve shows an evident plateau level and at this region, the current density is determined by the available buffer base amount. With reaching higher potential region, the current density is further improved. Comparing with pure water curve at high potential, the current density at low KPi concentration is almost comparable and we attributed to water acting as proton acceptor to accelerate proton transfer. In addition, by using in-situ Raman spectroscopy, we observed an obvious acidification at near electrode surface with increasing

applied potential and quantitatively analysed the dependent relationship between current density and proton concentration. In this work, electrochemical analysis via extended Tafel plots demonstrates the important role of buffer base for proton management acting as proton acceptor. In addition, local acidification was quantitatively analysed by in-situ Raman spectroscopy. It potentially emphasises preventing local acidification at neutral pH is necessary.

- [1] K. Klingan, F. Ringleb, I. Zaharieva, J. Heidkamp, P. Chernev, D. Gonzales, M. Risch, A. Fischer, H. Dau, , *ChemSusChem*, 2014, 7, 1301-1310.
- [2] H. Dau, C. Pasquini, *Inorganics*, 2019, 7, 20.