Electronic Supplementary Information (ESI)

Reversible Br₂/Br⁻ Redox Couple in Aqueous Phase as Highperformance Catholyte for Alkali-Ion Batteries

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Catholyte chemistry	Mw (g mol ^{−1})	E ^e vs. Li⁺/Li (V)	Theoretical Capacity ^[a]	Medium	References
Fe ^{3+/} Fe ²⁺	55.85	3.7	480	aqueous	S1
Fe(CN) ₆ ^{3–} /Fe(CN) ₆ ^{2–}	211.95	3.4	127	aqueous	S2, S3
₃ -/ -	126.90	3.6	211	aqueous	S4, S5
1,4-Benzoquinone	108.1	2.6 – 2.8	496	nonaqueous	S6
2,5Dipropoxy-1,4- benzoquinone	224.3	2.4 – 2.6	273	nonaqueous	S6
2,5-Diethoxy-1,4- benzoquinone	196.2	2.5 – 2.7	273	nonaqueous	S6
Polysulfide	32.07	2-2.4	1672	nonaqueous	S7
WO ₄ ^{2–} /WO ₄ ^{(2+x) –}	247.84	3.2	< 108	aqueous	S8
Br₂/Br⁻	80.92	4.1	331	aqueous	This work

Table S1. Representative redox couples for aqueous/nonaqueous catholyte.

^[a] mA h g⁻¹, calculated based on the molecular weight of the ions/molecules only



Fig. S1 Schematic illustration of the assembly process of the cylinder cell.



Fig. S2 Sampled-current voltammogram profile of 1M LiBr aqueous solution. $E_{1/2}$ was determined to be 1.136 V vs. SHE.



Fig. S3. Stable potential window of H_2O at room temperature.^{S9} At the pH value of the catholyte (4.5 – 5), the practical OER and HER take place at the potentials of 1.38 V and – 0.62 V (*vs.* SHE) or 4.42 V and 2.42 V (*vs.* Li⁺/Li), respectively.



Fig. S4 Equivalent circuits for the simulation of the impedance spectra of (a) the cylinder cells and (b) the solid electrolyte. Fitting of the Nyquist plots according to the equivalent circuit contained four different impedances: R_s , the responses from the liquid solutions, electrochemical reactions, bulk solid electrolyte and its internal parts; R_{ct} and C_1 , the charge transfer resistance and the Faradic charge-transfer impedance and double layer capacitance, respectively (charge transfer takes place between the electrolyte and current collector corresponding to the semicircle at high frequencies); R_{gb} and C_2 , the grain boundary impedance and capacitance of the solid electrolyte, respectively, corresponding to the semicircle at high-medium frequencies; R_{int} and C_3 , the interfacial impedance and capacitance, respectively, corresponding to the semicircle at medium-low frequencies.

	R _e (Ω·m)	R _{ct} (Ω·m)	R _{gb} (Ω·m)	<i>R</i> _{int} (Ω·m)
As-assembled cell	35.4	82.1	247.3	4243
Cell after initial cycle	39.2	83.2	245.1	77.9

Table S2. Fitted values of resistance contributions of the as-assembled cell and the cell after initial cycle



Fig. S5 Digital images showing the hydrophobic surface of the as-prepared acetylene black/PVDF current collector (left), and the hydrophilic surface of the acetylene black/PVDF current collector after the initial cycle (right).



Fig. S6 Polarization curve (black) and corresponding specific power density (blue) of the Br_2/Br^- catholyte at 40 °C. The rated power output is 1790 W kg⁻¹ at current density of 630 mA g⁻¹ (~ 1.9C) and peak power output of 2880 W kg⁻¹, respectively.



Fig. S7 Polarization curve (black) and corresponding specific power density (blue) of the Br_2/Br^- catholyte at 55 °C. The rated power output is 3230 W kg⁻¹ at current density of 1000 mA g⁻¹ (~ 3C) and peak power output of 4740 W kg⁻¹, respectively.



Fig. S8 Charge/discharge profiles of the as-synthesized KBr/LiBr catholyte with pH ~ 8.5. The capacity fading should be attributed to the formation of BrO⁻ via the reaction of Br₂ + 2OH⁻ \leftrightarrow Br⁻ + BrO⁻ + H₂O.



Fig. S9 Charge/discharge profiles of the KBr/LiBr catholyte with pH ~ 6.5 – 7 (adjusted by sulphuric acid). Compared with the catholyte with pH ~ 8.5, neutral pH value could partially supress the side reaction of $Br_2 + 2OH^- \leftrightarrow Br^- + BrO^- + H_2O$, as evident by the fact that less capacity fading was observed at neutral pH value.



Fig. S10 Charge/discharge profiles of the KBr/LiBr catholyte with pH \sim 3 – 3.5 (adjusted by sulphuric acid).



Fig. S11 X-ray diffraction patterns of the pristine solid electrolyte (black) and the one soaked in KBr/LiBr catholyte (pH 4.5 – 5) for 1 month (red). No obvious structural change could be observed.



Fig. S12 Nyquist plots of the pristine solid electrolyte (red) and the one soaked in KBr/LiBr catholyte with pH 4.5 – 5 for 1 month (blue). No obvious conductivity variation could be observed. Before he EIS measurement, the both sides of the solid electrolyte was sputtered a gold layer as the electrode. The simulated R_{gb} using the equivalent circuits shown in Fig. S4b is ~ 215 Ω ·m for the pristine solid electrolyte, corresponding well with that of the as-assembled cell (~ 247.3 Ω ·m) shown in Table S2.



Fig. S13 Effect of acidity on the ionic conductivity of the solid electrolyte. (a) Nyquist plots obtained from Li₂SO₄ (1M aq.) | solid electrolyte | Li₂SO₄ (1M aq.) symmetric cell at pH values of 0 (black), 2 (blue), 4 (red), 6 (green), and 10 (orange). The pH value of Li₂SO₄ solution was adjusted with H₂SO₄ or LiOH when necessary. In the measured pH values, the total cell resistance decreased with the increasing of pH, suggesting Li–ion diffusion is more favourable in neutral environment. (b) Nyquist plots obtained from H₂SO₄ (1M aq.) | solid electrolyte | H₂SO₄ (1M aq.) and Li₂SO₄ (1M aq.) | solid electrolyte | H₂SO₄ (1M aq.) and Li₂SO₄ (1M aq.) | solid electrolyte | Li₂SO₄ electrolyte, indicating protons could barely diffuse across the solid electrolyte. Ti foil was used as the current collector in the EIS measurement. All the EIS measurements were performed at the open-circuit voltage of the cell in the frequency range of 10⁶–0.1 Hz with ac signal amplitude of 10 mV.



Fig. S14 Diagram of capacity as a function of average discharge potential of similar batteries based on different redox reactions in aqueous/liquid phase: $K_3Fe(CN)_6$ (ref S3), I_2 (ref S4), KMnO₄ (ref S9), 1,4-Benzoquinone (BQ, ref S6), 2,5-Dimethoxy-1,4-benzoquinone (DMBQ, ref S6), 2,5-Dipropoxy-1,4-benzoquinone (DPBQ, ref S6), polysulfide (ref S7), FeCl₃ (ref S1), and Cu(NO₃)₂ (ref S10).

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