

Integrating Multiredox Centers into One Framework for High-Performance Organic Li-Ion Battery Cathodes

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S Supporting Information

ABSTRACT: Organic cathode materials are promising for developing high-energy and high-power Li-ion batteries (LIBs). However, the energy storage of most organic cathodes relies on the electron transfer of a single type of functional group, leading to either a low redox potential or a low capacity. Here we propose a new strategy for the structure design and performance optimization of organic materials. A new organic cathode, dithianon (DTN), containing three functional groups (-S-, C=0, C=N) in one framework, is reported. The -S- group increases the redox potential to 3.0 V, while C=O and C=N groups enable a three Li-ions-involved redox reaction. As a cathode, DTN delivers 270.2 mAh g⁻¹ at 0.5C for 300 cycles. Even at 5C, it still retains 161.5 mAh g^{-1} after 1000 cycles. The high-capacity, high-power, and stable DTN cathode offers great promise for high-performance and sustainable LIBs.



i-ion batteries (LIBs) have become dominant energystorage devices for portable electronics since their first commercialization in 1990s^{1,2} and now are penetrating to electric vehicles and smart grids. The energy density and power density of state-of-the-art LIBs are limited by the low energy density of intercalation-type cathodes. Considerable research efforts have been devoted to increasing the energy density and power density of intercalation-type transitionmetal oxide cathodes (e.g., LiCoO₂, LiFePO₄, Li- $Ni_{0.8}Mn_{0.1}Co_{0.1}O_2$ and Li-rich cathodes),³⁻⁸ and the capacities of intercalation-type transition-metal oxide cathodes are approaching their capacity limit of ~ 200 mA h g⁻¹.

As alternatives to the inorganic counterparts, organic cathode materials are promising candidates for high-energy and high-power-density LIBs due to the tunable molecular structure and high structural diversity.^{9,10} The reversible redox reactions of organic materials involve charge state change of electrochemically active organic functional groups such as the carbonyl group (C=O), imine group (C=N), organic free radicals, disulfide group (S–S), azo group (N=N), and cyano group $(C \equiv N)$.^{11–21} To date, a number of carbonyl groupbased organic materials (oxocarbon salts,²² poly-(anthraquinonyl sulfide),²³ and polyimide²⁴) and imine group-based organic materials (triquinoxalinylene²⁵ and alloxazine²⁶) have been reported for LIB cathodes. Among them, the organic cathode, cyclohexanehexone, can even reach an ultrahigh capacity up to 902 mA h g^{-1} , which is over 4

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Figure 1. Structural demonstration and investigation. (a-d) Structures of dithianon (DTN, a), anthraquinone (AQ, b), thianthrene (TTE, c), and 2,3-naphthalenedicarbonitrile (NLC, d). (e) Proposed reaction mechanism of DTN for LIBs with three participating Li ions. The white, gray, red, yellow, pink, and blue balls represent the H, C, O, S, Li, and N atoms, respectively. (f-i) XRD (f), Raman (g), FTIR (h), and TGA (i) results of DTN. The Raman spectra show consistent peaks with the FTIR. TGA reveals that the weight loss of DTN proceeds in two stages.

times higher than that of most intercalation-type transitionmetal oxide cathodes. Zhiqiang Luo et al. reported a twodimensional microporous covalent organic framework, poly-(imide-benzoquinone), polymerized with graphene as a highrate organic cathode for LIBs.²⁸ Nevertheless, the poor longterm cycling stability, sluggish reaction kinetics, and low redox potential limit the large-scale application of organic cathode materials. Therefore, it is still challenging to develop highenergy and high-cyclic-stability organic cathodes for sustainable LIBs.

In this work, we report exceptional electrochemical performance of a dithianon (DTN) cathode material, consisting of two carbonyl groups, two cyano groups, and two sulfur atoms (Figure 1a). The carbonyl group and cyano group in DTN serve to enhance the capacity, while the heteroatom (S) in DTN is to increase the redox potentials. To confirm the electrochemical activity of each functional group, the electrochemical behaviors of organic materials with only one type of each functional group such as anthraquinone (AQ, Figure 1b), thianthrene (TTE, Figure 1c), and 2,3-naphthalenedicarbonitrile (NLC, Figure 1d) were studied as controls. In DTN, both the carbonyl group and cyano group act as electrochemically active sites to react with Li⁺. As proposed in Figure 1e, DTN can reversibly react with three lithium ions step by step to deliver a theoretical capacity of 271.2 mA h g^{-1} . More importantly, the doping of heteroatoms into the organic material lowers the energy levels of the lowest unoccupied molecular orbital (LUMO), resulting in an increased redox potential.^{29–31} As a cathode, the DTN retains a high reversible capacity of 270.2 mA h g^{-1} after 300 cycles at 0.5C, with a long and flat plateau at ~2.9 V and a sloping plateau centered at 1.8 V, and 161.5 mA h g⁻¹ after 1000 cycles at 5C. Hence, DTN with two sulfur atoms and two types of electroactive groups is a promising organic cathode material for high-performance and sustainable LIBs.

Letter



Figure 2. Quantum chemistry calculation. Quantum chemistry calculated electronic structures and relative energies using B3LYP/6-31+G(d,p) in acetone solvent; the left axis represents the relative voltage (versus SHE), and the right axis stands for the relative energy level in vacuum. The dark red and dark green regions represent the deletion and accumulation of electrons, respectively.



Figure 3. Electrochemical comparison and predicted structural evolution during the lithiation process. (a-c) Charge-discharge curves of AQ (a), NLC (b), and TTE (c) in the cutoff window from 1.0 to 3.5 V, at 0.2C. (d) Discharge curve of DTN in the cutoff window from 1.0 to 3.5 V and predicted lithiated structures during the discharge process.

The structure and morphology of these four organic materials were characterized using scanning electron microscopy (SEM), solid-state NMR, X-ray diffraction (XRD), Raman spectroscopy, Fourier-transform infrared (FTIR) spectroscopy, and thermogravimetric analysis (TGA). The SEM images in Figure S1 demonstrate that NLC, TTE, AQ, and DTN samples consist of irregular shaped particles with a size in the range of $1-5 \mu m$, and the sharp XRD peaks in Figures 1f and S2 reveal that they display well-defined crystalline structure. The solid-state ¹³C magic-angle spinning



Figure 4. Electrochemical properties of DTN. (a) Charge–discharge curves of DTN in the cutoff window from 1.0 to 3.5 V. (b) Cyclic voltammetry of DTN with a scan rate of 0.1 mV s⁻¹. (c) Cycling performance of DTN cathode at 0.5C. (d) Rate capability of DTN cathode at various current densities from 0.2C to 15C. (e) Cycle performance of DTN cathode at 5C.

(MAS) NMR spectra are provided in Figure S3, and the different ¹³C resonances clearly demonstrate the typical chemical environments of C in DTN, AQ, TTE, and NLC. Furthermore, the Raman spectrum of DTN in Figure 1g confirms the existence of -S- stretching vibration at ~492 cm^{-1} ,³² C=O stretching vibration at ~1665 cm^{-1} ,³³ and the symmetric/asymmetric stretching vibrations of C≡N at 2215 and 2230 cm⁻¹.^{34,35} Similar C=O stretching at ~1665 cm⁻¹ was also observed for carbonyl groups in AQ (Figure S4), while the strong fluorescence of TTE and NLC leads to the increased baseline intensity in the Raman spectra, which overlaps with their characteristic Raman peaks. The FTIR results in Figures 1h and S5 provide more explicit evidence without fluorescence disturbance, and the typical IR peaks of DTN are consistent with those in the Raman spectra. The thermostabilities of DTN, AQ, TTE, and NLC were investigated by TGA; as shown in Figures 1i and S6, all of these organic materials are stable up to ~ 200 °C.

Quantum chemistry calculations were conducted to evaluate the redox properties of the four organic materials from an atomic scale.³⁶ The highest occupied molecular orbital (HOMO) and LUMO distributions of the four organic molecules are shown in Figure 2, and their energies resided on the LUMO and HOMO. The deeper the LUMO level, the better the electron affinity it would exhibit. As revealed, DTN delivers a much lower LUMO energy level of -5.68 eV than AQ (-1.15 eV), TTE (-3.17 eV), and NLC (-2.67 eV), suggesting that DTN owns greater electron affinities; therefore, it should exhibit a higher reduction potential than AQ, TTE, and NLC. The LUMO is mainly located on the C=C double bond and the top of S atoms, suggesting their electron acceptor roles during the reduction. In addition, DTN has a much lower gap (0.14 eV) between its HOMO and LUMO levels than AQ (4.22 eV), TTE (4.19 eV), and NLC (4.49 eV), indicating that DTN has the highest intrinsic electronic behavior among these four samples.

The role of each functional group in DTN was investigated by comparing the charge–discharge curves of AQ, TTE, NLC, and DTN acquired in coin-type half-cells with Li metal as a counter electrode, within the voltage range of 1.0-3.5 V. As shown in Figure 3a, AQ exhibits two pairs of redox plateaus at 2.1 and 2.3 V, with a discharge capacity of 145.5 mAh g⁻¹, corresponding to the reversible reaction between two carbonyl groups in AQ and two Li-ions. NLC (Figure 3b) shows a pair of redox plateaus centered at 1.4 V, with a discharge capacity of 138.8 mAh g⁻¹, corresponding to the reversible reaction



Figure 5. Structure evolution of DTN. (a) Low-range and (b) high-range ex situ Raman spectra of DTN cathode at different stages of the pristine DTN electrode before cycling, fully discharged, discharged to a voltage of 2.0 V, and fully charged back. In situ XRD pattern (c) with the discharge curve and corresponding contour maps (d) related to the evolution of the main characteristic diffraction peaks of DTN cathode during the first discharge process ($\lambda = 1.5416$ Å).

between cyano groups in NLC and Li-ions. As for the TTE electrode in Figure 3c, it exhibits a long sloping discharge curve below 1.3 V, with a discharge capacity of only 8.1 mAh g^{-1} , and the charge-discharge curves of conductive carbon black in Figure S7 reveal that the capacity of TTE is totally contributed by the conductive carbon black, demonstrating that TTE is electrochemically inactive in the voltage range from 1.0 to 3.5 V. The CV results of AQ, TTE, and NLC (Figure S8) are consistent with their charge-discharge curves. In comparison, the DTN (Figure 3d) displays a higher average discharge voltage than AQ, NLC, and TTE, with a high discharge capacity of 243.9 mAh g⁻¹, of which a long discharge plateau at \sim 2.9 V contributes a capacity of \sim 90 mAh g⁻¹ and a sloping discharge curve from 2.9 to 1.0 V contributes a capacity of ~154 mAh g^{-1} . Therefore, the electrochemical behaviors of these four organic materials demonstrate that carbonyl groups and cyano groups are electrochemically active sites in DTN, and the redox plateaus of carbonyl groups in AQ and cyano groups in TTE are lower than that in DTN, confirming that the doping of heteroatoms into the organic material serves to increase the redox potential. The electrochemical behaviors of DTN are consistent with the DFT results. To understand the multistep lithiation process of DTN, the structure simulation of DTN at different lithiation stages was conducted, and the optimized energy-favorable structures of DTN-xLi (x = 1, 2,and 3) were attached to the discharge curve of DTN in the cutoff window from 1 to 3.5 V. As shown in Figure 3d, the DFT results reveal that three Li ions can be inserted into the DTN in the cutoff window from 1 to 3.5 V, referring to a theoretical capacity of 271.2 mA h g^{-1} . Specifically, two sites of O atoms in DTN are the most energy favorable for Li-ion

accommodation, corresponding to average reduction potentials of 2.9 and 2.1 V (vs Li/Li⁺), respectively. The third Li-ion tends to interact with the -CN groups in DTN, which exhibit an average reduction potential of 1.4 V (vs Li/Li⁺). The corresponding calculated energy levels of DTN at different lithiation stages are offered in Figure S9.

The lithiation/delithiation capacities and redox potentials of the DTN were evaluated and compared to the results from Quantum chemistry calculations at a potential range of 1.0–3.5 V in coin cells using lithium metal as a counter electrode, in the electrolyte of 7 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1,2-dimethoxyethane (DME)/dioxolane (DOL) (volume, 1:1), (denoted as 7 M LiTFSI-DME/DOL). To further prevent the dissolution of DTN electrode in 7 M LiTFSI-DME/DOL electrolyte during the long cycling process (Figure S10), the atomic layer deposition (ALD) technique was used to deposit a thin layer (5 nm) of Al_2O_3 on the DTN electrode to protect the organic material from dissolution. The typical charge-discharge curves of Al₂O₃-coated DTN electrode in the 1st, 2nd, 5th, and 100th cycles at 0.5C are shown in Figure 4a, $(1C = 271.2 \text{ mAh g}^{-1})$. The gradual increase in Coulombic efficiency and discharge capacity from the first to fifth cycle is due to an activation process caused by coating of the insulating Al₂O₃. After the initial activation process, the Al₂O₃-coated DTN electrode displays discharge capacities of 243.9 and 246.4 mAh g^{-1} in the 5th and 100th cycles, with a long and flat plateau at \sim 2.9 V and a slopping plateau centered at 1.8 V, which are similar to the calculated potentials of DTN-1Li, DTN-2Li, and DTN-3Li in Figure 3d. In addition, the electrochemical behavior of DTN was also studied by cyclic voltammetry (CV) at a scan rate of 0.1 mV

s⁻¹, as shown in Figure 4b. A sharp peak at ~2.8 V and a broad peak at ~2.2 V were observed in the cathodic scan, corresponding to a sharp peak at ~3.3 V and a broad peak at ~2.8 V in the anodic scan. The CV results are consistent with the charge–discharge curves. The use of highly concentrated electrolyte of 7 M LiTFSI-DME/DOL and the coating of an electronic nonconductive Al_2O_3 layer enhanced the reversibility of DTN, as demonstrated by the similar peak areas for the oxidation and reduction peaks in Figure 4b.

The excellent cycling stability of Al₂O₃-coated DTN cathode is shown in Figure 4c. As revealed, it delivers a first discharge capacity of 228.2 mA h g^{-1} at 0.5C and then increases to 243.9 mA h g^{-1} after five activation cycles and maintains a reversible capacity of 270.2 mA h g^{-1} after 300 cycles. The capacity fluctuation in the long-term cycling is due to the roomtemperature variation during the battery test. An initial activation process is required to promote the electron and Li-ion transfer in the DTN cathode, which is also observed in the other literature.³⁷ To further confirm it, electrochemical impedance spectroscopy (EIS) from the 1st cycle to 100th cycle was performed. As shown in Figure S11, the depressed semicircle represents the interphase resistance, which decreases from \sim 180 to \sim 120 Ohm after the fifth cycle due to the initial activation process. Then, it increases to ~ 170 Ohm from the 5th to 20th cycle and stabilizes at ~150 Ohm after the 50th cycle, demonstrating the stable interphase layer of DTN cathode for the reversible lithiation/delithiation process. The rate capability of DTN at various current densities from 0.2C to 15C was also evaluated. As shown in Figure 4d, with elevated current densities from 0.2C to 15C, DTN exhibits average reversible capacities of 285.8, 276.4, 260.3, 239.1, 212.8, 184.4, and 153.6 mA h g^{-1} at 0.2C, 0.5C, 1C, 2C, 5C, 10C, and 15C, respectively. When the current density is reduced back to 0.2C, the capacity of DTN recovers to 281.2 mA h g^{-1} , comparable to its initial value. Moreover, the longterm cycling performance of DTN at a high current density of 5C was evaluated and is shown in Figure 4e. It delivers an initial discharge capacity of 184.3 mAh g^{-1} and retains a reversible capacity of 161.5 mA h g^{-1} after 1000 cyles, demonstrating a powerful robustness at the high current density. The superior electrochemical performance of DTN is not only beneficial from its structural property but also closely related to its reaction kinetics. Thus, the CV curves at different sweep rates from 0.1 to 2.0 mV s⁻¹ were conducted to analyze the reaction kinetics of the DTN cathode. As shown in Figure S12, with the increased scan rate, the anodic peak shifts to a lower value, while the cathodic peak shifts to a higher value due to the enhanced polarization. According to the equation proposed by Dunn et al.,^{38,39} the k_1 and k_2 constants are 0.76 and 0.82 based on the anodic scan (Figure S13a) and cathodic scan (Figure S13b), suggesting that the exceptional rate capability of the DTN cathode is attributed to its surfacedominated pseudocapacitance mechanism.

The structure evolution of DTN at different states of discharge and charge was investigated by ex situ Raman spectra (Figure 5a,b). When the DTN electrode is discharged to 2.0 V, the strong peak at 1665 cm⁻¹ attributed to the C=O stretching vibration is remarkably weakened (Figure 5b), while a new peak at 521 cm⁻¹ appears (Figure 5a), corresponding to the lithiated carbonyl group and formation of a Li–O bond. It is well-matched with the characteristic Raman peak for Li₂O. After full discharge to 1.0 V, the peak for C=O stretching at 1665 cm⁻¹ completely disappears (Figure 5b), and the peak for

the Li-O bond becomes stronger. Moreover, the symmetric/ asymmetric stretching vibrations of C≡N at 2215 and 2230 cm⁻¹ are merged into a broad peak and blue shifted, while other new peaks at 371, 392, 682, 695, 1290, 1335, 1408, 1477, 1577, and 1598 cm⁻¹ arise, which are in general agreement with the polypyrrole's Raman peaks.⁴⁰⁻⁴² The appearance of these new peaks indicates that the $C \equiv N$ groups transform to a polypyrrole-like structure during the discharge process. The disappearance of C=O stretching vibration, the alteration of C≡N stretching vibration, and the appearance of these new peaks reveal the strong chemical interaction between Li⁺ and O/N in DTN at 1.0 V. When DTN is fully charged back, most Raman peaks for DTN are recovered, revealing good reversibility of the DTN cathode during charge and discharge. The -S- stretching vibration at ~492 cm⁻¹ is retained during the charge-discharge process, confirming that the -S- group does not participate in the redox reaction. Hence, the first and second Li-ions are accommodated by the two O atoms in the carbonyl groups, and the third Li-ion interacts with cyano groups to form a polypyrrole-like structure. The Raman results are consistent with the proposed reaction mechanism in Figures 1e and 3d. To better demonstrate the phase evolution of DTN electrode, in situ XRD during the first discharge process was conducted (Figure 5c,d), and the corresponding discharge curve is shown on the left side of Figure 5c. To avoid the activation process, DTN without Al₂O₃ coating was used for in situ XRD characterization. On the basis of the proposed mechanism in Figures 1e and 3d, three lithiated structures are formed within the potential range from 1.0 to 3.5 V, which are named DTN-1Li, DTN-2Li, and DTN-3Li, respectively. During the first lithiation process corresponding to the potential plateau at \sim 2.9 V, the in situ XRD results unravel that the peak at 12.7° becomes stronger, the peaks at 25.9 and 26.3° shift to 25.1 and 25.6°, respectively, a new peak at 27.9° emerges and becomes stronger, and the peaks at 28.7 and 29.0° disappear at the end of this process, indicating the phase change from DTN to DTN-1Li. Upon further lithiation process corresponding to the sloping curve from 2.7 to 1.0 V, the in situ XRD shows continuous variation tendency of peaks, in which the new peaks at 12.0 and 24.3° emerge and become stronger and peaks at 12.7, 25.1, 25.6, and 27.9° turn to be weaker. Therefore, the crystal structure of DTN-3Li is analogous to that of DTN-2Li. By combining the information from in situ XRD patterns and DFT calculations in Figure 3d, we conclude that DTN mainly delivers two parts of structural evolution during its lithiation process. The initial lithiation process experiences the phase transformation from DTN to DTN-1Li at a potential plateau of 3.0-2.7 V, and the further lithiation is accompanied by continuous phase change from DTN-1Li to DTN-3Li in a sloping potential range of 2.7-1.0 V. The in situ XRD and ex situ Raman results clearly demonstrate the structure evolution and reversible lithiation/ delithiation mechanism of the DTN cathode.

In conclusion, DTN as a new organic cathode material was reported for sustainable and high-performance LIBs. The DFT calculations and experimental results unravel that two kinds of organic functional groups, a carbonyl group and cyano group, in DTN act as electrochemically active sites to react with three Li-ions in the potential range from 1 to 3.5 V, and the introduction of the heteroatom (S) into the DTN enhances its redox potentials. The DTN-based cathode delivers a reversible capacity 270.2 mA h g⁻¹ at 0.5C after 300 cycles and retains a reversible capacity of 161.5 mA h g⁻¹ at 5C for 1000 cycles.

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The ex situ Raman and in situ XRD spectra reveal its structure and phase evolution during discharge and charge processes and confirm its exceptional structure reversibility and stability. Therefore, this work not only provides a new promising organic cathode material (DTN) but also offers a new structure design and performance optimization strategy by incorporating multiredox centers in one framework to enhanced the redox potential and capacity of organic electrode materials for sustainable and high-performance LIBs.

ASSOCIATED CONTENT

G Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.9b02466.

Experimental details, SEM images, XRD patterns, NMR spectra, Raman spectra, FTIR spectra, TGA, charge–discharge curves, CV curves, calculated energy levels at different lithiation stages, cyclic performance, Nyquist plots, CV curves at various sweep rates, and corresponding peak current I_p as a function of square root of the scan rate $\nu^{1/2}$ (PDF)

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Notes

The authors declare no competing financial interest.

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