

Surface Passivation or Catalysis? Some Surprising Observations for CoPi-Catalyzed BiVO₄ Photoanodes

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To enhance the performance of metal oxide photoanodes for water splitting, such as BiVO₄ or Fe₂O₃, their surfaces are usually functionalized with water oxidation catalysts (e.g. IrO_x, CoO_x, NiFeO_x). These catalysts greatly enhance the photocurrent and appear to address the slow oxygen evolution kinetics of metal oxide surfaces. However, the true nature of semiconductor-catalyst interactions and the mechanism(s) of these improvements are still unclear.

In this study, we use intensity modulated photocurrent spectroscopy (IMPS) to examine the surface charge carrier dynamics of spray-deposited bismuth vanadate (BiVO₄) photoanodes and the effect of cobalt phosphate (CoPi) catalysts on its surface. An LED is used to illuminate the sample with a modulated intensity, and the real and imaginary parts of the opto-electrical impedance are recorded. To interpret the resulting spectra, we used a model developed by Peter et al. that allows one to distinguish the rate constants for surface recombination and charge injection into the electrolyte [1]. For bare BiVO₄, we find that at moderate applied bias potentials (< 1.0 V vs. RHE), the recombination rate does not depend on the applied bias, whereas the charge transfer rate increases with applied bias (Fig. 1). This behavior resembles that of a metal, and we interpret this as a manifestation of Fermi level pinning. At potentials > 1.0 V vs. RHE, the charge transfer rate is more or less constant, while the recombination rate decreases. This is the behavior one expects for a semiconductor, suggesting that Fermi level is no longer pinned in this potential range.

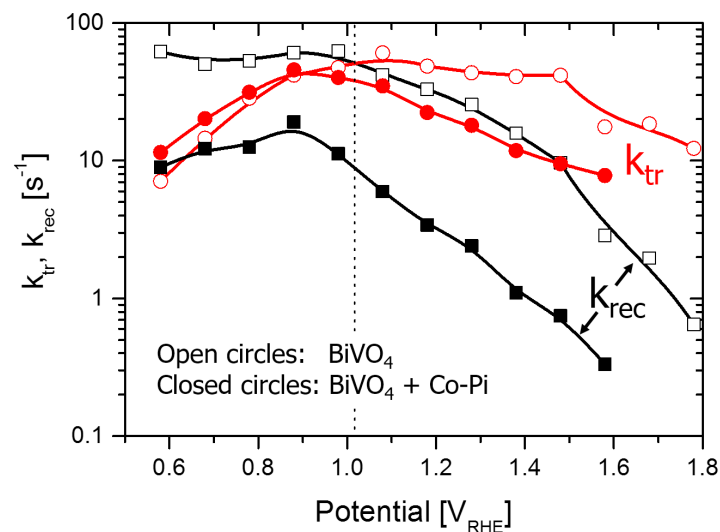


Figure 1. Charge transfer rate constant (red) and recombination rate constant (black) for the unmodified (open symbols) and the Co-Pi catalyzed BiVO₄ (closed symbols).

For CoPi-catalyzed samples, the surface recombination rate decreases by an order of magnitude, whereas the charge injection kinetics are much less affected. This suggests that i) BiVO₄ is already a good oxidation catalyst by itself, which is consistent with the relatively positive potential of the valence band edge, and ii) the main role of CoPi on BiVO₄ is that of a surface passivation agent. The latter is a surprising result, since CoPi is well known to be an efficient oxygen evolution catalyst [2], and this has also been thought to be its main role when applied to BiVO₄. Based on these results we predict that the modification of BiVO₄ surface with RuO_x, a well-known (non-passivating) oxygen evolution catalyst, does not improve the performance; our experiments show that this is indeed the case. These results allowed us to develop a modified semiconductor/catalyst model for BiVO₄ photoanodes. The model was verified by additional IMPS measurements in which the concentration of hole scavengers and background light intensities were systematically varied. The implications of the model will be discussed.

References

- [1] Ponomarev, E. A.; Peter, L. M. *J. Electroanal. Chem.* 396, 219 (1995).
- [2] Kanan, M. W.; Nocera, D. G. *Science* 321, 1072 (2008).