

Supplementary information for

**Low temperature operation of the solid-oxide Fe-air
rechargeable battery using $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ oxide ion
conductor**

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Experimental

Modification of Fe powder with a catalyst was performed via two methods. When the catalyst was a single metal or metal oxide, an aqueous solution of metal nitrate or metal chloride (Cr: $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Co: $\text{Co}(\text{NO}_3)_2 \cdot 8\text{H}_2\text{O}$, Mn: $\text{Mn}(\text{NO}_3)_2 \cdot 8\text{H}_2\text{O}$, Ni: $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Cu: $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, Pd: PdCl_2 , Rh: $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, Pt: $\text{H}_2\text{PtCl}_6 \cdot 3\text{H}_2\text{O}$) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with an Fe:catalyst ratio of 95:5 atomic percent was evaporated and calcined at 873 K. When the catalyst was a mixed oxide ($\text{Ce}_{0.6}\text{Mn}_{0.3}\text{Fe}_{0.1}\text{O}_2$, $\text{La}_{0.9}\text{Sr}_{0.1}\text{Fe}_{0.8}\text{Mn}_{0.2}\text{O}_3$, or $\text{LaSr}_3\text{Fe}_3\text{O}_{10}$), Fe_2O_3 powder was mixed with the mixed oxide catalyst in an Fe:catalyst weight ratio of 95:5 by ball-milling (400 rpm for 2 h) of the combined powders in ethanol. Oxidation of Fe by steam was evaluated by TG-DTA (Thermo Plus 2, Rigaku). Before the TG-DTA measurements, Fe powder was inserted into a tube-type furnace, followed by reduction at 673 K for 3 h under 2.8 vol% $\text{H}_2\text{O}-\text{H}_2$ flowing at 50 ml/min. Five milligrams of the obtained reduced Fe powder was used in the TG-DTA measurement. The temperature was increased from room temperature to 1273 K at 20 K/min, with the sample under 2.8 vol% $\text{H}_2\text{O}-\text{N}_2$ flowing at 50 ml/min. Reduction of Fe by H_2 was evaluated by TGA (Cahn, thermocahn 2000). Flow rate of H_2 was 100 ml/min.

A schematic of the electrochemical cell used in this study is shown in Figure 1. A tubular cell was fabricated using an extruded LSGM tube (1 mm thickness, 13 mm diameter, 9.7 mm length, 12.9 ml volume; NGK SPARK PLUG Co., Ltd.) for cyclic electrochemical charge-discharge

measurements. Ni–Fe(9:1, vol.%) and $\text{Ba}_{0.6}\text{La}_{0.4}\text{CoO}_3$ (BLC) were painted on the inside and outside of the LSGM tube, respectively, as electrodes; the tube was subsequently calcined at 1373 K for 30 min (surface area of electrodes: 10 cm^2). Ni–Fe (90:10, w/w) was synthesized by loading $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ onto NiO in aqueous solution. The obtained powder was calcined in air at 873 K to decompose the nitrate and produce the oxides. BLC was prepared by the solid-state reaction method. Pt mesh and Pt wire were applied as a current corrector and lead wire, respectively. Thirty milligrams of Fe oxide powder was inserted into a small alumina tube fixed in the LSGM electrolyte tube, and the LSGM tube was then closed with epoxy resin, except for the stainless steel gas lines used as a gas inlet and outlet. After the cell was heated to 773 K, 100 ml/min of H_2 with 3% of H_2O was fed to the anode side to reduce the Ni–Fe electrode and Fe oxide powder. Air was also fed at 100 ml/min of into the cathode side, which was open to air. After the Ni–Fe anode and Fe powder were reduced for 1 h at 773 K, the cell was cooled to 673 K. The anode gas was then changed to dilute H_2 (initial gas composition before discharge: 87.3% Ar, 9.7% H_2 , and 3% H_2O), and the inlet and outlet valves were closed. Charge–discharge measurements were performed at a constant current of 1 mA (0.1 mA cm^{-2}) using the two-probe method. Impedance analysis was performed using a Solartron 1260/1287 impedance analyzer under open-circuit conditions; the measurements were performed in the frequency range of 0.1–100,000 Hz using an ac amplitude of 30 mV. The shape of the Fe powder particles was observed by scanning electron microscopy (Keyence VE-7800) and

FIB-SEM (FEI Versa 3D HiVac).

Supplementary figures

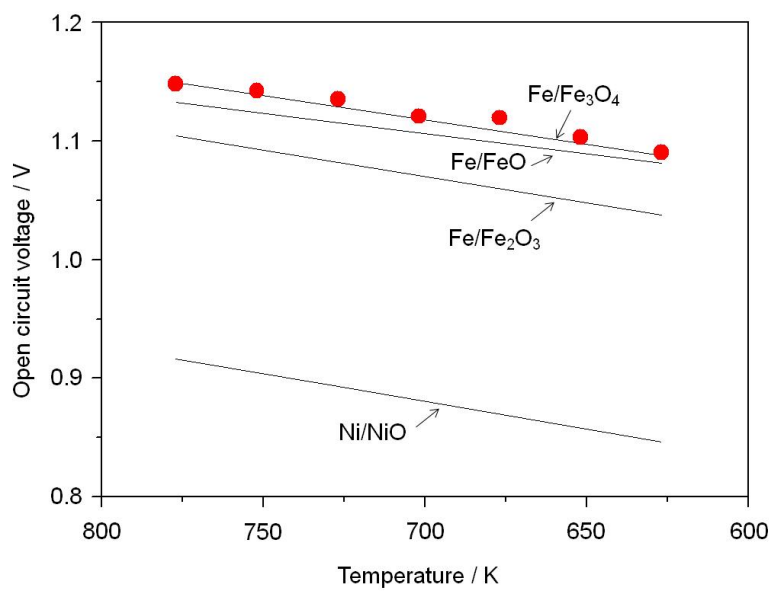


Figure S1 Observed open-circuit voltage of the Fe-air cell (dots). Lines indicate the theoretical EMF achieved by oxidation/reduction of various metals.

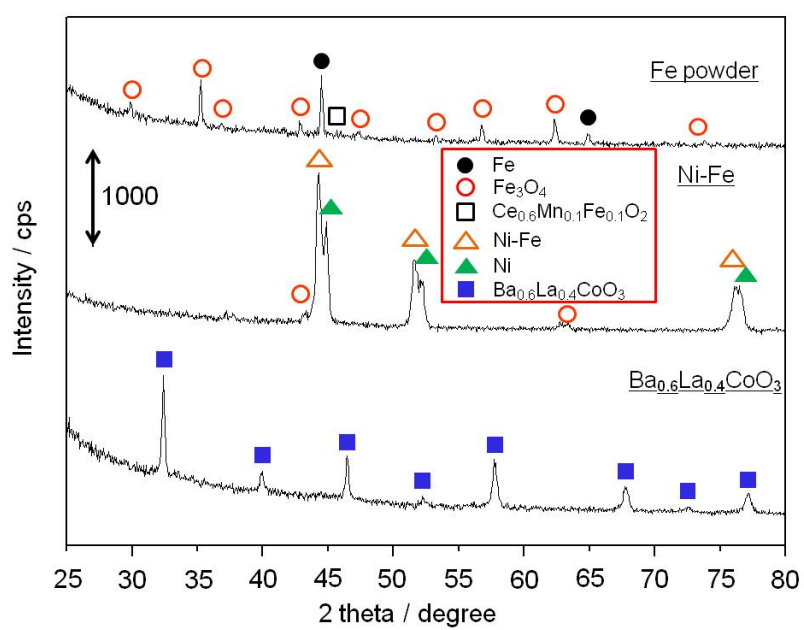


Figure S2 XRD patterns of the Fe-air battery components after the cycling test (after 21st discharge).

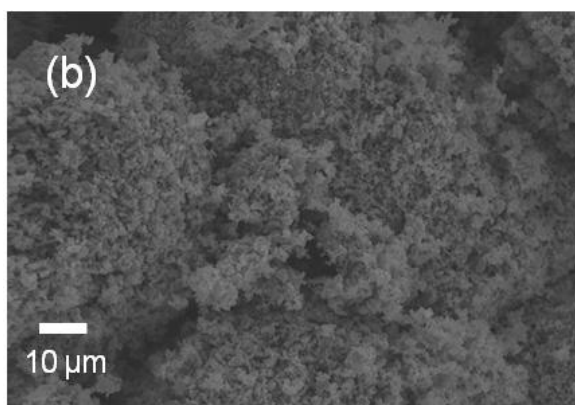
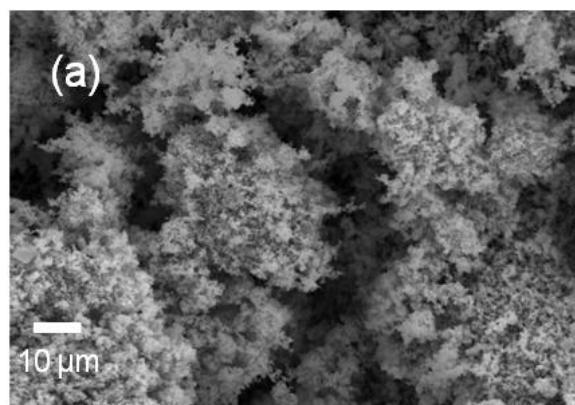


Figure S3 SEM images of Fe powder (a) before and (b) after charge–discharge cycling at 673 K.