Supporting Information

High Energy Density Aqueous Electrochemical Capacitors with a KI-KOH Electrolyte

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Calculation of the Usage of Limited Electrolyte in Coin Cells:

We first estimated the total volume of two film electrodes to be 14 μL based on the electrode area of 0.785 cm^2 each, and the average thickness of the film electrode of ~ 90 μm . We then calculated the **solid** volume occupied by carbon and binder in the electrode films. The volume occupied by solid carbon in both electrodes is estimated to be 5.6 μL , based on the density of 1.6 g/cc of the carbon before activation, measured by Archimedes' method. We assume that carbon black additive shares the same density as the amorphous carbon precursor. The volume of PTFE binder is calculated to be 0.45 μL based on its density of 2.2 g/cc. Therefore, the pore volume inside the electrodes equals to 7.95 μL ($=14 \mu\text{L} - 5.6 \mu\text{L} - 0.45 \mu\text{L}$).

We calculated the pore volume contributed from the separator based on its volume and porosity. The polycarbonate separator has a thickness of 9 μm and porosity of 17.7%. The total pore volume inside one separator (diameter: 1.9 cm) is calculated to be 0.454 μL .

So the total pore volume from both electrodes and separator is 8.40 μL ($7.95 \mu\text{L} + 0.454 \mu\text{L}$). Therefore, 10 μL of electrolyte is expected to be sufficient to fill up the porosity of a non-flooded coin cell.

Figure S1. N₂ isotherms of activated carbon at -196 °C, inset: Barrett-Joyner-Halenda (BJH) pore size distribution calculated from the adsorption curve.

Specific BET surface area and pore size distribution were measured by nitrogen sorption at -196 °C. A surface area of 2405 m²/g and pore volume of 1.0 cc/g were obtained, most of which is from pores with size less than 4 nm, exhibiting high EDL capacitance and providing surface for redox reactions.

Different concentrations of KI with and without the presence of 1 M KOH were tested using the galvanostatic charge-discharge technique. The specific capacitance is based on a full cell. Apparently, at each concentration, adding KOH helps increase capacitance. From Figure S2, the cell capacitance increases with a higher concentration of KI. With the presence of KOH, similar capacitance was found when using 4 M KI and 5 M KI. Considering the cost and electrolyte density, the optimal electrolyte is determined to be 4 M KI with 1 M KOH.

Figure S2. Galvanostatic discharge potential profiles for cells containing pure KI electrolytes with concentrations from 1 to 5 M (dashed lines) and the mixed electrolytes of KOH (1 M) plus KI with different concentrations from 1 M to 5 M (solid lines). The specific capacitance values here are calculated for the full cell level. For specific capacitance of individual electrode, a factor of four should be applied.

Figure S3. EDX results on the positive electrode (a) before switching from 1.5 to 1.6 V and (b) 2000 cycles after switching to 1.6 V.

Figure S4. Pourbaix diagram of iodine species. (Figure from reference S1)¹

The Pourbaix diagram in Figure S4 shows the iodine-containing species existing in different regions of potentials and pH values. At pH of 14, when I^- is oxidized, the product would be IO_3^- , or $H_2IO_6^{3-}$, corresponding to the +5 or +7 oxidation state of iodine, respectively.

Figure S5. Raman spectra of water, 0.1 M KIO_3 and mixed electrolyte: 4 M KI and 1 M KOH before and after charging.

From Figure S5, after charging, the mixture electrolyte of KI plus KOH shows the symmetric stretching vibration of IO_3^- (symmetry A_1) at $\sim 800 \text{ cm}^{-1}$, indicating the formation of iodate.

Figure S6. Comparison of electrochemical impedance spectroscopy results between the electrolytes of pure KI and the mixture of KI plus KOH. Inset: zoomed-in region at high frequencies.

Figure S6 shows the Nyquist plots of the pure KI electrolyte and the mixed electrolyte of KI plus KOH. From the intercepts on x-axis, it is evident addition of KOH decreases the equivalent series resistance (ESR) from 1.8 Ω to 1.2 Ω . The inset in Figure S6 shows a smaller diameter of the semicircle around 0.4 Ω with KOH, compared to 0.6 Ω without KOH. The smaller semicircle demonstrates lower Faradaic resistance, indicating that the redox reaction is kinetically faster in the presence of KOH. Furthermore, addition of KOH leads to an almost vertical line at lower frequency region, close to an ideal capacitor.

Figure S7. Cyclic voltammograms of pure KI (4 M) electrolyte and a mixed electrolyte of KI (4 M) + KOH (1M) for positive potentials vs. Ag/AgCl at (A) 1 mV/s, (B) 50 mV/s, and for negative potentials vs. Ag/AgCl at (C) 1 mV/s, (D) 50 mV/s.

Figure S7 compares cyclic voltammograms of pure KI (4 M) electrolyte and a mixed electrolyte of KI (4 M)-KOH (1M) at both cathode and anode potentials. At 1 mV/s, the cathodic peak shifts from 0.36 to 0.46 V vs. Ag/AgCl, which could help increase the cell voltage and therefore

improve energy density. At the anode potentials, small humps around -0.9 V vs. Ag/AgCl in Figure S6D indicate that redox reaction occurs when using KI + KOH electrolyte, which is attributed to hydrogen adsorption/desorption. The electrolyte of KI plus KOH also shows more desirable performance at higher scanning rates with the rectangular shape of the CV curves better retained. From galvanostatic charge-discharge profiles in three-electrode cells in Figure S7, both electrolytes show the well-defined plateaus close to 0.5 V vs. Ag/AgCl, but a higher current is observed in the KI-KOH mixed electrolyte. Enhanced hydrogen adsorption/desorption in the KI-KOH electrolyte helps increase charge storage on the anode, and therefore improves the specific energy of the full cell.

Figure S8. Galvanostatic charge-discharge profiles in three-electrode cells at 1 A/g with electrolytes of 4 M KI (A), and 4 M KOH + 1 M KOH (B).

Reference:

- S1. Parent, A. R.; Crabtree, R. H.; Brudvig, G. W. Comparison of Primary Oxidants for Water-Oxidation Catalysis. *Chem. Soc. Rev.* **2013**, *42*, 2247-2252.