Supporting Information for

Sulfide Electrolyte Additive Enables Multi-Ionic Transfer Pathways in the Alkaline Iron Redox

Divakar Arumugam,[a] AM Milinda Abeykoon,[b] Gihan Kwon,[b] Cheng-Hung Lin,[b] Lihua Zhang,[c] and Xiaowei Teng*[a]

a Department of Chemical Engineering, Worcester Polytechnic Institute, Worcester, Massachusetts 01609, United States
b National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, New York 11973, United States
c Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973, United States

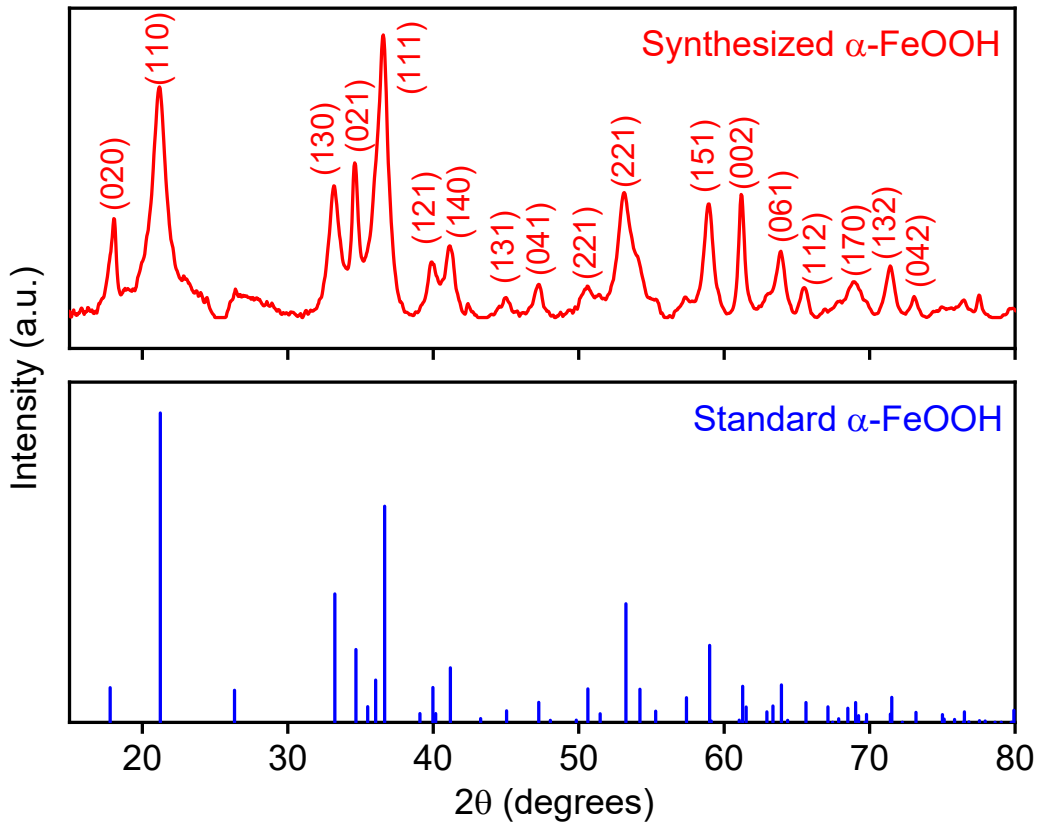

Figure S1. Structural characterization of as-made iron oxide. XRD analysis of as-made iron oxide shows a pure phase of α-FeOOH.

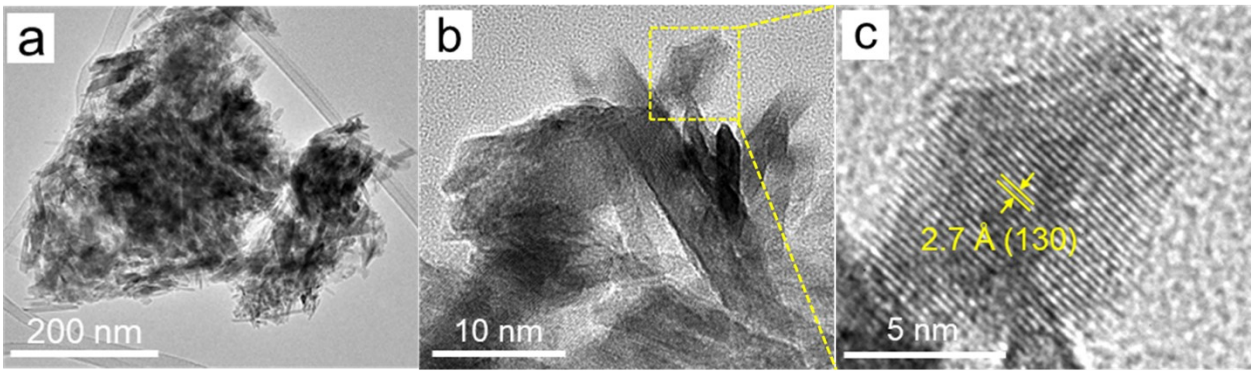

Figure S2. TEM characterization of as-made α-FeOOH. (a) Low-mag and (b, c) high-mag images of α-FeOOH materials.

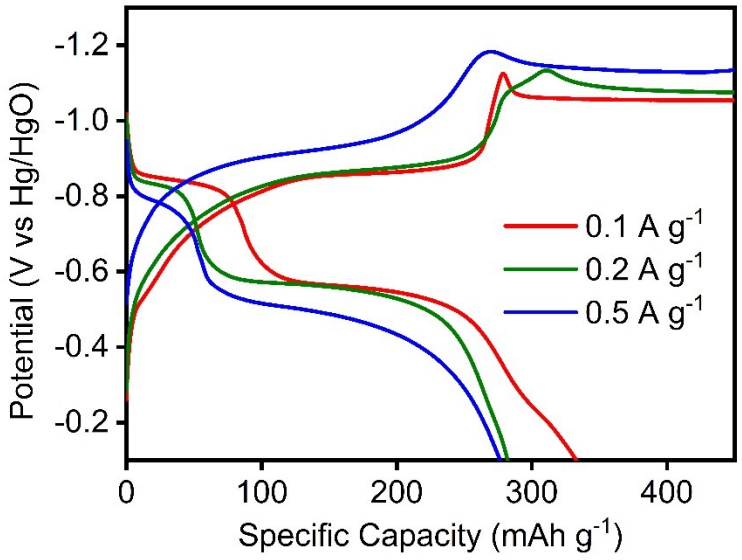

Figure S3. Effect of current density on Fe redox assessed by CP measurements. Discharge capacity of Fe^{2+}/Fe^{3+} redox in NaOH/Na_2SiO_3/Na_2S electrolytes increases from 276, 281, to 330 mAh g^{-1} as the current densities decrease from 0.5, 0.2 to 0.1 A g^{-1}.

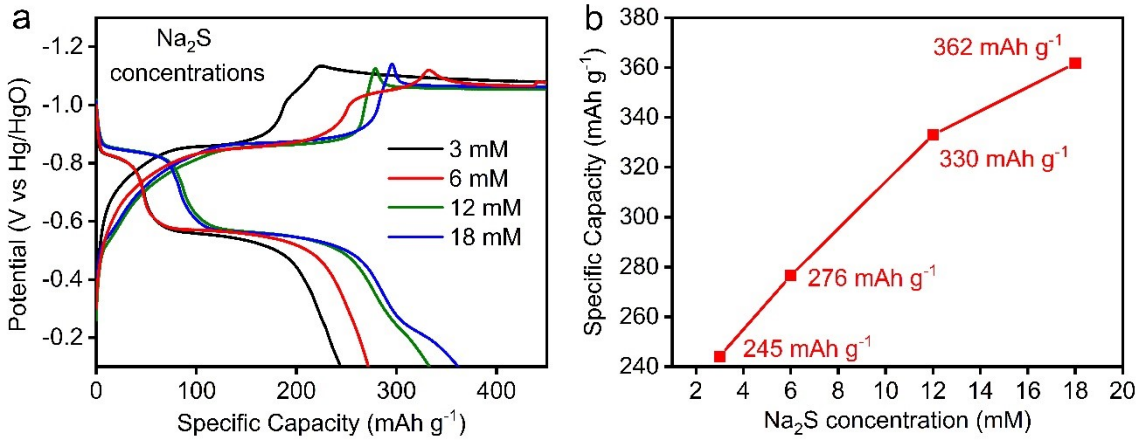

Figure S4. Effect of Na_2S additive on Fe redox assessed by CP measurements. Discharge capacity of Fe^{2+}/Fe^{3+} redox increases proportionally with Na_2S concentration in the low-concentration range, where additional increases in Na_2S have less significant contribution.

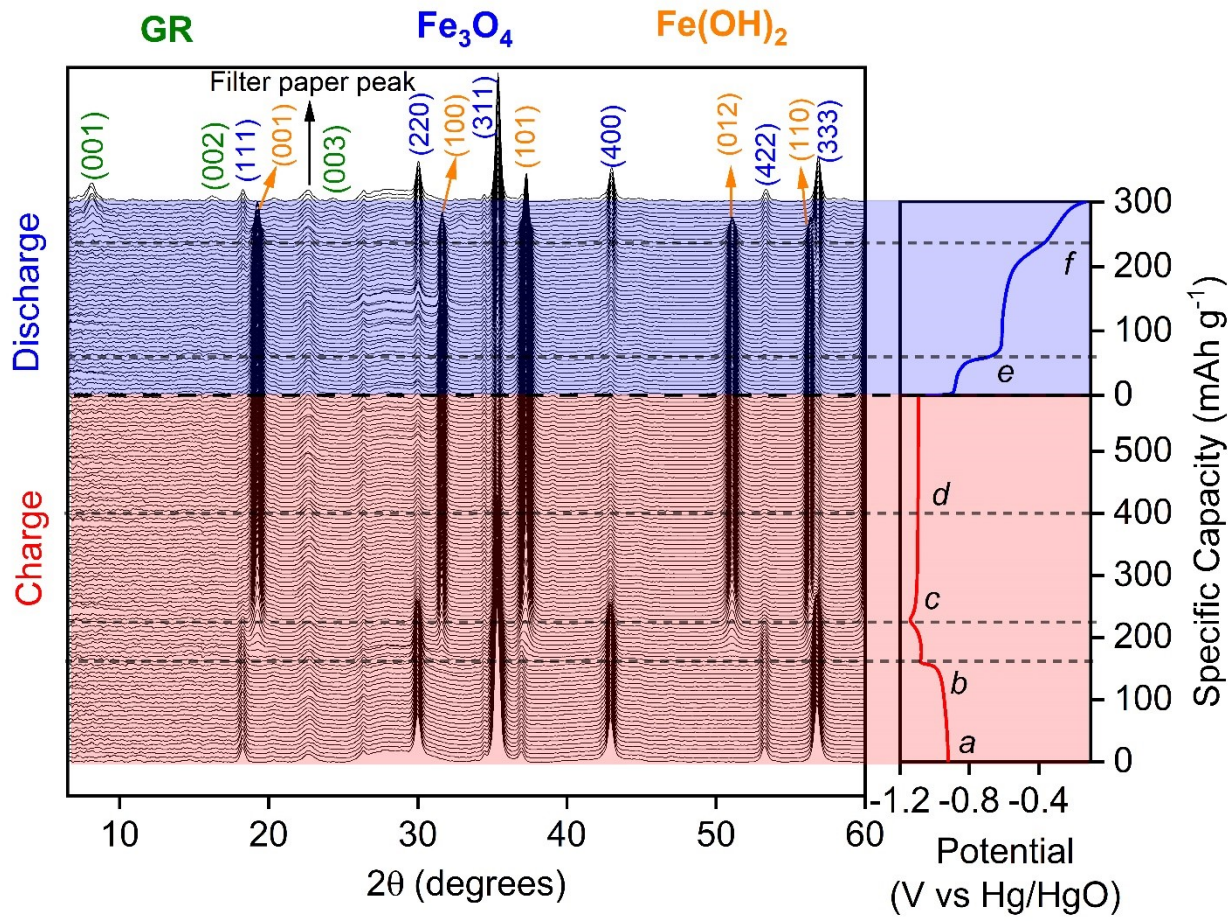

Figure S5. Stacked waterfall plots of *operando* XRD patterns acquired simultaneously with CP measurements at 0.1 A g^{-1} in NaOH/Na_2SiO_3/Na_2S electrolyte.

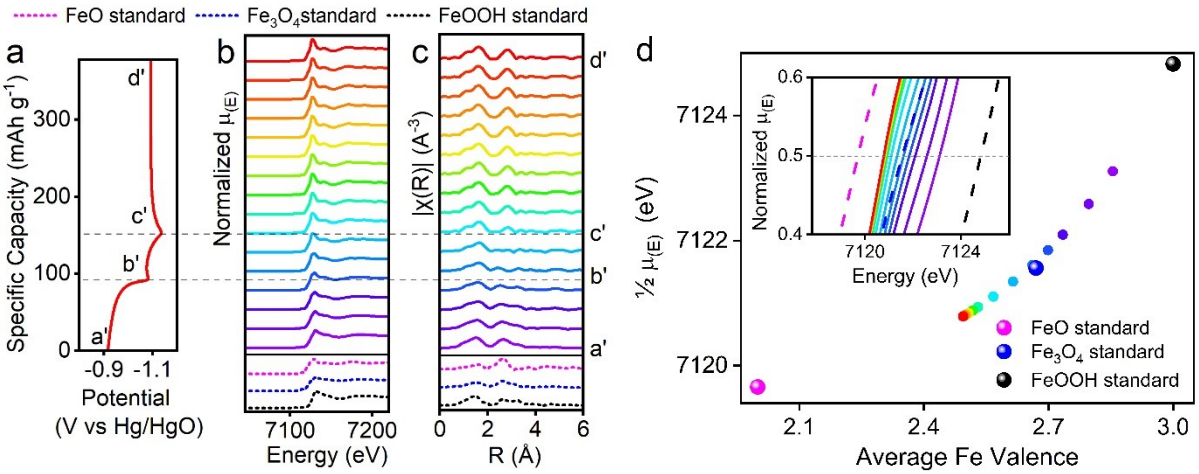

Figure S6. Operando XAS measurements in NaOH/Na_2SiO_3/Na_2S electrolyte. (a) CP measurement conducted at 0.2 A g^{-1}, waterfall plots of (b) Fe–K edge XAS spectra in energy-space (c) FT of XAS spectra in R-space and (d) Fe valence evolution compared with reference iron samples with defined valences. Zoom-in XAS spectra at 1/2 $\mu_{(E)}$ are shown in the inset.

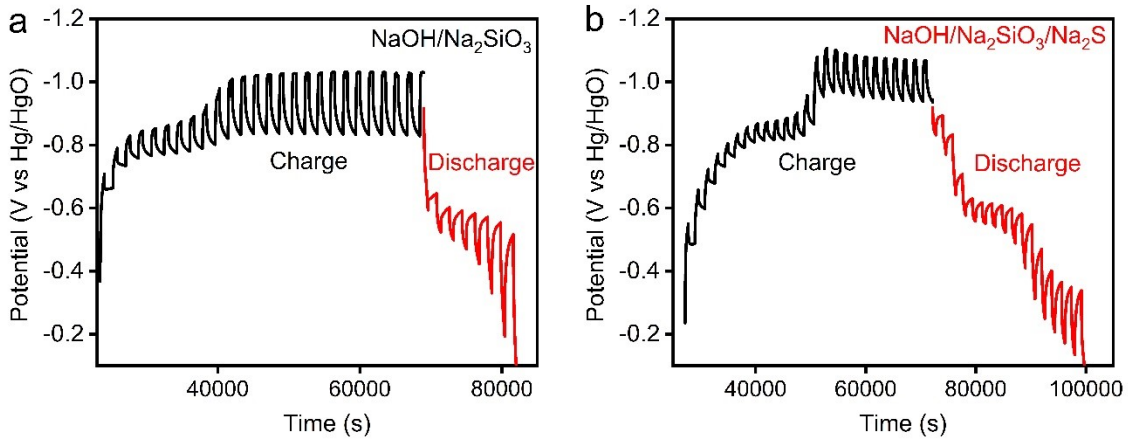

Figure S7. GITT tests conducted at 0.1 A g^{-1} in (a) NaOH/Na_2SiO_3 and (b) NaOH/Na_2SiO_3/Na_2S electrolytes.