Supporting Information

Bismuth ferrite: an abnormal perovskite with electrochemical extraction of ions from A site

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Full electrochemical processes:
Extracted Bi^{3+} reaction process:

$$Bi^{3+} + 3OH^- \rightarrow Bi(OH)_3, \quad \text{(S1)}$$

$$Bi(OH)_3 + OH^- \rightarrow BiO_2^- + 2H_2O, \quad \text{(S2)}$$

$$BiO_2^- + e \rightleftarrows BiO_2^{2-}, \quad \text{(S3)}$$

$$3BiO_2^{2-} + 2H_2O \rightleftarrows 2BiO_2^- + 4OH^- + Bi^{(0)}, \quad \text{(S4)}$$

$$Bi^{(0)} \xrightarrow{\text{deposite}} Bi_{(metal)}. \quad \text{(S5)}$$

$$Bi_{(metal)} \rightarrow Bi^+ + e, \quad \text{(S6)}$$

$$3Bi^+ \rightleftarrows Bi^{3+} + 2Bi_{(metal)}, \quad \text{(S7)}$$

$$Bi^{3+} + 3OH^- \rightarrow Bi(OH)_3, \quad \text{(S8)}$$

$$2Bi(OH)_3 \rightarrow Bi_2O_3 + 3H_2O. \quad \text{(S9)}$$

Iron oxide reaction process:

$$Fe(OH)_2 + 2e \rightleftarrows Fe + 2OH^-. \quad \text{(S10)}$$

Iron was found to disappear in the following scanning cycles, which should refer to the high concentration of OH^- and thus the production of iron was substantially suppressed. Alternatively, the major redox reaction based on Fe ions would be assigned as $Fe^{3+} \rightleftharpoons Fe^{2+}$ and the corresponding redox reaction in the following cycles is expected to be described as[1, 2]

$$Fe_2O_3 + 3H_2O + 2e \rightleftarrows 2Fe(OH)_2 + 2OH^-, \quad \text{(S11)}$$

$$3Fe(OH)_2 + 2OH^- \rightleftarrows Fe_3O_4 + 4H_2O + 2e. \quad \text{(S12)}$$

DFT calculations

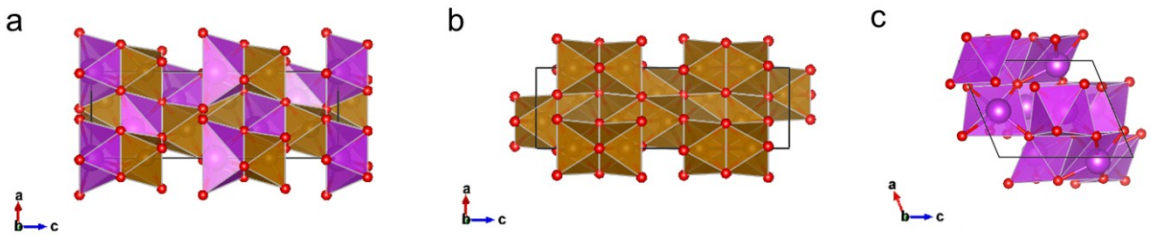

Figure S1 (a) Trigonal $FeBiO_3$ structure with a space group of R_3C. (b) Triclinic Fe_2O_3 structure with a space group of R_3C. (c) Monoclinic Bi_2O_3 structure with a space group of P21/C.

From an energetic point of view, the electrochemically driven bismuth evolution was considered according to the heat of enthalpy of the following reaction.

$$2FeBiO_3 = Fe_2O_3 + Bi_2O_3 \quad \text{(S13)}$$

The heat of enthalpy is calculated by the following equation:

$$\Delta H = E_{Fe2O3} + E_{Bi2O3} - 2E_{FeBiO3,} \quad \text{(S14)}$$

where E is the calculated total energy per f.u.

The $\Delta H = 285.378$ kJ mol^{-1} calculated by DFT is positive, showing that the bismuth evolution is a non-spontaneous process and the electrochemical process accounts for the evolution.

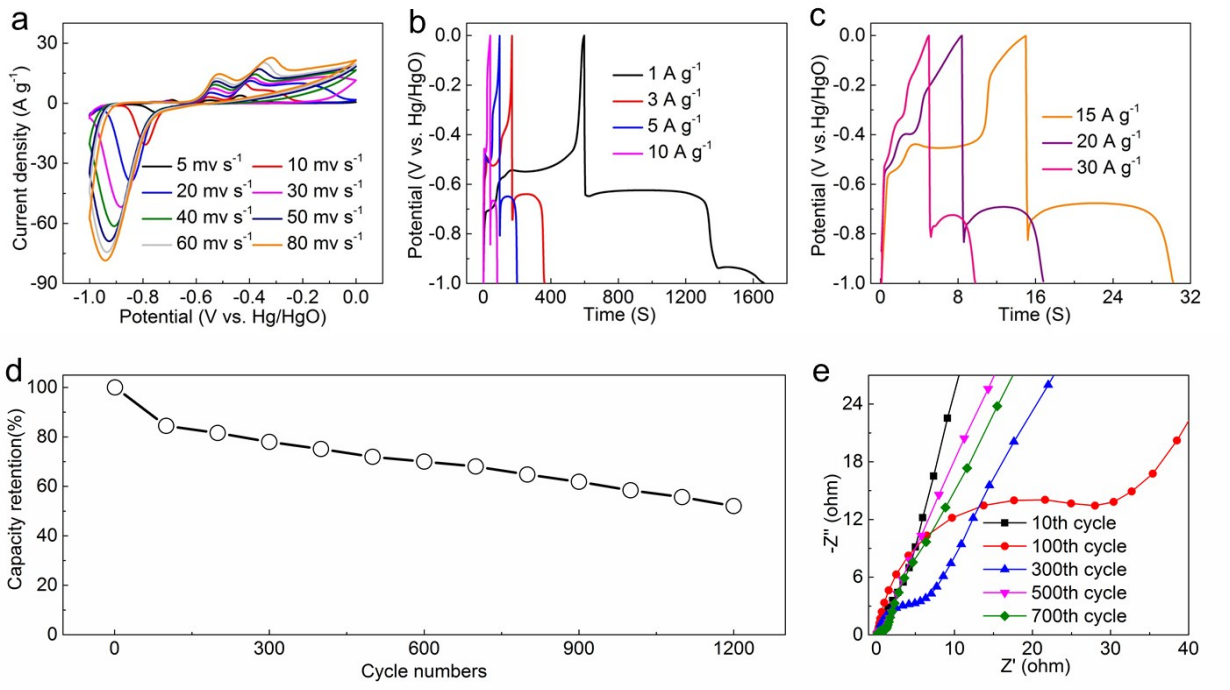

Figure S2 Electrochemical properties of as-prepared $BiFeO_3$ samples in three electrode systems: CV (a) and GCD (b-c) plots at various scan rates and current densities. (d) Cycling performances at current density of 5 A g^{-1}. (e) EIS curves of different cycle numbers.

To further investigate the electrochemical performance of $BiFeO_3$, CV, GCD, and EIS experiments were performed on a three-electrode test system, as presented in Figure S2. The CV curves display two oxidizing peaks and a reducing peak. The larger scan rates, the more incremental peak current densities, which indicate the good correspondence between electron and ion in the electrochemical reaction process (Figure S2 a). The GCD curves were shown Figure S2 b-c. It can be noted that as the current density increases, the time of the charge and discharge process decreases. This phenomenon was attributed to the fact that the diffusion of hydroxide cannot keep up with rapid potential changes, resulting in a decrease in the contribution of redox reactions.[3] The electrode of $BiFeO_3$ capacitor retention was not well. This was attributed to the fact $BiFeO_3$ micro-particles become nanoparticle during the phase decomposition process and a small amount of particles dissolve in the electrolyte (Figure S2 d). Figure S2 e displays EIS curves of different cycle numbers.

It can be found that the radius of the semi-circular arc largest of 100^{th} cycle, indicating that there is a large charge transfer resistance, which is due to the fact that the phase decomposition process produces more phase interfaces and increases the difficulty of charge transfer.[4]

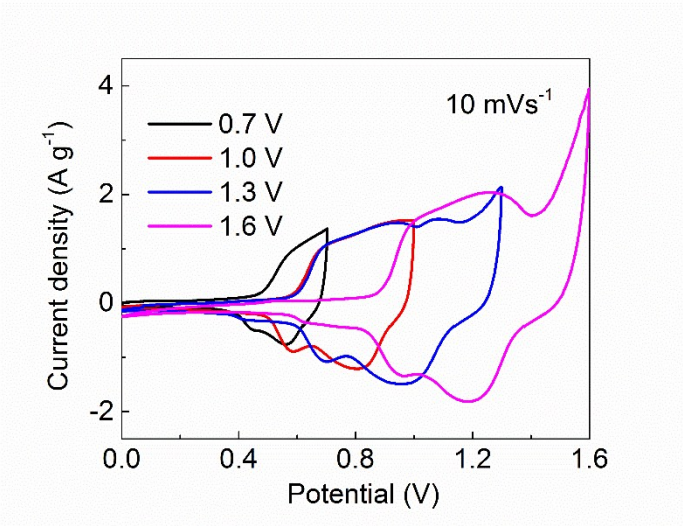

Figure S3 CV plots of hybrid electrochemical energy storage device at various potential windows in 6mol L^{-1} KOH aqueous solution at 10 mV s^{-1} scan rate.

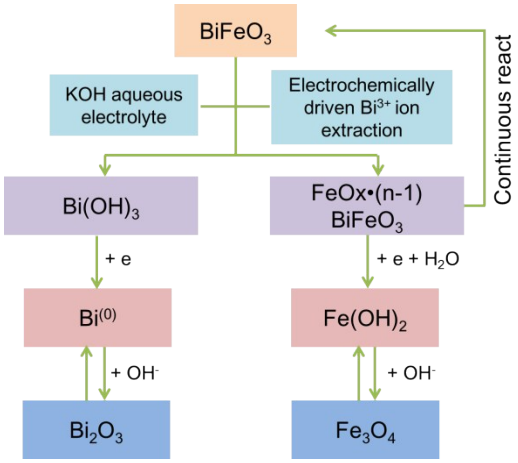

Figure S4 Evolution process of bismuth ion extraction from A site in BFO material.

In the process of electrochemical action, the Bi-O coordination bond is easily broken due to the strong polarity of the hydroxide to form bismuth hydroxide with the alkali aqueous solution. Singh et al. reported that the relative Gibbs free energy (0.19 eV/atom) of $BiFeO_3$ in aqueous media (PH=8.0) at 1.5 V (vs. RHE), and their decomposition products were Fe_2O_3 and Bi_4O_7 by the first-principles-based formalism[5]. Therefore, $Bi(OH)_3$ and FeO_x are further reduced. In the 6mol L^{-1} KOH alkaline water electrolyte, $Bi(OH)_3$ and $Fe(OH)_2$ would react with OH^- to form Bi_2O_3 and Fe_2O_3, respectively. The remaining part of $BiFeO_3$ undergo the same reaction processes, as shown in Figure S4.

Supplementary References

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[4] Y. Shao, M. F. El-Kady, C.-W. Lin, G. Zhu, K. L. Marsh, J. Y. Hwang, Q. Zhang, Y. Li, H. Wang and R. B. Kaner, *Adv. Mater*., 2016, **28**, 6719-6726.

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