Electronic Supplementary Material (ESI) for Energy & Environmental Science

Electrochemical and Photoelectrochemical Investigation of Water Oxidation with Hematite Electrodes

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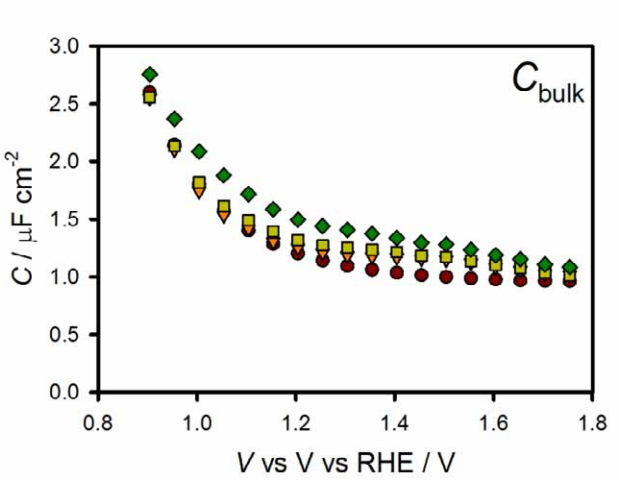
Supporting Information



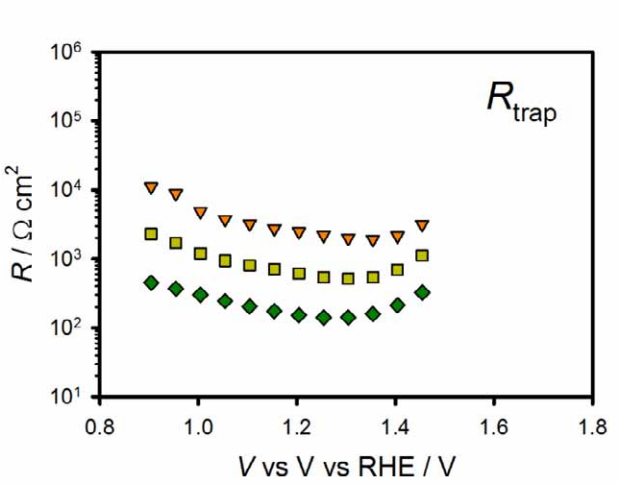


Figure S1. R_{trap} and C_{bulk} values fit from IS data of a hematite electrode in contact with a H_2O electrolyte in the dark (red circles), under 0.1 sun (orange triangles), 0.33 sun (yellow squares) and 1 sun (green diamonds) illumination.

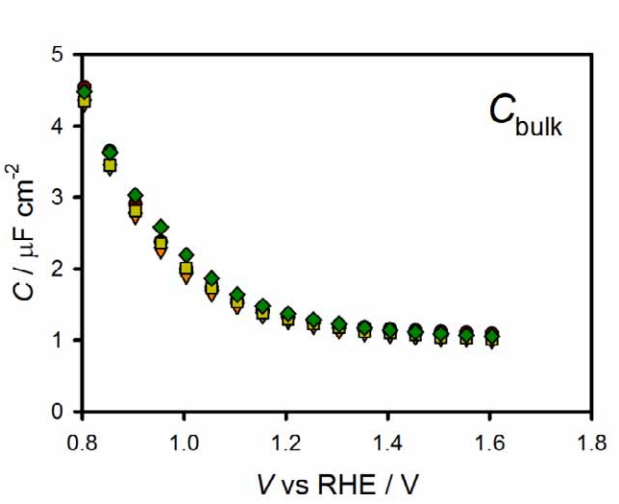


Figure S2. C_{bulk} values fit from IS data of a hematite electrode in contact with a $[Fe(CN)_6]^{3-/4-}$ electrolytes in the dark (red circles), under 0.1 sun (orange triangles), 0.33 sun (yellow squares) and 1 sun (green diamonds) illumination.

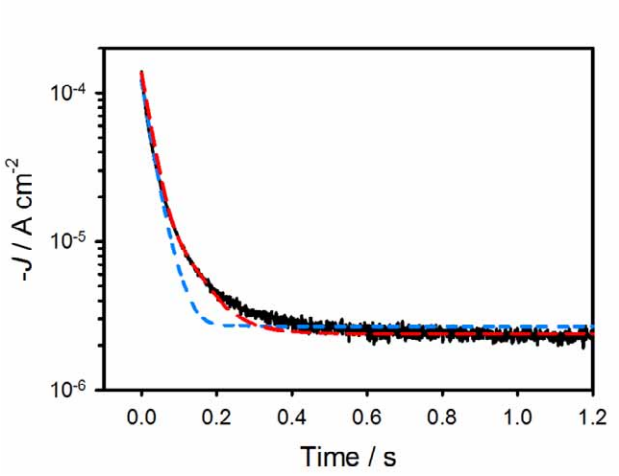


Figure S3. Experimentally measured decay measured at 1.2 V vs RHE (black line) and fits for a single exponential decay (blue small dashed line) and double exponential decay (red long dashed line)

The charge measured by the current transients can be related to C_{SS} by the equation $C_{SS} = \frac{Q}{\Delta V}$ where ΔV is the change in the quasi-Fermi level as a result of turning the light off at a constant potential. Since the surface states probed by IS and transients are expected to be the same, ΔV can be calculated by plotting C_{SS} from EIS vs Q measured from the transients. The inverse of the slope would thus be ΔV. ΔV was found to be 0.07 , 0.13 and 0.16 V for 0.1, 0.33 and 1 sun respectively. This corresponds to an increase of 92 mV per 10 fold increase in light intensity (inset of figure S4).

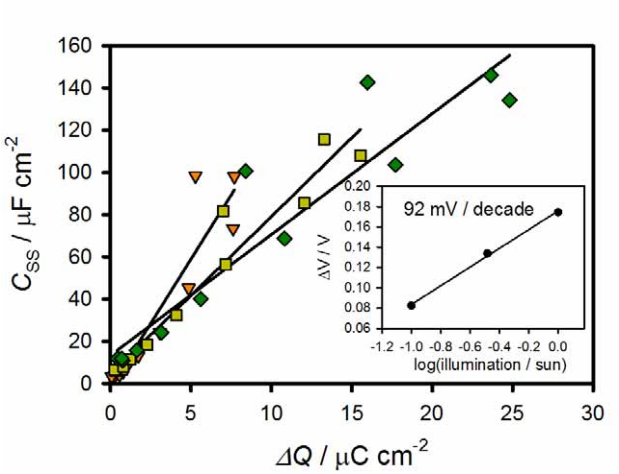


Figure S4.C_{SS} from EIS vs Q from transients for a given potential measured under 0.1 Sun (orange triangles), 0.33 sun (yellow squares) and 1 sun (green diamonds) illumination. Insert shows the slopes of C_{ss} vs Q (ΔV) as a function of log(illumination).

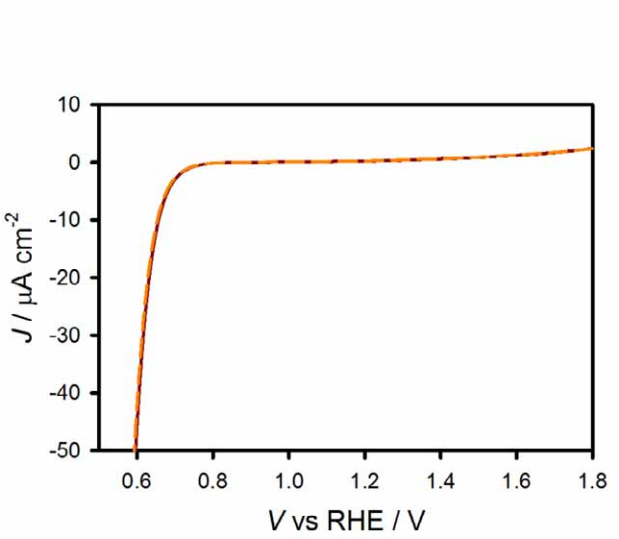


Figure S6. Cyclic voltammetry of hematite in $[Fe(CN)_6]^{3-/4-}$ electrolyte scanned at 200 mV s^{-1} after holding the electrode at a potential of 2 V vs RHE for 60 seconds under 1 sun illumination. The first cycle (solid red line) and the second cycle (dashed orange line) are overlapping.

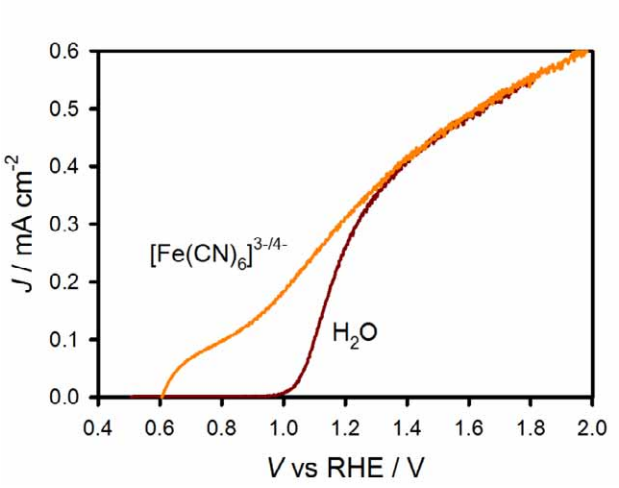


Figure S7. *J-V* curve measured for a hematite electrode in a $[Fe(CN)_6]^{3-/4-}$ electrolyte (orange curve) and in a H_2O electrolyte (red curve). The H_2O curve has been shifted by 200 mV to overlap with the $[Fe(CN)_6]^{3-/4-}$ curve.

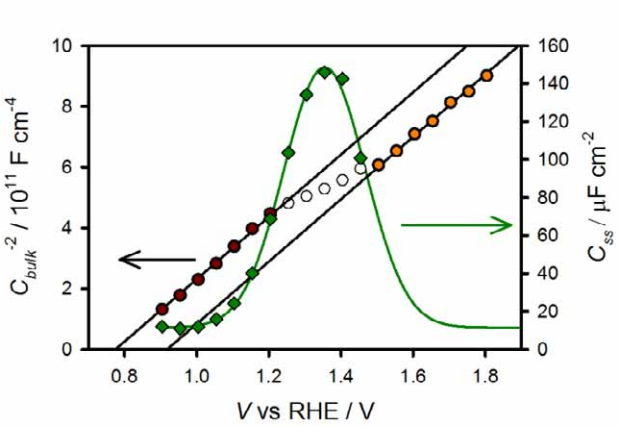


Figure S8. Mott Schotty plot made from C_{bulk} values measured under 1 sun illumination. The lines represent lines of best fit of the points measured at potentials negative (red circles) and positive (green circles) of the shift in the flat band. The white circles were not used in either fit. Both sets of data were made to share the same slope in the fit. Using this method, the shift in flat band potential is calculated to be 140 mV. Also included is the C_{ss} measured under one sun illumination (green diamonds) and the Gaussian fit (green line).