Supporting information for: The Impact of Electrocatalyst Activity and Ion Permeability on Water-splitting Photoanodes

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Experimental

Sample Fabrication

Preparation of n-TiO₂ substrates was based on the method used by Finklea.^{S1} Single crystal (100)-oriented n-TiO₂ substrates (MTI) were diced into squares 5 mm in length, cleaned in hot piranha (1:3 H₂O₂ to concentrated H₂SO₄ by volume) for 20 min, and doped n-type by annealing at 750 °C for 2 h under 15 sccm of 5% H₂ / 95% N₂. The doped n-TiO₂ substrates were then etched for 1 h in conc. H₂SO₄ heated to 260 °C on a hot plate.

Precursor solutions for thermal deposition of dense metal oxide catalysts were made by dissolving $Ni(NO_3)_2 \cdot 6H_2O$ (98%, Alfa-Aesar); $Co(NO_3)_2 \cdot 6H_2O$ (98+%, Sigma-Aldrich); $Fe(NO_3)_2 \cdot 9H_2O$ (Mallinckrodt analytical grade); and $IrCl_3 \cdot xH_2O$ (99.9%, Strem Chemicals) in ethanol at a concentration of 0.05 M for Ni, Co, Fe, and 0.025 M for Ir. Triton X-100 (J.T. Baker) was added to give 0.15 g Triton per mmol of metal ions. The precursor solution was spun-coat (3000 rpm, 30 s) onto n-TiO₂ or conductive substrates. The coated substrates were then annealed in air on a hot plate at 300 °C for 3 min to decompose the precursor into metal oxide film.^{S2} An ohmic contact was made to the back side of $n-\text{TiO}_2$ substrates using In-Ga eutectic and Sn-Cu wire or the edge of conductive substrates

using Ag paint and Sn-Cu wire. Epoxy (Loctite Hysol 1C) was used to cover the contact and attach the substrate onto one end of a 3.5 mm diameter glass tube such that the contact wire ran inside the tube and out of the other end.

Solutions for electrodeposition of ionpermeable Ni, Co, and Fe catalyst films were prepared by dissolving $NiSO_4$, $Co(NO_3)_2$, and $FeCl_2$ in 18.2 M Ω cm nanopure water to achieve a concentration of 0.1 M. The pH of the NiSO₄ solution was subsequently adjusted to \sim 7 with 1.0 M NaOH. Ion-permeable catalyst films were then anodically deposited onto n- TiO_2 electrodes under 1 sun illumination by cycling the potential of the n-TiO₂ between -0.1 V and +1.0 V versus Ag/AgCl reference electrode at 10 mV/s until the maximum photocurrent decreased by about 10%. Carbon cloth was used as counter electrode for all film depositions. The $IrO_x \cdot xH_2O$ catalyst film was anodically deposited from a IrO_x nanoparticle solution (prepared following Nakagawa *et al.*^{S3}) in a similar fashion except a UV LED (Thorlabs, M365L2 365 nm) was used to achieve a maximum photocurrent density of about 10 mA/cm^2 . The deposition of ion-permeable catalyst films from the above solutions onto conductive substrates were carried out by passing a typical anodic current density of about 0.5 mA/cm^2 for 60 s except for the deposition of $IrO_x \cdot xH_2O$, which required passing a current density of at least 2 mA/cm² for 10 min. Although direct measurement of the thickness of electrodeposited hydrous EC films was not performed, the decrease of photocurrent after EC deposition was monitored to keep the film thickness comparable among different ECs. Scanning electron microscopy (Zeiss Ultra 55 at 5 kV) was used to examine film morphology.

The Fe-free KOH electrolyte was prepared according to an established purification method.^{S4} Multiple samples were fabricated and tested for each experiment and representative data is reported. We were able to use the same n-TiO₂ substrate for multiple catalyst depositions because all electrochemically deposited catalysts, except IrO_x , were cleaned off easily by soaking in 2 M HCl for 15 min. Other electrodes which had the same catalysts deposited showed similar results, independent of deposition sequence. Additional structural and compositional information regarding the ECs used in this study can be found in works previously published by our group and oth- $\mathrm{ers.}^{\mathrm{S2-S6}}$

Measurements

Photoelectrochemical measurements were conducted in a three-neck, flat-bottom fused silica cell containing $\approx 15 \text{ mL}$ of 0.1 M KOH solution (Fluka Analytical TraceSelect, > 30%, diluted with 18.2 M cm water) using either a Autolab PGSTAT302N or a Bio-Logic SP200 potentiostat. A solar simulator (Abet technologies, model 10500, calibrated to 1 sun at the sample surface in the solution) was used to illuminate the n-TiO₂ photoanode via the flat bottom surface of the three-neck cell. A Pt coil was used as the counter, and the reference was either Hg/HgO filled with 0.1 M KOH (CH instruments) or a saturated calomel electrode (Fisher Scientific). The solution was stirred using a magnetic stir bar and sparged with pure O_2 . Unless stated otherwise, all potentials reported were referenced to the thermodynamic redox potential of OER at pH = 13 (E_{OER}), calculated using the Nernst equation with 0.1M OH⁻ and 1 atm O₂.

Impedance data modeling

Impedance data (|Z| and phase angle θ) were modeled using the EC-Lab software (v10.38, Bio-Logic Science Instruments) with a simple $R_s + R_p/C_p$ circuit to extract the apparent junction capacitance values at various applied potentials to construct the Mott-Schottky plots. Although impedance data were typically recorded over a frequency range of 100 Hz–100 kHz, only the region dominated by capacitive response was fitted to obtain Mott-Schottky data. An example of the original and fitted data is shown in Figure S1. Better fits of the impedance data could be obtained by increasing the complexity of the equivalent circuit. However, the interpretation of the results inevitably becomes more ambiguous with increased number of elements in the equivalent circuit. Because we were only interested in extracting the SC depletion region capacitance, fitting only the portion of data that exhibits strong purely capacitive behavior (phase angle -90°) allows us to use a the simplest and least-ambiguous equivalent circuit.

Due to possible complication from surface states and deep impurity states, slight changes in the slope of Mott-Schottky plots for *n*-TiO₂ electrodes are typically observed when a wide range of bias voltage is used. The slope variation increases the uncertainty of extracted $V_{\rm fb}$, therefore, for consistency we fit data points only from reverse biases (positive versus $E_{\rm OER}$) where the Mott-Schottky plots are linear to obtain $V_{\rm fb}$ values.

$V_{\rm fb}$ shift upon repeated EC deposition/cleaning

A general trend of cathodic shift in the apparent $V_{\rm fb}$ was observed when the *n*-TiO₂ electrode (with or without EC) undergoes repeated catalyst deposition/cleaning cycles. Data in Figure S2 shows that the order of catalyst deposition did not substantially affect the trend in $V_{\rm fb}$ with deposition/cleaning cycle.



Figure S1: A typical set of original impedance data collected during Mott-Schottky measurement (symbols) compared to the results of three-element (R-C/R) fit (lines). (a)–(d): results from samples with thermally deposited Co, Fe, Ir, and Ni catalyst, respectively. (e)–(h): results from samples electrodeposited Co, Fe, Ir, and Ni catalyst, respectively.

Ion permeability of electrodeposited EC films

We note the following lines of evidence that indicate the electrodeposited catalysts are ionpermeable. For Ni(Fe)OOH it has been demonstrated that all Ni sites are redox active, i.e. accessible to the electrolyte.^{S2,S4} Electrolyte accessibility is required for redox activity since ionic charge must compensate electronic charge associated with faradaic reactions. To provide further evidence of ion permeability for electrodeposited ECs, we conducted additional electrochemical impedance spectroscopy experiments to monitor the change of Au surface double layer capacitance before and after the electrodeposition of Ni, Fe, Co, and Ir catalysts. We found that as long as the Au substrate is held at a potential where Faradaic charging/discharging of the catalyst is minimized, the addition of Ni, Fe, and Co catalysts did not substantially change the apparent double layer capacitance (C_{dl}) of the underlying Au electrode (see Table S1).

Furthermore, C_{dl} was found to be independent of Ni(OH)₂ thickness (Figure S3). Since Ni(OH)₂, Co(OH)₂, and Fe(OH)₂ have previously been shown to be insulators, ^{S4,S5} one

Table S1: Apparent double layer capacitance of Au substrate with or without electrodeposited catalyst in 0.1 M KOH.





Figure S2: Changes in the extracted flat band potential $V_{\rm fb}$ in 0.1 M KOH of two *n*-TiO₂ electrodes – (a) and (b), with or without an ion-permeable catalysts on its surface. The data number indicates the sequential order of each Mott-Schottky measurement. Data from the same catalyst but deposited at different times were represented by the same color.

would expect C_{dl} of the EC-coated Au electrode to decrease (which was not observed) after the EC deposition if the films are impermeable to electrolyte. For the hydrous Ir catalyst, C_{dl} increased by a factor of four after EC deposition, due to the presence of redox capacitance over a wide range of the potential window. Murray and coworkers have also shown that all Ir sites in similarly prepared IrO_x nanoparticles are redox active and the entire electroflocculated film is microscopically accessible to electrolyte.^{S3,S6} These results support our assertion that electrolyte permeates throughout the electrodeposited EC film and makes direct contact to the underlying substrate.



Figure S3: Cyclic voltammogram of $Ni(OH)_2/NiOOH$ films of various thickness (deposition time) on Au substrate collected at a scan rate of 50 mV/s in 0.1 M KOH. The apparent double layer capacitance of each Au|EC electrode is also shown. The lack of correlation between EC film thickness and double layer capacitance suggest that EC film is completely ion permeable.

TiO_2 catalytic activity and carrier exchange with the catalyst layer

 TiO_2 is a very poor EC for water oxidation, as shown by experiment and theory (e.g. see Viswanathan and Norskov).^{S7} For 1 nm thick TiO_2 films (where lateral electrical transport through the TiO_2 is relatively fast) overpotentials of nearly 800 mV are required to pass 1 mA/cm^2 OER current. Illuminated n-TiO₂ is able to drive water oxidation efficiently because, given the large band gap, the hole quasi Fermi level, and thus surface potential of holes, is able to move very positive under illumination. At steady-state the hole quasi-fermi level in bare TiO_2 must be sufficiently anodic under illumination to drive the photocurrent (i.e., based on published data 800 mV more positive than the OER potential). However, if the surface is modified with a EC layer that has much faster kinetics than bare TiO_2 (as Fe, Ni, Co-based ECs all have - they pass 1 mA/cm² at < 400 mV overpotential), then, if the EC and SC surface exchange carriers relatively fast (which would be expected for two solid-state systems in direct contact) the catalysts will prevent the TiO₂ surface from reaching the very oxidizing potentials needed to drive OER on the bare TiO₂ and all the current will flow through the EC.

References

- (S1) Finklea, H. O. J. Electrochem. Soc. 1982, 129, 2003–2008.
- (S2) Trotochaud, L.; Ranney, J. K.; Williams, K. N.; Boettcher, S. W. J. Am. Chem. Soc. 2012, 134, 17253–17261.
- (S3) Nakagawa, T.; Beasley, C. A.; Murray, R. W. J. Phys. Chem. C 2009, 113, 12958–12961.
- (S4) Trotochaud, L.; Young, S. L.; Ranney, J. K.; Boettcher, S. W. J. Am. Chem. Soc. 2014, 136, 6744–6753.
- (S5) Burke, M. S.; Kast, M. G.; Trotochaud, L.; Smith, A. M.; Boettcher, S. W. J. Am. Chem. Soc. 2015, 137, 3638–3648.
- (S6) Nakagawa, T.; Bjorge, N. S.; Murray, R. W. J. Am. Chem. Soc. 2009, 131, 15578–15579.
- (S7) Viswanathan, V.; Pickrahn, K. L.; Luntz, A. C.; Bent, S. F.; Norskov, J. K. Nano Lett. 2014, 14, 5853–5857.