Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Highly stable and high performance iodine redox flow batteries using host-guest interaction of (2-Hydroxypropyl)-β-cyclodextrin additive

Mingyu Shin[1,‡], Chanho Noh[2,3,‡], and Yongchai Kwon[1,2*]

[1] Department of Chemical and Biomolecular Engineering, Seoul National University of Science and Technology, 232 Gongneung-ro, Nowon-gu, Seoul, 01811, Republic of Korea

[2] Department of New Energy Engineering, Seoul National University of Science and Technology, 232, Gongneung-ro, Nowon-gu, Seoul, 01811, Republic of Korea

[3] KEPCO Research Institute, Korea Electric Power Corporation, 105 Munji-ro, Yuseong-gu, Daejeon 34056, Republic of Korea

*Corresponding author. E-mail: kwony@seoultech.ac.kr (Y Kwon)

Author Contributions

‡ M. Shin and C. Noh contributed equally to this work.

Table of Contents

Experimental Procedures

Materials.

β-Cyclodextrin (β-CD, ≥97%), (2-Hydroxypropyl)-β-cyclodextrin (HP-β-CD, average Mw ~1,460), Potassium chloride (KCl, ≥99.0%), and Ammonium chloride (NH_4Cl, ≥99.5%) were purchased from Sigma Aldrich. Potassium iodide (KI, 99%), Iodine (I_2, 99+%), and Zinc iodide (ZnI_2, 99+%) were purchased from Alfa Aesar. All chemicals were used without further purification.

Preparation of active materials.

All solutions were prepared using deionized water (DIW). For UV-VIS spectroscopy analysis, iodine solutions were prepared by dispersing I_2 in DIW, and the solution was sonicated for 30 min and stirred. Solutions including HP-β-CD were prepared by mixing HP-β-CD in DIW and stirring them for more than 24 h. I_2/HP-β-CD mixed solutions were prepared by either adding I_2 to HP-β-CD solution or by adding HP-β-CD to a solution containing the predetermined amount of I_2, and they were sonicated for 30 min and stirred.

For Linear Sweep Voltammetry (LSV), Chronoamperometry (CA), and Electrochemical Impedance Spectroscopy (EIS) analyses, solutions were prepared by first dissolving 0.1M KI and 1M KCl in DIW, and the predetermined amount of β-CD or HP-β-CD was further included into the solutions [1]. The electrolytes for the symmetric RFB cell tests were prepared by dissolving 0.125 M I_2 and 0.25M KI in DIW, and 1M NH_4Cl was further included into the solution, and subsequently, the various amounts of HP-β-CD were added [2]. The electrolytes for RFB single cell tests were prepared by adding ZnI_2 to a solution including NH_4Cl dissolved in DIW, and the predetermined amount of HP-β-CD was further included into the electrolytes, and they were stirred for more than 24 h.

Electrochemical/chemical and spectroscopic evaluations.

The potential of HP-β-CD additive and the enhancement in solubility of I_2 were evaluated using a UV-VIS spectrometer (UV-2600i, Shimadzu). Measurements were taken at a range from 185 to 900 nm, and a path length of 1cm was maintained for each sample. A baseline was set by the peaks of DIW for each experiment.

The potential of HP-β-CD additive and the enhancement in solubility of I_2 were evaluated using a UV-VIS spectrometer (UV-2600i, Shimadzu). Measurements were taken at a range from 185 to 900 nm, and a path length of 1cm was maintained for each sample. A baseline was set by the peaks of DIW for each experiment. In addition, ^{1}H- Nuclear Magnetic Resonance (NMR) spectra of samples (0.05M HP-β-CD and 0.5M HP-β-CD + 0.5M I_2 samples in 1mL D2O) were recorded by a Varian 400MHz NMR (Varian,US/Broadband MERCURY,400MHz).

To overhaul the electrochemical reaction of iodine electrolyte and the removal of I_2 film occurred due to the addition of HP-β-CD additive, LSV was employed. A rotating disk electrode (RDE, glassy carbon, 0.1963cm^{-2}) was used as the working electrode at a rotating speed of 1000 RPM. A Pt wire was acted as the counter electrode, while a silver/silver chloride electrode was used as the reference electrode. The scan was conducted in a range of 0 to 0.9 V (vs. Ag/AgCl) at a scan rate of 10mV s^{-1}.

Chronoamperometry (CA) was executed to evaluate the electrochemical performance of iodine electrolyte improved due to the removal of I_2 film by the additive. In this case, a glassy carbon electrode (GCE, 0.1963cm^{-2}) was employed as the working electrode, and the reference and counter electrodes were the same as those used for LSV measurements. The potential applied during the experiment was 0.8 V vs. Ag/AgCl, and the duration was set at 2 min.

Electrochemical impedance spectroscopy (EIS) was conducted after CA tests to determine the resistance of electrolyte and its variation occurred with the addition of HP-β-CD. The potential applied for EIS measurements was 0.45V (vs. Ag/AgCl), and frequencies were measured from 800 kHz to 500 mHz. The electrodes used for these tests were the same as those used for CA tests.

To assess the performance of the solution in actual RFBs, symmetric cell tests and RFB single cell tests were carried out. In the RFB symmetric cell test, catholyte and anolyte were iodine solutions showing a state of charge (SOC) of 50%. The charge-discharge current density was set at 40 mA cm^{-2}, with cut-off voltages of 0.25 or 0.35V for charging and -0.25 or -0.35V for discharging. The RFB single cell tests utilized ZnI_2 solutions for catholyte and anolyte. The reactions occurring at cathode and anode can be seen in eqs.1, 2, 3 [3–5]. Here, the charge-discharge current density was set at 40 mA cm^{-2}, with cut-off voltages of 1.6 and 0.6V for charging and discharging. All RFB tests utilized Nafion 117 (Chemours) as ion exchange membrane, which was prepared by soaking it in DIW for 24 h prior to using it. Graphite felt (GFD 4.6, SGL carbon) of 2x2cm^{2} size was used as electrode for RFB cell tests.

(1) Cathode: $I_3^- + 2e^- \leftrightarrow 3I^-$ $E^0 =$ 0.331V vs. Ag/AgCl

(2) Anode: $Zn \leftrightarrow Zn^{2+} + 2e^-$ $E^0 =$ -0.967V vs. Ag/AgCl

(3) Overall reaction: $I_3^- + Zn \leftrightarrow Zn^{2+} + 3I^-$ $E =$ 1.298 V

Results and Discussion

Supplementary Figures.

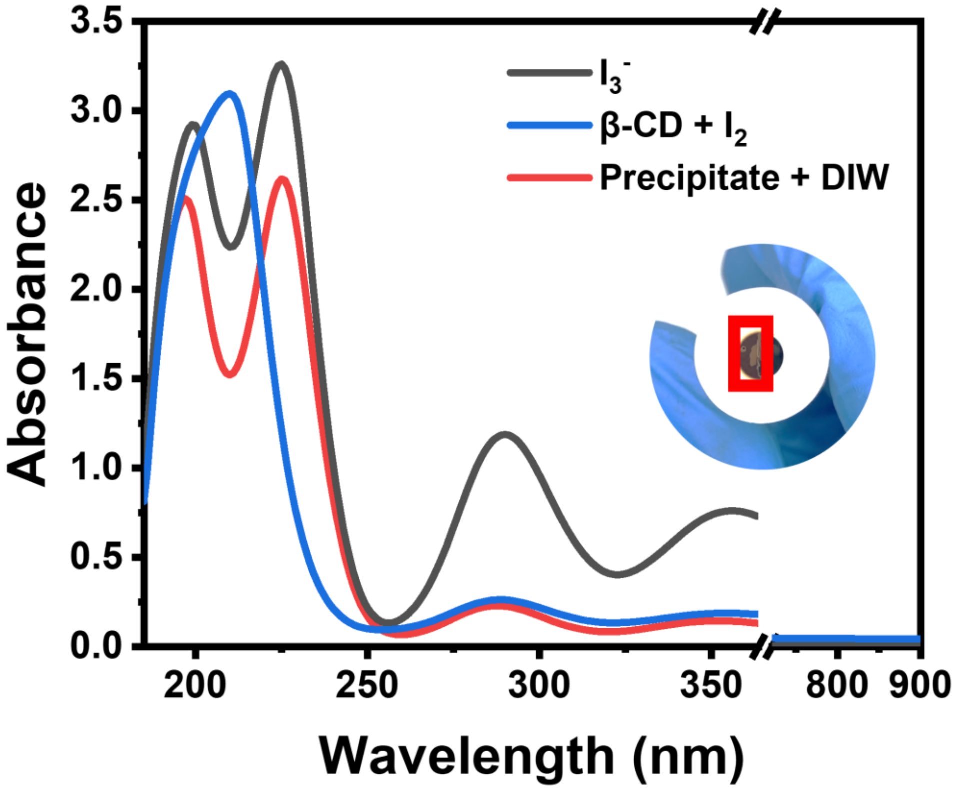

Figure S1. UV-VIS absorption spectra measured from dilute solutions of I_3^-, β-CD + I_2, and precipitates extracted after LSV tests.

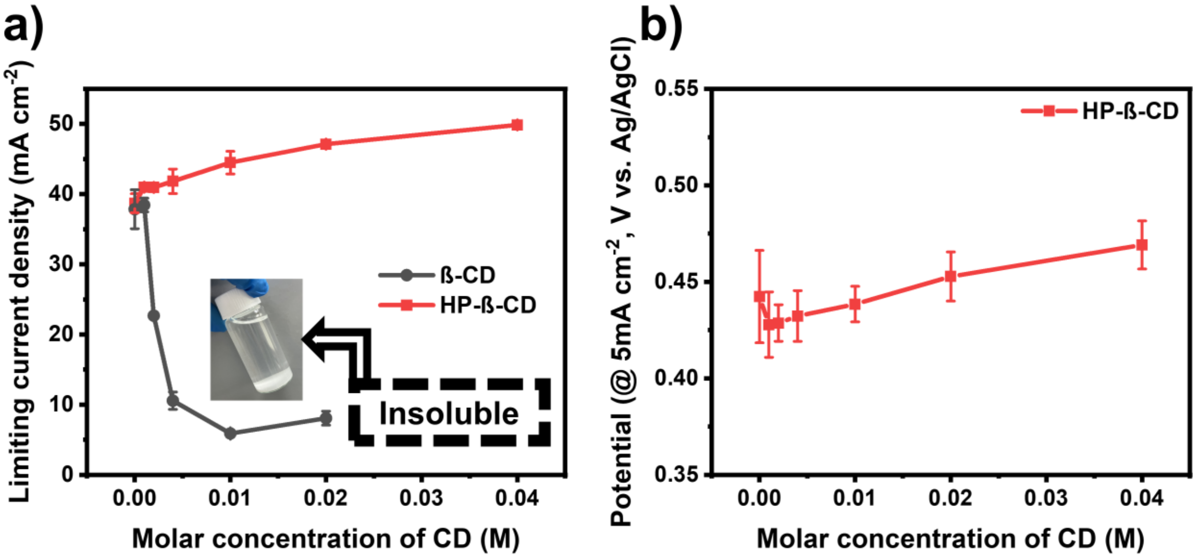

Figure S2. Graphs showing (a) limiting current density and (b) potential at 5mA cm^{-2} measured with change in the concentration of CD.

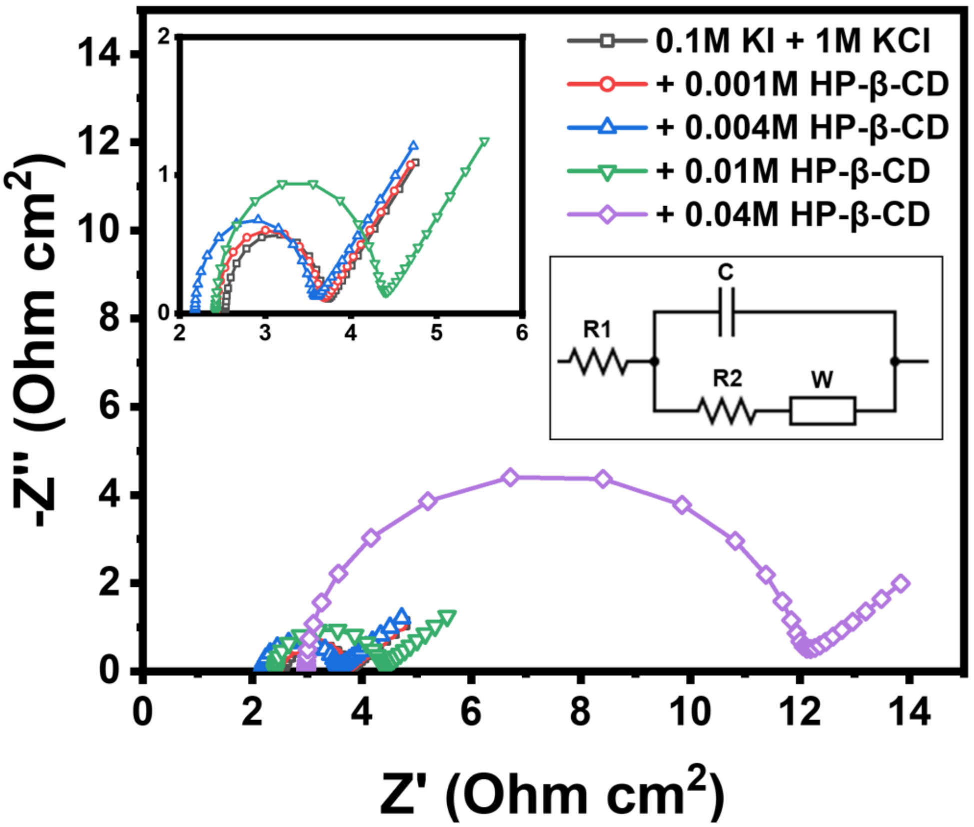

Figure S3. Nyquist plots of iodine electrolytes measured before and after the addition of HP-β-CD.

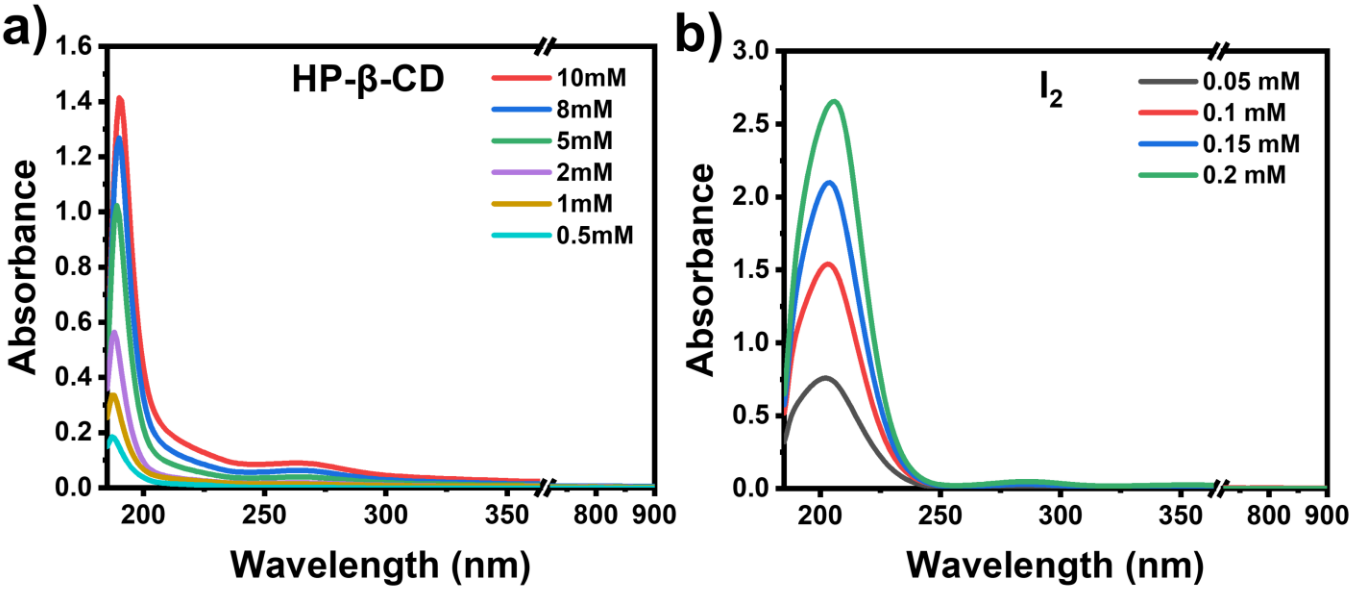

Figure S4. UV-VIS absorption spectra of (a) HP-β-CD and (b) I_2.

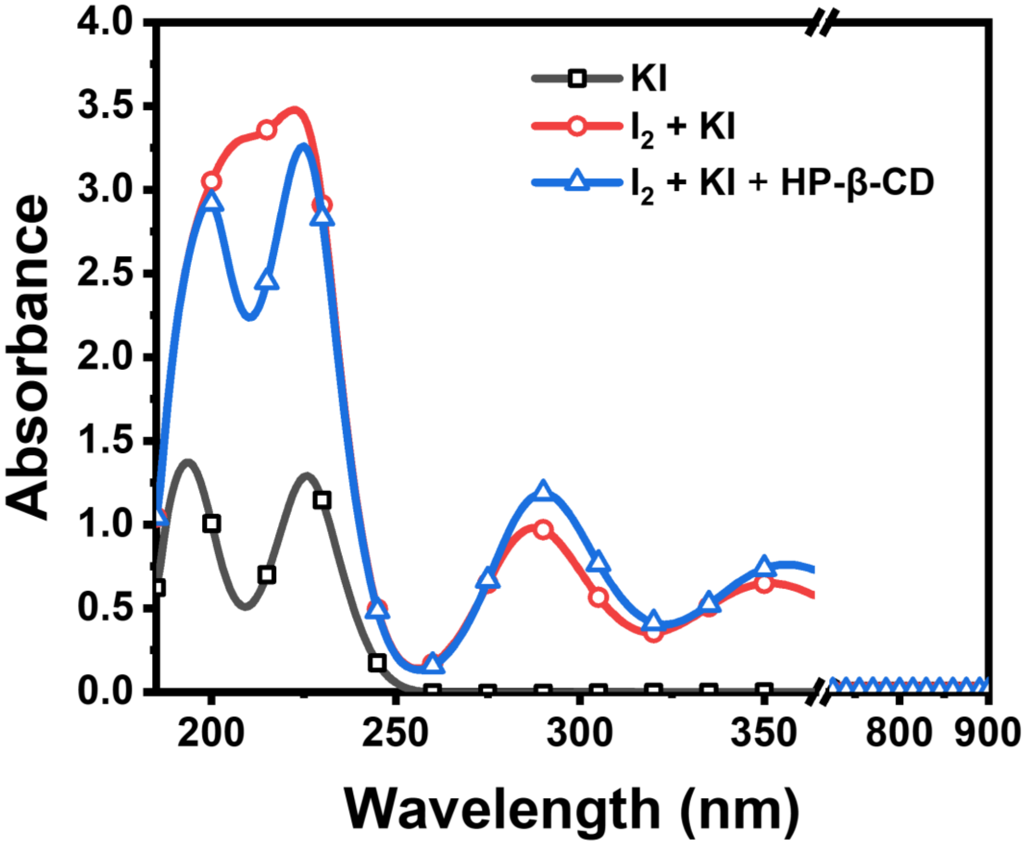

Figure S5. UV-VIS absorption spectra of solutions containing KI, KI + I_2, and KI + I_2 + HP-β-CD.

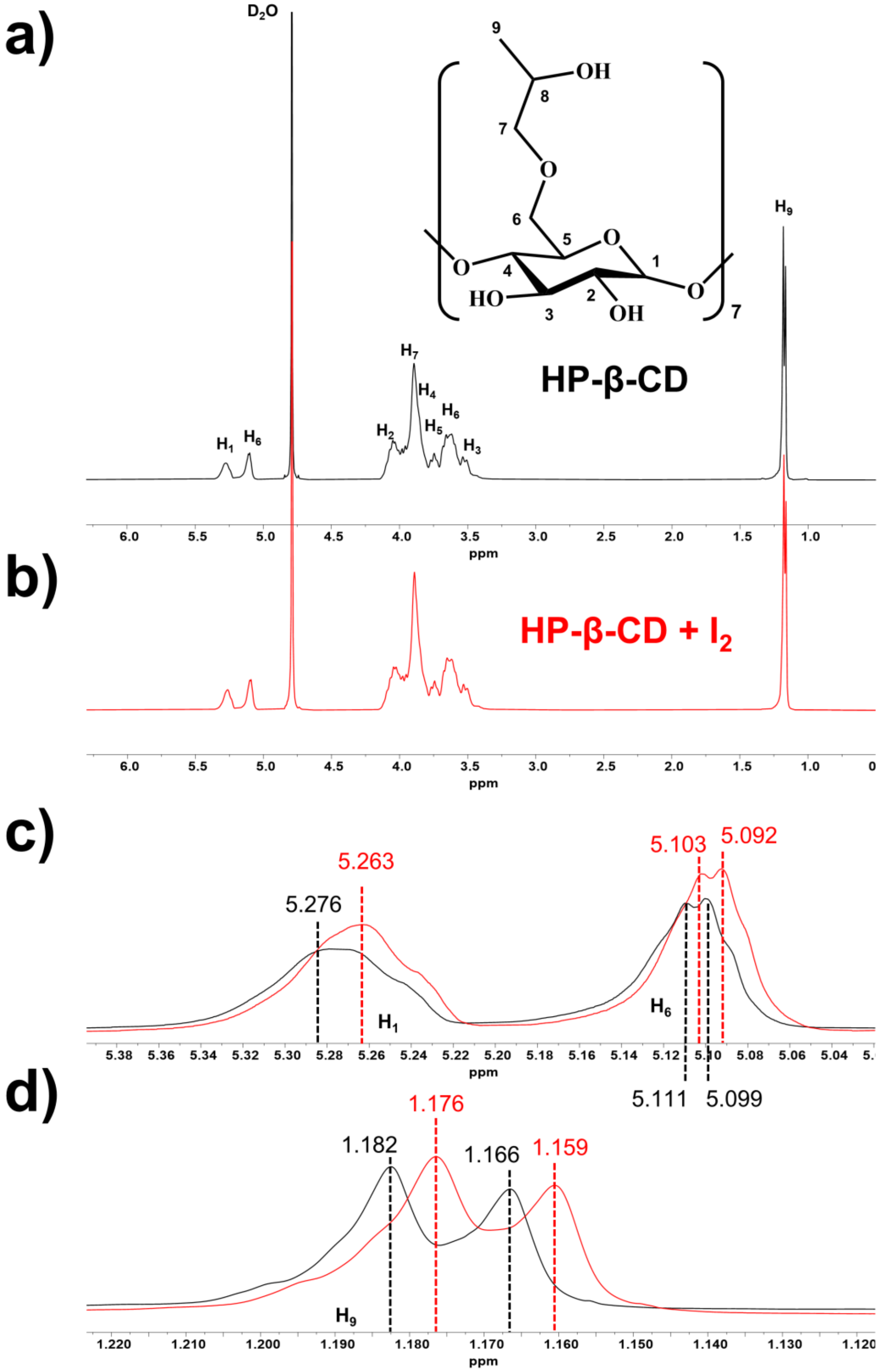

Figure S6. ^{1}H-NMR data of a) 0.05M HP-β-CD and b) 0.05M HP-β-CD + 0.05M I_2. Magnified NMR peaks representing for c) H_1 and H_6 areas, and d) H_9 area of each sample [6,7].

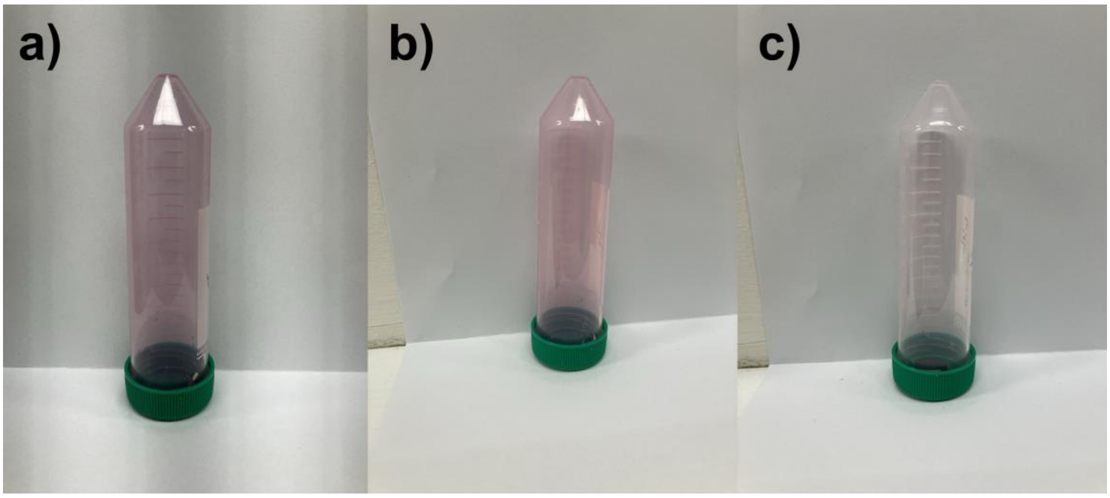

Figure S7. Photo images of a) I2 flake, b) an electrode collected from RFB symmetric cell using 0.125M I_2 + 0.25M KI + 1.0M NH_4Cl electrolyte, c) an electrode collected from RFB symmetric cell using 0.125M I_2 + 0.25M KI + 1.0M NH_4Cl + 0.05M HP-β-CD electrolyte.

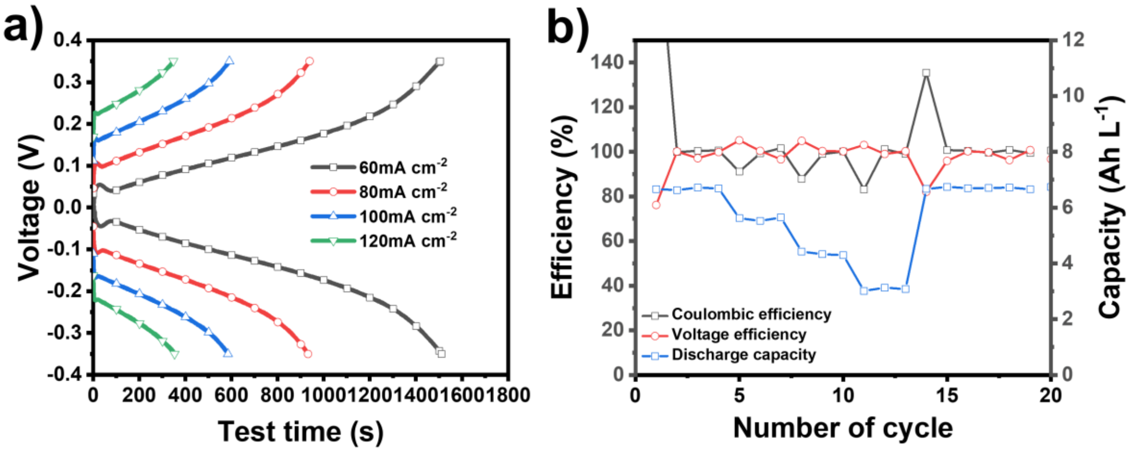

Figure S8. A) Time versus voltage graphs of symmetric RFBs using electrolyte including 0.05M HP-β-CD additive and b) Cycling graphs of symmetric RFBs using iodine electrolytes including HP-β-CD additive measured at four current densities of 60, 80, 100 and 120 mA cm^{-2}.

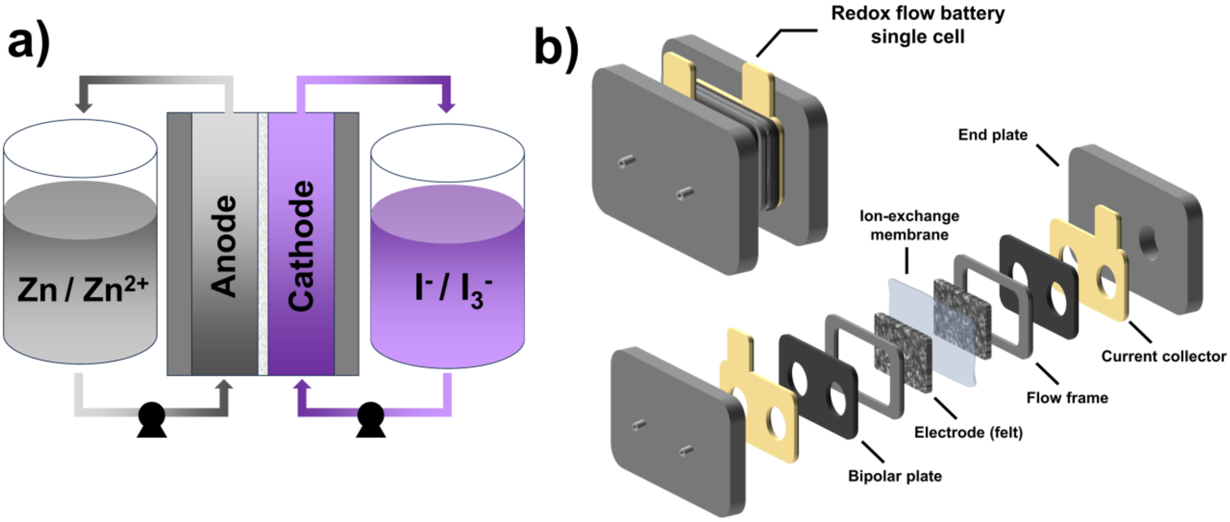

Figure S9. a) A schematic illustration of ZIRFB and b) the structure of RFB single cell.

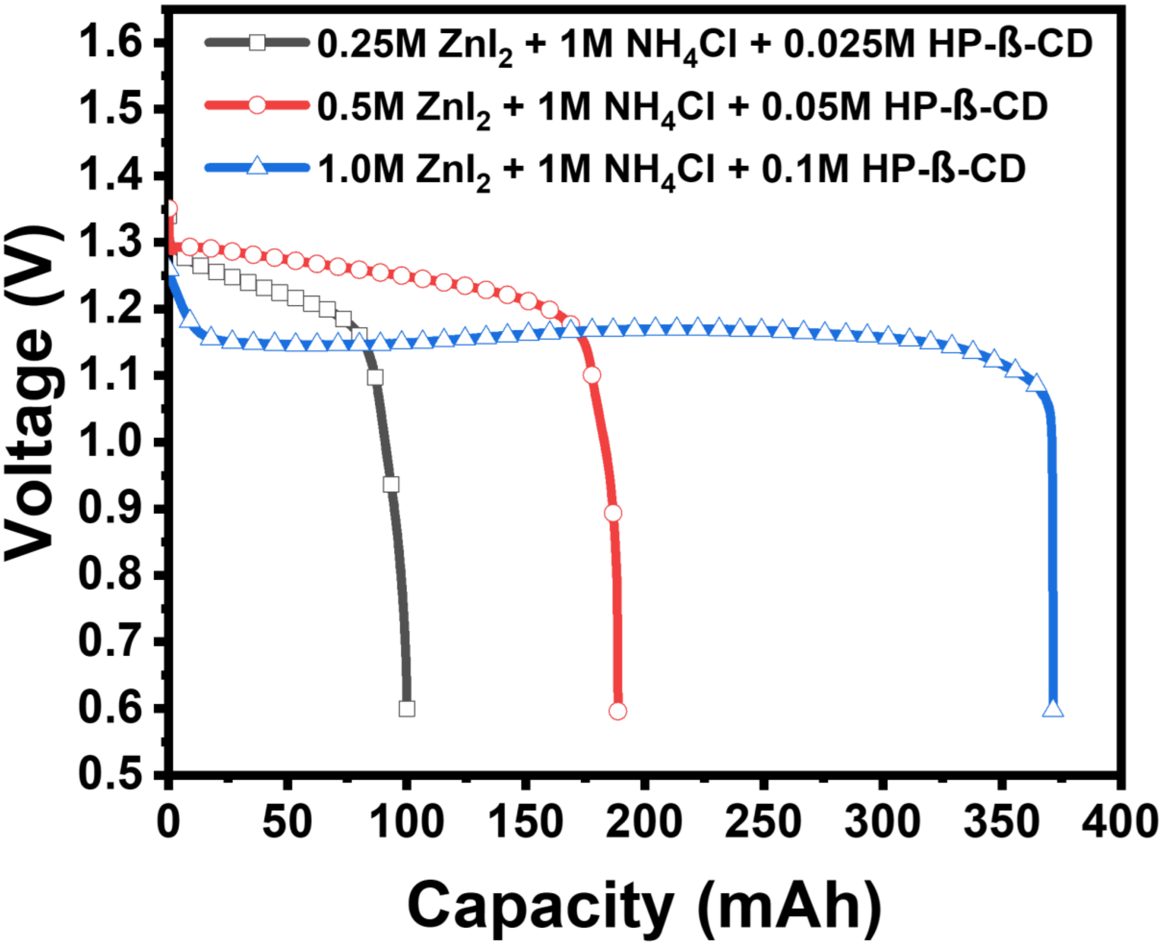

Figure S10. Capacity vs. voltage graphs of RFBs using electrolyte including 0.25M, 0.5M, and 1.0M iodine.

Supplementary Tables.

Table S1. Average resistances of all the electrolytes calculated from their Nyquist plots.

Electrolyte condition	Average R1 (ohmic resistance, Ohm cm^2)	Average R2 (charge transfer resistance, Ohm cm^2)
0.1M KI + 1M KCl	2.53	1.13
+ 0.001M HP-B-CD	2.44	1.19
+ 0.004M HP-B-CD	2.18	1.39
+ 0.01M HP-B-CD	2.41	1.85
+ 0.04M HP-B-CD	2.99	8.63

References

1 C. Park and J. Chang, *Electrochim. Acta*, 2021, **368**, 137650.

2 M. Mousavi, G. Jiang, J. Zhang, A. G. Kashkooli, H. Dou, C. J. Silva, Z. P. Cano, Y. Niu, A. Yu and Z. Chen, *Energy Storage Mater.*, 2020, **32**, 465–476.

3 A. Khor, P. Leung, M. R. Mohamed, C. Flox, Q. Xu, L. An, R. G. A. Wills, J. R. Morante and A. A. Shah, *Mater. Today Energy*, 2018, **8**, 80–108.

4 B. Li, Z. Nie, M. Vijayakumar, G. Li, J. Liu, V. Sprenkle and W. Wang, *Nat. Commun.*, 2015, **6**, 6303.

5 Z. Pei, Z. Zhu, D. Sun, J. Cai, A. Mosallanezhad, M. Chen and G. Wang, *Mater. Res. Bull.*, 2021, **141**, 111347.

6 H. Huang, H. Yu, D. Li, Y. Liu, F. Shen, J. Zhou, Q. Wang and G. Tang, *Int. J. Mol. Sci.*, 2008, 9, 2278–2289.

7 J. A. Pellicer, M. I. Rodríguez-López, M. I. Fortea, C. Lucas-Abellán, M. T. Mercader-Ros, S. López-Miranda, V. M. Gómez-López, P. Semeraro, P. Cosma, P. Fini, E. Franco, M. Ferrándiz, E. Pérez, M. Ferrándiz, E. Núñez-Delicado and J. A. Gabaldón, *Polymers*, 2019, 11.