Electronic Supplementary Information

Oxygen-evolution reaction in the presence of cerium(IV)

ammonium nitrate and iron (hydr)oxide: Old System, new findings

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Material and methods

All reagents and solvents were purchased from commercial sources and used without further purification. Milli-Q water (18-20 MQ \bullet cm⁻¹ at 27 °C) was used for the experiments.

Fe(III) oxide (FeO_xH_y): It was prepared by the reaction of $Fe(ClO_4)_3$ (10 mL, 0.01 M) and KOH (10, 0.10 M) solution under a stirrer (300 rpm). The solid was centrifuged, washed with water (5 × (10 mL)), and dried at 60 °C.

Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectrometry (EDX): Surface morphology and elemental composition of the sample were characterized by a TESCAN MIRA3 XMU SEM equipped with an Oxford Instruments EDX detector. When placed inside the SEM chamber under vacuum conditions, powder samples can potentially become airborne and disperse. To prevent this, it is crucial to take appropriate measures during sample preparation. For larger quantities of powder, compression into a solid pill-like form is recommended. On the other hand, for smaller amounts, the powder should be dispersed in a volatile solvent and then carefully dropped onto a suitable substrate. This method minimizes the risk of the powder becoming airborne and ensures that the samples remain in place for accurate SEM analysis.

Raman Spectroscopy: Raman spectra are collected before, after, and during the operation at 25 °C. Raman spectra were collected by ATR3110-633 from Optosky Company (633 nm). The Raman spectra were performed by the software "OptoskySpectra" from Optosky Company.

Oxygen-evolution measurement: The measurement of oxygen evolution from aqueous solutions in the presence of CAN was conducted using an HQ40d portable dissolved oxygen meter connected to an oxygen monitor with a digital display. The reactor, placed in a water bath, was consistently maintained at a temperature of 25.0 °C. During a typical experiment, the instrument's readout was calibrated by comparing it to air-saturated distilled water that was continuously stirred using a magnetic stirrer within a sealed reactor. Once a stable baseline reading was established, the water in the reactor was substituted with CAN. Under these experimental conditions, without the presence of a catalyst, CAN remained stable, and no oxygen evolution was observed. Following the removal of dissolved oxygen from the CAN solution using argon, specific compounds were introduced, and the subsequent oxygen evolution was measured using the oxygen meter while stirring the solution. The generation of oxygen occurred, and the rates of oxygen formation per iron site were determined by fitting the data with linear regression analysis.

Electron Paramagnetic Resonance (EPR): The EPR measurements were carried out using a Bruker EMX spectrometer working at a fixed frequency of 9.38 GHz (X-band). A 100 kHz magnetic field modulation and phase-sensitive detection were used to record the derivative of the absorbed microwave power.

X-ray absorption spectroscopy (XAS): Fe K-edge XAS measurements were performed on FeO_xH_y and CAN/FeO_xH_y along with the references of Fe-foil, FeO, and Fe₂O₃ at 1D KIST-PAL beamline in Pohang Accelerator Laboratory (PAL), South Korea. The electron storage ring at Pohang Light Source was operated in top-up mode at an energy of 3 GeV with a beam current of 250 mA. Si (111) double crystal monochromators were used to select energy from a broad range of

energies 4 to 16 keV with an energy resolution of 10⁻⁴. All the data were collected at room temperature using fluorescence mode. The as-obtained XAS data are processed using the Athena program and extended X-ray absorption fine structure (EXAFS) simulations are carried out using the Artemis program.¹ The EXAFS simulation is carried out in the ranges of 3 Å⁻¹ \leq k \leq 9 Å⁻¹ and 1 Å \leq R \leq 3 Å.



Figure S1 SEM images of FeO_xH_y prepared by the reaction of $Fe(CIO_4)_3$ and KOH solution at different magnifications.



Figure S2 EDX spectrum of FeO_xH_y prepared by the reaction of $Fe(ClO_4)_3$ and KOH solution.



Figure S3 UV-VIS spectra of the mixture of K_2 FeO₄ (0.6 mg, 3 mL) and 1-10 μ L CAN (0.10 M).



Figure S4 Oxygen evolution in the reaction of K_2FeO_4 (1.25 mM) with water (40 mL, pH \approx 6) (a). Oxygen evolution in the reaction of K_2FeO_4 (0.5 mM) with an acidic solution (40 mL, pH \approx 1 (HNO₃)) (b). Oxygen evolution in the reaction of K_2FeO_4 (0.5 mM) with CAN (40 mL, 0.10 M) (c).



Figure S5 Raman spectrum of Fe_2O_3 (blue) and in situ Raman spectra of Fe_2O_3 (red) in the presence of CAN (0.20 M) during the time.



Figure S6 Raman spectrum of Fe_2O_3 (blue) and in situ Raman spectra of Fe_2O_3 (red) in the presence of water during the time.



Figure S7 OER in the presence of FeO_xH_y (50 mg) and CAN (0.10 M).

Reference

1. B. Ravel, M. A. Newville, J. Synchrotron Radiat. 2005, 12(4), 537-541.