Supporting Information

Effect of Electrolyte Anions on the Cycle Life of a Polymer Electrode in Aqueous Batteries

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t-test

t-test analysis was carried out on the area of particles shown in Fig. 1 to identify whether particle volume evolution is statistically significant after 100 cycles. The statistical analysis of size distribution for pristine and cycled PBQS particles are listed in Table S1. For instance, to evaluate the particle area of pristine PBQS and the one cycled in $ZnSO_4$, the number of samples (*N*), average particle area (*M*), and standard deviation (*s*) are used in the calculation. The polled sample variance is calculated as:

$$s_p^2 = \frac{(N_1 - 1) \cdot s_1^2 + (N_2 - 1) \cdot s_2^2}{N_1 + N_2 - 2} = 7.8$$

The *t*-value for two sets of polled samples is calculated as:

$$t = \frac{M_1 - M_2}{\sqrt{s_p^2 \left(\frac{1}{N_1} + \frac{1}{N_2}\right)}} = -3.52$$

The *p*-value with 0.05 confidence interval (CI) based on two-tailed hypothesis is $p = 0.0005 < 0.05$. The difference in PBQS size distribution is considered statistically significant before and after cycling in $ZnSO_4$.[1]

Similarly, the difference of the size distribution for pristine and cycled PBQS particles in $Zn(CF_3SO_3)_2$ are evaluated with t-test. The t-value for two sets of samples is −2.03. The p-value with 0.05 CI based on two-tailed hypothesis is $p = 0.043 < 0.05$. The difference in PBQS size distribution is considered statistically significant before and after cycling in $Zn(CF_3SO_3)_2$.

To compare the difference of PBQS particles after 100 cycles in two electrolytes, we performed t-test on the area of particles shown in Fig. 1g and j. The t-value for two sets of samples is −2.07. The p-value with 0.05 CI based on two-tailed hypothesis is $p = 0.038 < 0.05$. The difference in PBQS size distribution after 100 cycles in $ZnSO_4$ and $Zn(CF_3SO_3)_2$ is also considered statistically significant. Statistical analysis justifies the remarkable influence of solvation structure on the microstructure of polymer electrodes.

Table S1. Size distribution for pristine and cycled PBQS in $ZnSO_4$ and $Zn(CF_3SO_3)_2$.

Parameters	Pristine	Cycled in $ZnSO_4$	Cycled in $Zn(CF_3SO_3)_2$
Number of samples N	339	261	266
Average particle area M (μm^2)	1.23	2.04	1.52
Standard deviation s (μm^2)	1.77	3.71	1.69

Table S2. FTIR vibrational peak assignment.

#	Functional Groups	Wavenumber (cm^{-1})
1	O–D	2350–2450. [2]
2	C=O	1630 [2]
3	C–O and Ar–S stretching	1400 [2]
4	Ar–S stretching	1540 [2]
5	S–O antisymmetric stretching	1060–1200 [3]
6	S–O bending	600–780 [3]
7	C–F stretching	1220–1240. [4]
8	C–F antisymmetric stretching	1150–1180. [4]
9	S–O stretching	1028 [4]

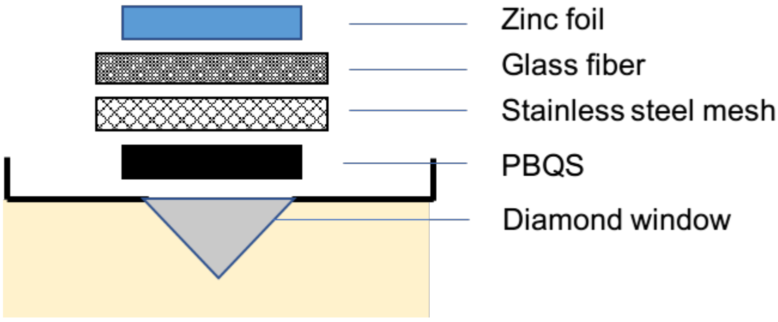

Figure S1. Schematics of an in situ cell for FTIR characterization.

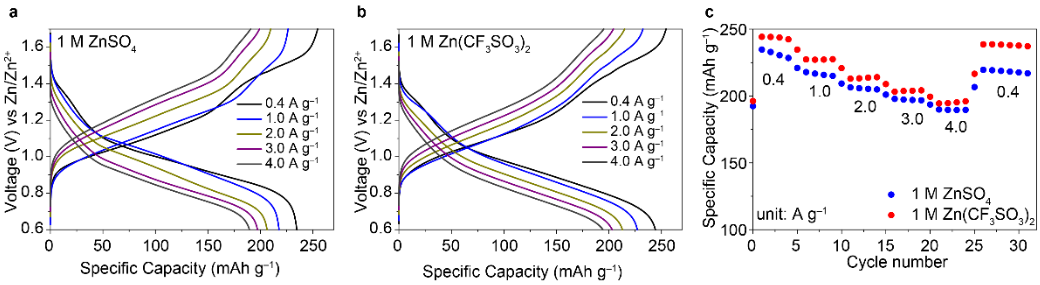

Figure S2. Voltage profiles of PBQS cathodes tested in **a,** 1 M $ZnSO_4$ and **b,** 1 M $Zn(CF_3SO_3)_2$ electrolyte under different current densities. **c,** discharge capacity vs. cycle number.

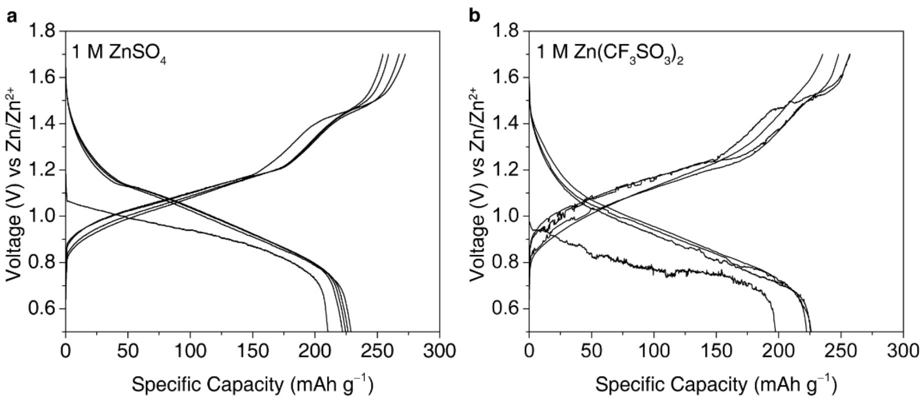

Figure S3. Cycle performance of PBQS/Zn cells during stack pressure monitoring in **a,** 1 M $ZnSO_4$ and **b,** 1 M $Zn(CF_3SO_3)_2$ electrolytes.

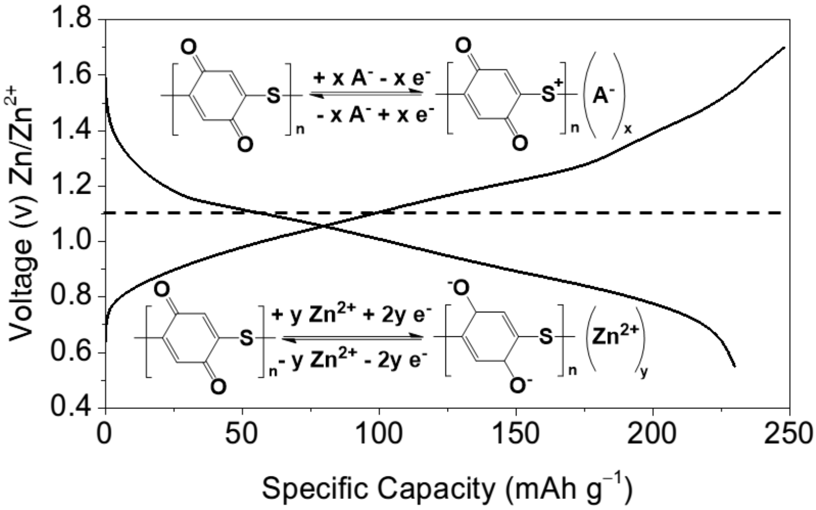

Figure S4. Doping mechanism of PBQS in different voltage ranges.

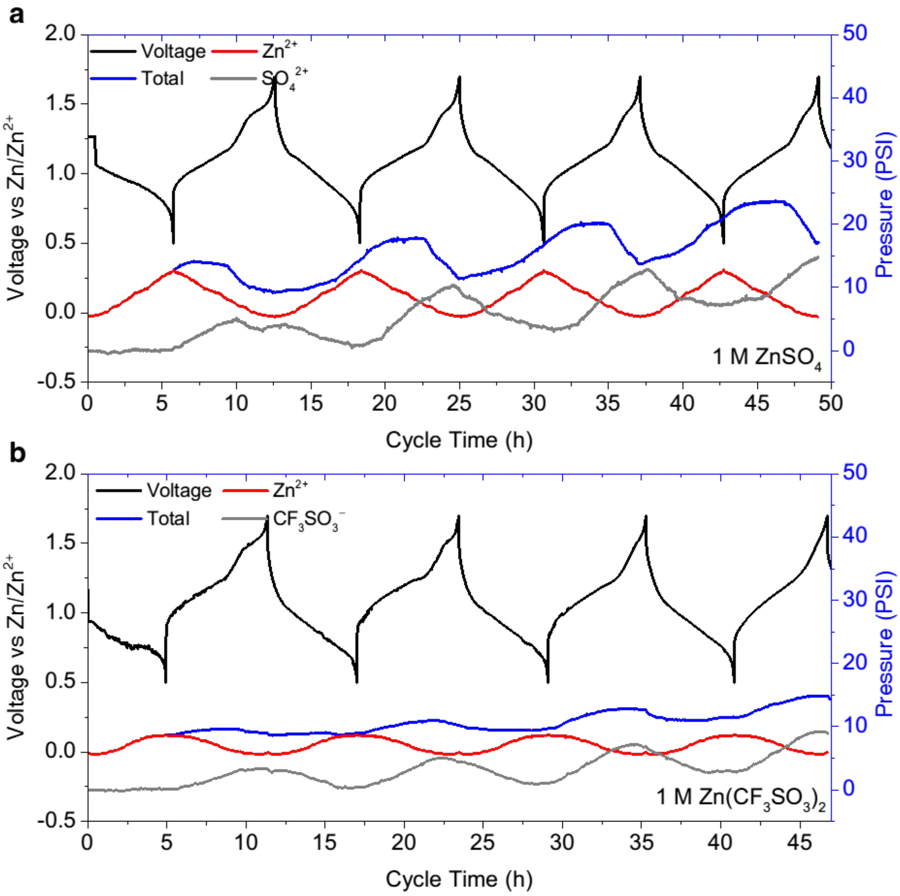

Figure S5. Voltage and pressure evolution profiles in **a,** 1 M $ZnSO_4$ and **b,** 1 M $Zn(CF_3SO_3)_2$ electrolytes. We assume that the pressure change in the first discharge is driven solely by Zn^{2+} and such change is fully reversible in later cycles. The pressure change contributed by Zn^{2+} and anions are marked in red and grey lines. It should be noted that the trapping of solvent and/or salt would affect pressure values but not the evolution trend.

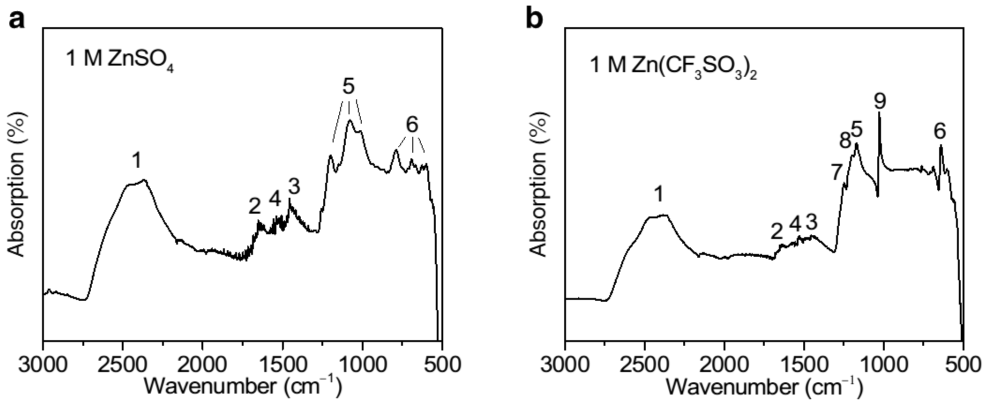

Figure S6. FTIR spectra of pristine PBQS electrode in **a,** 1 M $ZnSO_4$ and **b,** 1 M $Zn(CF_3SO_3)_2$ electrolytes.

Reference

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