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A one-dimensional π -d conjugated coordination polymer for sodium storage with catalytic activity in Negishi coupling

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Abstract: π -d Conjugated coordination polymers (CCPs) have attracted a lot of attention for various applications, although the chemical states and structures of many CCPs are still blurry. Here, we report a one-dimensional (1D) π -d conjugated coordination polymer for high performance sodium-ion batteries. We clearly revealed the chemical states of the obtained coordination polymer. Our results show that the electrochemical process undergoes a three-electron reaction and the structure transforms from C=N double bonds and Ni(II) to C-N single bonds and Ni(I), respectively. Our unintentional experiments provided visual proof of Ni(I). The existence of Ni(I) was further corroborated by its X-ray absorption near-edge structure (XANES) and its catalytic activity in Negishi cross-coupling.

Introduction

Growing demands on energy and rising interest in portable electronics and electric vehicles are driving the development of lithium-ion batteries (LIBs) and alternatives. Sodium-ion batteries (SIBs) have attracted tremendous attention in place of LIBs, in virtue of the abundance of sodium resources, eco-friendliness, low cost and similar electrochemical properties.^[1-7] However, SIBs are still unable to compete with LIBs in capacity and cycling stability, mainly due to the large size of sodium ions (1.02 vs. 0.76 Å). Of particular note are the anode materials, because commercial anode materials for LIBs (graphite) deliver very low sodium storage. Many efforts have been made to explore novel anode materials for SIBs^[8-12]; however, most of them either delivered low capacities or showed poor cycling life. The anode materials with high capacity and cycleability, therefore, are highly desirable for SIBs.

π-d Conjugated coordination polymers (CCPs)^[13-44] that are quite similar with π-π conjugated organic/polymeric materials (flexibility, low cost, functionalization through molecular design, low volume variation during cycling)^[2, 6, 45-49], arose extensive attention in recent years, due to the delocalization of electrons in

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the π -d systems (the hybridization of frontier π orbits of conjugated ligands and the d-orbits of transition metals). The delocalization of electrons in the π -d systems will improve the stabilities of the materials and their charged states, and enhance the conductivity of the materials.^[16-18, 29-34] These merits can be expected to benefit the long-term cycleability and the rate performance of batteries, which, however, hasn't been well investigated. On the other hand, although CCPs have been extensively studied, the exact chemical states or structures of most CCPs (e.g. the valence of metal ions^[50], the single/double bond characters^[15, 17], the presence or absence of counterions^{[19,} ^{51]} and radicals^[15, 17] etc.) are still blurry. The structure and state variation during electrochemical redox process can be expected to provide an efficient method for revealing the chemical structures. It is therefore highly imperative to systematically investigate the chemical states of CCPs and their applications and inner mechanisms in batteries.



Figure 1. (a) Schematic diagram of chemical structure and synthesis of Ni-BTA. (b) Schematic diagram of planar 1D conjugated coordination polymers Ni-BTA (side and top view, respectively). (c) Herringbone packing motif of Ni-BTA (view along the polymer chain).

Herein, we report the application of one-dimensional π -d metal-organic CCPs for SIBs. The square and planar coordination manner of the Ni (II) complex and the planar 1,2,4,5-benzenetetramine (BTA) guarantee the coplanarity^[52-53] and π -d delocalization of the Ni-BTA chains (Figure 1). The obtained Ni-BTA delivered high specific capacity of around 500 mAh g⁻¹ at 0.1 A g⁻¹ and superior rate performance (330 mAh g⁻¹ at 10 A g⁻¹). These performances are superior to most of the reported conjugated organic/polymeric materials for SIBs. The chemical states, the electrochemical properties and the storage mechanism of Ni-BTA were systematically studied. Our results showed that Ni-BTA can probably store three electrons for every unit through the transformation from C=N double bonds (two electrons) and Ni(II) (one electron) to C-N single bonds and Ni(I), respectively. What is more, our unintentional experiments provided visual proof of Ni(I). The existence of Ni(I) was further corroborated by its X-ray absorption near-edge structure (XANES) and its catalytic activity in Negishi cross-coupling reaction. The discovery of a novel type of materials for sodium storage, the unprecedented utilization of electrochemical process for achieving potential quasi-single-atom catalyst from CCPs and the precise identification of chemical states of the

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CCPs present new insights into relevant research areas and deepen our understanding of conjugated coordination polymers.



Figure 2. a) SEM and b) TEM images of Ni-BTA obtained via fast reaction processes, producing nanosheet morphologies. c) SEM and d) TEM images of Ni-BTA obtained via slow reaction processes, giving nanorods. e) SEM and f) HRTEM images of Ni-BTA obtained via vapor-diffusion processes, resulting in 3D nanobricks.

Results and Discussion

Synthesis and morphology control

The Ni-BTA CCPs were synthesized according to literature^[31]. The direct mixing of two reactants in the presence of ammonia and ambient air resulted in rapid reaction, which can be observed visually (Figure S1). In view of this, two conditions with different reaction speeds were conducted through controlling the temperature and bubbling. The literature^[17] has showed that oxygen is prerequisite to the reaction. Hence, the bubbling of air that will increase the liquid/oxygen interface can accelerate the coordination reaction, and thereby will increase the possible coordination of one Ni ion with more than two BTA molecules, forming cross-linked coordination polymers (Figure S2). Increasing the temperature has the similar impact on accelerating the cross-linked side reactions. Due to the planar coordination manner, the cross-linking tends to form twodimensional (2D) coordination polymers rather than 3D polymers. On the contrary, slow reaction benefits the precise coordination of every Ni ion with exact two neighbor BTA molecules, leading to one-dimensional (1D) coordination polymers, which hence should be more thermal stable than the cross-linked products. According to the Bravais-Friedel-Donnay-Harker (BFDH) law^[54] that can be used to predict the morphologies, the 1D CCPs will tend to form 1D morphologies (along the direction with strong π - π intermolecular interactions^[55] or along the long axis of the polymer^[56]) or 3D morphologies (for those with comparable intermolecular interactions along three or more directions)^[57]; while the 2D cross-linking polymers may form 2D morphologies^[57]. Figure 2a-d show the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the obtained Ni-BTA CCPs. As expected, the fast reaction produced 2D nanosheets (Figure 2a-b); while the slow reaction gave quasi-1D nanorods (Figure 2c-d). Encouraged by these achievements, we further decelerated the reaction by

using a vapor-diffusion method^[21, 57] (Figure S3). The slow diffusion of ammonia into the reactant mixture will significantly reduce the reaction speed. 3D small crystals with regular shapes therefore can be obtained, as shown in Figure 2e (The possible reason why 3D crystals were formed can be found in the following). These results showed that the synthesis, structure and the morphologies of Ni-BTA CCPs can be facilely controlled. **Determination of chemical states**

Tremendous efforts have been made to investigate the chemical states and structures of the similar conjugated coordination materials (e.g. small molecules: bis(ophenylenediamino)nickel (Ni(opda)₂)^[30, 52, 58-59], and CCPs: consisted of nickel ions and tetraamino^[22, 31] or hexaamino^{[17-18, 20,} ^{29-30, 32, 41-42]} ligands, Figure S4). According to the literature, it is plausible that the Ni ions are divalent and the whole molecule is neutral. The C-N bonds have partial double-bond characters and every nitrogen atom is connected to one hydrogen atom^[52, 58-59]. In order to confirm the formation of Ni-BTA and reveal its structure, energy dispersive spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), electron paramagnetic resonance (EPR) and elemental analyses (EA) were performed. The EDS showed that the atomic ratio of Ni, N and C is close to 1:4:6 (Figure S5), which indicated that charge-balancing cations do not exist (e.g. Ni²⁺ or NH₄⁺). EA results also proved that the contents of C, H, N and Ni were close to theoretical values in the proposed formula. The samples from slower reaction showed contents closer to the theoretical values (Table S1). Particularly, the faster reaction gave products with higher content of C, H and N, but lower content of Ni, indicating that coordination bonds were not formed at some sites of the ligands (Figure S2). These results confirmed the proposed chemical formula and the supposed reaction mechanism. The signal of CI was not observed in the EDS and XPS spectra (Figure 3a, S5), which again proved that there are no charge-balancing anions (CI⁻). The XPS spectra also indicated that the Ni ions should be divalent (Figure S6). In this case, the C-N bonds should have partial double-bond character, which can be further proved by the coexistence of stretching vibration of C=N (1627 cm⁻¹) and C-N (1410 cm⁻¹) bonds in IR spectra (Figure 3b). The absorption peaks at 3306 cm⁻¹ also confirmed the existence of N-H. The EDS mapping clearly demonstrated the uniform distribution of C, N, and Ni in Ni-BTA (Figure S7). Different from the results in hexaaminobenzene (HAB)-based CCPs,[17] strong EPR signal was observed in our sample with g-factor of 2.008 (Figure 3c). Owing to the dsp² hybridization of Ni2+, the EPR signals was not originated from Ni²⁺ and therefore, the strong EPR signal in Ni-BTA further solidified the partial double-bond characters of C-N bonds, as shown in Figure 1a and S8. All of these results proved the formation of proposed neutral conjugated coordination polymers (Ni-BTA) with proposed chemical structures. The chemical states and structures of Ni-BTA can also be further confirmed via their variations in the electrochemical studies.

Structure identification

Besides the morphologies and EA results, thermogravimetric analysis (TGA) measurements of the three samples obtained from different reaction speeds showed different behaviors. The samples obtained from slower reaction showed much higher thermal stability (Figure S9). This agrees well with our

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assumptions as mentioned above, due to the possible noncoordination or coordination of one Ni with more than two ligands at some sites in the faster reactions. The powder X-ray diffraction (PXRD) patterns revealed that the three samples have the same crystal phases with distinct peaks at $2\theta = 20.5$, 23.6, 29.1°, corresponding to d-spacing values of 4.3, 3.8, and 3.1 Å, respectively (Figure 3d). However, the three samples showed different diffraction intensities. The different intensities can also be interpreted by our assumption: the faster reaction will lead to cross-linked coordination and lower crystallinity (marked as L-Ni-BTA); while the slower reaction benefited the formation of highly ordered 1D CCPs (marked as M-Ni-BTA); the vapor-diffusion method produced the highest diffraction among them (marked as H-Ni-BTA). What is more, the vapor-diffusion method gave three additional distinct peaks at 14.2, 39.7 and 44.1°, corresponding to *d*-spacing values of 6.2, 2.3, and 2.1 Å, respectively (Table S2). The same crystal phase suggested that the cross-linking in the L-Ni-BTA was not in control. leading to low crystallinity rather than highly ordered 2D frameworks. The structure was therefore calculated by using density functional theory (DFT) calculations^[31] and further optimized with Dmol³. The optimized structure was shown in Figure 1b-1c. The polymeric chain had a planar nature and arranged as typical herringbone packing motif^[60]. The C-C bonds have partial double-bond characters, comparable with those in benzene rings (Figure S10). The C-N bonds have similar partial doublebond characters, similar to those in pyridine. Moreover, the bond length of Ni-N is shorter than that in the coordination materials containing saturated ligands (~1.92 Å)^[61]. All of these results agreed well with the experimental characterizations and indicated the strong π -d delocalization in Ni-BTA. This strong π d delocalization should be advantageous to the charge transport and high-rate performance. The XRD patterns could be well simulated by Pawley refinement with negligible difference between the experimental and simulated results. The six peaks thereby can be indexed to (011), (021), (030), (022), (042) and (033), respectively. High resolution TEM images (Figure 2f) showed clear lattice fringes with *d*-spacing about 3.7 Å, which is quite close to the d-spacing (23.6°, 3.77 Å) of (030). All of these confirmed the validity of our proposed structure. The structure had strong π -d conjugation along *a* axis (long axis of the polymer) and strong C-H… π or N-H… π intermolecular interactions along b and c axes. The comparable interactions along three directions are probably the reason for forming 3D nanobricks. The theoretical predicted BFDH morphology^[54] of Ni-BTA are also well consistent with the experimental results on both shapes and relative dihedral angles (Figure 2e,S3 and S11). **Electrochemical performance**

In order to study the possible application of π -d CCPs in SIBs, the electrochemical performances of all the three samples were evaluated. Figure 4a presents the typical cyclic voltammetry (CV) curves of H-Ni-BTA ranged from 0.01 to 2.5 V (vs. Na⁺/Na) at a scan rate of 0.5 mV s⁻¹. The cathodic scan showed three reduction peaks located at 1.09, 0.79 and 0.69 V, respectively. The two peaks moved to 1.21, 0.82 and 0.71 V from second scan, with relative anodic peaks located at 1.55, 0.88 and 0.78 V, respectively (the peaks at 0.1 V can be ascribed to the conductive additives, Figure S12). The significant difference between the second and the first cathode scan is

probably due to the synergistic effect created by the formation of solid-electrolyte interface (SEI)^[45] and the highly crystalline nature of H-Ni-BTA^[62]. The highly crystalline nature requires an activation process and a higher potential is necessary for relaxation of the strain/stress in the first cycle^[63] (see following). However, the CV curves afterward kept quasi-reversible and stable. The total transferred electrons are about three per unit for all the three samples. Moreover, the ratio of the integral areas for the three peaks of H-Ni-BTA is around 1:1:1 (the two peaks at lower electrode potentials overlapped with each other), which suggested that every peak might involve one-electron transfer (Figure S13). The CV curves of M-Ni-BTA and L-Ni-BTA showed two pairs of peaks, and the ratio of the integral areas for the two peaks is around 2:1, indicating that two peaks at lower electrode potentials in H-Ni-BTA overlapped thoroughly (Figure S13-S14). The two peaks fused into rectangular capacitor shapes in samples with lower crystallinity; while more separated peaks were found in samples with higher crystallinity. The difference in CV curves between the H-Ni-BTA and L-Ni-BTA can probably be ascribed to the higher crystallinity and purity of H-Ni-BTA and the relatively higher specific surface area of L-Ni-BTA (Figure S15).



Figure 3. (a) XPS spectra of Ni-BTA, showing the existence of only Ni, O, N and C. (b) FTIR spectra of Ni-BTA, exhibiting the clear presence of N-H, C=N and C-N bonds. (c) EPR spectra of Ni-BTA. No EPR signal was observed in the control experiment of divalent NiCl₂. (d) XRD patterns of Ni-BTA. Pawley-refined XRD patterns (simulated) were also shown for comparison, with very low differences from H-Ni-BTA.

Figure 4b displays the representative galvanostatic discharge-charge voltage profiles of the H-Ni-BTA at a current density of 0.1 A g⁻¹. The H-Ni-BTA electrodes delivered an initial discharge capacity of 861.7 mAh g⁻¹ and a recharge capacity of 531.8 mAh g⁻¹. The high discharge capacity in the first several cycles should be attributed to the formation of SEI layer.^[64] After 9 cycles, the capacity contribution from Ni-BTA is about 420 mAh g⁻¹ with Coulombic efficiency (CE) approaching to 100% (Figure 4c, S12, after deducting the contribution of super P), confirming a three-electron redox process for every unit

(theoretical capacity of 419 mAh g⁻¹). The capacity for the first plateau (~1.25 V) is about 140 mAh g⁻¹, quite close to oneelectron transfer. However, the charge-discharge curves below 1.2 V became sloping (including the second plateau (~0.75 V)), delivering capacity of about 280 mAh g⁻¹. These results indicated that the other two electron transfer occurs simultaneously, which agreed with the CV curves (two peaks overlapped with each other). The electrodes of M-Ni-BTA and L-Ni-BTA displayed a slightly lower capacity and stability than those of H-Ni-BTA, which reconfirmed the higher quality of H-Ni-BTA (Figure S16). Moreover, although the 2D nanosheet morphology and larger BET surface area of L-Ni-BTA facilitate the absence of activation process and capacitor-like voltage profiles (Figure S17), the rate performance of H-Ni-BTA is superior to those of L-Ni-BTA and M-Ni-BTA (Figure S18). The H-Ni-BTA electrodes still delivered a capacity of 330 mAh g⁻¹ at a current density of 10 A g⁻¹ (~18 C, 1C=558 mA g⁻¹). In addition, the typical discharge-charge profiles of H-Ni-BTA and M-Ni-BTA showed plateaus with small polarization (< 0.1 V) even at a rate of 10 A q^{-1} (Figure S19). When the current density returned back to 0.1 A g⁻¹, the capacity of H-Ni-BTA quickly recovered to 500 mAh g⁻¹. Figure 4d shows the cycling performance of the Ni-BTA at a current density of 1.0 A g⁻¹. The capacity of H-Ni-BTA electrodes remained 424 mAh g⁻ ¹ after 100 cycles without obvious capacity fading. After 400 cycles, the capacity of H-Ni-BTA electrodes still reached 378 mAh g⁻¹. The activation processes and the higher stabilities of H-Ni-BTA and M-Ni-BTA than those of L-Ni-BTA again proved the improved quality of H-Ni-BTA and M-Ni-BTA. We further performed the long-term cycling performance of Ni-BTA at high rate of 10 A g⁻¹ (Figure S20). Similar activation process, relatively higher capacity and better stability were observed for H-Ni-BTA and M-Ni-BTA. The cycling stability and rate performance of Ni-BTA electrodes are superior to most of the reported π-conjugated organic/polymeric materials for SIBs (Figure S21, Table S3). A full battery was hence assembled by using Ni-BTA as the anode (Figure S22). These results proved the potential application of Ni-BTA in SIBs.



Figure 4. (a) CV curves of H-Ni-BTA at a scan rate of 0.5 mV s⁻¹. (b) Discharge-charge voltage profiles of H-Ni-BTA at rate of 0.1 A g⁻¹. Cycling performance of Ni-BTA electrodes at (c) 0.1 and (d) 1 A g⁻¹. The solid squares represent the charge capacity and the open circles display the discharge capacity. The solid triangles are the Coulombic efficiency.

Determination of storage mechanism: from C=N to C-N

As mentioned above, the chemical states of Ni-BTA and analogues are still ambiguous. In order to fully understand the chemical states and storage mechanism of Ni-BTA, we examined the composition variation during cycling. Based on the above discussions, the electron transfer number is three for unit during charge/discharge process in every the electrochemical window from 0.01 to 2.5 V. According to literature^[17], the similar small molecule Ni(opda)₂ can receive two electrons, where Ni keeps as divalent, forming [Ni(II)(opda)2]2-. This mechanism is widely accepted in recent literatures^[17]. Some reports^[14, 42, 58] also suggested that Ni(opda)₂ can lose two electrons, leading to [Ni(II)(opda)2]2+ (Figure S23). This claim makes it plausible that Ni-BTA can even undergo four-electron redox reactions during cycling. However, this four-electron redox reaction mechanism should have three clear phenomena, which are contradictory to our results: 1) the first discharge cycle can only undergo two-electron redox reactions, which should deliver a theoretical capacity of ~280 mAh g⁻¹. This value was much lower than the actual results; 2) the charged states of Ni-BTA should involve the intercalation of charge-balancing anions (PF6-), which was not observed in the XPS results (Figure S24, S25); 3) the charged states of Ni-BTA will only have C=N double bonds without C-N bonds. Hence, the only possible charge storage mechanism of Ni-BTA is that it accepts more electrons through forming reduction states rather than oxidization states (Figure 5a). The open-circuit voltage of the as-prepared battery (same to the cutoff voltage) and the actual capacities also manifested this assumption. In this case, the ligand (BTA) can accept two electrons, forming BTA4-, which corresponds to a transformation from partial C=N double bonds to full C-N bonds. This mechanism can be proved by the XPS, FT-IR and Raman spectra of the charged/discharged states. From the C 1s spectra (Figure 6a), it is clear that the peak assigned to C-N bonds (285.5 eV) increased with decrease of C=N bonds (286.7 eV) after discharging.^[65] The relative intensity recovered after being recharged. The N 1s spectra (Figure S26) also confirmed this mechanism. Compared with the pristine electrodes, the signal of C-N single bonds (~399.4 eV) increased obviously with weak signal of C=N double bonds (~398.2 eV), after fully discharging. When being recharged to 2.5 V, the relative intensity returned back to its original state. From FT-IR spectra (Figure 6b), the strong vibration absorption at around 1633 cm⁻¹, which is assigned to the C=N stretching, decreased after discharging. On the other hand, the absorption from the C-N stretching increased significantly (1415 cm⁻¹). After being fully recharged to 2.5 V, the relative absorption of the C-N peaks decreased, which is reverse to the discharge process. The Raman spectra (Figure S27) showed that the aromatic ring stretch (C=C/C-C bonds) maintained stable during cycling, which indicated that the C-C/C=C did not participate in the reaction (also can be proved by the XPS and IR results). All of these results strongly proved that the ligands BTA can undergo a two-electron redox process (between BTA2- and BTA4-), accompanying with the transformation between C=N and C-N groups.

Determination of storage mechanism: from Ni(II) to Ni(I)

Although low valent Ni(I)^[37] and Ni(0) (such as Ni(PPh₃)₄)^[40, 66] have been reported in some coordination complexes, the assertion that Ni-BTA can accept more electrons forming low-

valent Ni still lacks substantial evidences. The ex-situ XPS spectra showed that the valence of nickel kept as +2 during cycling (Figure S25), which is contradictory to our assumption. However, we unintentionally observed that a clear white smoke with spark appeared immediately when we exposed the wet fully discharged samples containing some solvent (dimethoxyethane, DME) into air (Video S1 and Figure S28). This phenomenon only occurs when the discharged electrode was not fully dried after being washed by DME. These phenomena can be observed for every fully discharged sample but were never found for the pristine or fully charged samples. Considering that there are no any other highly active materials and every Ni atom/ions in the coordination polymers is separated by the ligands, the highly active material is probably low-valent Ni^[37] which behave like single-atom nickel. Based on the electrochemical performance, the valence of Ni after discharging should be +1. If there is no solvent, the highly active guasi-single-atom Ni may be oxidized in the air, thereby forming divalent nickel as found in the XPS results. However, in the presence of flammable DME, the highly reactive guasi-single-atom Ni(I) will react with some oxidative species and ignite the DME, forming smoke and leading to scorch on the substrate (Figure S28). In order to exclude the possibility that the smoke might come from the possible formation of highly active sodium metal in the fully discharged samples (0.01 V), we conducted the detailed experiments during cycling: when the samples were discharged to 1.1 V (after the first plateau), no smoke was observed; however, smoke can be observed when the samples were discharged to 0.75 V or 0.4 V, leading to scorch on the substrate afterwards (Figure S29 and Video S2). These results indicated that: 1) the smoke did not come from the sodium metal, because sodium metal is not likely formed at voltages as high as 0.75 V; 2) the sloping region (including the second plateau) probably involved the redox reaction of Ni(II) into Ni (I).



Figure 5. (a) Schematic diagram of the possible storage mechanism of Ni-BTA. The system can store three electrons for every unit, leading to reduction states (Ni-BTA-R3) rather than oxidization states (Ni-BTA-O). (b) Simplified structures to demonstrate the most possible sites of inserted Na ions. Left: Every unit accepts two electrons and two Na-ions. The two Na-ions are uniformly located at the top/bottom of the molecules (forming Ni-BTA-R2); Right: every unit accepts one more electron and one more Na-ion. The Na-ion

is located at the lateral position of the molecular plane (forming Ni-BTA-R3. the first two Na-ions are omitted for clarity).

Catalytic activity of discharged Ni-BTA in Negishi coupling

The high activity of the discharged samples (possibly presence as Ni(I)) inspired us to use the fully discharged sample as catalyst, because it has been widely reported that Ni(I) is the intermediate in Ni(0)-based Negishi coupling reactions^[67-68]. The fully discharged electrode was directly used for catalyzing the Negishi cross-coupling reaction (Figure 6c, S30-S32). Target products were observed with yield around 40% (after purification), which provides strong evidences for the existence of highly reactive Ni(I). As a control experiment, no product was observed by using either NiCl₂ powders, Ni-BTA powders, pristine Ni-BTA electrodes or fully charged Ni-BTA electrodes as catalyst, because nickel ions in all of them are divalent (Table S4). These results proved the catalytic activity of Ni(I) in the cross-coupling reaction and the reduction of Ni(II) ions into Ni(I) during discharging. This experiment also provides a novel strategy for achieving potential quasi-single-atom catalyst by using electrochemical process from coordination polymers.

Refined electrochemical process

To further refine the electrochemical process, we conducted the ex-situ EPR measurements and the catalytic activity of the electrodes during cycling. From Figure 6d, compared with the pristine electrode, it is clear that the EPR signal decreased for the electrodes discharged to 1.3 and 1.1 V with similar g-factor of 2.002. Based on our aforementioned analysis, the EPR signal of the pristine electrode can be ascribed to the radicals on ligands (Figure S8). Hence, the decrease of the EPR signal suggested the first reduction peak around 1.3 V can be assigned to the acceptance of electrons in the ligands, leading to decrease of radicals and the transformation from C=N double bonds to C-N single bonds. The presence of radicals at 1.1 V (though very weak) together with the electron transferring number indicated that Ni-BTA-R1 was formed after the first plateau (Figure 5a). The overlapping between the two redox peaks at lower electrode potential makes it difficult to distinguish the other two electrons. However, from the peak shapes in the CV curves, it can be inferred that the third redox peaks might come from the transformation from Ni(II) to Ni(I). Considering the d⁹ state of Ni(I) (unpaired electrons existed, as also reported in other Ni(I) complex^[37]), the further discharged samples should exhibit EPR signals. Therefore, we investigated the samples after discharging to 0.75 V. EPR signal indeed appeared again with g-factor of 2.001. This EPR signal further increased after being discharged to 0.4 V. These results indicated that Ni-BTA-R3 was formed afterwards (Figure 5a).

In view of the catalytic activity of Ni(I) in Negishi crosscoupling reactions, we conducted the catalytic reactions using discharged electrodes at different cutoff voltages: when the electrodes were discharged to 1.1 V (after the first plateau), no obvious products were observed by thin-layer chromatography (the yield is only 4% analyzed by gas chromatography (GC, Figure S33)); however, when the electrodes were discharged to 0.75 V or 0.4 V, the product can be isolated and the yield increased to 19.6 and 32.4% after purification, respectively (Table S4). These results, together with smoking experiments

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Figure 6. Characterization of Ni-BTA electrodes during cycling. (a) XPS C 1s spectra of Ni-BTA electrodes. (b) FTIR spectra of Ni-BTA electrodes (the broad peak at ~3400 cm⁻¹ can be ascribed to the moisture appeared during sample handling). (c) Catalytic activity of discharged Ni-BTA electrodes in Negishi cross-coupling reaction and the ¹H NMR spectra of the products obtained from the cross-coupling reaction. (d) EPR spectra of Ni-BTA electrodes. The three red lines showed a similar g-value of 2.002; while the two blue lines have a comparable g-value of 2.001. (e) Ni K-edge XANES and (f) EXAFS of Ni-BTA.

and the EPR measurements during cycling, again corroborated that the redox reaction of Ni from Ni(II) to Ni(I). All of these results suggested that Ni-BTA can store three electrons for every unit through the transformation from C=N double bonds (two electrons) and Ni(II) (one electron) to C-N single bonds and Ni(I), respectively. The combined function of metal ions and the ligands are the reasons that Ni-BTA can deliver high capacities.

It is therefore of great significance to reveal the chemical and crystal structure variation during cycling. The XRD patterns showed that the structure of Ni-BTA kept stable and no phase transition has been observed (Figure S34, S35). The Raman spectra (Figure S27) also showed that the chelate ring stretch (Ni-N coordination bonds) maintained stable during cycling, which indicated that the structure of the CCPs was stable during cycling (dsp² hybridization maintained). What's more, the N-H bonds also kept stable after cycling, which can be proved by the IR spectra (Figure 6b). We further performed the X-ray absorption spectroscopy (XAS) of Ni-BTA during cycling (Figure 6e-f). As shown in the XANES spectra, the shoulder peak at 8340 eV appeared in the powders, pristine and charged electrodes of Ni-BTA indicated the existence of Ni(II) and the low-spin square-planar configuration.[40] Moreover, the peaks at 8340 and 8354 eV shifted to 8338 and 8352 eV, respectively. The shifts of 2 eV suggested that Ni(II) was probably reduced to Ni(I).^[69-70] From the Fourier transformed extended X-ray absorption fine structure (EXAFS) spectra, clear Ni-N coordination bonds can be observed in the Ni-BTA samples (powders, pristine and charged samples) with bond length of about 1.83 Å, which coincides well with the aforementioned calculations (1.84 Å). What's more, Ni-N coordination bonds still existed in the discharged samples and the length of Ni-N bonds (1.87 Å) is slightly longer than the pristine and charged samples, which indicated the larger size of Ni(I) than Ni(II) (Figure S36 and Table S5). These results clearly confirmed that the structure

of Ni-BTA kept stable and the Ni-N coordination bonds remained, even when Ni became monovalent.

In order to investigate why three rather four electrons were accepted (leading to Ni(I) rather than Ni(0) in the discharged states) and where the intercalated Na ions exist, theoretical calculations were performed. The DFT calculations were carried out to simulate the geometry optimizations of Ni-BTA-R3 (three electrons and three Na ions, Ni(I)) and Ni-BTA-R4 (four electrons and four Na ions, Ni(0)), respectively. The calculations showed that Ni-BTA-R3 is much more stable than Ni-BTA-R4. The positive binding energy of Ni-BTA-R4 showed that Ni-BTA-R4 can't be formed, because the discharging process should be a spontaneous redox reaction. The calculations also showed that the three inserted Na ions in Ni-BTA-R3 are located in the following manner: two Na ions are located uniformly at the top/bottom of the molecular plane and the third Na ion is present at the lateral position (bay position) of the molecular plane (Figure 5b and S37-S39). In this case, all the most favorable sites (only three for per unit) have been occupied in Ni-BTA-R3. **Reaction kinetics of Ni-BTA electrodes**

To further understand the reaction kinetics of Ni-BTA, the conductivity, the electrochemical impedance spectra (EIS), the capacitive contribution in the Ni-BTA electrodes and the ionic diffusion properties were studied. The electric conductivity was measured by using two-terminal devices, in which the material itself was pressed into pellets (~120 μ m). All the three samples showed similar I-V curves (Figure S40). The samples with higher crystallinity had higher conductivity, which can probably be ascribed to the well π -d conjugation, lower defects and higher crystalline nature. The EIS measurements were performed to detect the charge transfer and ionic diffusion in the batteries (Figure S41). The Nyquist plots showed that all the three samples of Ni-BTA were of a very small internal resistance during cycling, which is one of the reasons that Ni-BTA can give

high rate performance. The H-Ni-BTA electrodes showed the lowest resistance of only ~1 Ω . Additionally, the resistance of L-Ni-BTA and M-Ni-BTA electrodes increased during cycling, which may be the reason that L-Ni-BTA and M-Ni-BTA electrodes showed inferior cycling stability than that of H-Ni-BTA. The capacity contribution^[71-73] from diffusion-control or capacitive effect was then analyzed by scanning the CV curves at different scan rates. Clearly, all the three samples showed capacitive effects (>70%, Figure S42 and Table S6). And the 2D nanosheet morphologies of L-Ni-BTA gave higher contribution of capacitive effects (Figure S43). Galvanostatic intermittent titration technique (GITT) method was further used to investigate the reaction kinetics. The results indicated that the calculated Na⁺ diffusion coefficient of three samples typically increased with the quality of the materials (Figure S44), although the grain size of H-Ni-BTA is larger than those of M-Ni-BTA and L-Ni-BTA. The higher Na-ion diffusivity of H-Ni-BTA can probably be ascribed to the high quality and the high crystallinity of H-Ni-BTA (ordered ionic diffusion channel). These results indicated that the high electrochemical performance of H-Ni-BTA is originated from the high quality and high crystallinity of the samples and the corresponding high Na-ion diffusivity.

Conclusion

In conclusion, we reported the 1D π -d conjugated coordination polymers for sodium-ion batteries. The high crystalline H-Ni-BTA electrodes delivered high specific capacity of around 500 mAh g⁻¹ at 0.1 A g⁻¹ and superior rate performance (330 mAh g⁻¹ at 10 A g⁻¹). These performances are superior to most of the reported conjugated organic/polymeric materials for SIBs anodes. The chemical states, the electrochemical properties and the storage mechanism of Ni-BTA were studied. We showed substantial evidence that Ni-BTA can store three electrons for every unit through the transformation from C=N double bonds (two electrons) and Ni(II) (one electron) to C-N single bonds and Ni(I), respectively. The reduction of Ni ions into highly active quasi-single-atom Ni(I) was also corroborated by the XAFS results and its catalytic activity in Negishi cross-coupling reaction. These results provide a novel strategy for achieving potential quasi-single-atom catalyst by using electrochemical process from coordination polymers. Through various characterizations, we clearly identified the electrochemical active centers and refined electrochemical reaction process. The discovery of a novel type of materials for sodium storage, the unprecedented utilization of electrochemical process for achieving guasi-single-atom catalyst from CCPs and the precise identification of chemical states of the CCPs present new insights into relevant research areas and deepen our understanding of conjugated coordination polymers.

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Keywords: π -d conjugated coordination polymers • organic sodium-ion batteries • mechanism • Negishi cross-coupling • single-atom catalyst

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RESEARCH ARTICLE

Entry for the Table of Contents

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A conjugated coordination polymer is reported for sodium-ion batteries. The chemical states of the obtained coordination polymer clearly are revealed, indicating that the electrochemical process undergoes a three-electron reaction and the structure transforms from C=N double bonds and Ni(II) to C-N single bonds and Ni(I), respectively. Furthermore, the discharged electrodes (Ni(I)) can be used as quasi-single-atom catalyst in Negishi cross-coupling.



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A one-dimensional π -d conjugated coordination polymer for sodium storage with catalytic activity in Negishi coupling