Supporting Information

A novel rechargeable aqueous bismuth-air battery

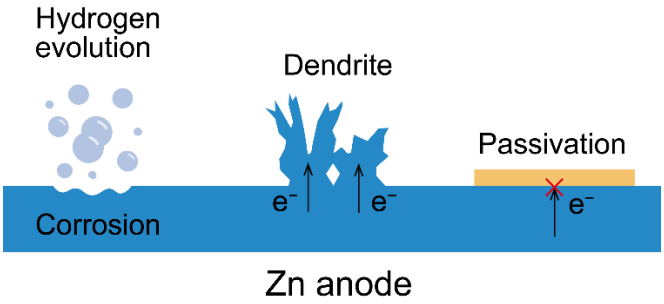

Figure S1. Scheme of repeated plating/stripping on Zn anode. The Zn anode suffers from a poor cycling stability in aqueous electrolytes due to H_2 evolution reaction, passivation layer formation (such as zinc hydroxides and zincates), and Zn dendrite growth.

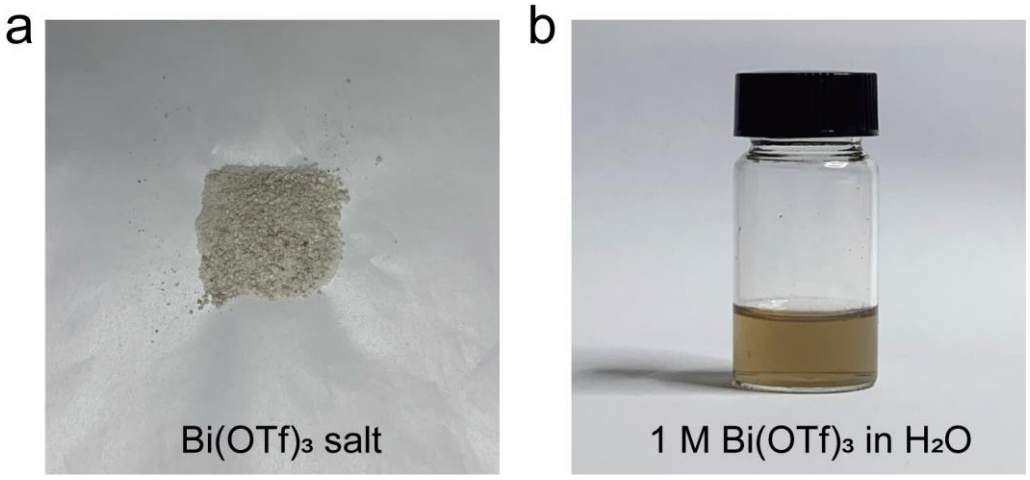

Figure S2. Photographs of (**a**) $Bi(OTf)_3$ salt and (**b**) 1 M $Bi(OTf)_3$ aqueous electrolyte.

Figure S3. The pH of 1 M $Bi(OTf)_3$ aqueous electrolyte.

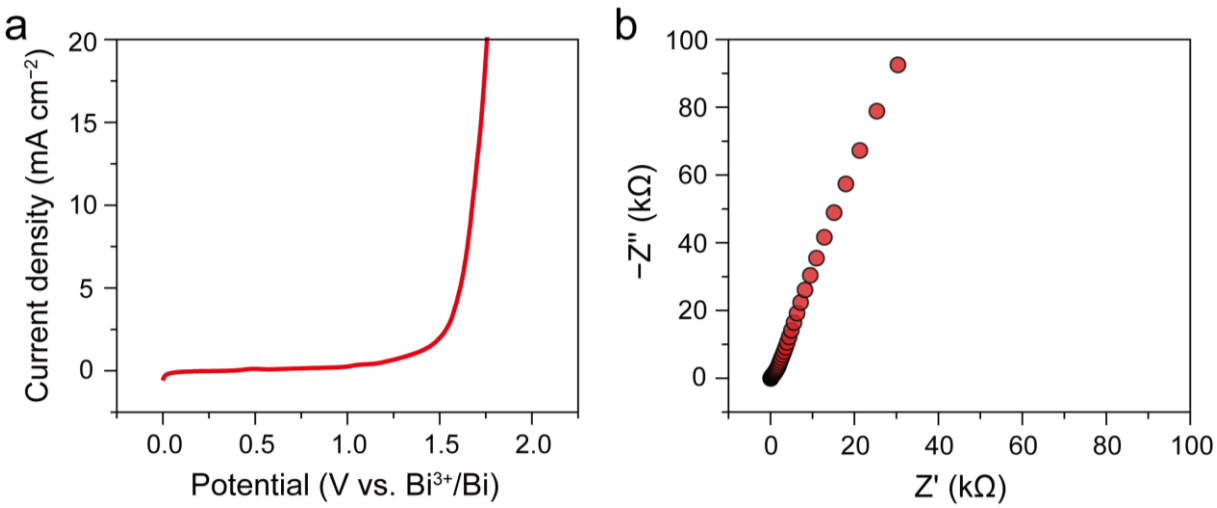

Figure S4. (**a**) Electrochemical stability window and (**b**) ionic conductivity of the 1 M $Bi(OTf)_3$ electrolyte. The ionic conductivity was calculated from $\sigma = l / (R_b \times A)$ where σ is the ionic conductivity (S cm^{-1}), l is the thickness (0.5 cm), A is the area (1 cm^2), and R_b (Ω) is the bulk resistance in impedance spectroscopy.

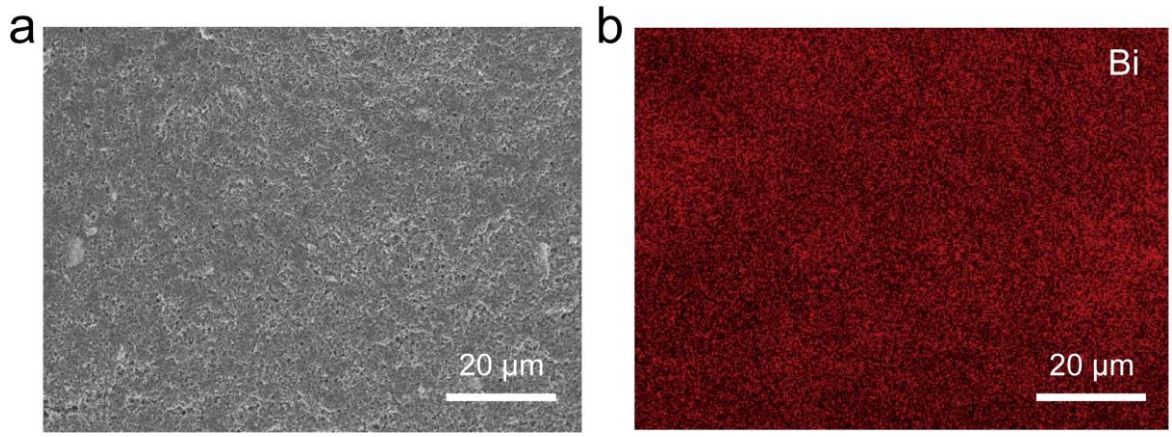

Figure S5. (**a**) SEM image and (**b**) the corresponding element mapping of Bi anode.

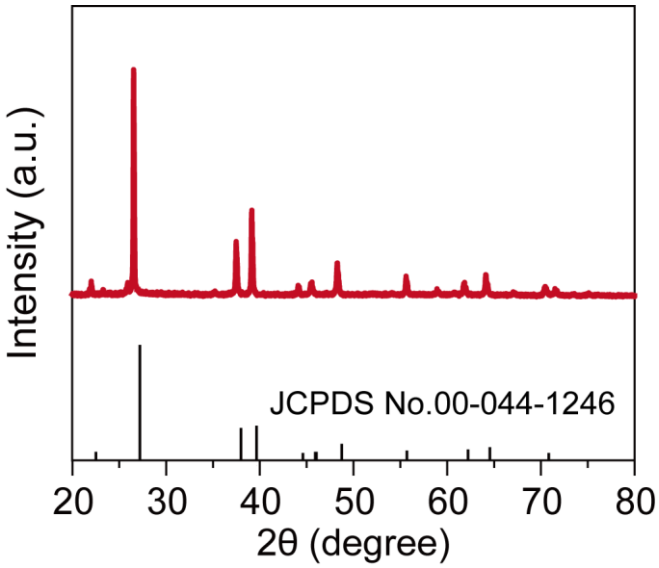

Figure S6. XRD pattern of Bi anode.

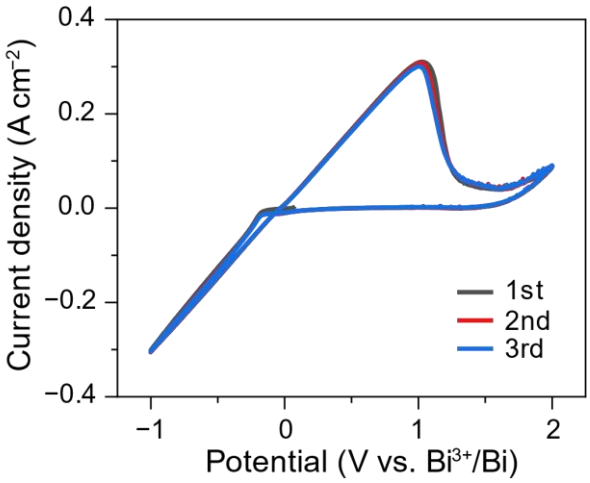

Figure S7. CV curves at a scan rate of 10 mV s^{-1} in a three-electrode cell using 1 M $Bi(OTf)_3$ electrolyte. Carbon paper was used as working electrode, and Bi metal plates were used as counter electrode and reference electrode.

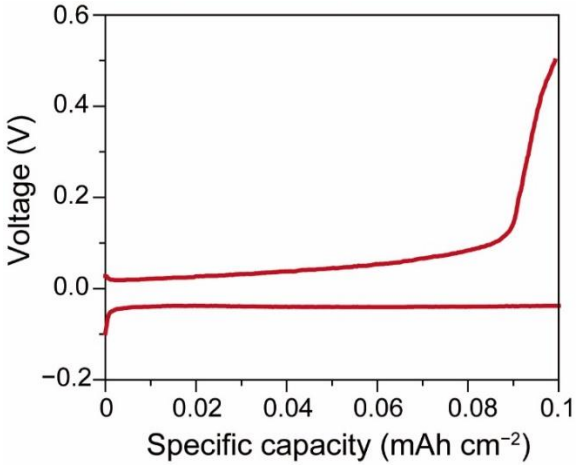

Figure S8. Voltage profiles of the C||Bi cells using the $Bi(OTf)_3$ electrolyte at 0.1 mA cm^{-2} with the capacity of 0.1 mAh cm^{-2} and cut-off voltage of 0.5 V.

The specific capacity of Bi anode

$$= \frac{\text{stripped capacity of bismuth anode}}{\text{the mass of plated bismuth}}$$

$$= \frac{\text{stripped capacity of bismuth anode}}{\text{plated capacity bismuth}} \times \text{theoretical specific capacity of bismuth}$$

$$= \frac{0.0996}{0.1} \times 385 \text{ mAh g}^{-1} = 383\ mAh\ \text{g}^{-1}$$

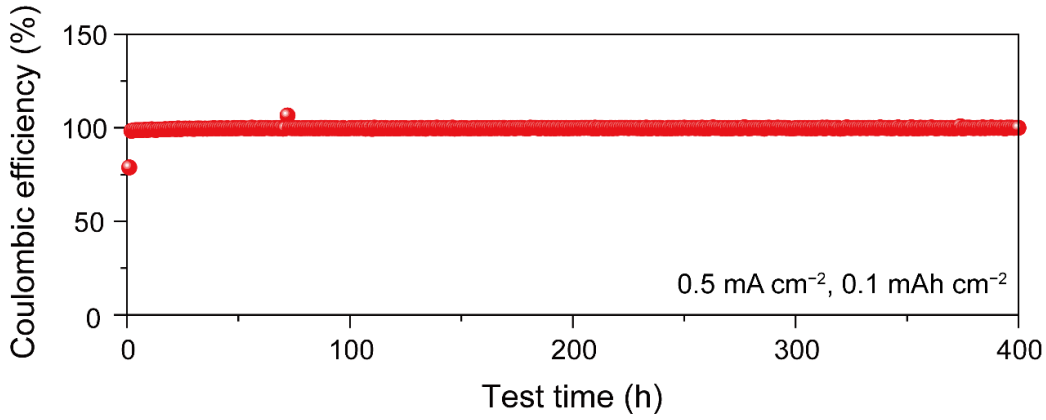

Figure S9. Coulombic efficiency of C||Bi cells using the $Bi(OTf)_3$ electrolyte at 0.5 mA cm^{-2} with the capacity of 0.1 mAh cm^{-2} and the cut-off voltage of 0.5 V.

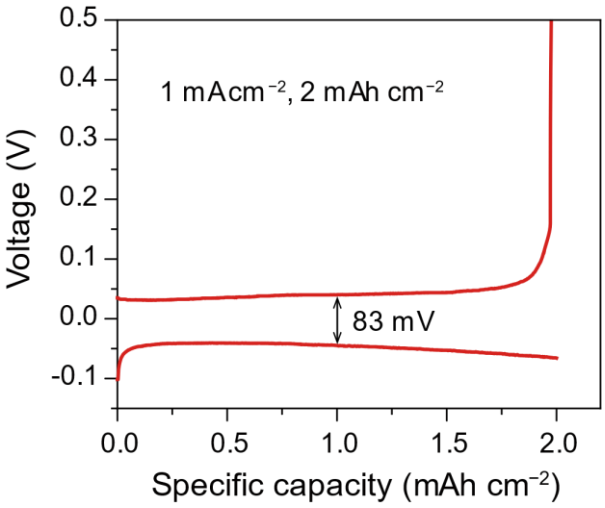

Figure S10. Voltage profile of the C||Bi cell using the $Bi(OTf)_3$ electrolyte at 1 mA cm^{-2} with the capacity of 2 mAh cm^{-2}.

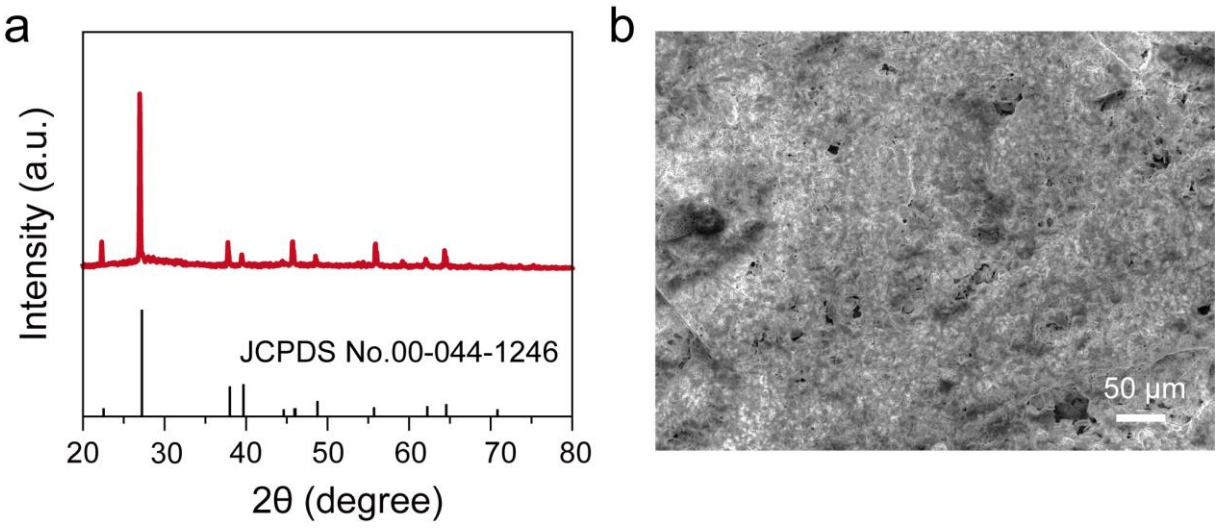

Figure S11. (**a**) XRD pattern and (**b**) SEM image of Bi electrode extracted from Bi symmetric cells using 1 M $Bi(OTf)_3$ aqueous electrolyte after 100 cycles at 1 mA cm^{-2} and 0.5 mAh cm^{-2}.

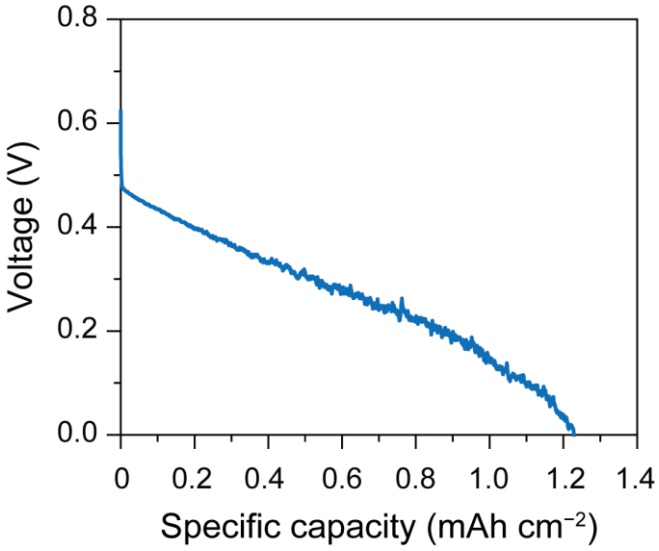

Figure S12. The galvanostatic discharge profile of Bi-air batteries using 6 M KOH electrolyte at 0.1 mA cm^{-2} with the cut-off voltage of 0 V.

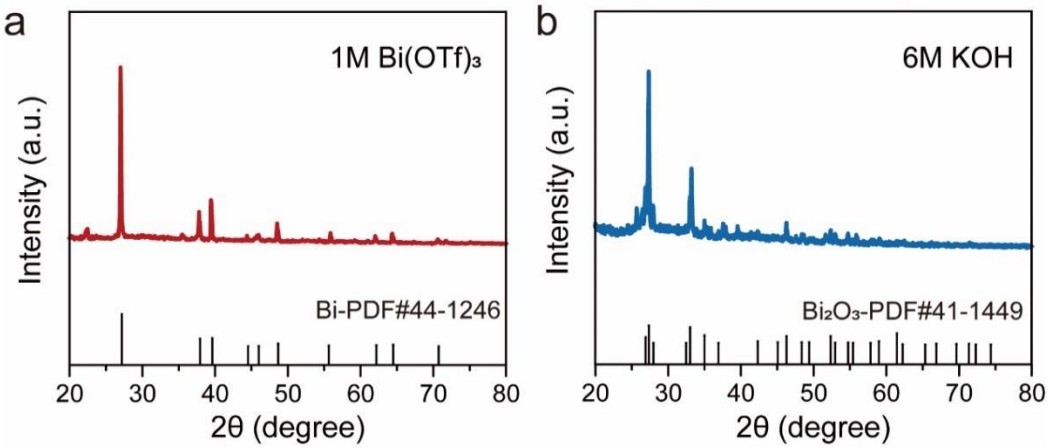

Figure S13. XRD patterns of Bi anode after immersed in 1 M $Bi(OTf)_3$ aqueous electrolyte and 6 M KOH aqueous solution for 12 h.

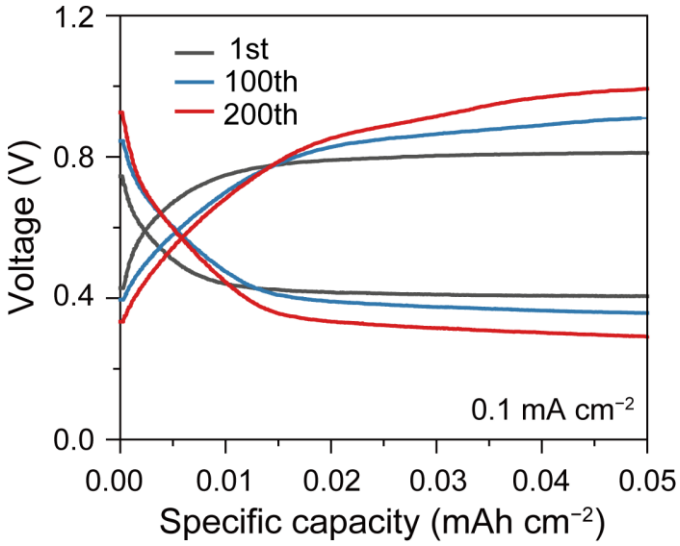

Figure S14. The galvanostatic discharge/charge profiles of Bi-air battery at a current density of 0.1 mA cm^{-2} with the capacity of 0.05 mAh cm^{-2}.

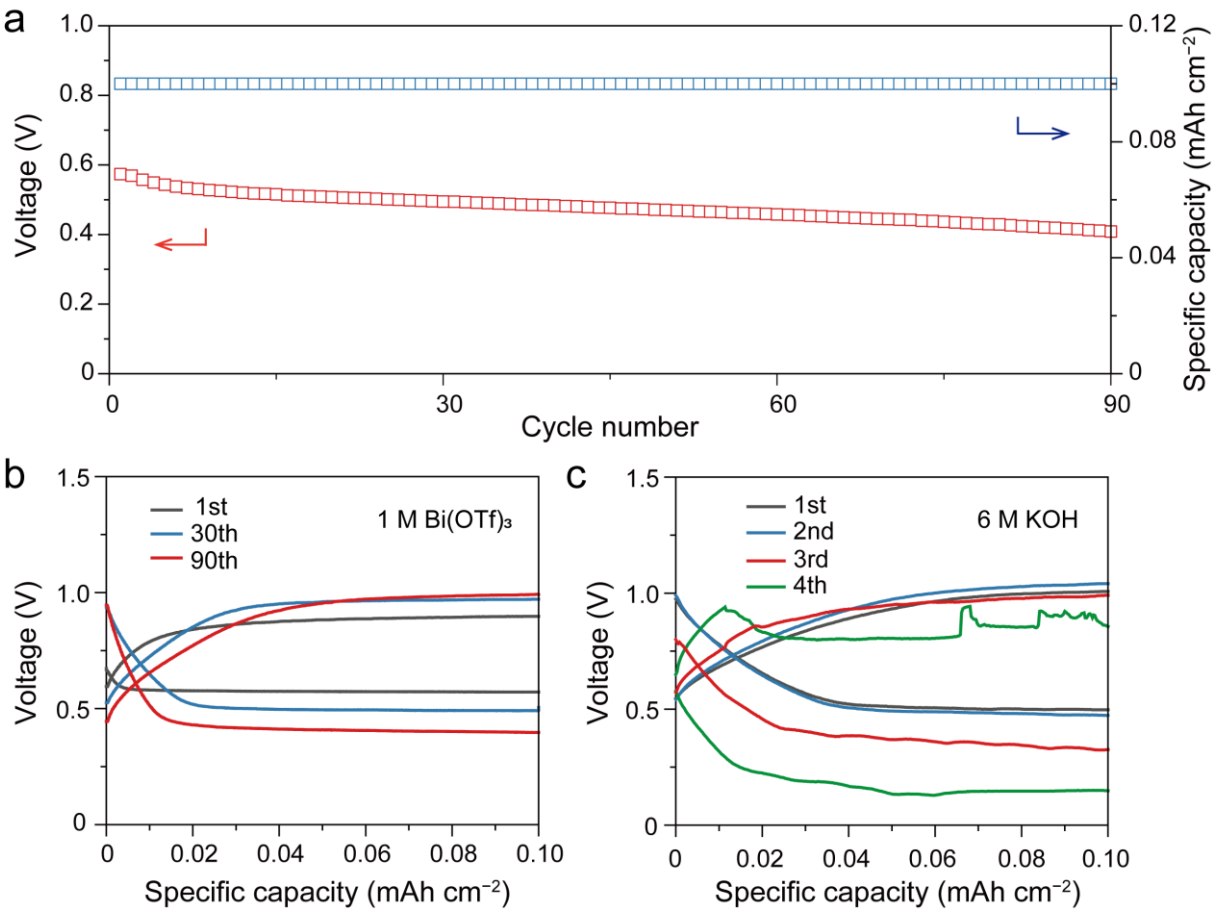

Figure S15. (**a**) Cycling performance of Bi-air battery using 1 M $Bi(OTf)_3$ electrolyte at the current density of 0.1 mA cm^{-2} with the capacity of 0.1 mAh cm^{-2}. (**b**) The corresponding discharge/charge profiles of Bi-air battery. (**c**) The galvanostatic discharge/charge profiles of Bi-air battery using 6 M KOH electrolyte at the current density of 0.1 mA cm^{-2} with the capacity of 0.1 mAh cm^{-2}.

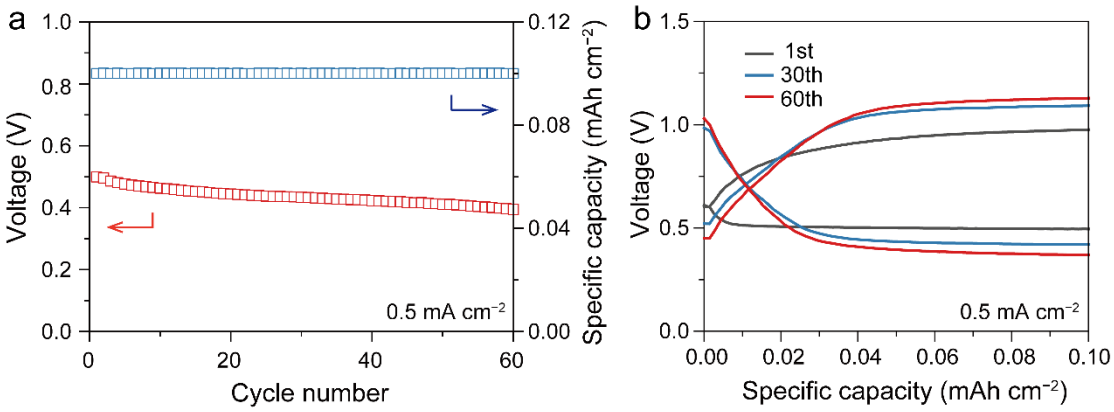

Figure S16. (**a**) Cycling performance of Bi-air battery using 1 M $Bi(OTf)_3$ electrolyte at the current density of 0.5 mA cm^{-2} with the capacity of 0.1 mAh cm^{-2}. (**b**) The corresponding discharge/charge curves of Bi-air battery.

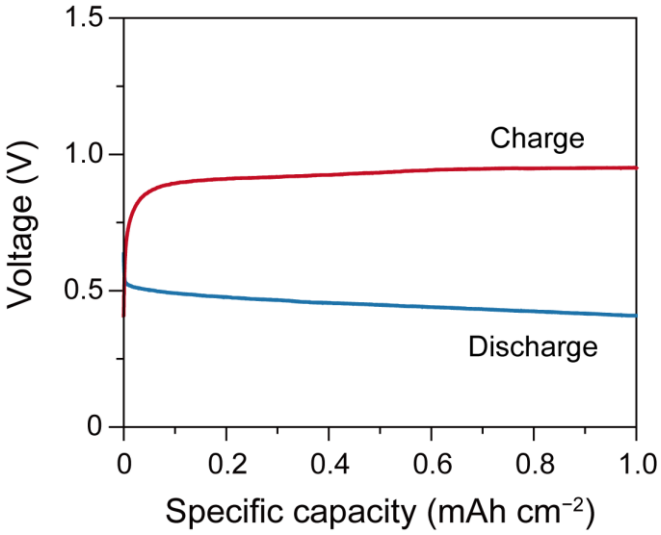

Figure S17. Discharge/charge profiles of Bi-air batteries using $Bi(OTf)_3$ electrolyte at 0.1 mA cm^{-2} with the capacity of 1 mAh cm^{-2}.

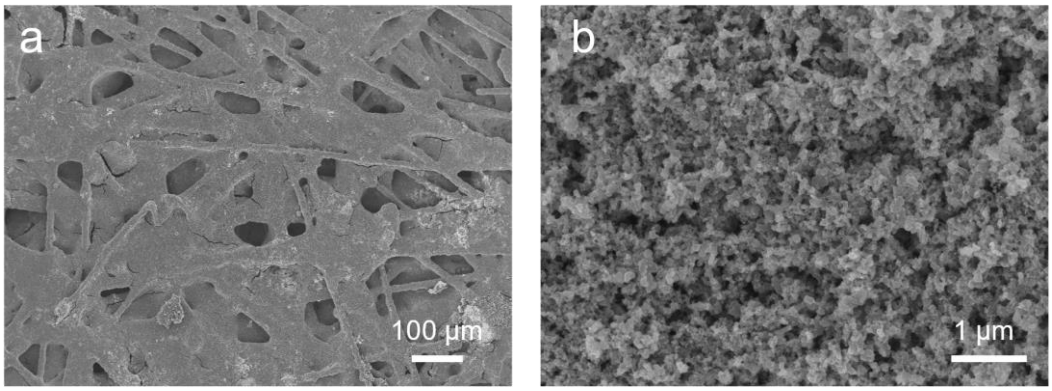

Figure S18. SEM images of pristine air cathode with the loading of 1 mg cm^{-2} Pt/C catalyst.

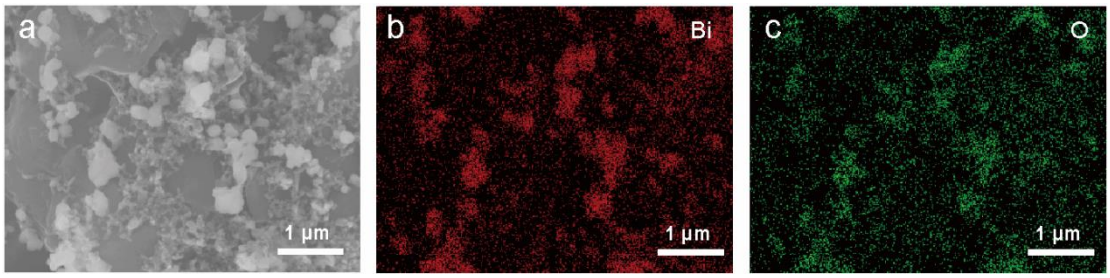

Figure S19. (**a**) SEM image and (**b**) corresponding elemental mappings of discharged air cathode.

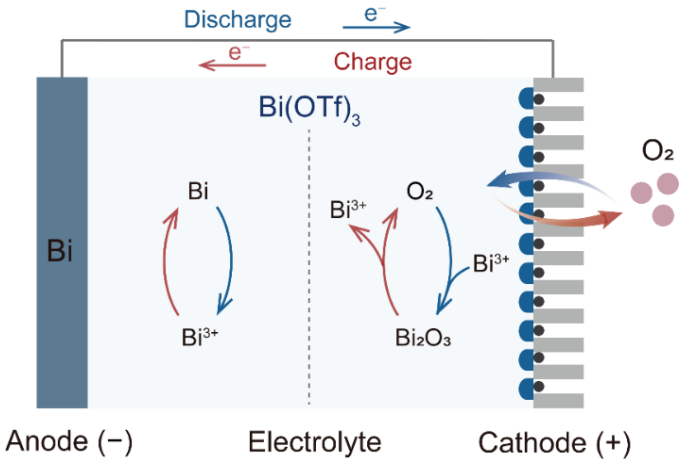

Figure S20. Schematic of the electrically rechargeable Bi-air battery using $Bi(OTf)_3$ electrolyte.

$$\text{Anode: } 4Bi \leftrightarrow 4Bi^{3+} + 12e^{-}$$

$$\text{Cathode: } 3O_2 + 12e^{-} + 4Bi^{3+} \leftrightarrow 2Bi_2O_3$$

$$\text{Overall: } 4Bi + 3O_2 \leftrightarrow 2Bi_2O_3$$

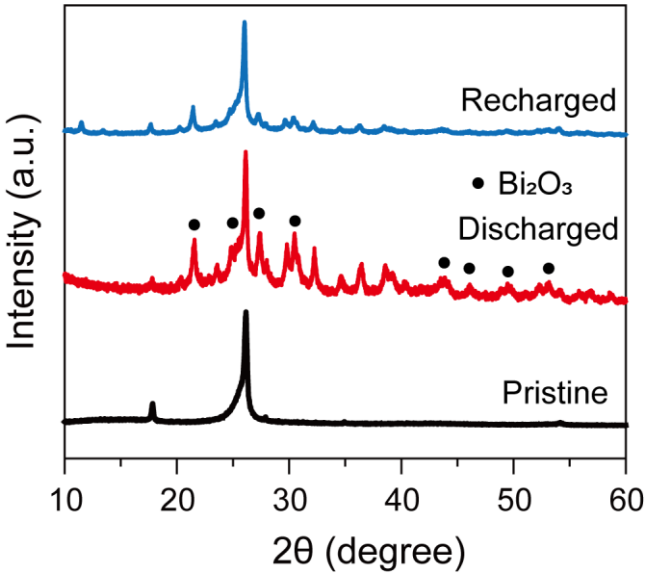

Figure S21. XRD patterns of air cathode extracted from Bi-air batteries after 200th discharge-charge process at the current density of 0.1 mA cm^{-2} with the capacity of 0.05 mAh cm^{-2}.

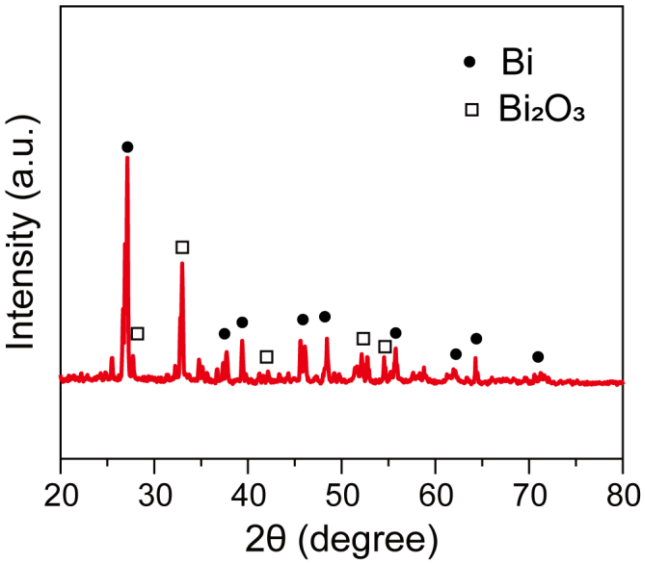

Figure S22. XRD pattern of Bi anode extracted from Bi-air batteries after 200th discharge-charge process at the current density of 0.1 mA cm^{-2} with the capacity of 0.05 mAh cm^{-2}.