Towards understanding nanoscale water electrolysis via photocatalytic overall water splitting

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Abstract: Nanoscale water electrolysis is substantially different from macroscale systems (such as conventional electrolyzers) in terms of local electric field, ohmic loss, and the role of supporting ions in steady-state catalysis. Clear advantage of nanoscale electrolysis are shown in simulations using the Poisson-Nernst-Planck (PNP) equations which were solved for redox sites less than 100 nm apart and showed negligible ohmic and Nernstian potential losses from the formation of a pH gradient when working at rates of 10 mA cm^{-2}. Herein, CrO_x/(Pt or Rh)/$SrTiO_3$ was observed to have substantial improvement in photocatalytic rates when buffer ions were introduced under near-neutral conditions and under high photon flux. Electrocatalytic measurements and the solved PNP equations confirmed contribution of mass transport events and the presence of buffer ions decreased the kinetic overpotential significantly (400 mV) for the hydrogen evolution reaction (HER).

Keywords: Nanoscale, photocatalysis, electrocatalysis, water splitting, buffers, electrolyte

1. Introduction

Solar fuel production is considered an attractive solution to meet the ever-increasing global energy demands. Promising methods of solar fuel generation includes photovoltaic cells conjugated with an electrolyzer, photoelectrochemical water splitting, and photocatalytic water splitting. Photocatalysis using semiconductor powder can be considered a microphotoelectrochemical device which enables the co-generation of H_2 and O_2 from the same surface at a nanometer-scale distance between redox sites through complex physicochemical phenomena from solid-state physics, catalysis, and electrochemistry. The complexity of this system makes it challenging to achieve substantial solar-to-hydrogen conversion efficiencies. This study discusses benefits of the co-generation of H_2 and O_2 at the nanoscale which can overcome the typical drawbacks of macro-sized electrolyzers. The presented nanoelectrochemistry in this study demonstrates the knowledge transfer from electrocatalysis to photocatalysis and can be correlated with the development of applications in fields ranging from energy to bioanalysis.

2. Results and discussion

Electrocatalytic water splitting is composed of the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), which proceed via the following reactions in acidic to near-neutral media:

HER: $4H_3O^+ + 4e^- \rightarrow 2H_2 + 4H_2O$
OER: $6H_2O \rightarrow O_2 + 4H_3O^+ + 4e^-$

while the following equations rule them in near-neutral pH to alkaline conditions:

HER: $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$
OER: $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$

There is a significant kinetic overpotential required for the dissociation of the O-H bond in H_2O compared to the dissociation of the hydronium ion for the HER.[1] In unbuffered near-neutral pH conditions, H_2O molecules are the primary reactant instead of unavailable hydronium or hydroxide ions leading to diffusion limitations.[2] Fig. 1a shows the points of the reactant switching based on H^+ and OH^- diffusion limitation at different current densities. Fig. 1b shows the apparent quantum efficiency (AQE) in the photocatalytic system using $CrO_x/Pt/SrTiO_3$ in unbuffered and various buffered electrolytes. The improvement in AQE can be attributed to the reactant switching from kinetically demanding H_2O reduction to the facile H_3O^+ reduction. The difference in kinetic overpotential between these two reactions were calculated and are shown in Fig. 1c,d where the PNP equations were solved and the potentials required for water splitting were analyzed according to the thermodynamics, kinetics and mass transport contributions. To sustain 10 mA cm^{-2} in a system where the anode and cathode are 10 nm apart, an overall voltage of 2.0 V (Fig. 1c) and 2.4 V (Fig. 1d) is required for hydronium ion reduction and water molecule reduction, respectively. Therefore, a 400 mV improvement was observed with the introduction of buffer at near-neutral pH.

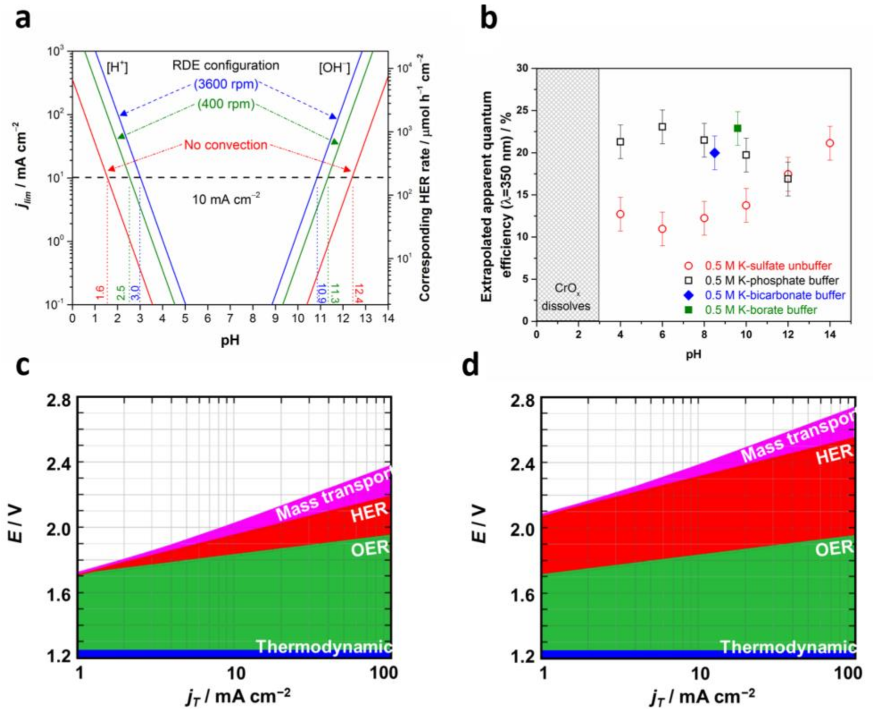

Fig 1: **(a)** Expected limiting diffusion current density for the reduction of H^+ and oxidation of OH^- on a substrate. **(b)** AQE of photocatalytic H_2 evolution using $CrO_x/Pt/SrTiO_3$ in buffered and unbuffered solutions ($300 < \lambda < 800$ nm, 50 mg of photocatalyst). Water electrolysis simulations via the PNP equations of the relative potential distribution as a function of the logarithm of the current density in the system, assuming an inter-particle distance of 10 nm where the HER exchange current density was assumed as **(c)** $10^{-a/b} = 1$ mA cm^{-2} (hydronium ion reduction) and **(d)** $10^{-a/b} = 1\times10^{-3}$ mA cm^{-2} (water molecule reduction).

3. Conclusions

Nanoscale water electrolysis performed via photocatalytic overall water splitting, was investigated by combined studies from theoretical modeling and electrocatalytic measurements. Both theory and experiments quantitatively confirm the benefits of H_2/O_2 co-generation at the nanoscale as the ohmic drop and pH gradient are negligible, even using ultra-pure water as a reactant, when the distance between the cathode and anode is maintained at less than 100 nm at ~10 mA cm^{-2}. The presence of buffer ions at near-neutral pH drastically improved the water splitting rates in comparison to ultra-pure or unbuffered water splitting in both photocatalytic and electrocatalytic HER. This work demonstrates that microelectrochemical systems are capable of achieving an efficient photocatalytic water splitting reaction under benign conditions, and this work can be further generalized to advance electrochemical systems performing any catalytic reaction at the nanoscale.

References

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