Quantitative description to stabilize local pH shift in a solar-driven water splitting device and demonstration of coupled reductive upgrading of biomass feedstock

([1]*Institute for Solar Fuels, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH*, [2]*Graduate School of Engineering, The University of Tokyo,* [3]*Department of Chemistry, Technische Universität Berlin*) ○Keisuke Obata,[1,2] Michael Schwarze,[3] Roel van de Krol,[1,3] Reinhard Schomäcker,[3] Fatwa F. Abdi[1]

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Neutral pH buffer electrolyte is an attractive media to safely perform solar-driven water splitting in a wide area. However, local pH shifts close to the electrodes lead to concentration overpotentials.[1] In this study, a pH-sensitive fluorescence sensor foil was introduced between Pt model electrodes to *in situ* observe the local pH during water splitting, which successfully captured a pH shift of ca. 1 unit in 0.1 M potassium phosphate solution even at 1 mA cm^{-2} (Fig. 1a).[2] The observed shift was reproduced by multiphysics simulations containing electrochemistry, mass-transport, and fluid dynamics. The simulations revealed that the buoyancy effect due to the concentration change generates a convection close to the electrode, which partly helps to stabilize the pH shift.

Production of value-added products is a promising way for deep implementation of photoelectrochemical technique. This study further investigates hydrogenation of itaconic acid (IA), one of the major biomass feedstocks, to methylsuccinic acid (MSA) using (photo)electrochemically *in situ* generated H_2 and Rh based homogeneous catalyst. Although Pt can heterogeneously reduce IA to MSA, its production rate dropped within one hour most likely due to the passivation of the active sites (Fig. 1b). In the presence of Rh catalyst, MSA was continuously produced highlighting the great advantage of the present coupled catalytic approach. Solar-driven upgrading from IA to MSA has been successfully demonstrated using either $BiVO_4$ photoanode or GaInP/GaAs/Si tandem photovoltaic cell.

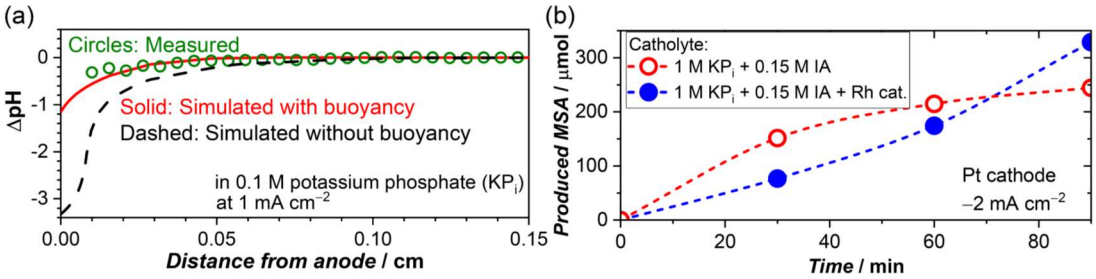

Figure 1 (a) Measured and simulated pH profile close to the anode. (b) Time course of MSA production during chronopotentiometry using Pt cathode.

1) M. R. Singh, et al., *Energy Environ. Sci.* **2015**, *8*, 2760. 2) K. Obata, *et al.*, *Energy Environ. Sci.* **2020**, *13*, 5104.