

Communication

A 2D covalent organic framework as a high-performance cathode material for lithium-ion batteries

Manman Wu^a, Yang Zhao^a, Binqiao Sun^a, Zhenhe Sun^a, Chenxi Li^a, Yu Han^a, Lingqun Xu^a, Zhen Ge^a, Yuxin Ren^a, Mingtao Zhang^a, Qiang Zhang^b, Yan Lu^{b,**}, Wei Wang^c, Yanfeng Ma^a, Yongsheng Chen^{a,*}

^a State Key Laboratory and Institute of Element-Organic Chemistry, Centre of Nanoscale Science and Technology and Key Laboratory of Functional Polymer Materials, College of Chemistry, Nankai University, Tianjin, 300071, China

^b Tianjin Key Laboratory for Photoelectric Materials and Devices, Key Laboratory of Display Materials & Photoelectric Devices, Ministry of Education, School of Materials Science & Engineering, Tianjin University of Technology, Tianjin, 300384, China

^c State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou, Gansu, 730000, China



ARTICLE INFO

Keywords:

Lithium-ion batteries
Organic cathode
Covalent organic frameworks
High capacity
Cycle and rate performance

ABSTRACT

Organic cathode materials for lithium storage have attracted wide attention owing to their very diverse structures and largely tuned engineered molecular levels. However, it remains a great challenge to design a cathode material with simultaneously combined features of high specific capacity, cycle life and rate performance. Here, based on our proposed strategy, we design and report a BQ1-COF consisting of maximum active groups (C=O and C=N) with minimal inactive groups, which when used as cathode materials for lithium-ion batteries give a reversible capacity of 502.4 mA h g⁻¹ at 0.05C, so far the highest capacity among polymer-based cathode materials. More importantly, the stable framework structure delivers an excellent capacity retention (81% after 1,000 cycles at 1.54 A g⁻¹), and it is noted that the rate performance (170.7 mA h g⁻¹ even at 7.73 A g⁻¹) is far superior to previous related reports. These results indicate that maximizing the loading of redox active groups in a stable network structure is an effective strategy to design organic cathode materials simultaneously with high capacity and outstanding cycle and rate performance for next generation lithium-ion batteries.

High-performance lithium-ion batteries (LIBs) have attracted growing attention for satisfying the demands of communication, portable electronic devices, electric vehicles (EVs) and hybrid EVs (HEVs) [1]. The essential is to have applicable electrode materials with high-performance. In particular, cathode material is probably a bigger bottleneck due to its low theoretical capacity compared to that of anode materials, such as Si-based and Li metals anodes [1,2]. With the advantages of abundant resource, wide structural diversity and being environmentally friendly [3,4], organic/polymeric materials have been explored as electrode materials and in some cases with high capacity [2, 5,6]. However, there have been some intrinsic and challenging issues remained to be solved, and the main one is their dissolution into electrolytes, which leading to a fast capacity fading during cycling. Many strategies have been applied to address such an issue, including polymerizing the redox-active compound [7–9], elongating the molecular conjugation length [10,11], forming a salt with organic carbonyl

compounds and so on [12–16]. Nevertheless, while these strategies succeed in enhancing the cyclability, they come with the cost of reduced specific capacity due to a large amount of existence of inactive units. The inherent low conductivity and redox voltage for organic materials also limit the electrochemical performance of their LIBs [17]. Thus, it is still a great challenge to design appropriate cathode materials with high capacity, outstanding cyclability and rate performance all together.

For the capacity issue, on the basis of the relationship between theoretical capacity and chemical structure [18,19], the most intrinsic approach to achieve the highest theoretical capacity is to increase redox group loading and reduce inactive group loading as much as possible, thus with the maximum electron transfer per repeating unit. In theory, the compounds that consist of only redox groups without any inactive groups could deliver the highest capacity. This comes to the case such as (CO)₆, with only redox active C=O group [19], exhibiting the highest theoretical capacity (957 mA h g⁻¹) among conjugated carbonyl

* Corresponding author.

** Corresponding author.

E-mail addresses: luyan@tjtu.edu.cn (Y. Lu), yschen99@nankai.edu.cn (Y. Chen).

<https://doi.org/10.1016/j.nanoen.2020.104498>

Received 26 December 2019; Received in revised form 13 January 2020; Accepted 13 January 2020

Available online 21 January 2020

2211-2855/© 2020 Elsevier Ltd. All rights reserved.

compounds. Nevertheless, its cycle and rate performance need to be further improved for practical application. Clearly, the most effective way to obtain high capacity and long cycle life simultaneously is to maximize the loading of redox active groups in a stable polymeric network structure to have monolithic materials.

With this, we propose a series of possible materials that meet the above requirements with the most widely used redox groups (C=N, C=O), as shown in Scheme 1 and Table S1, including linear polymers and covalent organic frameworks (COFs). In particular, COFs exhibit more distinct advantages as electrodes materials for LIBs due to its rather stable framework structure and regular porous channel, which should facilitate both ion and electron transport for both better cycling stability and rate performance [20–26]. Therefore, the designed COFs (Scheme 1) with the maximum electron transfer per repeating unit are expected to not only deliver a high capacity but also afford outstanding cycle and rate performance for LIBs.

Among above proposed structures, considering both the structural stability for cycling issue and theoretical capacity together with easy access, BQ1-COF was chosen and synthesized directly by a simple polycondensation reaction of hexaketocyclohexane (HKH) and tetramino-benzoquinone (TABQ) [25] as shown in Fig. 1a and more details are given in the Methods. The abundant C=O and C=N groups and minimal inactive groups in this structure render it a theoretical capacity of 773 mA h g^{-1} corresponding to 18 electrons redox per repeating molecular unit. When applied as the cathode material for LIBs, it delivers an ultrahigh experimental capacity of $502.4 \text{ mA h g}^{-1}$ corresponding to a maximum number of 12 electrons transfer per repeating molecular unit, so far the highest capacity among polymer-based cathode materials. The stable framework structure affords an excellent capacity retention of 81% after 1,000 cycles at 1.54 A g^{-1} . The well-defined channel and extended conjugated system promote a rapid Li^+ diffusion and electron transport, delivering an outstanding rate performance ($170.7 \text{ mA h g}^{-1}$ at 10C), which is far superior to previous related reports.

FT-IR and solid-state ^{13}C NMR were carried out to confirm the chemical composition and structure of BQ1-COF (Figs. S1 and S2). The emerging C=N group (1550 cm^{-1}) in the FTIR spectrum of BQ1-COF and the peak with a chemical shift of around 146 ppm in the solid-state ^{13}C NMR spectrum, indicating the formation of the expected π -conjugated C=N linkages, consistent with the structures proposed in Fig. 1a. The chemical composition and structure of BQ1-COF were also characterized and supported by X-ray photoelectron spectroscopy (XPS) (Fig. S3) and Elemental analysis (Table S2).

As shown in Fig. 1c, the Brunauer-Emmett-Teller (BET) surface area was measured by N_2 adsorption-desorption measurement and is calculated to be $94.73 \text{ m}^2 \text{ g}^{-1}$ in the range of $P/P_0 = 0.05\text{--}0.2$. Its isotherm

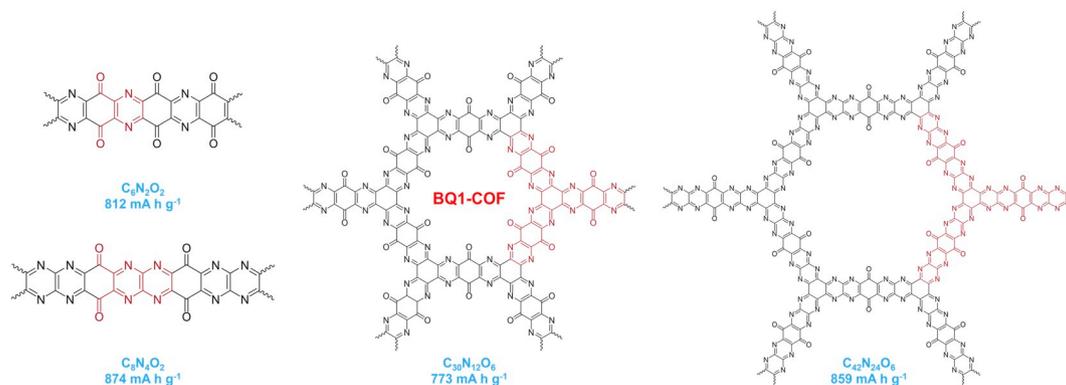
plots exhibit a classic type I isotherm, revealing the microporous character of BQ1-COF [20]. The pore size distribution demonstrates that BQ1-COF forms a well-defined channel structure, and the dominant pore size observed at 1.35 nm is close to the calculated pore size (1.39 nm) as shown in Fig. 1a. And Energy-dispersive X-ray spectroscopy (EDS) elemental mapping (Fig. S5) from the SEM images show the homogeneous spatial distributions of C, N, O of BQ1-COF, and the atomic ratio of C to N is about 2.33, which agrees with the theoretical calculated value of 2.5.

Its XRD pattern (Fig. S6) exhibits clear peaks at 11.88° , 15.56° , 18.06° and 19.92° , which are assigned to the (110), (101), (210) and (201) planes, respectively, indicating a good crystallinity. The PXRD diffraction peaks for BQ1-COF is consistent with the result of simulated AB stacking structure (Fig. S7). It is worth noting that BQ1-COF does not show a diffraction peak of (100) instead of exhibiting a strong diffraction peak at 28.80° , which is assigned to the (002) plane representing a π -stacking distance of 0.315 nm. The result is probably induced by the strong π - π interaction between neighbor layers of BQ1-COF with extended π -conjugated structure [27,28]. In addition, in high-resolution transmission electron microscopy (HRTEM) images of BQ1-COF (Fig. 1d, e and S8), the clearly observed lattice fringes with an estimated d spacing of 0.23 nm is close to the inter-spacing of (420) plane (0.24 nm). The observed hexagonal electron diffraction (SAED) pattern (inset in Fig. 1d) is also in consistent with the observed (420) plane in HRTEM. All these indicate a good crystallinity of BQ1-COF.

Furthermore, its Raman spectrum (Fig. S9) exhibits a band at $\sim 1520 \text{ cm}^{-1}$, reflecting the in-plane bond-stretching vibrations of sp^2 carbon atoms in the 2D honeycomb structure [29], which further confirms the graphene-like 2D structure of BQ1-COF. Its high thermal stability was demonstrated in the TGA analysis (Fig. S10), which indicates the material is stable up to $\sim 360^\circ\text{C}$ without clear degrading/decomposition. The lowest unoccupied molecular orbital (LUMO) energy level of BQ1-COF (Fig. S11) (-4.20 eV) is lower than most organic materials, which implies larger electron affinity and higher reduction potential and thus a high working voltage [30–32]. And compared to other reported COFs [33,34], the LUMO-HOMO gap (3.41 eV) is much smaller, indicating possibly a high electrical conductivity [30]. This was consistent with the observed conductivity of $3.1 \times 10^{-6} \text{ S m}^{-1}$ (Fig. S12), several orders higher than most organic materials [31].

The electrochemical performance of BQ1-COF was evaluated as the cathode material for LIBs with metal lithium as the counter/reference electrode. Fig. 2a shows that the typical cyclic voltammograms (CV) of BQ1-COF electrodes in the initial three-cycle, displaying three clear reduction peaks at 2.64, 2.20 and 1.2 V vs. Li^+/Li , which clearly point to the multiple-electron redox reactions during the charging/discharging processes. Correspondingly, three clear discharge plateaus at about

Our strategy



Scheme 1. Some proposed organic cathode materials with ultrahigh theoretical capacity with typical redox active groups (C=N, C=O). The structural repeating units are marked by red. The chemical formulae of repeating units and calculated theoretical capacity of each structure are shown below the corresponding structures.

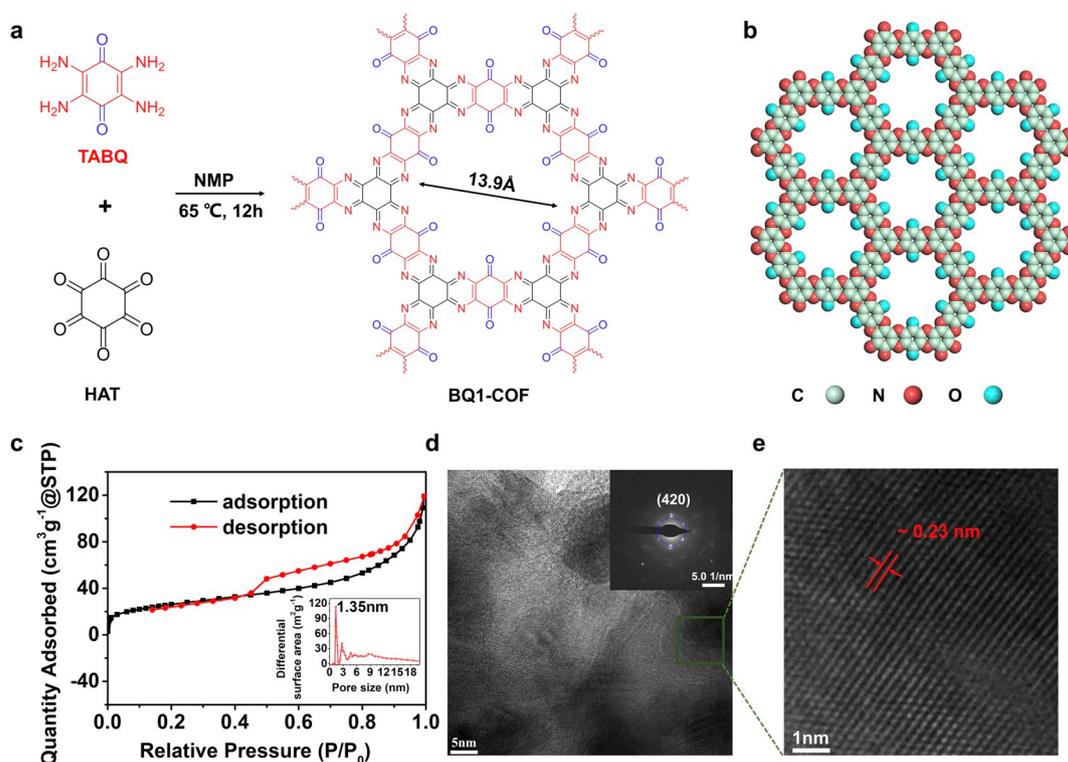


Fig. 1. (a) Scheme for the synthesis of BQ1-COF. (b) Graphic representation of one-layer-conjugated skeleton of BQ1-COF. (c) Pore-size distribution and N_2 adsorption-desorption isotherms of BQ1-COF. (d, e) Transmission electron microscopy images of BQ1-COF. Inset: SAED pattern of BQ1-COF.

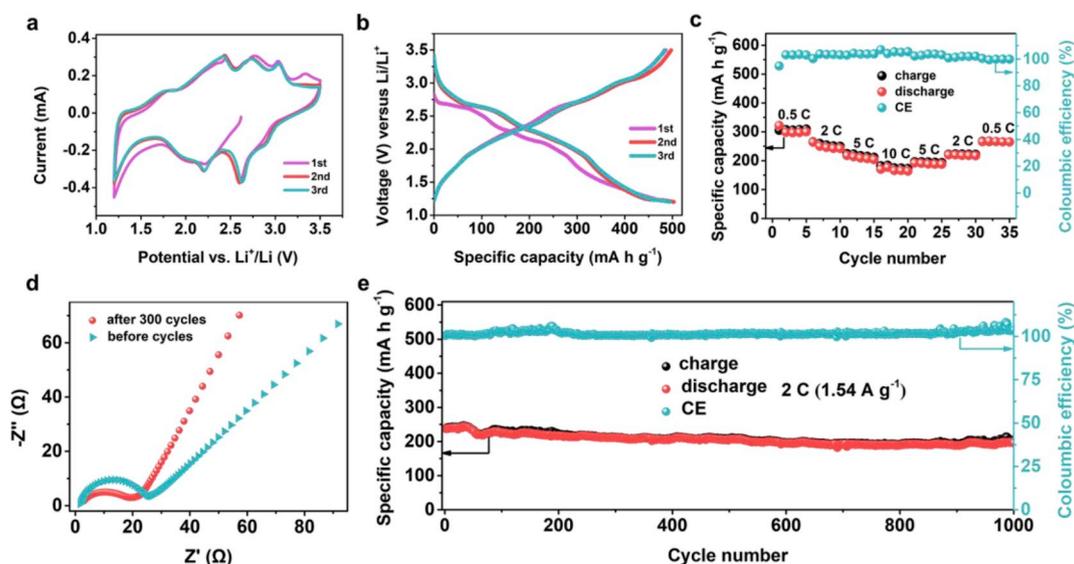


Fig. 2. (a) The initial three-cycle CV curves of BQ1-COF at a scan rate of 0.5 mV s^{-1} . (b) The initial three-cycle capacity-voltage profile of BQ1-COF at a current of $0.05C$. (c) Rate capabilities of BQ1-COF at various current rates. (d) Nyquist plots of BQ1-COF before and after 300 cycles at a current of $2C$. (e) Long-term cycling performance of BQ1-COF at a current of $2C$ for 1,000 cycles.

$3.20\text{--}2.47 \text{ V}$, $2.47\text{--}2.11 \text{ V}$ and $1.4\text{--}1.2 \text{ V}$ can be distinguished from the fully reversible galvanostatic charge/discharge curves in Fig. 2b. The first cycle CV curve shows an extra anodic peak at 3.36 V compared to the next cycles, which is due to the formation of the SEI film [10,35]. The second and third CV curves display a good reversibility of the redox process. In Fig. 2b, the first galvanostatic charge/discharge curve shows a high initial capacity of 494 mA h g^{-1} with a high coulombic efficiency of 98.4% , and the charge/discharge curves of the second and third cycles are also consistent each other. These results indicate the highly

reversible nature of BQ1-COF as cathode material for LIBs. It's worth of noting that the cathode exhibits an ultrahigh capacity of $502.4 \text{ mA h g}^{-1}$ in second cycle at $0.05C$. To our knowledge, the reversible capacity of BQ1-COF is the highest among all reported organic COF or polymer-based cathode materials (Fig. 4c, Table S3) [7–9,15,20–23,25,34,36–38]. Furthermore, BQ1-COF exhibits an average discharge voltage of 2.06 V , and the energy density, calculated based on the reversible capacity and average discharge voltage above, can reach up to 1033 W h kg^{-1} , much higher than the capacity ($100\text{--}140 \text{ W h kg}^{-1}$) of

traditional commercial cathode materials such as LiCoO_2 and LiMn_2O_4 [31]. Even at a higher current density of 10C (7.73 A g^{-1}), the cathode material can still afford a high energy density ($\sim 350 \text{ W h kg}^{-1}$) with also a high power density (12.6 kW kg^{-1}) (Figs. S13 and S14).

The rate capabilities of BQ1-COF (Fig. 2c) were investigated at various current density. Notably, BQ1-COF can still show a reversible specific capacity of $170.7 \text{ mA h g}^{-1}$ even at an ultrahigh current density of 10C (7.73 A g^{-1}). The rate capabilities are far superior to previous related reports (Fig. 4d, Table S4) [7–9,20–23,25,30,34,36–38], which is contributed to its well-defined channel structure and extended π -conjugated systems. To investigate the kinetics of BQ1-COF, electrochemical impedance spectroscopy (EIS) of BQ1-COF was measured, before and after 300 cycles at 2C (Fig. 2d). The charge-transfer resistance (R_{ct}) of the cathode material (23.3Ω before cycling) decreases to be 20Ω after 300 cycles, suggesting a fast and stable reaction kinetic of the cathode [20,39].

In addition, BQ1-COF exhibited outstanding long-term cycling stability (Fig. 2e), while maintaining $198.4 \text{ mA h g}^{-1}$ with 81% capacity retention after 1,000 cycles at a current density of 2C, and the Coulombic efficiency remains approximately 100% during all the cycling. Furthermore, even at higher current density of 5C (3.87 A g^{-1}), BQ1-COF can still deliver capacity of 158 mA h g^{-1} after 1,500 cycles, (Fig. S15), revealing an excellent electrochemical stability of BQ1-COF.

To explore the lithium storage mechanism of BQ1-COF, DFT and ex situ XPS were carried out. For the extended conjugated system constructed by C=O groups and neighboring C=N groups, N and O atoms work as the collaborative centers during the lithium intercalation, which can form a stable five-membered chelate rings (C–N–Li–O–C) [40–42]. In addition, electroactive pyridine N and pyrazine N atoms in a π -conjugated C=N system can strongly coordinate with lithium ion, affording high-capacity lithium storage with multiple electron redox reaction [31, 41]. In the initial stage, there are three possible ways of lithiation, the two possible simultaneous coordination of N and O to Li (N–Li–O) and the similar chelating effect of N–Li–N. The DFT calculations for three situations are carried out and the optimization results (Fig. S16)

indicated that lithium ions are expected to firstly chelate with oxygen atom and adjacent interior nitrogen atoms to form the configuration of five-membered ring (C–N–Li–O–C). Considering the structural symmetry, three lithium ions could be chelated at the same time in each stage. In the second stage, three possible configurations can be obtained as shown in Fig. S16, together with their calculated total energy, which suggest that lithium ions prefer to coordinate with the nitrogen and oxygen of the same side at this stage. For the next two stages, there are two possibilities for COF–9Li (Fig. S16) and only configuration for COF–12Li (Fig. S17), where six lithium ions might correlate with the COF via chelating with the other three carbonyl groups and six neighboring conjugated C=N groups as observed before [40]. At the final two stages of the lithiation processes, the lithium storage should be mainly contributed to the remaining six electroactive C=N groups of the COF–12Li. As indicated by Fig. S17, COF–15Li should be formed by accepting three lithium ions that bond with three pyridine nitrogen atoms. Afterwards, with the insertion of another three lithium ions, the final lithiated structure of COF–18Li can be achieved. Therefore, one repeating unit of BQ1-COF that contains 6C=O groups and 12C=N groups can reversibly accept 18 lithium ions in theory, making full advantage of redox groups (C=O, C=N) and offering an ultrahigh theoretical capacity of 773 mA h g^{-1} .

Nevertheless, it is also noted that the binding energies (ΔE) elevate significantly after inserting 12 lithium ions (Table S5), so the following lithiation will be much more difficult. This can be explained by the steric hindrance effect and decreased stability of the produced molecule after 18 Li^+ insertion as shown in Figure S17 [40]. Therefore, the stepwise actual lithium-storage process of BQ1-COF can be divided into four stages (Fig. 3), and a maximum of 12 lithium ions can be stored experimentally in a COF repeating unit in the operating voltage window of 3.5–1.2V. The total energy of BQ1-COF and lithiated COF–nLi ($n = 3, 6, 9, 12$) at each stage are marked by orange in Fig. S18, the trend of energy change is well consistent with the discharge curve.

Ex situ XPS scans were performed to identify the structural evolution of BQ1-COF during its discharging/charging process. As shown in

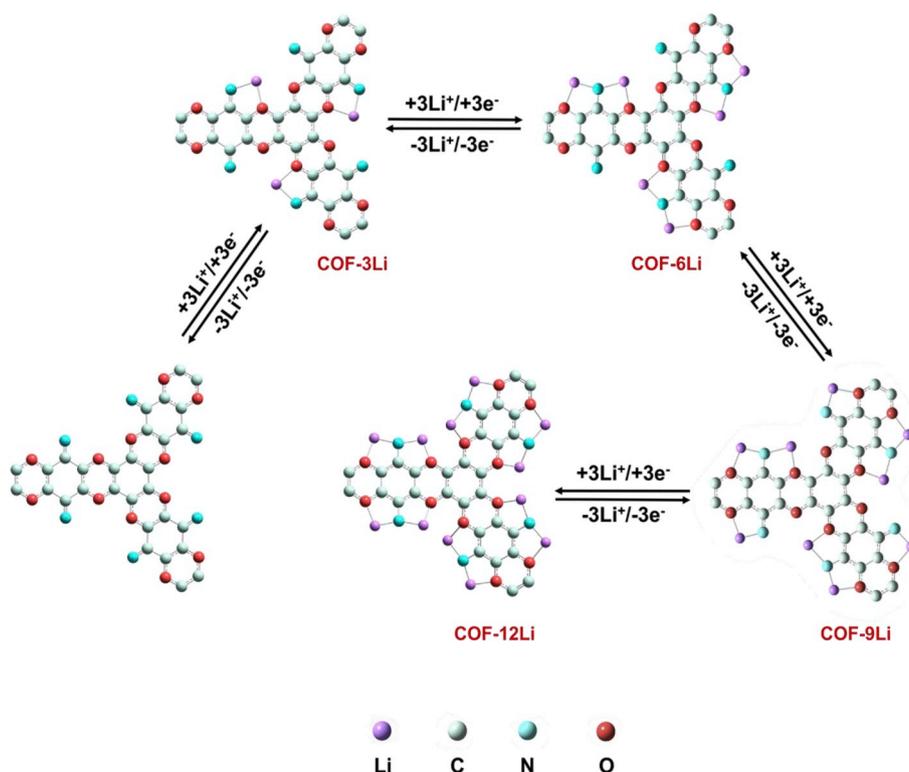


Fig. 3. Scheme for the structure revolution during the 12 lithium ions insertion and extraction process with a COF repeating unit.

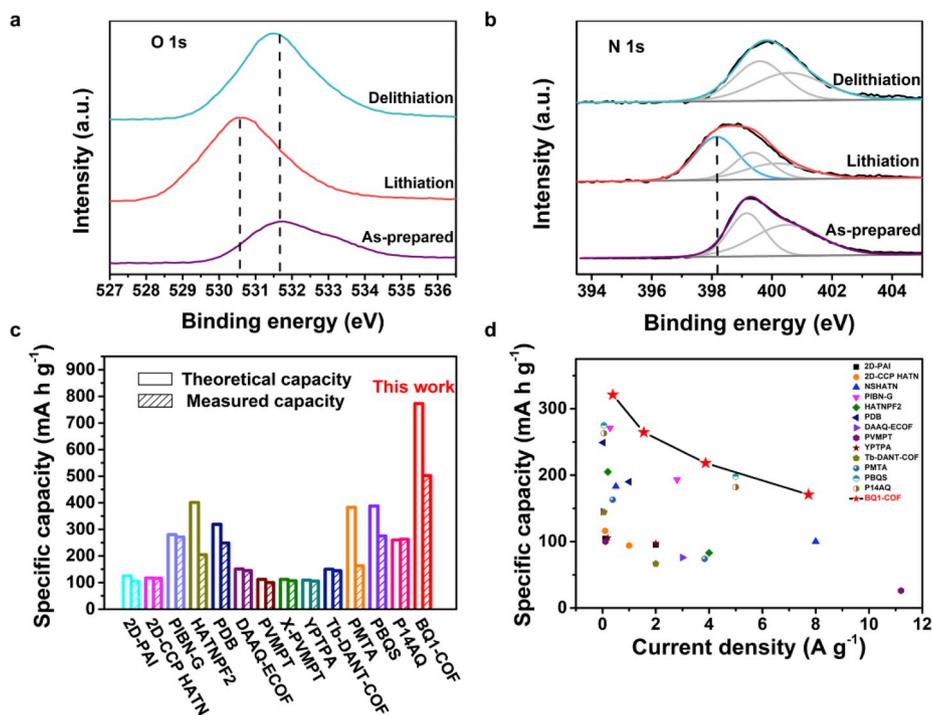


Fig. 4. (a) Ex-situ XPS local scan spectra of O 1s and (b) N 1s regions at different states during lithiation and delithiation process, respectively. (c) Theoretical and measured capacities and (d) rate performance comparison of BQ1-COF with some previously reported COF and related polymer-based cathode materials, respectively.

Fig. 4a, the peak for O 1s spectrum shifted toward lower binding energy during the lithiation process and then recovered to the initial state during the following delithiation process. This indicates that the C=O groups of the cathode participate in the reversible redox reaction with lithium ions [41–43]. As shown in Fig. 4b, for the as-prepared cathode, the N 1s spectrum could be divided into two peaks located at 399.17 and 400.5 eV, which are assigned to the conjugated (sp^2) pyrazine and non-conjugated (sp^3) amino-groups, respectively. After lithiation, the intensity of C=N bond decreased, while an additional peak evolved at a lower binding energy of 398.0 eV, corresponding to the formation of a new bond (N–Li) between N and Li atoms [41,43], which implies that C=N groups are also redox-active centers similar to C=O groups. For the delithiation cathodes, the restoration of C=N peak was observed, while the N–Li peak was disappeared, suggesting the reversible Li^+ insertion C=N bonds during the redox process. These ex situ XPS results confirm that there happens reversible change involving both C=O and C=N groups in the molecular structure of the cathode during the redox reaction.

In summary, a 2D BQ1-COF with multiple redox sites was designed and prepared as the cathode material for LIBs and exhibited an excellent overall battery performance. The observed ultrahigh reversible capacity is contributed to the abundant active sites associated with not only C=O but also π -conjugated C=N groups, delivering the highest capacity and ultrahigh energy density among polymer-based cathode materials. Moreover, the stable 2D conjugated network of BQ1-COF avoids the common dissolution of small molecular-based organic cathode materials and endows this cathode material with excellent cycling life. In addition, the well-defined channel and extended conjugated framework can promote the rapid Li^+ diffusion and electron transport, leading to a prominent rate performance. Our design strategy is expected to offer one way towards the development of high performance organic cathode materials for next generation LIBs with high specific capacity and outstanding cycling stability as well as rate performance all together.

Acknowledgments

The authors gratefully acknowledge the financial support from Ministry of Science and Technology of China (MoST, 2016YFA0200200), the National Natural Science Foundation of China (NSFC, 21421001, 51633002) of China, Tianjin city (16ZXCLGX00100) and 111 Project (B12015).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.nanoen.2020.104498>.

References

- W. Guo, Y.X. Yin, S. Xin, Y.G. Guo, L.J. Wan, Superior radical polymer cathode material with a two-electron process redox reaction promoted by graphene, *Energy Environ. Sci.* 5 (2012) 5221–5225.
- Y. Liang, Z. Tao, J. Chen, Organic electrode materials for rechargeable lithium batteries, *Adv. Energy Mater.* 2 (2012) 742–769.
- D. Larcher, J.M. Tarascon, Towards greener and more sustainable batteries for electrical energy storage, *Nat. Chem.* 7 (2015) 19–29.
- T.B. Schon, B.T. McAllister, P.F. Li, D.S. Seferos, The rise of organic electrode materials for energy storage, *Chem. Soc. Rev.* 45 (2016) 6345–6404.
- B. Tian, G.-H. Ning, W. Tang, C. Peng, D. Yu, Z. Chen, Y. Xiao, C. Su, K.P. Loh, Polyquinoneimines for lithium storage: more than the sum of its parts, *Mater. Horiz.* 3 (2016) 429–433.
- M. Park, D.S. Shin, J. Ryu, M. Choi, N. Park, S.Y. Hong, J. Cho, Organic-catholyte-Containing flexible rechargeable lithium batteries, *Adv. Mater.* 27 (2015) 5141–5146.
- Z. Song, Y. Qian, M.L. Gordin, D. Tang, T. Xu, M. Otani, H. Zhan, H. Zhou, D. Wang, Polyanthraquinone as a reliable organic electrode for stable and fast lithium storage, *Angew. Chem. Int. Ed.* 54 (2015) 13947–13951.
- Z. Song, Y. Qian, T. Zhang, M. Otani, H. Zhou, Poly(benzoquinonyl sulfide) as a high-energy organic cathode for rechargeable Li and Na batteries, *Adv. Sci.* 2 (2015) 1500124.
- H. Wu, Q. Meng, Q. Yang, M. Zhang, K. Lu, Z. Wei, Large-area polyimide/SWCNT nanocable cathode for flexible lithium-ion batteries, *Adv. Mater.* 27 (2015) 6504–6510.
- J. Wu, X. Rui, C. Wang, W.-B. Pei, R. Lau, Q. Yan, Q. Zhang, Nanostructured conjugated ladder polymers for stable and fast lithium storage anodes with high-capacity, *Adv. Energy Mater.* 5 (2015) 1402189.

- [11] J. Wu, X. Rui, G. Long, W. Chen, Q. Yan, Q. Zhang, Pushing up lithium storage through nanostructured polyazaacene analogues as anode, *Angew. Chem. Int. Ed.* 54 (2015) 7354–7358.
- [12] Z. Song, Y. Qian, X. Liu, T. Zhang, Y. Zhu, H. Yu, M. Otani, H. Zhou, A quinone-based oligomeric lithium salt for superior Li-organic batteries, *Energy Environ. Sci.* 7 (2014) 4077–4086.
- [13] S. Wang, L. Wang, K. Zhang, Z. Zhu, Z. Tao, J. Chen, Organic $\text{Li}_4\text{C}_8\text{H}_2\text{O}_6$ nanosheets for lithium-ion batteries, *Nano Lett.* 13 (2013) 4404–4409.
- [14] D. Chen, A.J. Avestro, Z. Chen, J. Sun, S. Wang, M. Xiao, Z. Erno, M.M. Algaradah, M.S. Nassar, K. Amine, Y. Meng, J.F. Stoddart, A rigid naphthalenediimide triangle for organic rechargeable lithium-ion batteries, *Adv. Mater.* 27 (2015) 2907–2912.
- [15] O. Fabian, K. Martin, B. Jens, W. Martin, B. Peter, E. Birgit, Unlocking full discharge capacities of poly(vinylphenothiazine) as battery cathode material by decreasing polymer mobility through cross-linking, *Adv. Energy Mater.* 8 (2018) 1802151.
- [16] D. Sui, L. Xu, H. Zhang, Z. Sun, B. Kan, Y. Ma, Y. Chen, A 3D cross-linked graphene-based honeycomb carbon composite with excellent confinement effect of organic cathode material for lithium-ion batteries, *Carbon* 157 (2020) 656–662.
- [17] J. Xie, Q.C. Zhang, Recent progress on rechargeable lithium batteries with organic materials as promising electrodes, *J. Mater. Chem.* 4 (2016) 7091.
- [18] Z. Song, H. Zhou, Towards sustainable and versatile energy storage devices: an overview of organic electrode materials, *Energy Environ. Sci.* 6 (2013) 2280–2301.
- [19] Y. Lu, X. Hou, L. Miao, L. Li, R. Shi, L. Liu, J. Chen, Cyclohexanexone with ultrahigh capacity as cathode materials for lithium-ion batteries, *Angew. Chem. Int. Ed.* 58 (2019) 7020–7024.
- [20] S. Xu, G. Wang, B.P. Biswal, M. Addicoat, S. Paasch, W. Sheng, X. Zhuang, E. Brunner, T. Heine, R. Berger, X. Feng, A nitrogen-rich 2D sp²-Carbon-Linked conjugated polymer framework as a high-performance cathode for lithium-ion batteries, *Angew. Chem. Int. Ed.* 58 (2019) 849–853.
- [21] G. Wang, N. Chandrasekhar, B.P. Biswal, D. Becker, S. Paasch, E. Brunner, M. Addicoat, M. Yu, R. Berger, X. Feng, A crystalline, 2D polyarylimide cathode for ultrastable and ultrafast Li storage, *Adv. Mater.* 31 (2019) 1901478.
- [22] S. Wang, Q. Wang, P. Shao, Y. Han, X. Gao, L. Ma, S. Yuan, X. Ma, J. Zhou, X. Feng, B. Wang, Exfoliation of covalent organic frameworks into few-layer redox-active nanosheets as cathode materials for lithium-ion batteries, *J. Am. Chem. Soc.* 139 (2017) 4258–4261.
- [23] C. Zhang, X. Yang, W. Ren, Y. Wang, F. Su, J.X. Jiang, Microporous organic polymer-based lithium ion batteries with improved rate performance and energy density, *J. Power Sources* 317 (2016) 49–56.
- [24] Z. Lei, X. Chen, W. Sun, Y. Zhang, Y. Wang, Exfoliated triazine-based covalent organic nanosheets with multielectron redox for high-performance lithium organic batteries, *Adv. Energy Mater.* 9 (2019) 1801010.
- [25] Z. Luo, L. Liu, J. Ning, K. Lei, Y. Lu, F. Li, J. Chen, A microporous covalent-organic framework with abundant accessible carbonyl groups for lithium-ion batteries, *Angew. Chem. Int. Ed.* 57 (2018) 9443–9446.
- [26] X. Chen, Y. Li, L. Wang, Y. Xu, A. Nie, Q. Li, F. Wu, W. Sun, X. Zhang, R. Vajtai, P. M. Ajayan, L. Chen, Y. Wang, High-lithium-affinity chemically exfoliated 2D covalent organic frameworks, *Adv. Mater.* 31 (2019) 1901640.
- [27] C. Jiang, M. Tang, S. Zhu, J. Zhang, Y. Wu, Y. Chen, C. Xia, C. Wang, W. Hu, Constructing universal ionic sieves via alignment of two-dimensional covalent organic frameworks (COFs), *Angew. Chem. Int. Ed. Engl.* 57 (2018) 1–6.
- [28] D.A. Vazquez-Molina, G.S. Mohammad-Pour, C. Lee, M.W. Logan, X. Duan, J. K. Harper, F.J. Uribe-Romo, Mechanically shaped two-dimensional covalent organic frameworks reveal crystallographic alignment and fast Li-ion conductivity, *J. Am. Chem. Soc.* 138 (2016) 9767–9770.
- [29] Z.Q. Lin, X. Jian, Z. Bo-Wei, L. Jie-Wei, W. Jiena, S. Rong-Bin, H. Xiao, Z. Hao, L. Hai, L. Ye, J.X. Zhichuan, H. Wei, Z. Qichun, Solution-processed nitrogen-rich graphene-like holey conjugated polymer for efficient lithium ion storage, *Nano Energy* 41 (2017) 117–127.
- [30] J. Wang, Y. Lee, K. Tee, S.N. Riduan, Y. Zhang, A nanoporous sulfur-bridged hexaazatriphenylene framework as an organic cathode for lithium ion batteries with well-balanced electrochemical performance, *Chem. Commun.* 54 (2018) 7681–7684.
- [31] C. Peng, G.-H. Ning, J. Su, G. Zhong, W. Tang, B. Tian, C. Su, D. Yu, L. Zu, J. Yang, M.-F. Ng, Y.-S. Hu, Y. Yang, M. Armand, K.P. Loh, Reversible multi-electron redox chemistry of π -conjugated N-containing heteroaromatic molecule-based organic cathodes, *Nat. Energy* 2 (2017) 17074.
- [32] H. Banda, D. Damien, K. Nagarajan, A. Raj, M. Hariharan, M.M. Shaijumon, Twisted perylene diimides with tunable redox properties for organic sodium-ion batteries, *Adv. Energy Mater.* 7 (2017) 1701316.
- [33] J. Wang, K. Tee, Y. Lee, S.N. Riduan, Y. Zhang, Hexaazatriphenylene derivatives/GO composites as organic cathodes for lithium ion batteries, *J. Mater. Chem.* 6 (2018) 2752–2757.
- [34] J. Wang, C.S. Chen, Y. Zhang, Hexaazatriphenylene-based porous organic polymers as organic cathode materials for lithium-ion batteries, *ACS Sustain. Chem. Eng.* 6 (2018) 1772–1779.
- [35] J. Xu, J. Mahmood, Y. Dou, S. Dou, F. Li, L. Dai, J.-B. Baek, 2D frameworks of C_2N and C_3N as new anode materials for lithium-ion batteries, *Adv. Mater.* 29 (2017) 1706498.
- [36] X. Jian, W. Zilong, J.X. Zhichuan, Z. Qichun, Toward a high-performance all-plastic full battery with a single organic polymer as both cathode and anode, *Adv. Energy Mater.* 8 (2018) 1703509.
- [37] M. Kolek, F. Otteny, P. Schmidt, C. Mück-Lichtenfeld, C. Einholz, J. Becking, E. Schleicher, M. Winter, P. Bieker, B. Esser, Ultra-high cycling stability of poly(vinylphenothiazine) as a battery cathode material resulting from π - π Interactions, *Energy Environ. Sci.* 10 (2017) 2334–2341.

- [38] D.H. Yang, Z.Q. Yao, D. Wu, Y.H. Zhang, Z. Zhou, X.H. Bu, Structure-modulated crystalline covalent organic frameworks as high-rate cathodes for Li-ion batteries, *J. Mater. Chem.* 4 (2016) 18621–18627.
- [39] Z. Lei, Q. Yang, Y. Xu, S. Guo, W. Sun, H. Liu, L.P. Lv, Y. Zhang, Y. Wang, Boosting lithium storage in covalent organic framework via activation of 14-electron redox chemistry, *Nat. Commun.* 9 (2018) 576.
- [40] S.-Y. Yang, Y.-J. Chen, G. Zhou, Z.-W. Fu, Multi-electron fused redox centers in conjugated aromatic organic compound as a cathode for rechargeable batteries, *J. Electrochem. Soc.* 165 (2018) A1422–A1429.
- [41] J. Hong, M. Lee, B. Lee, D.-H. Seo, C.B. Park, K. Kang, Biologically inspired pteridine redox centres for rechargeable batteries, *Nat. Commun.* 5 (2014) 5335.
- [42] A. Shimizu, Y. Tsujii, H. Kuramoto, T. Nokami, Y. Inatomi, N. Hojo, J.I. Yoshida, Nitrogen-containing polycyclic quinones as cathode materials for lithiumion batteries with increased voltage, *Energy Technol.* 2 (2014) 155–158.
- [43] M. Lee, J. Hong, D.H. Seo, D.H. Nam, K.T. Nam, K. Kang, C.B. Park, Redox cofactor from biological energy transduction as molecularly tunable energy-storage compound, *Angew. Chem. Int. Ed.* 52 (2013) 8322–8328.



Manman Wu received her B.S. degree from the School of Materials Science and Engineering of Zhengzhou University in 2016. She is currently studying for a doctoral degree in Prof. Yongsheng Chen's Group in Nankai university. Her research focus on organic electrode materials for lithium-ion batteries.



Yang Zhao received her B. S. degree in Chemical biology from College of Chemistry, Nankai University. She is a master student of Nankai University now. Her research focus on Organic Cathode Materials for Lithium-ion Batteries.



Binqiao Sun is a master student from the department of chemistry in Nankai University. He majors in Analytical Chemistry currently. He received his B.S. degree (2018) from Northeastern University of Applied Chemistry. His research interest is the Computational Chemistry.



Zhenhe Sun received his B.E. and B.S. degree from the Molecular Science and Engineering department of Nankai University in 2015. He is currently studying for a doctoral degree in Prof. Yongsheng Chen's Group. His research interests include the synthesis and modification of lithium-rich cathode materials and supercapacitors based on carbon materials.



Prof. Chenxi Li received his PhD degree from the State Key Laboratory and Institute of Element-Organic Chemistry at Nankai University in 1990. Since 1997, he has been a Professor of Chemistry at Nankai University. His research interests include the organic and polymeric functional materials and organic photovoltaics energy devices.



Mingtao Zhang is an associate professor from the department of chemistry in Nankai University. He received his B.S. degree and Ph. D. degree from Nankai University in 1993, 2004, respectively. His research interests focus on Molecular Modeling as well as Cheminformatics and Computational Chemistry.



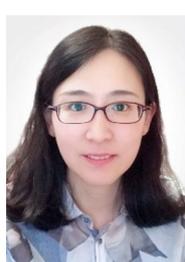
Yu Han is currently a master student at Nankai University under the direction of Prof. Yongsheng Chen. She obtained her B.S. degree from Lanzhou University in 2017. Her main research interests focused on gel electrolyte and related applications in energy storage.



Qiang Zhang received his PhD degree in 2015 at Nankai University. He joined Prof. Yan Lu's group at Tianjin University of Technology in 2015. His current research interests include synthesis of conjugate polymers and photoelectric materials.



Lingqun Xu received her B.S. degree in Polymer Material and Engineering from the Yanshan University. Now as a post-graduate, her research focuses mainly on improving the cycling performances of lithium sulfur batteries, with an emphasis on the cathode development.



Yan Lu received her B.S. degree from Department of Chemistry, Jiangsu Normal University in 1999 and Ph.D. degree in polymer chemistry and physics at College of Chemistry, Nankai University in 2004. She then moved in 2004 to School of Materials Science and Engineering, Tianjin University of Technology. In 2011, she became a professor. Her current research interests focus on design, synthesis, and properties of conjugated polymers, solar cells and biosensors.



Zhen Ge graduated from Nankai University with a Ph.D. degree in materials physics and chemistry in 2019 and then joined Nankai University for his postdoctoral studies. His research interests mainly focus on graphene composites, porous materials and energy storage.



Prof. Wei Wang received his PhD degree in physical organic chemistry from Lanzhou University in 1998. After his post-doctoral research at University of Stuttgart (2000–2001) and at University of Southern California (2001–2002). In 2006, he moved back to Lanzhou University and was appointed as the Cheung Kong Professor from the Ministry of Education of China. The research in his laboratory focuses on homogeneous and heterogeneous organocatalysis, organic porous materials, and solid-state NMR spectroscopy.



Yuxin Ren received his B.S. degree in Material Chemistry from the Nankai University. Now as a postgraduate, his research focuses mainly on the research of Physical and chemical properties of two-dimensional materials.



Yanfeng Ma received her B.S. (1994) in Physical Chemistry and Ph.D. (2003) in Physical Chemistry from Nankai University. Since 2003, she has been an Associate Professor of Chemistry at Nankai University. Her research interests focus on controlled synthesis and application of carbon nanomaterials (graphene and carbon nanotubes), carbon-based functional materials, nanocomposites, and nanodevices.



Prof. Yongsheng Chen graduated from the University of Victoria with a Ph.D. degree in chemistry in 1997 and then joined the University of Kentucky and the University of California at Los Angeles for postdoctoral studies from 1997 to 1999. From 2003, he has been a Chair Professor at Nankai University. His main research interests include: i) carbon-based nanomaterials, including carbon nanotubes and graphene; ii) organic and polymeric functional materials, and iii) energy devices including organic photovoltaics and supercapacitors.