Supporting Information

Heterocyclic Conjugated Polymer Nanoarchitectonics with Synergistic Redox-Active Sites for High-Performance Aluminium Organic Batteries

X. Peng, Y. Xie, A. Baktash, J. Tang, T. Lin, X. Huang, Y. Hu, Z. Jia, D. J. Searles, Y. Yamauchi*, L. Wang*, B. Luo*
Heterocyclic Conjugated Polymer Nanoarchitectonics with Synergistic Redox-active Sites for High-performance Aluminium Organic Battery

Xiyue Peng,[a]† Yuan Xie,[a]† Ardeshir Baktash,[a,b] Jiayong Tang,[a,b] Tongen Lin,[a,b] Xia Huang,[a,b] Yuxiang Hu,[d] Zhongfan Jia,[e] Debra J. Searles,[a,c] Yusuke Yamauchi,*[a,b] Lianzhou Wang,*[a,b] Bin Luo*[a]

Supporting Information
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Abstract: The development of cost-effective and long-life rechargeable aluminium ion batteries (AIBs) shows promising prospects for sustainable energy storage applications. Here, we report a heteroatom π-conjugated polymer featuring synergistic C=O and C=N active centres as a new cathode material in AIBs using a low-cost AlCl₃/urea electrolyte. Density functional theory (DFT) calculations reveal the fused C=N sites in polymer not only benefit good π-conjugation but also enhance the redox reactivity of C=O sites, which enables the polymer to accommodate four AlCl₃(urea)₂⁺ per repeating unit. By integrating the polymer with carbon nanotubes, the cathode exhibits a high discharge capacity and a long cycle life (295 mAh g⁻¹ at 0.1 A g⁻¹ and 85 mAh g⁻¹ at 1 A g⁻¹ over 4000 cycles). The achieved specific energy density of 413 Wh kg⁻¹ outperforms most Al-organic batteries reported to date. The synergistic redox-active sites strategy sheds light on the rational design of organic electrode materials.

DOI: 10.1002/anie.2021XXXXX
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1. Experimental Section

Materials

Pyrene, CH₂Cl₂, CH₃CN, NaIO₄, RuCl₃·xH₂O, tetrachlorobenzoquinone, potassium phthalimide, acetonitrile, hydrazine monohydrate, polyphosphoric acid, N-Methyl-2-pyrroldione, tetrahydrofuran, dimethoxyethane (DME), dimethylformamide, acetone, carboxyl methyl cellulose, Mo foil, AlCl₃ (99.99%), urea (99.0-100.5%), and Glass microfiber filters (GF/A, Whatman) were purchased from Sigma-Aldrich. Multiwall carbon nanotube (CNT) was purchased from Nanjing XFNANO Materials Tech Co., Ltd. Ketjen black was purchased from Suzhou Sinero Tech Co., Ltd. All the materials were used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

Synthesis of pyrene-4,5,9,10-tetraone (PYT)

Pyrene (5.06 g, 25 mmol) was dissolved in a mixture of CH₂Cl₂ (100.0 mL) and CH₃CN (100.0 mL). NaIO₄ (43.788 g, 0.205 mol), H₂O (125 mL), and RuCl₃·xH₂O (0.625 g, 3 mmol) were then added into the solution. The dark brown suspension was heated at 35 ℃ overnight. The reaction mixture was poured into H₂O (500 mL), and the solid was collected by filtration. After that, the dark green phase was extracted by CH₂Cl₂ and the organic phase was washed with water for a few times. The solvent was then removed under reduced pressure to afford a dark red solid. The resultant was combined with the dark green solid and purified by column chromatography using CH₂Cl₂ as an eluent to give pure products as a bright golden powder (18% yield).

Synthesis of tetraaminobenzoquinone (TABQ)

Tetrachlorobenzoquinone (4.92 g, 20.0 mmol) and potassium phthalimide (15.24 g, 82.3 mmol) were added to a round bottom flask, where hydrazine monohydrate (40 mL, 840 mmol) in 40 mL water was added dropwise over an hour in an ice-bath. After that, the reaction was then allowed to stir for an additional half hour at room temperature followed by 2 hours at 80 ℃. The reaction mixture was isolated through vacuum filtration and the product was washed successively with water and ethanol to give 1.75 g of purple powder (76% yield).

Synthesis of_pyrene-

Preparation of cathodes

The cathodes were prepared by mixing the active materials, such as PYTQ-CNT, PYTQ, or CNT, with ketjen black and carboxyl methyl cellulose at a weight ratio of 6:3:1. Then the slurry was pasted onto Mo foil followed by vacuum drying at 80 ℃ overnight. The typical average areal mass loading of electrodes was about 1.0 mg cm⁻².

Preparation of electrolytes

The electrolyte for AIBs was formulated by mixing anhydrous AlCl₃ (99.99%) with urea (99.0-100.5%) with the mole ratio of 1.3:1 in an argon-filled glove box at room temperature. After stirred for 30 mins, the AlCl₃/urea electrolyte was rested for 12 hours before usage.

Cell assembly and electrochemical tests

The Swagelok-type configurations were used to assemble the AIBs in an argon-filled glove box (H₂O and O₂ < 0.01 ppm) at room temperature with the active materials as cathodes, glass fibers (Whatman) as a separator, and Al foil (0.25 mm, 99.999%) as an anode. Galvanostatic charge/discharge tests were conducted on a LAND battery test system (CT2001A, Wuhan, China) in the voltage range of 0.2-2.1 V (vs. Al) at 25 ℃. EIS was measured between frequencies of 100 kHz-5 Hz. Cyclic voltammograms were measured at the scan speed in the range of 0.2-1.0 mV s⁻¹ using the same voltage set as the regular cells. To analyse the various states of charged/discharged batteries, the cathodes were disassembled in the argon-filled glove box and washed by pure DME solvent followed by drying in vacuum chamber overnight. In order to characterize the Al anode after cycling performances, the batteries were stopped after 500 cycles at 1 A g⁻¹ and then disassembled in the glove box. For comparison, another Al foil was soaked in the rested battery for the same time to investigate the influence of the electrolyte. After quick washing by pure DME solvent, the collected Al anodes were sealed in the glove box to avoid any surface oxidation before further characterizations.
Characterizations

Solid state NMR experiments were performed on a Bruker Avance III spectrometer with a 300 MHz magnet equipped with a 4 mm double air bearing, magic angle spinning probe. The powdered samples were placed in zirconia rotor with a Kel-F cap and rotated at 5 kHz. $^{13}$C spectra were recorded with CPMAS and SP-hpdec pulse sequences, the CPMAS data used to confirm peak positions. For CPMAS method cross-polarization time was 3 ms, decoupling power 100 kHz. For SP-hpdec method repetition delay was 30 s, verified as sufficient for full relaxation. Decoupling power was 100 kHz as well. All liquid state NMR spectra were recorded on a Bruker DRX 400 MHz spectrometer at 25 °C using an external lock (CDCl$_3$ or (CD$_3$)$_2$SO) and referenced to the residual nondeuterated solvent (CHCl$_3$ or DMSO). FTIR spectra were collected using a diamond/ZnSe crystal ATR accessory on a Perkin-Elmer 400 FT-IR/FT-FIR Spectrometer. Spectra were recorded in the range between 4000 and 1000 cm$^{-1}$ by acquiring 32 scans at 4 cm$^{-1}$ resolution with an OPD velocity of 0.2 cm s$^{-1}$. Samples were pressed onto the diamond internal reflection element of the ATR without further sample preparation. EA was performed by a CHNS-O Analyser (Thermo Scientific FlashEA™ 1112 HT Elemental Analyzer). The XPS analysis was obtained with monochromatic Al Kα excitation source. XRD analysis was performed on a D8-Advance X-ray diffractometer using Cu radiate ($\lambda = 0.15406$ nm). High resolution transmission electron microscopy (FE-TEM, JEOL-7100) were operated to study the morphologies of the materials. Energy dispersive spectroscopy (EDS) mapping was obtained on Hitachi SU3500 fitted with an Oxford Xmax SDD EDS detector. TGA was conducted on TGA/DSC 1 Thermogravimetric Analyzer (Mettler Toledo Inc) from room temperature to 800 °C under nitrogen atmosphere at a heating rate of 10 °C min$^{-1}$. The nitrogen adsorption isotherms and BET surface area were measured at 77 K with Micromeritics ASAP Tristar II 3020 system. A four-probe electroresistance analyzer (ST2258C) was used to analyse the sheet resistances of the samples.

DFT calculations

In this paper, the DFT was implemented in the Vienna Ab Initio Package (VASP)[1] to study the interaction of PYTQ polymer and AlCl$_2$(urea)$_2$$. The GGA-PBE functional are used for all the calculations[2]. A D3-BJ dispersion correction is also considered to correct the Van der Waals interactions[3,4]. The binding energy between PYTQ polymer and AlCl$_2$(urea)$_2$ is used to calculated according to the equation

$$E_b = E_{mol+R} - \left[E_{mol} + E_R\right]$$

where $E_b$ is the binding energy, $E_{mol+R}$ is the energy of the interacted PYTQ polymer and AlCl$_2$(urea)$_2$, $E_{mol}$ and $E_R$ are the energy of isolated AlCl$_2$(urea)$_2$ and PYTQ polymer, respectively. A force tolerance of $10^{-4}$ eV Å$^{-1}$ is chosen as the convergence criteria for geometry optimization. An energy cutoff of 600 eV and a k-point grid of $1 \times 2 \times 1$ are selected for the energy optimization and calculations. To study the charge of the ions, the Bader charge analysis method developed by Henkelman et al. is applied for this study[5].

Energy density and power density calculations

The mass energy density ($D_e$, Wh kg$^{-1}$) of the electrodes can be calculated according to the equation of

$$D_e = C \times U$$

where $C$ is the battery discharge capacity (mAh g$^{-1}$) based on the mass of active material in electrode, $U$ is the battery average discharge voltage (V).

The power density ($D_p$, W kg$^{-1}$) of the electrodes can be estimated according to the equation of

$$D_p = \frac{I \times U}{m}$$

where $I$ represents the applied current (A), $U$ is the battery average discharge voltage (V), and $m$ is the mass of active material in electrode (g).
2. Results and Discussion

(1) Synthesis of PYT

(2) Synthesis of TABQ

(3) Synthesis of PYTQ

Figure S1. Material synthesis route of PYT, TABQ monomers, and PYTQ polymer.
Figure S2. $^1$H NMR (400 MHz, DMSO-d$_6$) of TABQ.
Figure S3. $^{13}$C NMR (100 MHz, DMSO-$d_6$) of TABQ.
Figure S4. $^1$H NMR (400 MHz, DMSO-$d_6$) of PYT.

Note: $^{13}$C NMR of PYT (N/A, solubility too low).
**Figure S5.** Comparison of FTIR spectra of PYT, TABQ and PYTQ.
Figure S6. Single-pulsed solid-state $^{13}$C NMR spectrum of PYTQ. (Note: SSB: spinning side bands)
Figure S7. CPMAS solid-state $^{13}$C NMR spectrum of PYTQ.
Figure S8. SEM images of (a-c) PYTQ and (d-e) PYTQ-CNT.
Figure S9. (a) TEM images and (b) HRTEM images of PYTQ. TEM images of (c) PYTQ-CNT and (d) CNT.
Figure S10. (a) XPS survey spectra and high-resolution XPS spectra of (b) PYTQ polymer and (c, d) PYTQ-CNT hybrid.
Figure S11. XRD patterns of CNT, PYTQ, and PYTQ-CNT.
**Figure S12.** TGA curves of PYTQ and PYTQ-CNT.
Figure S13. (a) Adsorption-desorption isotherms of CNT, PYTQ and PYTQ-CNT. (b) Pore size distribution profiles of PYTQ and PYTQ-CNT.
**Figure S14.** Optimized structure of PYTQ polymer in coordination with the second AlCl$_2$(urea)$_2^-$: (a) on the opposite side, and (b) on the same side. The numbers in the structures show the calculated Bader charge values for the N and O atoms of the polymer after interaction with two AlCl$_2$(urea)$_2^-$. 
Figure S15. CV profile of Mo foil at 0.5 mV s⁻¹.
Figure S16. Cycling stability of PYTQ-CNT electrodes at the current density of 2 A g⁻¹.
Figure S17. Cycling stability of PYTQ electrodes at the current density of 1 A g⁻¹.
Figure S18. Chemical bonds percentage of (a) C 1s and (b) N 1s regions in the PYTQ cathode at different states.
Figure S19. Characterizations of Al anodes. SEM images of Al anodes (a, b) after cycling tests, and (c, d) after soak in electrolyte, where (a, c) show the cross-sections of Al foils; and (b, d) display the surface of Al foils. (e) High-resolution XPS spectra Al 2p region of the Al anodes. EDS mapping on the surface of the Al anodes (f) after cycling tests, and (g) after soak in electrolyte.
Figure S20. Nyquist impedance plots and Equivalent circuits of electrodes of (a) PYTQ-CNT before cycling, (b) PYTQ-CNT and PYTQ after 10 cycles. R1 is regarded as the diffusion resistance in the electrolyte, R2 indicates the resistance from the electrode/electrolyte interface (passivation layer), and R3 is the charge transfer resistance$^b$.
Table S1. Elemental analysis of PYTQ polymer.

| Sample ID | C %   | N %   | O %   | H %   | C/N   |
|-----------|-------|-------|-------|-------|-------|
| PYTQ-1    | 61.88 | 12.69 | 23.12 | 2.31  |       |
| PYTQ-2    | 62.50 | 12.59 | 22.5  | 2.41  |       |
| PYTQ-3    | 62.32 | 12.56 | 22.54 | 2.58  |       |
| PYTQ-4    | 62.01 | 12.29 | 23.15 | 2.55  |       |
| Average   | 62.18 | 12.53 | 22.83 | 2.46  |       |

Theoretical results based on the formula C_{236}H_{66}N_{40}O_{24}

| Sample ID | C %   | N %   | O %   | H %   | C/N   |
|-----------|-------|-------|-------|-------|-------|
| PYTQ      | 73.71 | 14.57 | 9.99  | 1.73  | C/N=5.06 |

EA results

C/N=4.96
Table S2. Atomic distances between O atom of PYTQ polymer and the atoms from AlCl$_2$(urea)$_2$.$^+$

| O atom from PYTQ polymer vs atoms from AlCl$_2$(urea)$_2$.$^+$ | Atomic distance for (Figure 1b) (Å) | Atomic distance for (Figure 1d) (Å) |
|---------------------------------------------------------------|-------------------------------------|-------------------------------------|
| O-Al                                                          | 4.45                                | 5.26                                |
| O-Cl1                                                         | 5.17                                | 3.54                                |
| O-Cl2                                                         | 6.19                                | 6.63                                |
| O-O1                                                          | 4.46                                | 6.35                                |
| O-O2                                                          | 3.08                                | 5.49                                |
| O-H1                                                          | 1.93                                | 4.98                                |
| O-H2                                                          | 1.59                                | 6.13                                |
| O-N1                                                          | 2.70                                | 5.95                                |
| O-N2                                                          | 2.63                                | 6.37                                |
| O-C1                                                          | 3.99                                | 6.66                                |
| O-C2                                                          | 3.29                                | 6.06                                |
Table S3. Atomic distances between O/N atoms from PYTQ polymer and H atoms from AlCl$_2$ (urea)$_2$$^+$. 

| Optimised structure                                      | O/N atoms from PYTQ polymer vs H atoms from AlCl$_2$ (urea)$_2$$^+$ | Atomic distance (Å) |
|---------------------------------------------------------|-------------------------------------------------------------------|---------------------|
| Polymer with two AlCl$_2$ (urea)$_2$$^+$ on the opposite side (Figure S14a) |                                                                   |                     |
| O-H1                                                    |                                                                   | 2.00                |
| O-H2                                                    |                                                                   | 1.97                |
| O-H3                                                    |                                                                   | 2.01                |
| O-H4                                                    |                                                                   | 2.02                |
| N-H1                                                    |                                                                   | 3.11                |
| N-H2                                                    |                                                                   | 3.26                |
| N-H3                                                    |                                                                   | 3.70                |
| N-H4                                                    |                                                                   | 2.98                |
| Polymer with two AlCl$_2$ (urea)$_2$$^+$ on the same side (Figure S14b) |                                                                   |                     |
| O-H1                                                    |                                                                   | 2.72                |
| O-H2                                                    |                                                                   | 2.07                |
| O-H3                                                    |                                                                   | 2.14                |
| O-H4                                                    |                                                                   | 2.11                |
| N-H1                                                    |                                                                   | 1.98                |
| N-H2                                                    |                                                                   | 2.87                |
| N-H3                                                    |                                                                   | 3.40                |
| N-H4                                                    |                                                                   | 2.75                |
Table S4. Chemical bonds percentage of N 1s, O 1s and C 1s regions in the PYTQ electrodes at different states.

| Chemical bonds | Pristine | Discharge-0.2V | Charge-2.1V |
|----------------|----------|----------------|-------------|
| **N 1s**       |          |                |             |
| C-N            | 83.52%   | 11.13%         | 72.6%       |
| C-N            | 16.48%   | 88.87%         | 27.4%       |
| **O 1s**       |          |                |             |
| C=O            | 16.7%    | 12.71%         | 21.47%      |
| C-O            | 10.01%   | 15.42%         | 14.6%       |
| O-C=O          | 73.29%   | 71.87%         | 63.93%      |
| **C 1s**       |          |                |             |
| C=C            | 42.78%   | 47.99%         | 47.46%      |
| C-O            | 15.91%   | 27.49%         | 17.91%      |
| C=N            | 27.27%   | 12.82%         | 21.03%      |
| C=O            | 9.02%    | 3.48%          | 6.4%        |
| O-C=O          | 4.03%    | 8.22%          | 4.98%       |
**Table S5. Comparison of representative cathode materials in AIBs.**

| Cathode material | Redox centre | Electrolyte | Discharge voltage | Discharge capacity/Current density | Cycles/Capacity retention/Current density | Reference |
|------------------|--------------|-------------|-------------------|------------------------------------|------------------------------------------|-----------|
| PYTQ-CNT         | synergistic C≡O/C≡N redox | AlCl3/urea  | 1.8/1.4 V         | 294.5 mAh g⁻¹/0.1 A g⁻¹              | 4000 cycles/85 mAh g⁻¹/1 A g⁻¹ | This work |
| TPB              | C=O          | AlCl3/urea  | 2.0/1.5/1.0 V     | 178 mAh g⁻¹/0.1 A g⁻¹                | 50 mAh g⁻¹/1 A g⁻¹                        | [7]       |
| PAQS-MWCNT       | C=O          | AlCl3/EMIC  | 1.0 V             | 190 mAh g⁻¹/0.5 C                    | 50 mAh g⁻¹/1 A g⁻¹                        | [9]       |
| PQ-graphite      | C=O          | AlCl3/EMIC  | 1.4 V             | 120 mAh g⁻¹/0.2 A g⁻¹                | 50 mAh g⁻¹/1 A g⁻¹                        | [9]       |
| TDK-AC blend     | C=O          | AlCl3/EMIC  | 1.3 V             | 226 mAh g⁻¹/0.1 A g⁻¹                | 50 mAh g⁻¹/1 A g⁻¹                        | [10]      |
| PI/MOF           | C=O          | AlCl3/EMIC  | 1.0 V             | 83 mAh g⁻¹/1 A g⁻¹                    | 1800 cycles/73 mAh g⁻¹/1 A g⁻¹            | [11]      |
| Pyrazine         | C=N          | AlCl3/EMIC  | 0.7 V             | 145 mAh g⁻¹/0.05 A g⁻¹               | 100 cycles/92 mAh g⁻¹/0.05 A g⁻¹          | [12]      |
| H2TPP            | C=N          | AlCl3/EMIC  | 1.6 V             | 101 mAh g⁻¹/0.1 A g⁻¹                | 500 cycles/84.8 mAh g⁻¹/0.2 A g⁻¹         | [13]      |
| TCNQ             | C≡N          | AlCl3/EMIC  | 1.6 V             | 180 mAh g⁻¹/0.5 A g⁻¹                | 2000 cycles/115 mAh g⁻¹/0.5 A g⁻¹         | [14]      |
| Pyrene           | NA           | AlCl3/EMIC  | 1.7 V             | 20 mAh g⁻¹/0.2 A g⁻¹                 | 300 cycles/10 mAh g⁻¹/0.2 A g⁻¹           | [15]      |
| Polypyrene       | NA           | AlCl3/EMIC  | 1.7 V             | 70 mAh g⁻¹/0.2 A g⁻¹                 | 300 cycles/70 mAh g⁻¹/0.2 A g⁻¹           |           |
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Author Contributions

X.P. and Y.X. contributed equally to this work. B.L., Y.Y., and L.W. guided the project. X.P. and Y.X. designed the research, conducted material synthesis, characterization, and electrochemical measurements. A.B. performed the theoretical work and analyzed the data. D.J.S. aided in the simulation and discussion of the theoretical part of the project. J.T., T.L., X.H., Y.H., and Z.J. contributed to the discussion of the results. X.P. drafted the manuscript with further revision from Y.X., A.B., Z.J., L.W., Y.Y., and B.L. All the authors discussed the results and commented on the manuscript.