Electronic Supplementary Information

Synergistic Effect of Multi-Electron Conversion and Anion Redox Media Chemistry for
High Performance Rechargeable Aqueous Zn Ion Batteries

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Experimental Section

Materials preparation: In a typical synthesis route, BiOI was prepared by dissolving Bi(NO$_3$)$_3$·5H$_2$O (1.5 mmol) into ethanol (20 mL) and kept stirring about 20 min. Next, the KI (1.5 mmol) was dispersed into distilled water (40 ml) with stirring in a separate glass beaker, then added to the aforementioned solution drop by drop. The PH value of the final solution was adjusted to 7 by using the ammonia solution (1.5 mol L$^{-1}$) before reacting in an oil bath at 80 °C for 3 h. In the end, the obtained precipitate was washed and collected with distilled water and ethanol, and then dried in vacuum at 60 °C overnight. The PAM gel electrolyte was prepared by adding 2 g acrylamide into 20 mL DI and stirring for 30 min, then 2 mg N,N-dimethyldiacrylamide and 10 mg potassium peroxodisulfate were dissolved into the above solution as cross-linking agent and initiator. The obtained solution was stirred for 60 min and vacuumized for a night, and then dried in vacuum at 60 °C for 4 h.

Materials characterization: Powder X-ray diffraction (XRD) is collected with PANalytical X’Pert PRO using Cu Kα radiation at room temperature. Thermogravimetric analysis measurement is implemented under air atmosphere with the temperature range from room temperature to 1000 °C. Scanning electron microscopy (SEM; Hitachi, SU 8010) and transmission electron microscopy (TEM; Talos F200X) are utilized to analyze the morphology and microstructure of the prepared bismuth oxyiodide, and cycled electrodes as well. The X-ray photoelectron spectroscopy (XPS, ESCLAB 250Xi) spectra are obtained to examine surface chemical component characterizations of the initial and electrochemical cycled materials.
**Electrochemical measurements:** All the electrodes were fabricated by traditional suspension coating method and carbon paper was as current collector, in which the active material (prepared BiOI powders), Super P (conductive agent), and polyvinylidene fluoride (PVDF; binder agent) were mixed with a mass ratio of 70:20:10, and then evenly dispersed in N-methyl-2-pyrrolidone (NMP) solvent as coating slurry. The fresh electrodes were dried at 60 °C in a vacuum oven and the mass loading of the synthesized BiOI powders was about 2~3 mg cm$^{-2}$. The CR-2032 stainless steel coin cells were used for electrochemical measurement, in which the BiOI electrode and Zn metal foil was as cathode and anode, the glass microfiber paper and filter membrane were served as separators, 1 M Zn(CF$_3$SO$_4$)$_2$ aqueous solution with 0.2 M ZnI$_2$ was employed as electrolyte. The assembled cells were tested on the Neware test system with the voltage range of 0.2-1.6 V. The cyclic voltammetry experiments were carried out on the CHI-660 electrochemical workstation.

**Computational method:** We have employed the Vienna Ab Initio Package (VASP)$^{[1,2]}$ to perform all the density functional theory (DFT) calculations within the generalized gradient approximation (GGA) using the PBE$^{[3]}$ formulation. We have chosen the projected augmented wave (PAW) potentials$^{[4,5]}$ to describe the ionic cores and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 400 eV. Partial occupancies of the Kohn-Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The electronic energy was considered self-consistent when the energy change was smaller than $10^{-5}$ eV. A geometry optimization was considered convergent when the force change was smaller than 0.02 eV/Å. Grimme’s DFT-D3 methodology$^{[6]}$ was used to describe the dispersion interactions.

The equilibrium lattice constants of hexagonal Bi unit cell were optimized, when using a 7×7×7 Monkhorst-Pack k-point grid for Brillouin zone sampling, to be $a=4.570$ Å, $c=11.715$ Å. It was then used to construct a Bi (001) sheet model with p (3×3) periodicity in the x and y directions and 1 stoichiometric layer (6 atomic layers) in the z direction separated by a vacuum
layer in the depth of 15 Å in order to separate the surface slab from its periodic duplicates. This Bi(001) surface model contains 54 Bi atoms. During structural optimizations, the gamma point in the Brillouin zone was used for k-point sampling, and the bottom half stoichiometric layer was fixed while the top half was allowed to relax.

The equilibrium lattice constants of tetragonal BiOI unit cell were optimized, when using a 10×10×4 Monkhorst-Pack k-point grid for Brillouin zone sampling, to be a=4.000 Å, c=9.011 Å. It was then used to construct a BiOI (001) sheet model with p (3×3) periodicity in the x and y directions and 1 stoichiometric layer in the z direction separated by a vacuum layer in the depth of 15 Å in order to separate the surface slab from its periodic duplicates. This BiOI (001) surface model contains 18 Bi, 18 O and 18 I atoms. During structural optimizations, the gamma point in the Brillouin zone was used for k-point sampling, and all atoms were allowed to relax.

The adsorption energy (Eads) of adsorbate A was defined as

\[ E_{ads} = E_{A/surf} - E_{surf} - E_{A(g)} \]

where \(E_{A/surf}, E_{surf}\) and \(E_{A(g)}\) are the energy of adsorbate A adsorbed on the surface, the energy of clean surface, and the energy of isolated A molecule in a cubic periodic box with a side length of 20 Å and a 1×1×1 Monkhorst-Pack k-point grid for Brillouin zone sampling, respectively.
Figure S1. The N$_2$ adsorption isotherm of BiOI.

Figure S2. The full XPS spectrum of BiOI.

Figure S3. The XPS spectrum of I 3d.
Figure S4. Rate performance with various electrolyte systems.

Figure S5. The CV curves of BiOI-ZnI$_2$ under various scan rates.

Figure S6. a) The polarization voltage at various scan rates; b) The CV curve of BiOI at 0.1 mV/s.
Figure S7. Cycling performance at 0.5 A/g.

Figure S8. (a) Charge/discharge curves and (b) cycling performance of BOI-ZI at 0.5 A/g with different electrolyte additive concentrations.

Figure S9. Raman spectrum under different discharge-charge stages.
**Figure S10.** The Nyquist plots of BiOI and BiOI-ZnI$_2$.

**Figure S11.** Cycling performance of Zn-BiOI battery at different operation temperature.

**Figure S12.** Electrochemical performance of quasi-solid-state Zn-BiOI battery under different bending degrees.
Figure S13. The photographs of LEDs lighted by quasi-solid-state batteries.

Reference


