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Electronic Supporting Information (ESI) for

Efficient Oxygen Evolution on Hematite at Neutral pH Enabled by Proton-Coupled Electron Transfer

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Contents

ESI. 1 Experimental methods

Electrode Preparation. Hematite (α-Fe_2O_3) electrodes were prepared by following the procedure reported previously. An $Fe(OH)_3$ colloidal solution was synthesized by adding 20 mL of 1 M ferric chloride ($FeCl_3 \cdot 6H_2O$, Kanto Kagaku, > 99.0%) solution dropwise to 230 mL of boiling water while vigorously stirring. After boiling for 10 min, the solution was allowed to cool to room temperature and was then dialyzed for 2 days to remove chloride ions. The thus-prepared $Fe(OH)_3$ solution was diluted and then sprayed onto a clean conducting glass substrate (FTO-coated glass, resistance 20 Ω/square) fixed on a 250 °C hot plate using an automatic spray gun. The red film that formed on the substrate was thoroughly rinsed with pure water and then calcinated at 500 °C in air for 2 h.

Electrochemical Measurement. Polarization curves were obtained with a commercial potentiostat and potential programmer (HZ-5000, Hokuto Denko) using a platinum (Pt) wire as the counter electrode and a silver/silver chloride electrode (Ag/AgCl/KCl (sat.)) as the reference electrode. The electrolyte solution (0.1 M sodium sulfate (Na_2SO_4)) was prepared by dissolving Na_2SO_4 (Kanto Kagaku, > 99.0%) in highly pure Milli-Q water (18 MΩ·cm), and the pH was adjusted using 0.5 M sulfuric acid (H_2SO_4, Kanto Kagaku, > 99.0%) and 1 M sodium hydroxide (NaOH, Kanto Kagaku, > 99.0%). No reagent for pH buffering was added to the electrolyte solution to avoid any effect of the adsorption of multivalent anions. The prepared electrolyte was bubbled with argon (Ar) gas prior to the measurement. To minimize changes in the pH near the electrode surface, the polarization curve was measured by performing a potential sweep from negative to positive. The concentration of O_2 dissolved in the electrolyte solution was monitored simultaneously with the polarization curve measurements using a needle-type oxygen microsensor (Microx TX3-trace, PreSens). A gas chromatograph equipped with a TCD detector (GC-8A, Shimadzu) was used to monitor the amount of oxygen in the head-space of electrochemical reactors. Pyridine and its derivatives were obtained from Kanto Kagaku, and isotopic reagents (D_2O, D_2SO_4, and NaOD for pD adjustment) were purchased from Sigma-Aldrich.

ESI. 2 Effects of proton acceptors on the onset potential at an alkaline pH

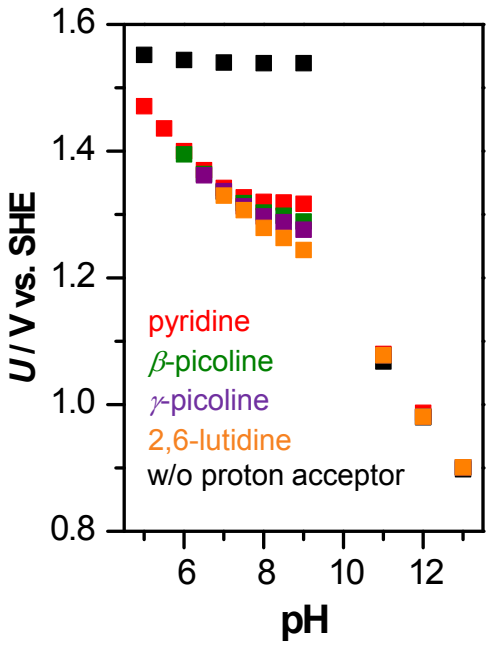

Fig. S1 Plots of pH versus potential showing the pH dependence of the onset potential for oxygen evolution, defined as the potential at a current density of 100 μAcm^{-2} in the presence of the pyridine derivatives at pHs ranging from 5 to 13.

ESI. 3 Comparison of the effect of pyridine on polarization curves measured under neutral and alkaline pH conditions

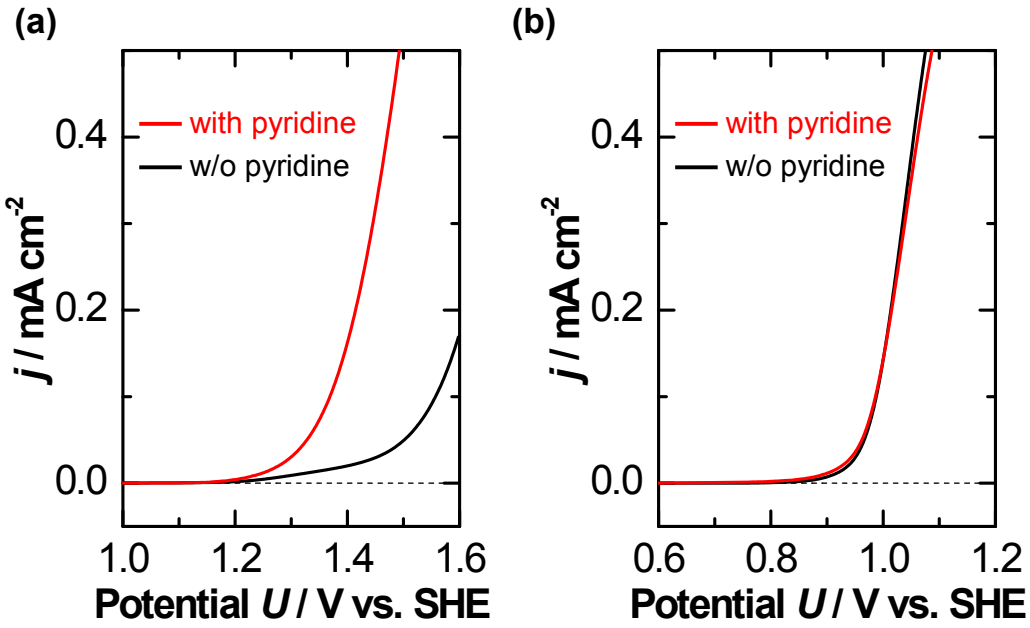

Fig. S2 Polarization curves of α-Fe_2O_3 electrodes measured at (a) pH 7 and (b) pH 13 (red line: with pyridine, black line: without pyridine).

ESI. 4 Polarization curves measured to examine the KIE effect

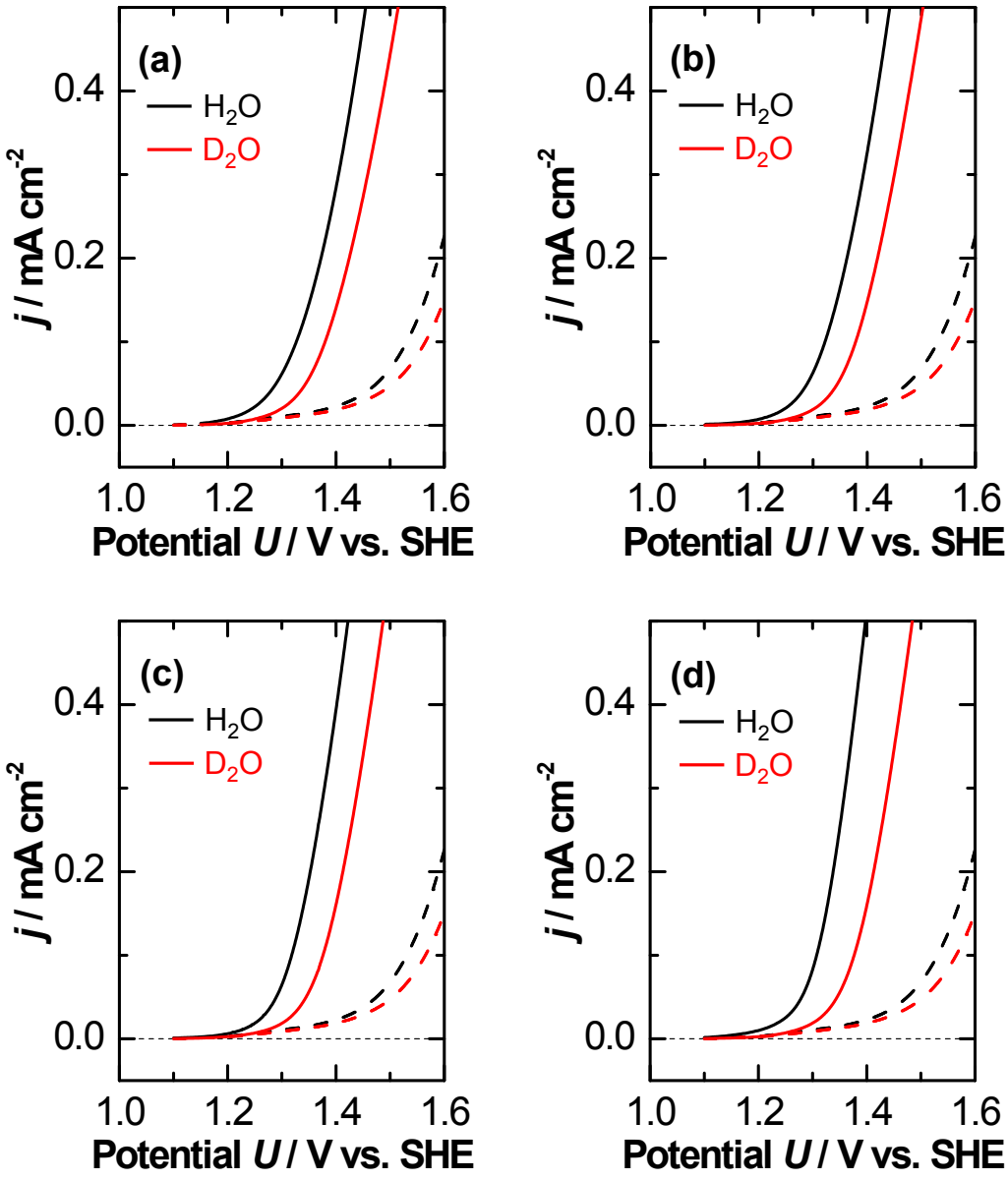

Fig. S3 Polarization curves of α-Fe_2O_3 electrodes measured to examine the KIE effect (black line: H_2O, red line: D_2O). The measurements were conducted at pH (pD) 7 in the presence of (a) pyridine, (b) β-picoline, (c) γ-picoline, and (d) 2,6-lutidine. Polarization curves measured without a proton acceptor (dashed lines) were also shown for reference.