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Supplementary Material

New insights into the charge storage chemistry of polymer cathodes in aqueous Zn batteries

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1. Calculation for the Activation Energy Using CV Curves

For a CV loop, the redox peak current I_p is expressed as:

$$I_P = A\sqrt{\upsilon e^{-E_A/RT} / T} \qquad \text{(S1)}$$

Where A is a constant, υ is the voltage scan rate, E_{Arr} is the activation energy, R is the gas constant, and T is the absolute temperature. Eq.(1) can be transformed into:

$$lnI_p = ln + \frac{1}{2}\left(ln\frac{\upsilon}{T} - \frac{E_A}{RT} - lnT \right) \qquad \text{(S2)}$$

When at constant υ, using the reduction peak intensities, I_1 and I_2, of two CV curves at temperatures of T_1 and T_2, respectively, we obtain:

$$E_A = \frac{\left(2ln\frac{I_1}{I_2} - ln\frac{T_2}{T_1} \right) RT_1T_2}{T_1 - T_2} \qquad \text{(S3)}$$

Using the reduction peaks of two sets of CV loops at 2 and 5 mV s^{-1}, and at two different temperatures, respectively, we are able to estimate E_A. For instance, for the poly(4-HDPA)/AC electrode, the reduction peak intensities of CV curves at 2 mV s^{-1} are 9.48 mA cm^{-2} at 25 °C (298.15 K) and 7.53 mA cm^{-2} at 15 °C (288.15 K). Hence, using Eq.(S3) we obtain E_A = 32.31 kJ mol^{-1}. In the temperature range form 15 to 5 °C, the E_A is 33.99 kJ mol^{-1}. Similarly, when using the CV curves at 5 mV s^{-1}, we obtain E_A values of 31.08 kJ mol^{-1} (25 -15°C) and 34.30 kJ mol^{-1} (15 - 5°C). Thus, the averaged E_A is 32.9 kJ mol^{-1}. More information about parameters and calculation results for polymer cathodes can be found in Table S5 and S6.

1. Supporting Figures and Tables

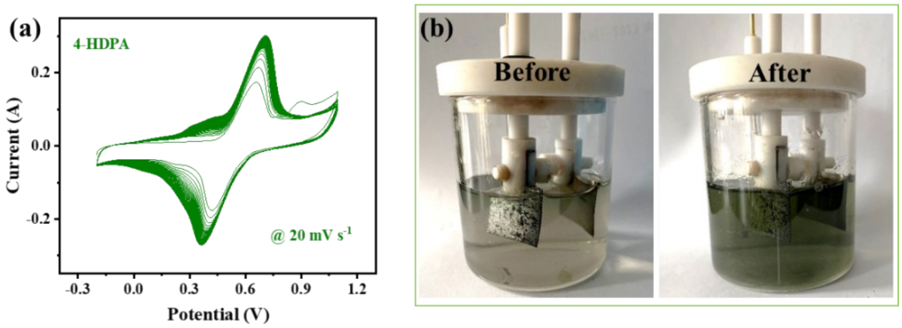

Fig. S1. (a) Evolution of CV loop in the electropolymerization process. (b) Optical photographs of a three-electrode cell before and after the electrodeposition of poly(4-HDPA).

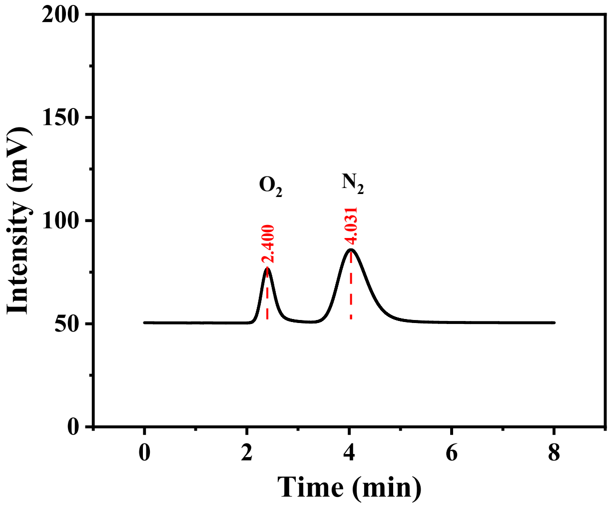

Fig. S2. GC spectrum of a Zn//poly(4-HDPA)/AC full cell after GCD test.

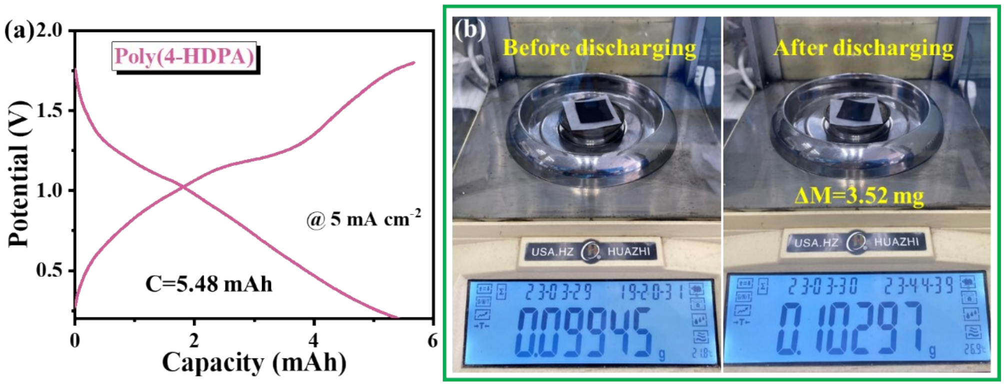

Fig. S3. (a) GCD curve of poly(4-HDPA) cathode at 5 mA cm^{-2}. (b) Weight of poly(4-HDPA)/AC cathode before discharging and after discharging.

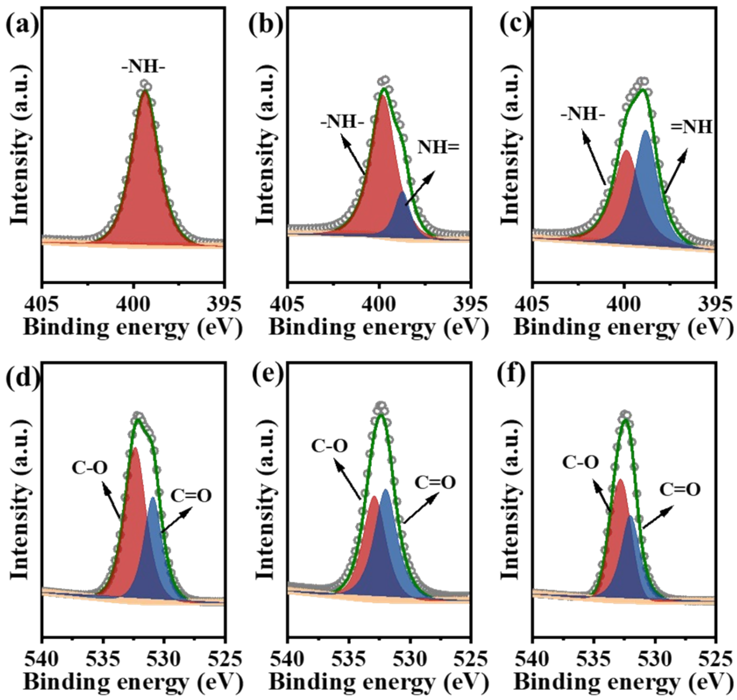

Fig. S4. (a-c) High-resolution N 1s XPS spectra collected from poly(4-HDPA), poly(4-AP), and poly(1,5-NAPD), respectively. (d-f) High-resolution O 1s XPS spectra collected from poly(4-HDPA), poly(4-AP), and poly(2,6-DHN), respectively.

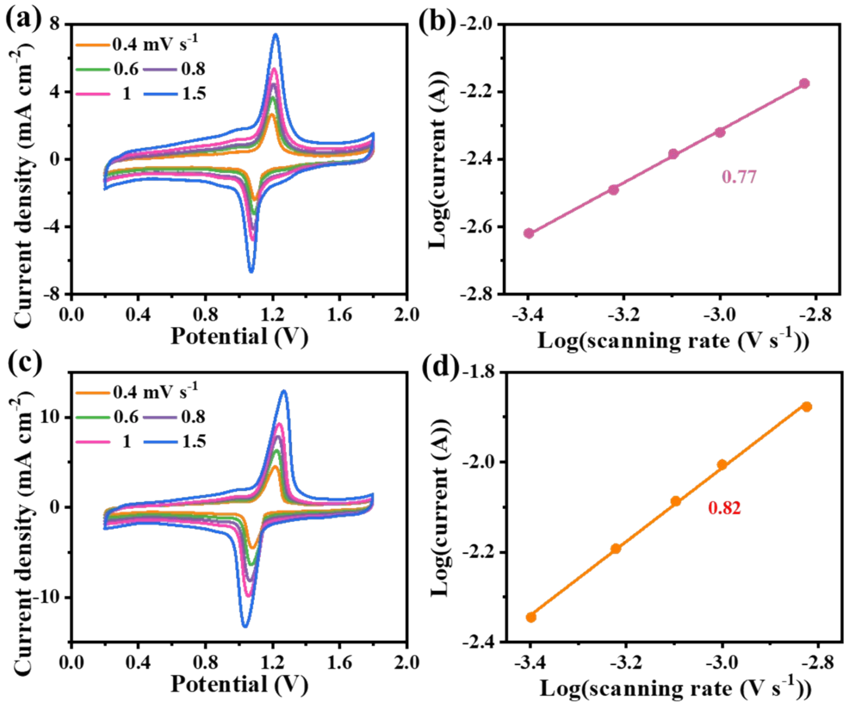

Fig. S5. (a) CV curves at scan rate ranging from 0.4 to 1.5 mV s-1 and (b) b-value for reduction peak of Zn//poly(4-HDPA)/AC cell. (c) CV curves at scan rate ranging from 0.4 to 1.5 mV s-1 and (d) b-value for reduction peak of Zn//poly(4-AP)/AC cell.

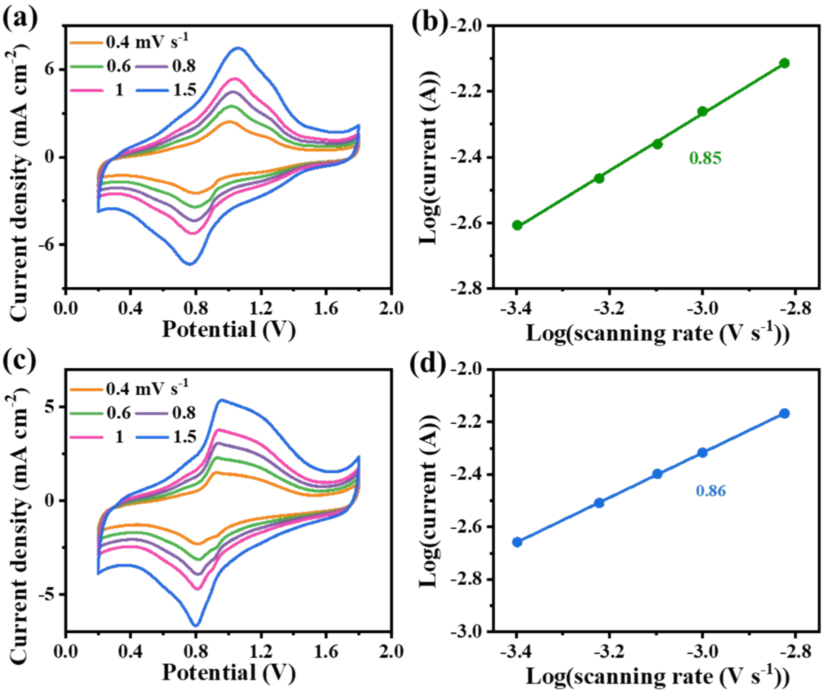

Fig. S6. (a, c) CV loops at low voltage scan rates from 0.4 to 1.5 mV s^{-1} collected from Zn||poly(1,5-NAPD)/AC and Zn//poly(1,6-DHN)/AC cells, respectively. (b, d) Plots for deducing b-values using the reduction peaks of poly(1,5-NAPD) and poly(1,6-DHN), respectively.

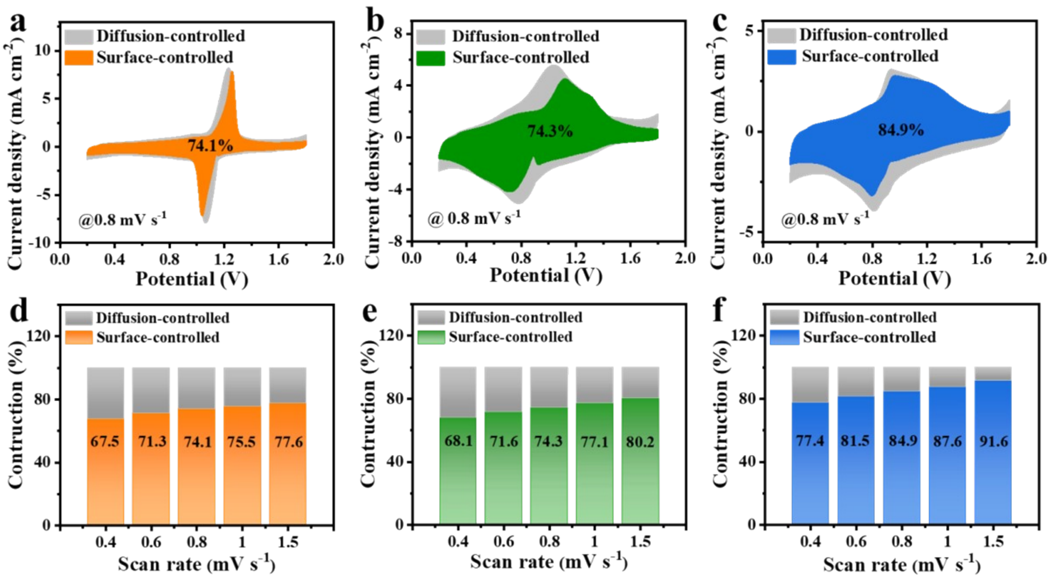

Fig. S7. (a-c) CV curves at 0.8 mV s^{-1} showing the contribution fractions of diffusion-controlled and surface-controlled charge storage processes for poly(4-AP), poly(1,5-NAPD), and poly(1,6-DHN), respectively. (d-f) Specific contributions of the two types of charge storage processes at different voltage scan rates for poly(4-AP), poly(1,5-NAPD), and poly(1,6-DHN), respectively.

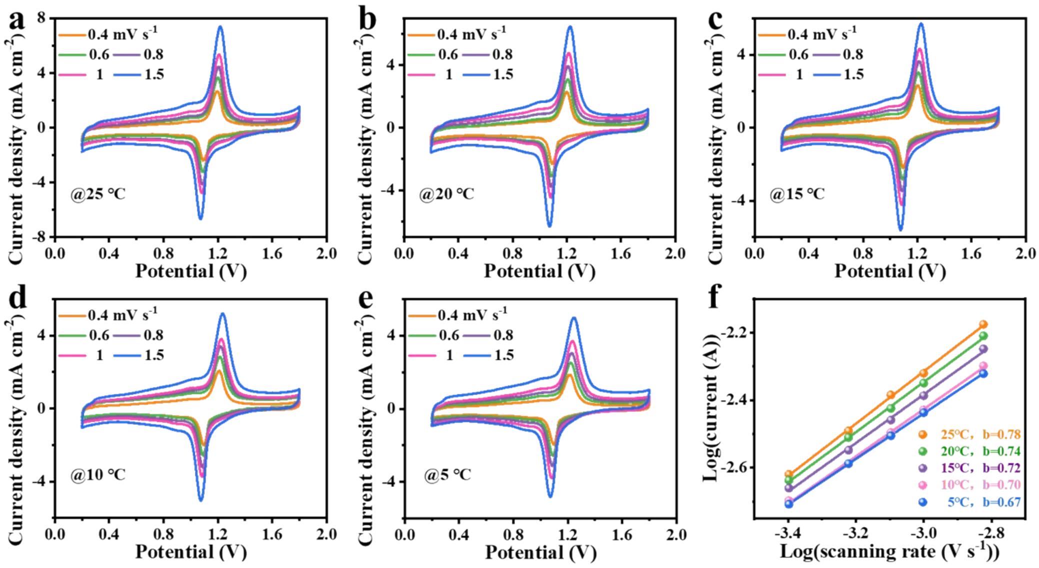

Fig. S8. CV curves collected from a Zn//poly(4-HDPA)/AC cell at (a) 25, (b) 20, (c) 15, (d) 10, and (e) 5 ºC. (f) Plots for deducing b-values of the poly(4-HDPA)/AC cathode at different temperatures using the reduction peak intensities.

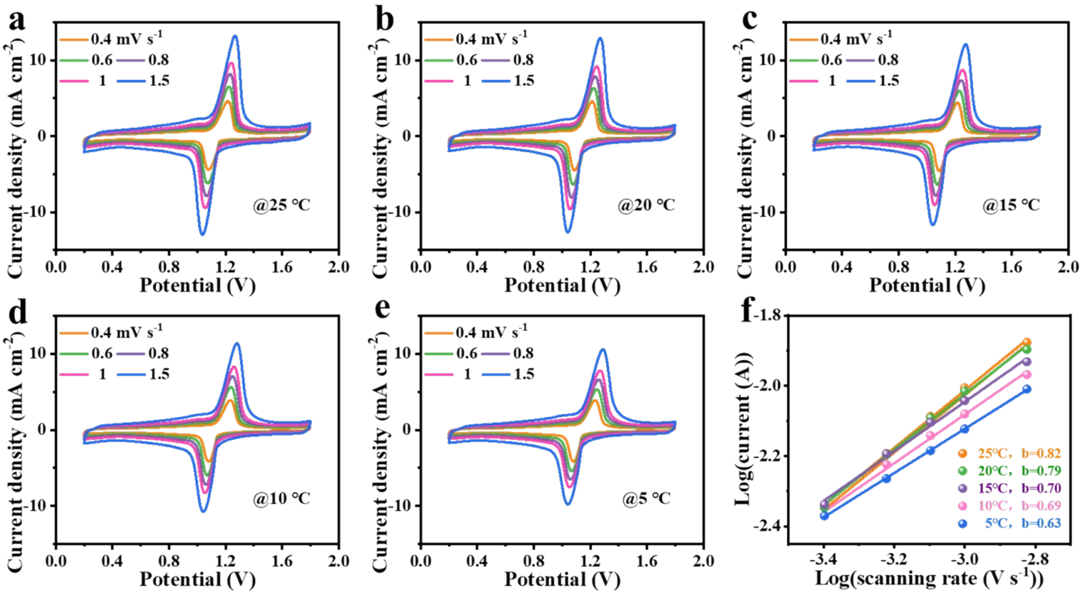

Fig. S9. CV curves collected from a Zn//poly(4-AP)/AC cell at (a) 25, (b) 20, (c) 15, (d) 10, and (e) 5 ºC. (f) Plots for deducing b-values of the poly(4-AP)/AC cathode at different temperatures using the reduction peak intensities.

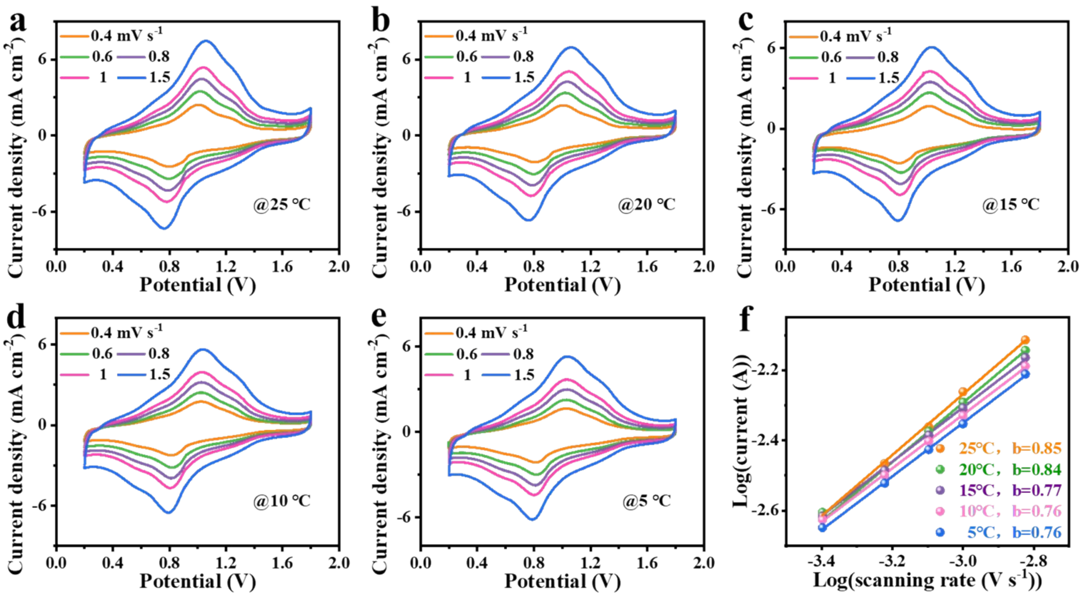

Fig. S10. CV curves collected from a Zn//poly(1,5-NAPD)/AC cell at (a) 25, (b) 20, (c) 15, (d) 10, and (e) 5 ºC. (f) Plots for deducing b-values of the poly(1,5-NAPD)/AC cathode at different temperatures using the reduction peak intensities.

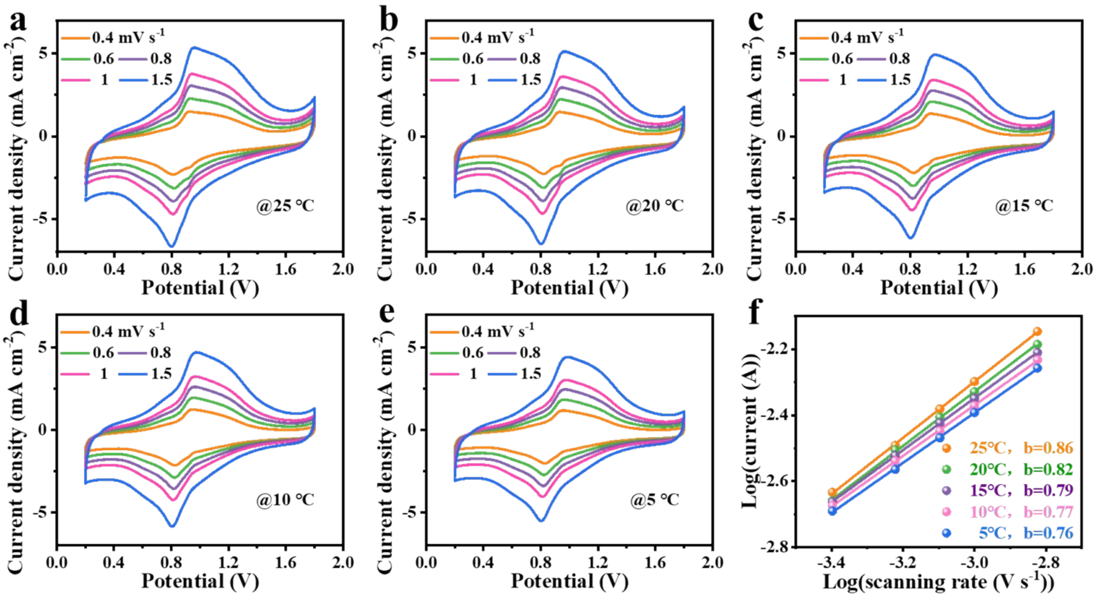

Fig. S11. CV curves collected from a Zn//poly(1,6-DHN)/AC cell at (a) 25, (b) 20, (c) 15, (d) 10, and (e) 5 ºC. (f) Plots for deducing b-values of the poly(1,6-DHN)/AC cathode at different temperatures using the reduction peak intensities.

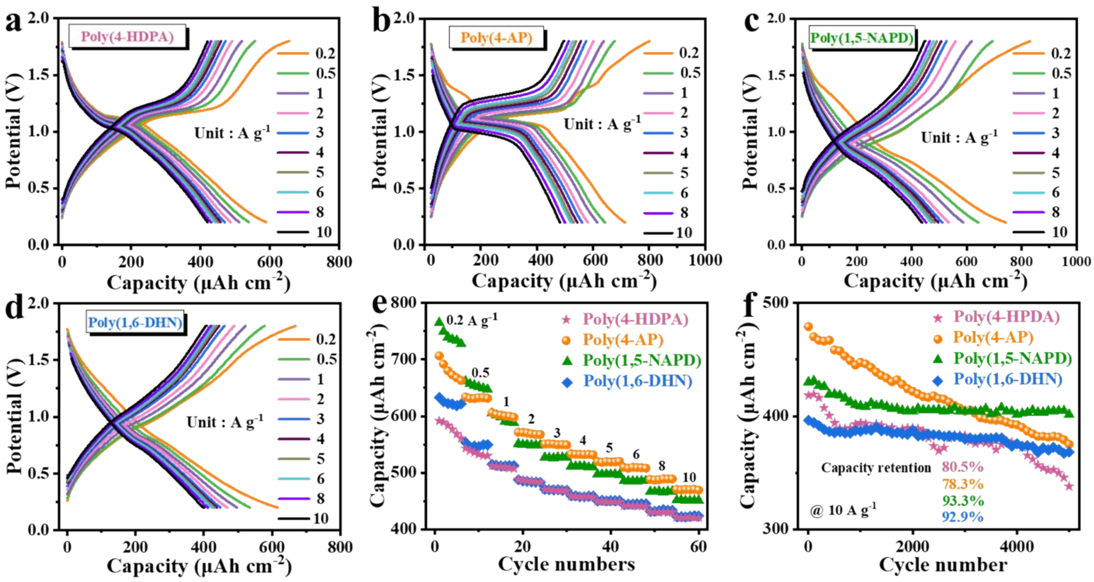

Fig. S12. GCD profiles at different current densities for (a) Zn||poly(4-HDPA)/AC, (b) Zn||poly(4-AP)/AC, (c) Zn||poly(1,5-NAPD)/AC and (d) Zn||poly(1,6-DHN)/AC cells. (e) Rate performances and (f) cycling stabilities of the four cells.

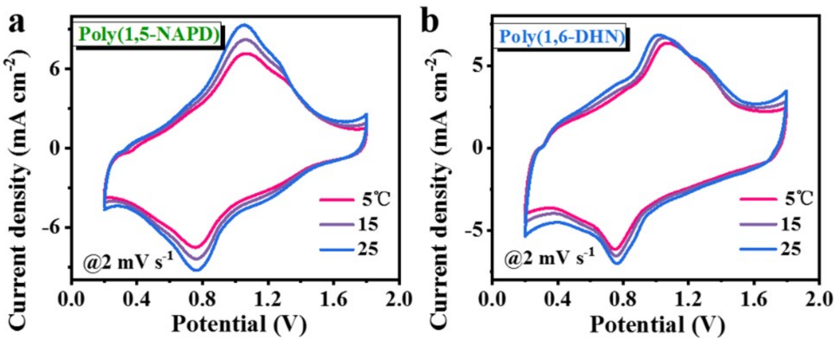

Fig. S13. Temperature-dependent CV loops at 2 mV s^{-1} collected from (a) Zn||poly(1,5-NAPD)/AC and (b) Zn||poly(1,6-DHN)/AC cells, respectively.

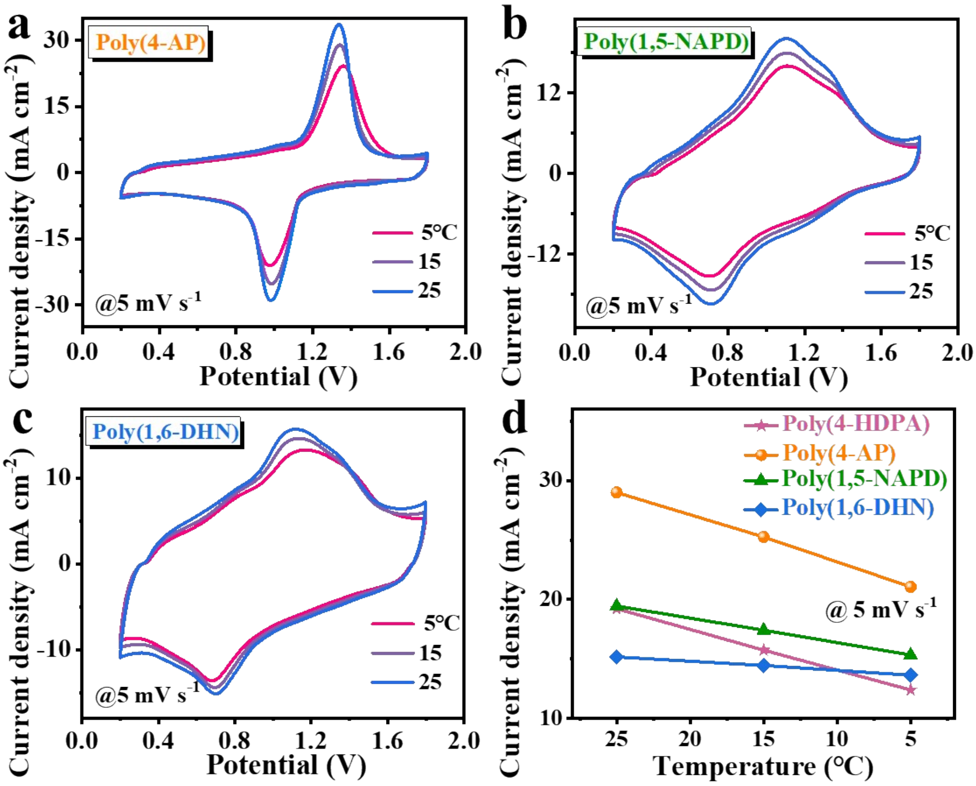

Fig. S14. (a-c) Temperature-dependent CV loops at 5 mV s^{-1} from Zn||poly(4-AP)/AC, Zn||poly(1,5-NAPD)/AC, and Zn||poly(1,6-DHN)/AC cells, respectively. (d) Plots of reduction peak current versus temperature at 5 mV s^{-1} for the Zn||poly(4-HPDA)/AC cell.

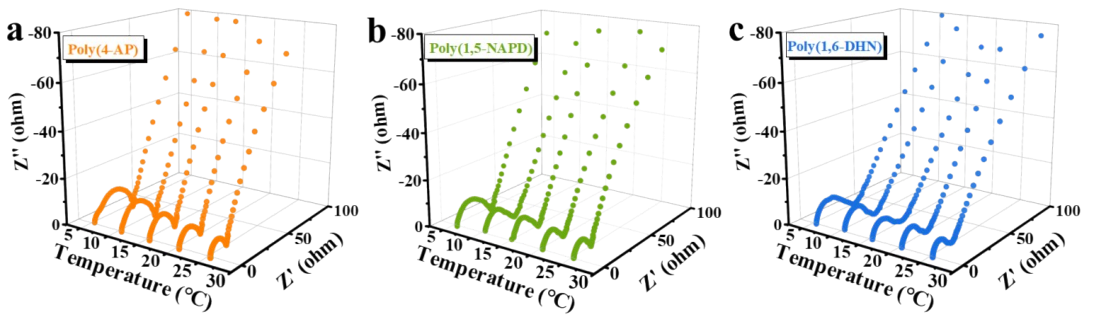

Fig. S15. Temperature-dependent EIS spectra of (a) Zn||poly(4-AP)/AC, (b) Zn||poly(1,5-NAPD)/AC, and (c) Zn||poly(1,6-DHN)/AC cells, respectively.

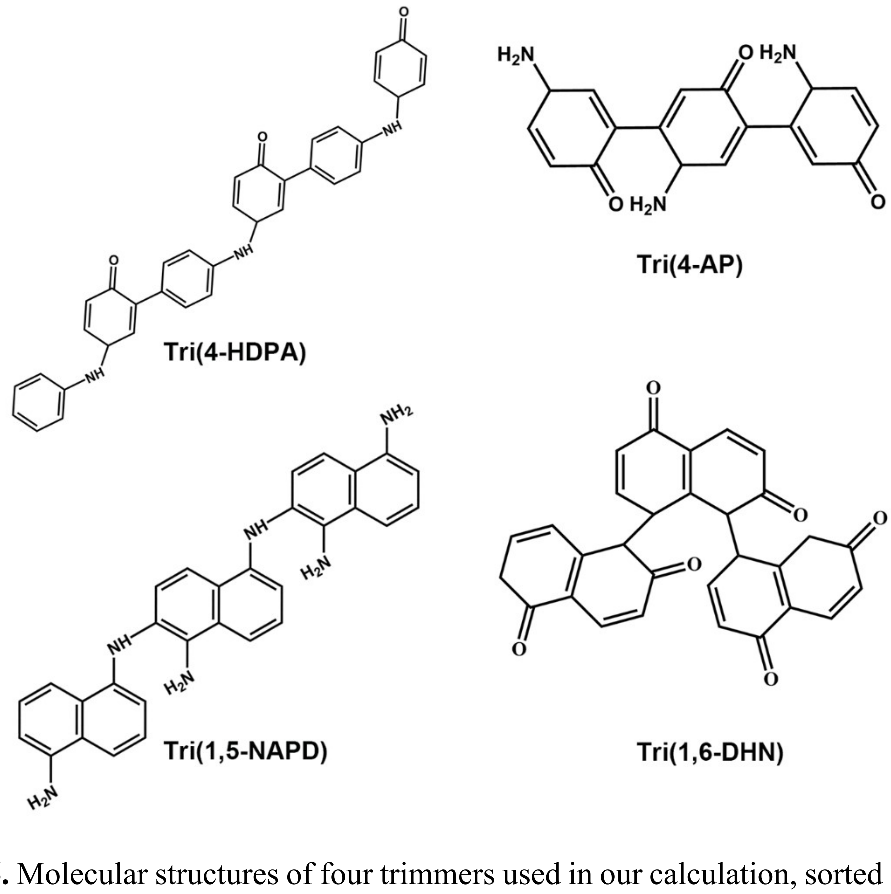

Fig. S16. Molecular structures of four trimmers used in our calculation, sorted out from many possible structures according to the lowest-energy principle in polymerization.

Table S1. Experimental data of poly(4-HDPA) cathode for the calculated fractions of H^+ uptake.

Sample	Mass before discharge (g)	Mass after Discharge (g)	ΔM (mg)	Discharge Capacity (mAh)	Quantity of H^+ (mmol)	Quantity of Zn^{2+} (mmol)	H^+ Percentage (%)
1	0.12887	0.13239	3.52	5.48	0.0992	0.0526	65.34
2	0.10859	0.11068	2.09	3.24	0.0584	0.0313	65.13
3	0.10974	0.11187	2.13	3.31	0.0598	0.0318	65.25
4	0.10768	0.11005	2.37	3.68	0.0664	0.0354	65.21
5	0.10975	0.11227	2.52	3.92	0.0709	0.0377	65.30
6	0.11449	0.11765	3.16	4.91	0.0887	0.0473	65.25
7	0.09795	0.10082	2.87	4.45	0.0802	0.0429	65.14
8	0.10247	0.10512	2.65	4.11	0.0741	0.0396	65.15
9	0.10644	0.10897	2.53	3.92	0.0706	0.0378	65.11
10	0.10426	0.10672	2.46	3.82	0.0690	0.0368	65.22
Averaged value: (65.21 ± 0.08)%							

Table S2. Experimental data of poly(4-AP) cathode for the calculated fractions of H^+ uptake.

Sample	Mass before discharge (g)	Mass after Discharge (g)	ΔM (mg)	Discharge Capacity (mAh)	Quantity of H^+ (mmol)	Quantity of Zn^{2+} (mmol)	H^+ Percentage (%)
1	0.10126	0.10480	3.54	5.42	0.0963	0.0530	64.50
2	0.10429	0.10750	3.21	4.94	0.0883	0.0480	64.76
3	0.10664	0.10982	3.18	4.87	0.0865	0.0476	64.52
4	0.09867	0.1012	2.53	3.88	0.0691	0.0379	64.59
5	0.10421	0.10697	2.76	4.23	0.0752	0.0413	64.57
6	0.10323	0.10626	3.03	4.64	0.0824	0.0453	64.51
7	0.10879	0.11187	3.08	4.73	0.0843	0.0461	64.66
8	0.10648	0.10945	2.97	4.54	0.0805	0.0445	64.42
9	0.10364	0.10619	2.55	3.92	0.0700	0.0382	64.71
10	0.10335	0.10613	2.78	4.27	0.0761	0.0416	64.67
Averaged value: (64.59 ± 0.11)%							

Table S3. Experimental data of poly(1,5-NAPD) cathode for the calculated fractions of H^+ uptake.

Sample	**Mass before discharge (g)**	**Mass after Discharge (g)**	**ΔM (mg)**	**Discharge Capacity (mAh)**	**Quantity of H^+ (mmol)**	**Quantity of Zn^{2+} (mmol)**	**H^+ Percentag e (%)**
1	0.09846	0.10159	3.13	4.61	0.07811	0.047	62.46
2	0.08689	0.0895	2.61	3.84	0.06498	0.0392	62.40
3	0.09934	0.10228	2.94	4.31	0.07259	0.0441	62.20
4	0.09867	0.10110	2.43	3.58	0.06068	0.0365	62.47
5	0.09986	0.10275	2.89	4.24	0.07149	0.0434	62.24
6	0.09949	0.10252	3.03	4.47	0.0759	0.0454	62.55
7	0.09916	0.10234	3.18	4.68	0.07922	0.0477	62.41
8	0.09855	0.10152	2.97	4.38	0.07434	0.0445	62.53
9	0.09946	0.10201	2.55	3.75	0.06342	0.0383	62.37
10	0.09984	0.10252	2.68	3.94	0.0666	0.0402	62.36
Averaged value: (62.40 ± 0.11)%							

Table S4. Experimental data of poly(1,6-DHN) cathode for the calculated fractions of H^+ uptake.

Sample	Mass before discharge (g)	Mass after Discharge (g)	ΔM (mg)	Discharge Capacity (mAh)	Quantity of H^+ (mmol)	Quantity of Zn^{2+} (mmol)	H^+ Percentage (%)
1	0.10246	0.10471	2.25	3.28	0.0545	0.0338	61.89
2	0.10689	0.10911	2.22	3.24	0.0543	0.0333	61.95
3	0.11934	0.12147	2.13	3.10	0.0517	0.0320	61.80
4	0.11868	0.12101	2.33	3.39	0.0565	0.0350	61.78
5	0.10975	0.11267	2.92	4.26	0.0713	0.0438	61.93
6	0.10949	0.11250	3.01	4.38	0.0731	0.0452	61.79
7	0.09997	0.10302	3.05	4.45	0.0745	0.0458	61.93
8	0.10247	0.10544	2.97	4.33	0.0724	0.0446	61.89
9	0.10334	0.10587	2.53	3.69	0.0617	0.0380	61.91
10	0.10326	0.10583	2.57	3.75	0.0624	0.0386	61.94
Averaged value: (61.88 ± 0.07)%							

Table S5. Reduction peak current (I_p) densities and calculated activation energies for poly(4-HDPA) and poly(4-AP) cathodes.

<table>
<tr><th></th><th colspan="2">25 °C</th><th colspan="2">15 °C</th><th colspan="2">5 °C</th><th></th></tr>
<tr><td>I_p@2 mV s^{-1} (mA cm^{-2})</td><td colspan="2">9.48</td><td colspan="2">7.53</td><td colspan="2">5.94</td><td rowspan="5">**Poly(4-HDPA)**</td></tr>
<tr><td>I_p@5 mV s^{-1} (mA cm^{-2})</td><td colspan="2">19.22</td><td colspan="2">15.73</td><td colspan="2">12.38</td></tr>
<tr><td>E_A@2 mV s^{-1} (kJ mol^{-1})</td><td colspan="3">32.31</td><td colspan="3">33.99</td></tr>
<tr><td>E_A@5mV s^{-1} (kJ mol^{-1})</td><td colspan="3">31.08</td><td colspan="3">34.30</td></tr>
<tr><td>Averaged E_A (kJ mol^{-1})</td><td colspan="6">**32.9**</td></tr>
<tr><td>I_p@2 mV s^{-1} (mA cm^{-2})</td><td colspan="2">16.09</td><td colspan="2">8.39</td><td colspan="2">7.52</td><td rowspan="5">**Poly(4-AP)**</td></tr>
<tr><td>I_p@5 mV s^{-1} (mA cm^{-2})</td><td colspan="2">29.02</td><td colspan="2">25.26</td><td colspan="2">21.06</td></tr>
<tr><td>E_A@2 mV s^{-1} (kJ mol^{-1})</td><td colspan="3">22.52</td><td colspan="3">24.28</td></tr>
<tr><td>E_A@5 mV s^{-1} (kJ mol^{-1})</td><td colspan="3">22.16</td><td colspan="3">26.58</td></tr>
<tr><td>Averaged E_A (kJ mol^{-1})</td><td colspan="6">**23.9**</td></tr>
</table>

Table S6. Reduction peak current densities and calculated activation energies for poly(1,5-NAPD) and poly(1,6-DHN).

	25 °C	15 °C	5 °C	
I_p@2 mV s^{-1} (mA cm^{-2})	9.27	8.39	7.52	Poly(1,5-NAPD)
I_p@5 mV s^{-1} (mA cm^{-2})	19.45	17.41	15.32	
E_A@2 mV s^{-1} (kJ mol^{-1})	16.68		16.64	
E_A@5mV s^{-1} (kJ mol^{-1})	18.26		19.40	
Averaged E_A (kJ mol^{-1})	**17.7**			
I_p@2 mV s^{-1} (mA cm^{-2})	7.02	6.55	6.15	Poly(1,6-DHN)
I_p@5 mV s^{-1} (mA cm^{-2})	15.16	14.44	13.62	
E_A@2 mV s^{-1} (kJ mol^{-1})	12.34		10.75	
E_A@5 mV s^{-1} (kJ mol^{-1})	9.39		10.15	
Averaged E_A (kJ mol^{-1})	**10.7**			