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Authors: Zhiwei Tie, Luojia Liu, Shenzhen Deng, Dongbing Zhao, and Zhiqiang Niu

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Proton Insertion Chemistry of Zn/Organic Battery

Zhiwei Tie, Luojia Liu, Shenzhen Deng, Dongbing Zhao, and Zhiqiang Niu*

Dedicated to 100th anniversary of Nankai University

Abstract: The proton storage in rechargeable aqueous zinc-ion batteries (ZIBs) are attracting extensive attention due to the fast kinetics of H⁺ insertion/extraction. However, up to now, it is not achieved in organic materials-based ZIBs with a mild electrolyte. Herein, we developed aqueous ZIBs based on diquinoxalino [2,3-a:2',3'-c] phenazine (HATN) in a mild electrolyte. Electrochemical and structural analysis confirm for the first time that such Zn/HATN batteries experience a H⁺ uptake/removal behavior with highly reversible structural evolution of HATN. The H⁺ uptake/removal endows the Zn/HATN batteries with enhanced electrochemical performance. Proton insertion chemistry will broaden the horizons of aqueous Zn/organic batteries and open up new opportunities to construct high-performance ZIBs.

Rechargeable aqueous zinc-ion batteries (ZIBs) are attracting more attention since the Zn anode possesses low redox potential (-0.76 V vs. standard hydrogen electrode (SHE)), high specific capacity (820 mAh g⁻¹), excellent stability in water and low cost.^[1] The electrochemical performance of ZIBs mainly depends on the design of cathode materials.^[2] Recently, various active materials such as transition metal oxides or sulfides (based on vanadium^[3] and manganese^[4]), Prussian blue analogues^[5] and organic compounds^[6] were developed to serve as the cathode materials of aqueous ZIBs. Among them, organic materials are considered as a promising candidate because of their renewability, environmental friendliness, low cost and structural diversity.^[7]

Generally, the energy storage/release mechanism of Zn/organic battery is the coordination/incoordination reaction between Zn²⁺ and active group carbonyl.^[6b]. However, the electronic conductivity of organic active materials is intrinsically inferior and their corresponding discharge products often dissolve in H₂O. As a result, they usually suffer from poor rate performance and limited cycle life.^[8] Apart from Zn²⁺, H⁺ is also considered as an attractive charge carrier due to its small ionic radius and low relative atomic mass.^[9] Recently, the energy-storage based on H⁺ has been achieved in inorganic materials-based ZIBs.^[10]. Furthermore, these ZIBs with H⁺ insertion/extraction display excellent electrochemical performance due to the fast kinetics of the H⁺ insertion/extraction. In some cases of organic materials, their redox-active groups such as carbonyl (C=O) could incorporate H⁺ by a coordination

Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Renewable Energy Conversion and Storage Center, College of Chemistry, Nankai University Tianjin, 300071, P. R. China

- E-mail: zqniu@nankai.edu.cn
- Prof. D. Zhao

State Key Laboratory and Institute of Elemento-Organic Chemistry, College of Chemistry, Nankai University Tianjin, 300071, P. R. China

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Figure 1. a) The mechanism of proton insertion chemistry in the aqueous Zn/HATN battery system. b) SEM image of HATN. c) STEM-HAADF image and STEM-EDS mapping of C, N distributions in HATN. d) HRTEM of HATN (Inset shows the SAED pattern).

reaction in a three-electrode cell with 1M H₂SO₄ electrolyte.^[11] However, it could not be used in two-electrode Zn/organic batteries because of the violent chemical reaction between Zn anode and acidic electrolyte. As a result, until now, H⁺ energy storage has not been observed in organic materials-based aqueous ZIBs with mild electrolytes. If H⁺ uptake/removal could be realized in aqueous Zn/organic batteries, their energy density would be enhanced significantly and the horizons of aqueous ZIBs chemistry could be also broadened.

The π -conjugated aromatic compounds with imino moiety =N is a kind of neutral organic base, where the imino moiety =N will have an ability to chelate proton by a coordination reaction.^[12] Furthermore, a lone pair of electrons in imino moiety =N ensure these π -conjugated aromatic compounds with high redox activity.^[13] Inspired by this, we developed an aqueous Zn/organic battery system based on diquinoxalino [2,3-*a*:2',3'-*c*] phenazine (HATN) in mild electrolyte. The Zn/HATN systems display H⁺ uptake/removal by coordination/incoordination reaction rather than conventional Zn²⁺ insertion/extraction (Figure 1a). As a result, they achieve enhanced specific capacity and rate performance due to the fast kinetics of H⁺ uptake/removal. Furthermore, reversible structural evolution of HATN guarantees long-term cycle life of Zn/HATN batteries.

The HATN compound was synthesized by a simple dehydration condensation reaction between hexaketocyclohexane octahydrate and o-phenylenediamine. HATN exhibits a nano-belt morphology with about 100 μ m in length and 400-600 nm in width (Figure 1b; Figures S1 and S2, Supporting Information). Impressively, the HATN possesses good polycrystalline nature with the homogeneous distributions of C and N, which is different from conventional organic compounds with poor crystallinity (Figure 1c, d).^[6b] Its chemical structure is confirmed by ¹H NMR, ¹³C NMR, ESI-MS and FTIR spectra (Figures S3-S6, Supporting Information). Furthermore, there is only one peak at 385.1 in the ESI-MS spectrum, which

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Figure 2. a) Charge-discharge curves in first two cycles under a current density of 100 mA g⁻¹. Various ex situ tests of HATN-based electrodes at the marked points in the charge-discharge curves: b) and c) Ex situ FTIR spectra. d) Ex situ XPS spectra of N 1s. e) Ex situ ¹H solid-state NMR spectra. f) and g) Ex situ XRD profile. h)-l) SEM images at the marked points of 1, 4, 7, 10 and 13, respectively.

suggests the high purity of HATN.

The favorable morphological features of HATN would be beneficial for the fast kinetics of coordination/incoordination reaction. Based on HATN, the cathodes were prepared by a conventional method (Figure S7, Supporting Information). Then the typical coin-type cells were assembled. Figure 2a shows the charge/discharge curves of Zn/HATN battery at 100 mA g⁻¹ in the initial two cycles. Owing to the activation of electrode, the initial discharging curve is different from subsequent case.^[14] After that, Zn/HATN battery shows normal charge-discharge behavior with three voltage platforms, which indicates that there are three-steps coordination/incoordination reactions during the charging-discharging process. In general, the energy storage/release mechanism of Zn/organic battery is the coordination/incoordination reaction between Zn2+ and active groups. However, in our case, Zn element is not observed in the STEM-EDS and SEM mapping images of the HATN electrode at the discharged states (Figures S8 and S9, Supporting Information). It confirms that Zn²⁺ would not insert into the HATN nanobelt by a coordination reaction to realize the energy storage. To further understand the energy storage mechanism of Zn/HATN battery, various ex situ tests including FTIR, Raman, XPS, solid state ¹H nuclear magnetic resonance (¹H NMR) and X-ray diffraction (XRD) were employed to analyze the HATN electrodes at the selected states of initial two charge/discharge cycles, as marked in Figure 2a. In the FTIR spectra, the peaks of C=N (1520 cm⁻¹) and C-C (1127 cm⁻¹) groups gradually disappeared in the discharge processes,[15] indicating that the redox active centers of HATN are C=N groups (Figure 2c). Simultaneously, the FTIR spectra show that the peaks of C-N (1160 cm⁻¹) and N-H (3307, 3232, 3166 and 1642 cm⁻¹) groups are enhanced (Figure 2b).^[16] It suggests that C=N groups of HATN are reduced to C-N step by step and H⁺ ions were stored to form -NH- by three-steps coordination reactions in the discharge processes. It can be also reflected by the ex situ Raman spectra (Figure S10, Supporting Information). In HATN molecules, there are three pairs of electroactive pyrazine N atoms, which can strongly coordinate with H⁺. As a result, three protonated HATN structures will be achieved during the discharge processes, corresponding to three voltage platforms in the discharge curves. According to the discharge capacities at different voltage platforms of the second cycle, the calculated electron-transfer number is about 2 at each voltage platform (Supplementary Methods), which is ascribed to the uptake of 2 H⁺. Therefore, the discharged products at the end of three voltage platforms are defined as HATN-xH (x = 2, 4, 6), respectively. This is to say, all six electroactive pyrazine N atoms in a HATN molecule will react with H⁺. The gradual formation of -NH- groups in the discharged HATN can be also reflected by ex situ XPS (Figure 2d). The peak corresponding to -NH- group is obviously observed in N 1s XPS,^[6d, 17] suggesting the structural evolution from HATN to HATN-6H. Reversibly, in the following charging processes, three voltage platforms are also found, corresponding to the removal of H⁺ from three pairs of electroactive pyrazine N atoms in the HATN molecule, as suggested by FTIR spectra. The FTIR spectra show that the peaks of C=N and C-C groups gradually recover to the initial state, while the peaks of C-N and -NH- groups become weaker and disappear. At the same time, the corresponding peak of -NHgroup also disappears in N 1s XPS spectrum. These suggest that H⁺ ions remove from -NH- groups successively and structural evolution from HATN-6H to HATN is gradually achieved during the charging process.

Above reversible H⁺ uptake/removal can also be confirmed by ex situ ¹H solid-state NMR (Figure 2e). The ¹H solid-state NMR shows that the pristine HATN exhibits a wide peak from 10.0 to 5.0 ppm, which represents the H of benzene ring with two different chemical environments. During the discharging processes, a new peak at about 3.0 ppm emerged and gradually enhanced. This peak is ascribed to H resonances in -NH- groups of the discharged HATN-2H, HATN-4H and HATN-6H, confirming that the H⁺ ions participate in the coordination reaction with the C=N groups of HATN. Furthermore, it is noted that the gradual widening of the wide peak from 10.0 to 5.0 ppm indicates that the chemical environments of H in discharge products are different from the pristine HATN since the H⁺ ions participate in coordination reaction. Reversibly, in the subsequent charging process, this peak recovers to initial state and the peak at about 3.0 ppm is gradually invisible, indicating the H⁺ removal from HATN-6H.

As discussed above, the H⁺ ions take part in the energy storage of the Zn/HATN systems by the structural evolution from HATN to HATN-6H. These H⁺ ions come from the decomposition of water in the aqueous ZnSO4 electrolyte. Accompanying with the consumption of H⁺, a large amount of OH⁻ will yield synchronously. To reach a neutral charge system, these OHcould not exist in the electrolyte. They would move to the surface of HATN-based electrodes and react with ZnSO4 to form Zn₄SO₄(OH)₆·5H₂O (JCPDS:39-0688) successively during the discharge process, which is detected by the ex situ XRD analysis (Figure 2f, g). Furthermore, SEM images display that Zn₄SO₄(OH)₆·5H₂O possesses a flake-like morphology and the corresponding SEM-EDS mapping images display the uniform distribution of the elements C, N, Zn, O, S, further confirming the formation of Zn₄SO₄(OH)₆·5H₂O (Figures 2h, i and k; Figure S8, Supporting Information). More impressively, in the subsequent charging process, Zn₄SO₄(OH)₆•5H₂O can be gradually decomposed after charging from 0.3 to 1.1 V, as revealed by the XRD and SEM images (Figure 2j, I). These results indicate the reversible formation/decomposition of Zn₄SO₄(OH)₆·5H₂O on the



Figure 3. a) Calculated MESP distribution on the van der Waals surface of HATN molecule. b) Optimized structure and calculated frontier molecular orbital energy of HATN molecule. c) Calculated structural evolution and protonation pathway at discharging process.

HATN electrode along with the uptake and removal of H^+ during the charge/discharge processes, which was also proved by the FTIR spectra (Figure 2c; Figure S11 and S12, Supporting Information).

To further understand the H⁺ uptake in HATN molecule in the discharging process, we conducted theoretical calculations with density functional theory (DFT). The molecular electrostatic potential (MESP) method was employed to speculate the electrophilic and nucleophilic reaction-active sites to get further insight into the active-sites of H⁺ uptake.^[18] On the van der Waals surface of a HATN molecule (Figure 3a), the red region represents the positive MESP value (nucleophilic center) and blue region stands for the negative MESP value (electrophilic center). Obviously, the sites with more negative MESP are attractive for the uptake of carriers.^[6b] As a result, the pyrazine nitrogen atoms with negative MESP are the highly active sites for H⁺ ions uptake. It suggests that the acceptance of H⁺ is prior to Zn²⁺ in the Zn/HATN systems (Figure S13, Supporting Information). In addition, on the basis of the minimum energy principle, the protonation pathway of HATN was calculated and shown in Figures 3c and S14 (Supporting Information). Such calculated structural evolutions of HATN along with the protonation pathway are in accordance with the experimental results. Besides, we also conducted the frontier molecular orbitals of HATN, including the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) (Figure 3b). The energies of LUMO and HOMO in the system were calculated to be -2.78 and -6.46 eV, respectively. Therefore, the energy gap (ΔE) between HOMO and LUMO is 3.68 eV, which is lower than most of the organic electrodes, indicating the intrinsic electronic conductivity of HATN is higher than those organic materials.^[19] It will be beneficial to enhancing the electrochemical properties of HATN.

The unique H⁺ energy storage mechanism would endow Zn/HATN batteries with enhanced electrochemical performance. Their typical cyclic voltammetry (CV) curves are presented in Figure 4a. They display three pairs of redox peaks, which are



Figure 4. a) The CV curves of aqueous Zn/HATN batteries (0.01 mV s⁻¹). b) Rate capabilities of Zn/HATN batteries at various current rates. c) Cycle performance of Zn/HATN batteries under a current density of 5 A g⁻¹ for 5000 cycles. d) Comparison of electrochemical performance of aqueous Zn/organic batteries.

ascribed to the reversible structural evolution from HATN to HATN-2H, HATN-4H and HATN-6H, respectively, which agree well with their galvanostatic charge/discharge curves (Figure 2a). More importantly, these CV curves show similar shapes, indicating that Zn/HATN battery possesses excellent capacity retention. Owing to the uptake of six H⁺ ions, the Zn/HATN battery exhibits an initial discharge capacity of 405 mAh g⁻¹ at a current density of 100 mA g⁻¹ (Figure S15 and S16, Supporting Information), which is close to its theoretical capacity of 419 mAh g⁻¹ (Supplementary Methods for details) and higher than the cases of previously reported organic electrode materials of ZIBs.^[6-7] Apart from the high capacity, the Zn/HATN batteries also exhibit outstanding rate performance due to the π -conjugated aromatic structure and fast kinetics of H⁺ coordination/incoordination reaction (Figure 4b). They can display a high capacity of 123 mAh g⁻¹ even at a high current density of 20 A g⁻¹ (the charge/discharge process was completed in 44 s), maintaining 33.2% of that at 0.1 A g⁻¹. Furthermore, when the current density goes back to 0.1 A g⁻¹ after 150 cycles, the corresponding specific capacity can be recovered to 320 mAh g⁻¹.

The morphology and structural evolution of HATN and Zn anode during the charge/discharge processes play an important role in the stable electrochemical properties of Zn/HATN batteries (Figure S17 and S18, Supporting Information). Even after 5000 cycles, the HATN nanobelts in the cathodes still display a similar morphology without obvious change. It is ascribed to the π -conjugated aromatic structure of HATN, which strengthens π - π intermolecular interactions and suppresses the dissolution of HATN in aqueous electrolyte (Figure S19, Supporting Information). Such reversible structural evolution will endow the Zn/HATN batteries with stable long-term cycling performance. After 10 cycles at the current density of 0.1 A g⁻¹, the Zn/HATN battery delivers a specific capacity of about 150 mAh g⁻¹ and remains around 140 mAh g⁻¹ after 5000 cycles under a current density of 5 A g⁻¹ (Figure 4c), corresponding to a high capacity retention of 93.3%. As a result, the H⁺ uptake in HATN nanobelts results in enhanced electrochemcial performance than other previously reported Zn/organic system in common aqueous electrolytes $(ZnSO_4 \text{ or } Zn(CF_3SO_3)_2)$ (Figure 4d; Table S1, Supporting Information).

In summary, aqueous Zn/HATN batteries with H⁺ insertion chemistry were developped in mild electrolyte. The H⁺ uptake/removal behavior of HATN is deeply discussed by

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combining various ex situ characterization techniques and DFT calculations. The pyrazine nitrogen atoms with negative MESP are the active sites of H⁺ ions uptake in HATN and six H⁺ ions will react with these pyrazine nitrogen atoms by reversible structural evolution from HATN to HATN-2H, HATN-4H and HATN-6H, respectively. Owing to the fast kinetics of H⁺ uptake/removal behavior, the Zn/HATN batteries not only exhibit an initial discharge capacity of 405 mAh g⁻¹ at 100 mA g⁻¹, but also display excellent rate performance, and long cycle stability with a high capacity retention of 93.3% after 5000 cycles at 5 A g⁻¹. Proton insertion chemistry will broaden the horizons of aqueous Zn/organic batteries and provide a strategy to enhance the electrochemical performance of aqueous ZIBs.

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Proton insertion chemistry: The proton insertion chemistry based on organic aqueous ZIBs was developped in mild electrolyte. The H⁺ insertion/extraction endows the battery system enhanced electrochemical performance. Moreover, the proton insertion chemistry will broaden horizons of aqueous ZIBs.

Zhiwei Tie, Luojia Liu, Shenzhen Deng, Dongbing Zhao, and Zhiqiang Niu*

Proton Insertion Chemistry of Zn/Organic Battery