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New Insights into the Electrochemistry of Carbonyl- and Amino-Containing Polymers for Rechargeable Zinc—Organic Batteries

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ABSTRACT: Organic electrode materials have a large variety of types and could be a replacement for metal compounds in building highperformance rechargeable Zn-ion batteries. Polymers with redox activity can be divided into amino-containing aromatics and quinones, and they show different electrochemical behaviors. Here, we compare two representative polymers, poly(1,5-naphthalenediamine) and poly-(1,5-dihydroxynaphthalene), that are electrodeposited onto nanoporous carbon to make cathodes for Zn-ion batteries. Electrochemical energy storage performances of the two polymers are tested at different temperatures ranging from 20 to -20 °C, and the influence of low temperature on their capacity loss, charge transfer resistance, and activation energy is determined. By combining experiment with theory, we unravel key factors of the polymer that favor energy storage performance. The entropy change in the Zn-ion uptake process of an



organic electrode material is found to play a key role in the energy storage performance in terms of cycling stability and capacity retention in a cold environment.

queous rechargeable Zn-ion batteries (ZIBs) have received a great deal of attention due to the many merits of the Zn negative electrode, such as its earth abundance, divalent ion, high theoretical capacity (820 mAh g^{-1}), low redox potential of Zn²⁺/Zn, and environmental benignity.^{1,2} The cathode materials of ZIBs play a key role in energy storage performance, while their majorities have been limited to the manganese family, including different phases of MnO₂ and Mn₃O₄.^{3–5} Vanadium oxides were also used in ZIBs, and some of them exhibited a high specific capacity of >400 mAh g⁻¹, but such cells show a low discharge median voltage (~0.6 V).^{6,7} Drawbacks of metal oxide-based cathodes include unsatisfactory cycling stability, high resistance at a high mass loading, and gradual dissolution of metal oxide in an aqueous electrolyte.⁸

Beyond inorganic compounds that have a few types for ZIB cathodes, organic electrode materials have plenty of options due to the diversity of their molecular structures and different redox-active groups and could be a replacement for inorganic compound electrodes.^{9,10} Although charge storage polymers may have low electrical conductivity, they can be combined with nanoporous carbon to achieve a high areal mass loading of >10 mg cm⁻² while maintaining a low internal resistance.^{11,12}

Organic electrode materials for aqueous ZIBs are mainly aromatics containing carbonyl groups, amino groups, or both.^{11–15} Note that carbonyl and amino groups show different electrochemical behaviors. Zhao et al. used calix[4]quinone (C4Q) as a cathode material to make ZIBs, which showed a flat discharge voltage plateau around 1 V.¹⁴ Wan et al. reported a Zn//polyaniline battery that was operated within the voltage range of 0.5–1.5 V and showed a slopelike discharge profile.¹⁶ Upon the selection of optimal polymers for making high-performance Zn–organic batteries, a systematic study of the charge storage kinetics of quinones and aminocontaining aromatics is in high demand. In the literature, the widely used electrolyte for ZIBs is the 2 M ZnSO₄ solution that has a freezing point of around -12 °C. From a practical point of view, it is worth concocting a low-temperature resistant

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Figure 1. (a) Schematic illustration for the Zn-polymer cell. Molecular structures of two polymers as cathode materials are shown. (b and c) SEM images of typical poly(1,5-DHN)/AC and poly(1,5-NAPD)/AC cathodes, respectively. (d) Survey and (e) C 1s XPS spectra of poly(1,5-NAPD)/AC, poly(1,5-DHN)/AC, and the bare AC coating. (f) High-resolution O 1s XPS spectra of poly(1,5-DHN)/AC and bare AC.



Figure 2. (a-c) Temperature-dependent CV loops at 2 mV s⁻¹ from Zn//poly(1,5-NAPD)/AC, Zn//poly(1,5-DHN)/AC, and Zn//AC cells, respectively. (d) Plots of R peak current vs temperature for Zn//poly(1,5-NAPD)/AC and Zn//poly(1,5-DHN)/AC, deduced from CV loops at 2 and 5 mV s⁻¹. (e) Plots of capacity vs temperature for the three cells using poly(1,5-NAPD)/AC, poly(1,5-DHN)/AC, and bare AC coating anodes. (f) Dependence of the *b* value on temperature for poly(1,5-NAPD)/AC and poly(1,5-DHN)/AC cathodes.

electrolyte and understanding the energy storage performances of carbonyl- and amino-containing polymers in a bitterly cold environment.

Herein, by combining experiment with theory, we look into the different charge storage performances of two polymers containing carbonyl and amino groups, respectively. 1,5-Dihydroxynaphthalene (DHN) and 1,5-naphthalenediamine (NAPD), which share a similar molecular backbone structure, were electropolymerized and electrodeposited over nanoporous activated carbon (AC) granules to make cathodes. As-fabricated Zn-polymer batteries were tested within a wide temperature range from 20 to -20 °C, attributed to our antifreeze ZnSO₄ electrolyte with a methanol additive (freezing point of -35 °C). This study reveals factors accounting for the different electrochemical behaviors of poly(1,5-NAPD) and poly(1,5-DHN), such as the capacity decay at low temperature, cycling stability, and charge diffusion, paving the way toward advanced Zn-polymer batteries in the future.

Figure 1a shows the molecular structures of 1,5-DHN and 1,5-NAPD monomers, and the configuration of a Zn-polymer cell. Details of the electropolymerization process can be found in the Supporting Information. High-resolution scanning electron microscopy (SEM) images of poly(1,5-DHN)/AC and poly(1,5-NAPD)/AC cathodes are shown in panels b and c of Figure 1, respectively, revealing different morphologies of the two polymers. The slurry-coated AC had a specific surface area of 1820 m² g⁻¹ after being dried. After the electrodeposition process, the poly(1,5-DHN)/AC and poly(1,5-NAPD)/AC coatings showed specific surface areas of 351 and 160 m² g⁻¹, respectively (Figure S3a). X-ray photoelectron spectroscopy (XPS) spectra of bare AC, poly(1,5-DHN)/AC, and poly(1,5-NAPD)/AC samples are shown in Figure 1d. The bare AC powder made from coconut shell naturally contains a small oxygen fraction (4.8 atom %) without nitrogen. Among the three samples, poly(1,5-DHN)/AC shows the highest O content (13.5 atom %) and poly(1,5-NAPD)/AC shows the highest N content (2.9 atom %). Highresolution C 1s XPS spectra of the three samples are compared in Figure 1e. According to the O 1s XPS spectra in Figure 1f, the ratio of C=O to C-O in AC is \sim 20%. For the poly(1,5-DHN)/AC sample, this ratio is 25%. More characterizations, such as Raman and Fourier transform infrared spectroscopy, for our cathode materials can be found in Figure S4.

Two cells, Zn//poly(1,5-NAPD)/AC and Zn//poly(1,5-DHN)/AC, were tested at different temperatures ranging from 20 to -20 °C, and their cyclic voltammetry (CV) loops at 2 $mV s^{-1}$ are shown in panels a and b of Figure 2, respectively. In each cell, the areal mass loading of the AC coating in the cathode was $\sim 3.5 \text{ mg cm}^{-2}$. After the electropolymerization process, the mass loadings of poly(1,5-NAPD)/AC and poly(1,5-DHN)/AC composites were 5.0 and 4.4 mg cm⁻², respectively. It can be found that the oxidation (O) and reduction (R) peaks of poly(1,5-DHN)/AC are narrower than those of poly(1,5-NAPD) due to the coordination reaction between carbonyl groups and Zn²⁺. The relatively sharp R peak of poly(1,5-DHN) leads to an obvious voltage plateau in the galvanostatic discharge curve (Figure S5b). For comparison, we also made a Zn//AC hybrid supercapacitor, which relies on physical adsorption of ions for charge storage,¹⁷ to collect CV loops at different temperatures. In Figure 2c, the weak redox peaks of this Zn//AC cell were contributed by oxygenated groups in AC. To study the influence of temperature on the redox activity of poly(1,5-NAPD) and poly(1,5-DHN), we extracted the dependence of the R peak current (I_p) on the temperature from a series of CV loops at 2 mV s⁻¹, measured from 20 to -20 °C. As shown in Figures 2d, the peak current of poly(1,5-NAPD) decreases faster than that of poly(1,5-DHN) with a decrease in temperature. Figure 2e shows plots of capacity versus temperature for poly(1,5-NAPD)/AC//Zn, poly(1,5-DHN)/AC//Zn, and AC//Zn (Figure 2e), deduced from galvanostatic charge-discharge (GCD) curves at 2 mA cm⁻². At 20 °C, the specific capacities of Zn//poly(1,5-NAPD)/AC and Zn//poly(1,5-DHN)/AC reached 591 and 395 μ Ah cm⁻², respectively. The maximum capacity of the Zn//AC cell was 153 μ Ah cm⁻². When the temperature was decreased to -20 °C, the specific capacities of Zn//poly(1,5-NAPD)/AC and Zn//poly(1,5-DHN)/AC were decreased to 305 and 314 μ Ah cm⁻², respectively, corresponding to capacity retentions of 51.6% and 79.5%, respectively. The capacity retention of Zn//AC at -20 °C was 82.2%. Further GCD tests revealed that poly(1,5-DHN)/AC is better than Zn//poly(1,5NAPD)/AC in rate performance (Figure S5). In addition, the Zn//poly(1,5-NAPD)/AC and Zn//poly(1,5-DHN)/AC cells were cycled at 0 °C, showing capacity retentions of 90% and 94% after 3000 cycles, respectively (Figure S7). Therefore, the amino-containing poly(1,5-NAPD) shows higher capacity at room temperature but suffers from larger capacity loss under cold conditions. The quinone-type poly(1,5-DHN) is superior to poly(1,5-NAPD) in terms of rate performance, low-temperature capacity retention, and cycling stability.

According to the Randles–Sevcik equation,¹⁸ the peak current, I_p , for electrically reversible electron transfer processes involving freely diffusion redox species can be expressed as $I_p \propto \sqrt{Dv/T}$, where *D* is the diffusion coefficient, *v* is the voltage scan rate, and *T* is the absolute temperature. The Arrhenius equation relates *D* with *T*, as $D = D_0 \exp(-E_{Arr}/RT)$, where D_0 is a constant, E_{Arr} is the activation energy, and *R* is the gas constant.¹⁹ For an electrode-adsorbed species, $I_p \propto v/T$, which means the higher the temperature, the lower the peak current. However, for our Zn//AC cell showing weak redox peaks, the peak current was enhanced by increasing the temperature. Therefore, in our case, the component of $I_p \propto v/T$ is neglected and the redox peak current is expressed as

$$I_{\rm p} = A \sqrt{\nu e^{-E_{\rm Arr}/RT}/T}$$
(1)

where *A* is a constant. Using eq 1 and the data in Figure 2d, we deduced E_{Arr} values for the two cathodes (Table S1). In the temperature range of 10–20 °C, the averaged $E_{\rm Arr}$ values are 20.0 kJ mol⁻¹ for poly(1,5-DHN) and 24.4 kJ mol⁻¹ for poly(1,5-NAPD). From -20 to -10 °C, the averaged $E_{\rm Arr}$ values are 16.3 kJ mol⁻¹ for poly(1,5-DHN) and 23.2 kJ mol⁻¹ for poly(1,5-NAPD). Overall, poly(1,5-NAPD) shows an activation energy that is higher than that of poly(1,5-DHN). Using $I_p = av^{b}$, 20,21 where *a* and *b* are adjustable parameters, the temperature-dependent b values can be deduced using CV loops, and the results are shown in Figure 2f. Here a b of 0.5 indicates a diffusion-controlled process, whereas a b of 1.0 suggests a surface-controlled process. When at 20 $^{\circ}$ C, the b values of poly(1,5-DHN) and poly(1,5-NAPD) were 0.88 and 0.86, respectively. Both polymers showed that, with a decrease in temperature from 20 to 0 $^{\circ}$ C, the *b* value was reduced to a minimum value of ~ 0.75 and then increased with a further decrease in temperature from 0 to -20 °C. It should be noted that the large specific surface area of AC favors the capacity of our polymer/AC composite, although the specific surface area of the composite is $<400 \text{ m}^2 \text{ g}^{-1}$ (Figure S3). Polymer molecules filling the nanosized pores, with a mean size \sim 2 nm, of AC granules play an important role in enhancing the capacity, because ions can diffuse deeper inside the nanopore and fully utilize the functional groups along molecular chains to store charge. This assumption is based on the idea that the interspace between bundled molecular chains and the inner wall of the nanopore allows water molecules and ions to diffuse freely. Thus, the redox reactions inside the nanopore are mainly surface-controlled, and the b value is relatively high at room temperature. In addition to Zn²⁺, H⁺ ions also participate in the redox reaction, because the polymer is redox-active when tested in the H_2SO_4 electrolyte (Figure S10). On the contrary, both poly(1,5-NAPD) and poly(1,5-DHN) show two redox peaks in the $ZnSO_4$ electrolyte (Figure S9), implying a dual-ion effect. With a decrease in temperature from 20 to 0 °C, the diffusion depth of ions into the nanopores is reduced, and the redox species at the molecular chain/carbon interface



Figure 3. (a and b) Temperature-dependent EIS spectra of Zn//poly(1,5-NAPD)/AC and Zn//poly(1,5-DHN)/AC, respectively. (c) Dependence of the charge transfer resistance on temperature for poly(1,5-NAPD)/AC and poly(1,5-DHN)/AC cathodes. (d and e) Arrhenius plots used to deduce the activation energies for poly(1,5-NAPD)/AC and poly(1,5-DHN)/AC, respectively.



Figure 4. (a) Simulated electrostatic potential diagrams of tri(1,5-DHN) and tri(1,5-NAPD) molecules. (b and e) Illustrations for possible Zn^{2+} uptake processes of tri(1,5-DHN) and tri(1,5-NAPD), respectively. Their calculated ΔG values are also shown. (c and f) Calculated LUMO and HOMO levels of 1,5-DHN and 1,5-NAPD dimers, respectively. (d) ΔG values after Zn^{2+} uptake reactions at different temperatures, calculated for poly(1,5-DHN) and poly(1,5-NAPD) trimers.

are less utilized to store charge, leading to capacity decay. The fraction of redox reactions contributed by ions inserted into either the bunches of macromolecules inside the nanopore or the polymer coating over the outer surface of the AC granule is increased, resulting in the decrease in the *b* value. From 0 to -20 °C, the agitation of ions in water medium was greatly suppressed, and individual Zn^{2+} ions were surrounded by more polarized water molecules and anions due to the ion atmosphere effect. The clusters with a Zn^{2+} in the center were larger and more sluggish at lower temperatures, even blocked by narrow sections of nanochannels in the AC granule.

Due to the increased resistance of the polymer, the ion insertion depth as well as the diffusion-controlled redox component were reduced. Therefore, along with a larger capacity loss, the surface-controlled redox reactions, contributed by more H⁺ and less Zn^{2+} , turned out to be dominant and the *b* value was increased at a low temperature of -20 °C.

Panels a and b of Figure 3 show temperature-dependent electrochemical impedance spectra (EIS) of Zn//poly(1,5-DHN)/AC and Zn//poly(1,5-NAPD)/AC cells, respectively. The charge transfer resistance, R_{ctr} can be extracted from the EIS spectrum by using an equivalent circuit (Figure S11c).

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Figure 3c shows the dependencies of $R_{\rm ct}$ on temperature for the two cathodes. From 20 to -20 °C, the $R_{\rm ct}$ values were increased from 6.4 to 90.1 Ω for poly(1,5-NAPD)/AC and from 20.9 to 70.3 Ω for poly(1,5-DHN)/AC. Although the poly(1,5-NAPD)/AC electrode is more conductive than poly(1,5-DHN)/AC at room temperature, it suffers from a larger resistance increment after being cooled to -20 °C. The energy barrier, $E_{\rm av}$ can be calculated using the Arrhenius equation:²²

$$1/R_{\rm ct} = A \, \exp(-E_a/RT) \tag{2}$$

where A is a constant. Using the two linear fittings in panels d and e of Figure 3, the E_a values of poly(1,5-NAPD)/AC and poly(1,5-DHN)/AC are deduced to be 25.2 and 18.8 kJ mol⁻¹, respectively. Therefore, these E_a values are in agreement with the results presented above deduced from the temperature-dependent CV curves.

Our density functional theory calculation gave two electrostatic potential diagrams for 1,5-DHN and 1,5-NAPD trimers, as shown in Figure 4a. One can see that regions around O and N atoms, marked by blue color, are more attractive to cations such as Zn^{2+} and H⁺. For binding of tri(1,5-DHN) and tri(1,5-NAPD) with Zn²⁺, the changes in Gibbs free energy (ΔG) at 20, 0, and -20 °C were calculated, as shown in Figure 4d. Overall, the ΔG for tri(1,5-DHN) is more negative than that for tri(1,5-NAPD) in the Zn^{2+} uptake process. From 20 to -20°C, the difference between ΔG values for tri(1,5-DHN) (11.6 kJ mol⁻¹) is larger than that for tri(1,5-NAPD) (7.7 kJ mol⁻¹). According to the Gibbs–Helmholtz equation, $\Delta S = -(\partial \Delta G/\partial G)$ ∂T)_{*n*}, where ΔS is the change in entropy and T is the absolute temperature, we obtain ΔS values of -0.29 and -0.19 kJ mol⁻¹ K^{-1} for tri(1,5-DHN) and tri(1,5-NAPD), respectively, after the Zn^{2+} uptake process. The entropy is a measure of the number of specific ways in which a thermodynamic system may be arranged. Our calculation suggests that the entropy of tri(1,5-DHN) is higher than that of tri(1,5-NAPD) (Figure S12). This can be understood from their equilibrium geometries of molecules, as the poly(1,5-NAPD) molecular chain spontaneously coils into a spiral structure, while the poly(1,5-DHN) molecular chain curls randomly and has a higher degree of disorder (Figure S13). The capacity decay of a polymer electrode either after long-term cycling or at low temperatures means the number of molecules participating in redox reactions is decreased. Our former study of Zn-polymer batteries revealed that Zn^{2+} or SO_4^{2-} ions stuck between molecular chains could block paths for insertion and extraction of other ions, resulting in capacity decay.¹¹ A redox-active polymer with a higher entropy would be more stable in terms of molecular geometry, chemical activities, and thermal vibrations of functional groups, with a variation in temperature. Therefore, the higher entropy of poly(1,5-DHN)/AC could be a key factor behind its higher capacity retention, better cycling stability, and smaller resistance increment in a cold environment.

Hydroxyl and carbonyl groups may coexist in poly(1,5-DHN), and amino groups in poly(1,5-NAPD) could be divided into $-NH_2$ and =NH. After binding with Zn^{2+} , the ΔG values for two possible redox processes of tri(1,5-DHN), named as hydroxyl (P2) and carbonyl (P1) modes, were calculated, as shown in Figure 4b. The change in potential energy involved in the P1 route is -30.4 eV, which is much lower than that of the P2 route (40.9 eV). Hence, the carbonyl groups are responsible for charge storage. Similarly, the two possible processes for the binding of tri(1,5-NAPD) to Zn^{2+} were also calculated, as shown in Figure 4e. ΔG values for uptake of Zn^{2+} by tri(1.5-NAPD) with =NH (P2) and -NH₂ (P1) groups are -30.3 and 46.7 eV, respectively, suggesting that the redox at =NH sites, instead of -NH₂, is responsible for energy storage. The energy levels of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) for tri(1,5-DHN) and tri(1,5-NAPD), as well as their frontier molecular orbital diagrams, are shown in panels c and f of Figure 4, respectively. For tri(1,5-DHN), upon conversion of -OH into =O, both HOMO and LUMO levels are decreased, as from -1.0 to -3.9 eV for $E_{\rm LUMO}$ and from -5.2 to -6.3 eV for $E_{\rm HOMO}$. The quinonetype poly(1,5-DHN) is an n-type electrode material that receives electrons from the AC base to its LUMO level in the discharge process. The work function of graphitic carbon is generally in the range from -4.5 to -5.1 eV.^{23,24} The lower the LUMO level, the more favorable for electrons to hop between the carbon base and poly(1,5-DHN) due to the reduced energy barrier. For the tri(1,5-NAPD), upon conversion of $-NH_2$ into =NH, E_{LUMO} is largely decreased $(-1.0 \text{ eV} \rightarrow -4.1 \text{ eV})$, and the HOMO level is slightly shifted upward (-4.8 eV \rightarrow -4.6 eV). This also leads to the narrowing of the energy bandgap, as from 3.8 to 0.5 eV, implying that the tertiary amine-based poly(1,5-NAPD) is a semiconductor. This amino-containing polymer is p-type and donates electrons from its HOMO level to inserted Zn²⁺. A higher HOMO level of poly(1,5-NAPD) favors its redox activity.

In summary, two polymers, the amino-containing poly(1,5)-NAPD) and the quinone-tyle poly(1,5-DHN), were electrodeposited onto nanoporous AC to make ZIB cathodes and their electrochemical performances at different temperatures ranging from 20 to -20 °C were investigated, using our antifreeze aqueous ZnSO4 electrolyte. Influences of the cold environment on the capacity decay, charge storage kinetics, and resistance of the two polymers were studied both experimentally and theoretically, unravelling key factors behind their different energy storage performances. (1) At room temperature, the specific capacity of the poly(1,5-NAPD)/AC cathode $(0.59 \text{ mAh cm}^{-2})$ is much higher than that of the poly(1,5-DHN)/AC cathode (0.4 mAh cm⁻²). Also, poly(1,5-DHN)/AC cathode (0.4 mAh cm⁻²). NAPD) has a narrower energy bandgap and a higher conductivity compared to those of poly(1,5-DHN). (2) Although poly(1,5-NAPD)/AC shows a higher specific capacity at room temperature, it suffers from greater capacity loss and larger resistance increment at low temperature. (3) Compared to poly(1,5-NAPD), poly(1,5-DHN) has a higher entropy and undergoes a larger change in entropy after the Zn^{2+} uptake process, and has a lower activation energy for ion diffusion, accounting for its better cycling stability and rate performance, higher capacity retention, and smaller resistance increment at low temperatures. (4) Our calculation reveals that the redox of carbonyl groups is responsible for the charge storage of poly(1,5-DHN). For poly(1,5-DHN), Zn²⁺ uptake via = NH groups, instead of $-NH_2$, dominates the charge storage process. This work suggests clues for searching and designing better polymer electrodes for making advanced aqueous Zn-polymer batteries, i.e., higher entropy, higher HOMO level, and narrower energy bandgap of the polymer.

METHODS

See the Supporting Information for details of the materials and methods.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.1c00139.

Detailed experimental procedures and chemical materials, calculation details, BET, SEM images, CV and GCD curves, EIS spectra, and calculation results for the enthalpy and entropy of tri(1,5-NAPD) and tri(1,5-DHN) (PDF)

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Notes

The authors declare no competing financial interest.

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