

High Performance Rechargeable Aluminium Ion Batteries Enabled by Strategy of Covalent Organic Frame Material

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Abstract

Emerging rechargeable aluminium-ion batteries (RAIBs) are a sustainable option for the next generation of low-cost, high-safety and large-scale energy storage technologies. While the unsatisfying availability of traditional inorganic materials has limited the development of RAIBs, the advance of organic materials is expected to be a breakthrough towards high-performance cathode. However, the existing extensive research often focuses on the selection of appropriate organic monomers or stay in the tentative stage of preliminary polymerization. It is difficult to break through the inherent characteristics of the instability of small organic

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ones and the easy aggregation and accumulation of macromolecular polymers, which is no doubt ignoring the huge potential of organic compounds for structural design at the molecular level. In this connection, our study demonstrates a material design strategy that introduces active functional groups to small molecular monomers and polymerizes them into REDOX active covalent organic framework (COF) with multiple N-containing groups. Theoretical simulations and *ex-situ* analysis revealed the key function of C-N and C=N as active sites for reversible storage of AlCl_2^+ ions. In addition, the macro-ring frame brings enhanced structural stability and environmental tolerance for COF in complex electrolyte, resulting in significantly improved electrochemical performance. At 1 A g^{-1} , it exhibits a high specific capacity of 161.2 mAh g^{-1} and an excellent cycle life of approximately 100% coulombic efficiency after more than 3,000 cycles. This work fully demonstrates the operability of the design strategy to synthesize COF from small molecular organics by introducing reactive functional groups and its great potential in the role of cathode materials in RAIBs. The success meanwhile provides an inspiration for the development of COF-based organic battery system in large-scale energy storage.

Keywords: Rechargeable aluminium ion batteries; Covalent organic frameworks material; Triphenylamine

1. Introduction

Aluminium (Al), the most abundant metallic element in the crust of earth (8.2%), is addressing the attention of the next generation for sustainable energy storage solutions with the increasing global demands[1-3]. Rechargeable aluminium ion batteries (RAIBs), due to their low cost, high safety and environmental friendliness, ideal theoretical capacities (2981 mAh g⁻¹ and 8046 mAh cm⁻³), are also considered as potential substitutes for other expensive rechargeable metal ion batteries[4, 5]. However, the main challenge remaining for RAIBs is to find the suitable cathode material to solve the problem of guaranteeing the high-level discharge capability and long-term cycle stability under a complicated circumstance[6-8].

The performance of traditional inorganic material cathode in RAIBs is not a satisfactory[9]. Carbon-based materials such as graphite cathode are limited by inferior energy density with non-ideal discharge capacity and low power density, as well as difficult preparation[10-12]. Meanwhile, the transition metal sulfide/oxide-based cathode maintain no eligible electrochemical performance under long cycles due to the irreversible phase transition and slow reaction kinetics[13, 14]. In addition, the structural simplicity of inorganic materials also makes the research and preparation process of cathode materials lack diversity and operability[15, 16]. Hence attentions are turning, and great efforts have been made to explore emerging organic materials based on the structural diversity offered by sustainable and lightweight elemental compositions such as C, H, O and N, as well as the great potential and economics in molecular design and functional modulation[17]. Among them, small molecular organic matter is limited by the characteristics of easy to dissolve in the electrolyte, and subsequent research is more inclined to preliminary polymerization for improved stability[18, 19]. However, the common rapid polymerizing process will inescapably result in the formation of heterogeneous agglomeration or dense aggregates, resulting in the actual capacity and ion/electronic conductivity of the electrode as these dense polymers will be inevitable hinders[20, 21]. Therefore, it is quite important to optimize the structure and enhance the performance of organic compounds and polymerization processes under the guideline of a specific strategy[22].

58 Covalent organic framework (COF) materials, named for their modular structure and the construction of
59 structural connections between organics through strong covalent bonds, are an emerging but ideal platform for
60 structural adjustment and design at the molecular level[23]. Its macro-ring structure with high porosity, could
61 maintain the extended organic polymer network in the complex electrolyte environment and effectively improve
62 the ion transport efficiency between it and the active site[24]. In addition, a variety of active units for REDOX
63 (Reduction-Oxidation) reaction that interacting with Al-Cl carriers could be reasonably introduced in the
64 molecular design to further improve the energy transport and storage capacity of the electrode in the
65 electrochemical reaction while forming the connection bridge of the framework structure[25]. The
66 characteristics of high functionalization and complex environmental tolerance are extremely targeted to face
67 the problems of low specific discharge capacity and short cycle life of existing cathode materials, which makes
68 COF materials have the potential to be expectable in energy storage devices, though its application is still in the
69 preliminary stage[26]. Further, not to mention, the exploration and understanding of the complex structure-
70 properties of COF materials in RAIBs, as well as the control and improvement mechanism, need more attempts,
71 studies and discussions in both theory and experiments[27, 28].

72 We demonstrate for the first time a controlled growth strategy for COF materials by introducing reactive
73 functional groups from organic precursors and then repolymerizing them and compare it with common simple
74 organic polymerization strategies. It was previously reported that functional groups such as C=N and C-N can
75 have a good storage capacity of large volume Al-Cl carriers through a unique and efficient ionic coordination
76 process[21]. Therefore, as shown in Fig. 1, the triphenylamine (TPAn, white powder) containing N element
77 sites was selected as the initial body, and the -NH₂ from tris(4-aminophenyl)amine (TPA-NH₂, grey powder)
78 together with -CHO from tris(4-formylphenyl)amine (TPA-CHO, pale yellow powder) as functional groups.
79 They were introduced as the linking combination keys and additional reaction sites to successfully synthesize
80 TPA-COF (yellowish-brown powder), with polytriphenylamine (PTPAn, yellow powder) as comparing
81 products of traditional synthesis. A more detailed discussion is presented in Tab. S1, Fig. S1 and the

Experimental part of the Supporting Information document. DFT (Density Functional Theory) calculation and various chemical analyses show that multiple C-N and C=N groups in the structure act as coordination sites with AlCl_2^+ and realize multi-electron Al storage mechanism during multiple REDOX reaction. Compared with TPAn and PTPAn, the capacity of TPA-COF cathode is up to 168.5 mAh g^{-1} at 0.1 A g^{-1} and 108.2 mAh g^{-1} at 5 A g^{-1} , showing significantly improved rate performance. At 1 A g^{-1} , TPA-COF demonstrates a specific capacity of about 161.2 mAh g^{-1} and maintains 84.8% after a long time cycling of 3000. This enhanced cyclic stability is due to the stable hexagonal-like macro-ring structure and the resistance of the COF material itself in the complex electrolyte environment. Our strategy of designing and synthesizing TPA-COF not only helps to explore and improve the performance limits of RAIBs, but also provides a new angel of view for the rational allocation and design of organic materials for energy storage applications.

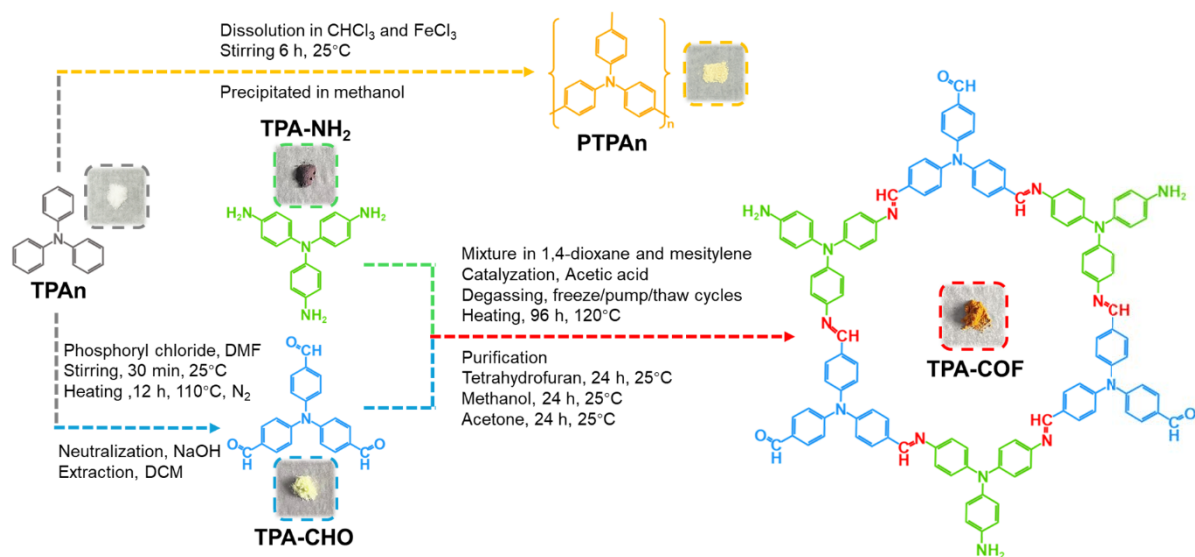


Fig. 1. Design and synthetic strategy of TPA-COF.

2. Results and Discussion

2.1. Theoretical calculations of TPA-COF

In case of serving as the cathode of RAIBs, its repeating unit of 1/6 structure for cationic storage is calculated and analysed in detail based on density functional theory (DFT). All DFT theoretical calculations have been carried out using the Gaussian 09 program package[29]. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are calculated and shown in Fig. 2a. The REDOX properties of the material are closely related to the electronic structure of the molecule, and the LUMO and HOMO energies in the system are calculated as -1.76 eV and -4.51 eV. Further, the gap (ΔE) between the two orbitals is 2.75 eV. This value of HOMO-LUMO gap is relatively low compared to other TPA samples in Fig. S3 with 4.62 eV, 3.82 eV, 3.97 eV and 3.74 eV. More specifically, the active site of the electrophilic reaction was inferred by molecular electrostatic potential (MESP) in Fig. 2b, and the exact active site of cationic uptake was determined. N atoms and carbonyl groups with more negative MESP values (red regions) indicate higher electronegativity, resulting in electrophilic cations (AlCl_2^+) being easily attracted to these locations. As can be seen in Fig. 2c, the binding energy of reaction sites in TPA-COF units with one to five units of AlCl_2^+ is negative, indicating that active localization such as N has been effectively utilized. Based on the above analysis, TPA-COF macrocyclic structure composed of repeating units demonstrates a highly expectable potential for efficient separation/combination with AlCl_2^+ groups.

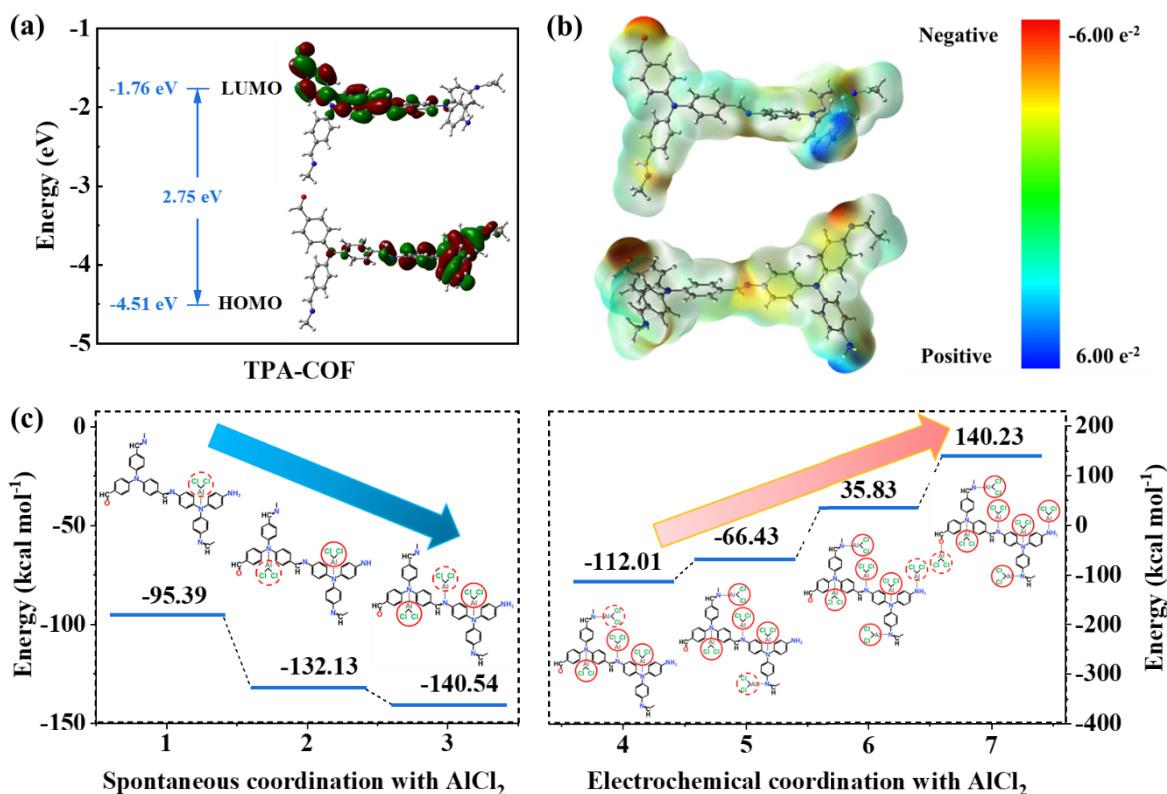


Fig. 2. (a) Optimized structure and calculated energy level of molecular orbital of repetitive units in TPA-COF, (b) Calculation of MESP distribution of repetitive units in TPA-COF, (c) Binding energy for repetitive units in TPA-COF with the most stable structure at each AlCl₂⁺ complexation stage.

2.2. Characterizations of TPA-samples

As can be seen from the SEM images, the TPAⁿ monomer in Fig. 3a has an irregular large block structure with a size of more than 50 μm, and TPA-NH₂ in Fig. 3d and 3g presents a rectangular rod-like structure with a very smooth surface. TPA-CHO in Fig. 3e and 3h showed a sugar cube shape with hollow holes on the surface of the cube, PTPAn in Fig. 3b and c showed a cross-linked leaf like structure, and TPA-COF in Fig. 3f and 3i showed a rose-like stacked nano petal structure with the particle size of about 5 μm. It is suggested from the

changes of surface morphology that the volume of TPA_n monomer could be reduced by the addition of different functional groups in the synthesis reaction, while the bulk products with high length-diameter ratio and low length-diameter ratio are attained, respectively.

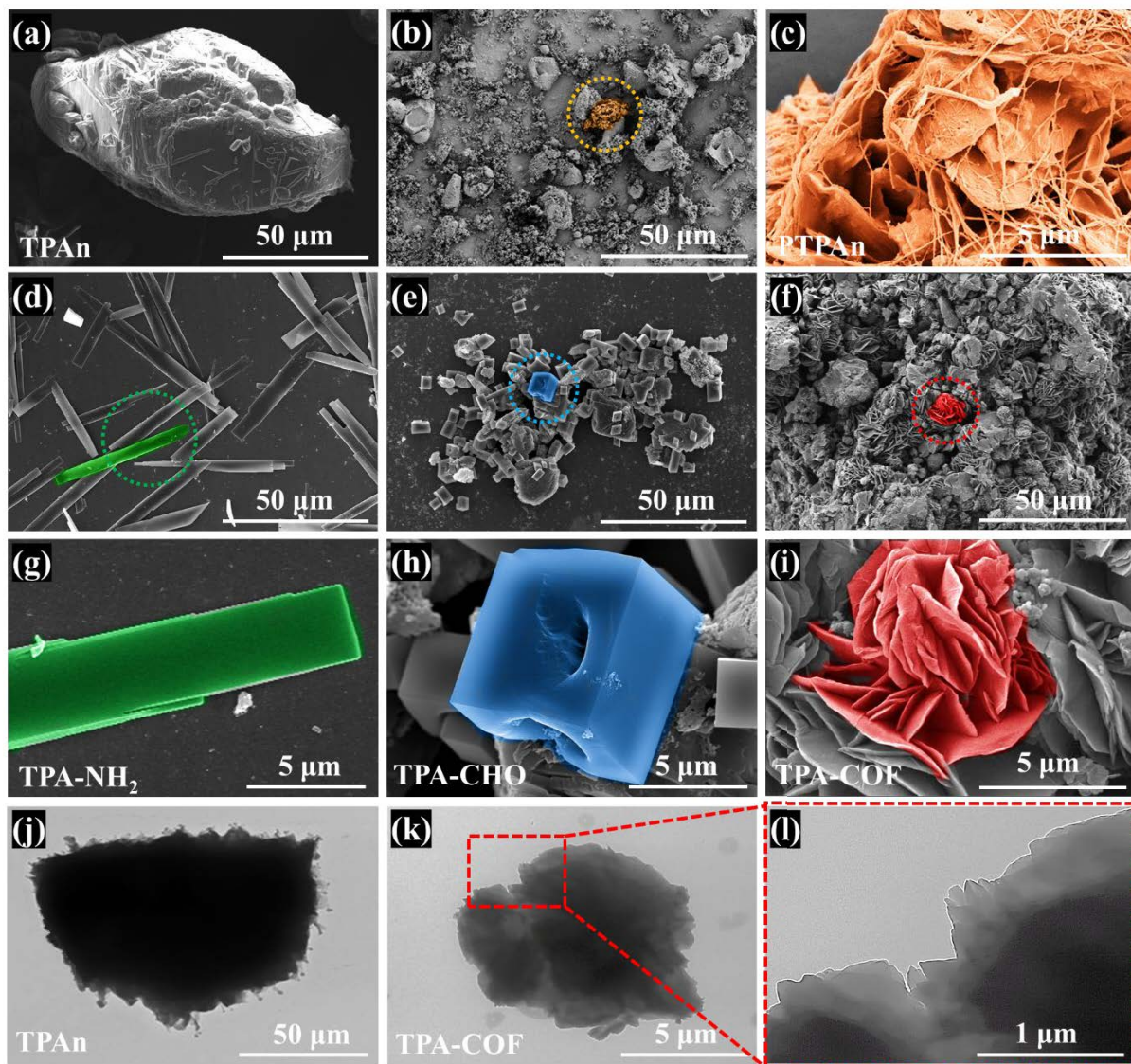


Fig. 3. SEM images of (a) TPA_n; (b), (c) PTPAn; (d), (g) TPA-NH₂; (e), (h) TPA-CHO; and (f), (i) TPA-COF; TEM images of (j) TPA_n and (k), (l) TPA-COF.

In the polymerization reaction, TPAn monomers first intertwine with each other to form thicker main chains, forming more network structures and hollow holes. Furthermore, TPA-COF alleviates the chain agglomeration and stacking effect, exposing more theoretical reaction sites.

The N_2 sorption isotherms in Fig. 4a is in accordance with the SEM characterization results, the surface of TPAn monomer is smooth and lacks holes, so it exhibits a lower adsorption capacity, while the two derivatives (TPA-NH₂ and TPA-CHO) exhibit the same adsorption and desorption curves due to their irregular surfaces. Furthermore, due to the formation of a better spatial network structure, the maximum adsorption capacity of the PTPAn has been significantly increased. To be noticed, the adsorption capacity of TPA-COF material is about 350 cm³ g⁻¹ when the relative pressure reaches 1.0, which is not only more than three times higher than that of PTPAn, but also has a qualitative improvement compared with TPAn monomer. This result is also consistent with the pore size distribution in Fig. 4b. Monomer of TPAn shows almost no pore distribution, while the two derivatives show a certain amount of pore size around 5 nm and 4 nm, respectively. PTPAn further shows the pore size distribution in the range of 2-9 nm. It is worth noting that TPA-COF shows an obvious pore size near the width of 2 nm, and its relatively complex surface morphology would suggest a promising leading to electrochemical performance. Meanwhile Fig. 4b shows the TG curves of the five samples under a nitrogen atmosphere. In the range of 200-300 °C, the three samples with small molecular structures, TPAn, TPA-NH₂ and TPA-CHO, all show a large amount of mass loss, and the polymeric PTPAn shows improved thermal stability with an obvious mass loss only after 500 °C, and a remaining of 76.3% over 600 °C. The mass retention rate of TPA-COF is 83.1% at 600 °C, showing the best thermal stability, which is due to its stable repeating macrocyclic structure.

As can be seen from the XRD images in Fig. 4c, TPAn, TPA-NH₂ and TPA-CHO samples with obvious crystal structure, show distinct characteristic peaks. On the contrary, for PTPAn and TPA-COF, without quantities of obvious characteristic peaks, there is a wider overall characteristic peak between 12-25° instead, showing obvious amorphous characteristics. The refine and calculation of PXRD results in Fig. 4d indicate that

the unit cell of the material belongs to the hexagonal crystal system ($P3$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, $a = b = 21.149$ Å, $c = 4.382$ Å). Additionally, the simulated XRD pattern shows excellent agreement with the experimental data (RWP = 0.38%, RP = 0.24%). The diffraction peaks at 4.92° and 9.71° can be assigned to the (100) and (200) crystal planes, respectively. These findings confirm the high crystallinity of the COF material, which could be further verified in the subsequence of FTIR. It can be seen from the FTIR data in Fig.4e that the characteristic peak representing bending vibration of N-H at 3336 and 3402 cm^{-1} in TPA-NH₂ sample and of C=O group at 1688 cm^{-1} in TPA-CHO sample appear as a large characteristic peak at 3423 cm^{-1} in the TPA-COF curve. The decreased intensity of these two bending vibrations and the increased intensity of the C=N bending vibration near 1660 cm^{-1} indicate the consumption changes of -NH and -CHO groups and the formation of repeated macrocyclic structures during the condensation process of TPA-COF. The terminal NH₂ groups on the surface of the resultant COFs appeared as weak signals at $3300\text{-}3500\text{ cm}^{-1}$, indicating that the most of the -NH groups are combined with -CHO groups. This significant reduction in the intensity of the N-H and C=O group eigen peaks suggests the depletion of them during the condensation reaction to form COF materials, while the appearance of new eigen peaks representing the C=N bond confirms the structure of the TPA-COF with poly-Schiff bases[30].

To further confirm the successful synthesis of TPA-COF, it can be seen from the ¹³C MAS-NMR spectra in Fig. 4f, the Quinone ring peaks at $127\text{-}140\text{ ppm}$ and C-N peaks at $152\text{-}156\text{ ppm}$ exhibited strong signals, which demonstrated the verification of macro-ring framework of TPA-COF. And the key connection characterization of C=N double bond formed by the condensation reaction of the two precursors TPA-NH₂ and TPA-CHO, was observed at around 163 ppm , indicating the anticipated synthesis of TPA-COF.

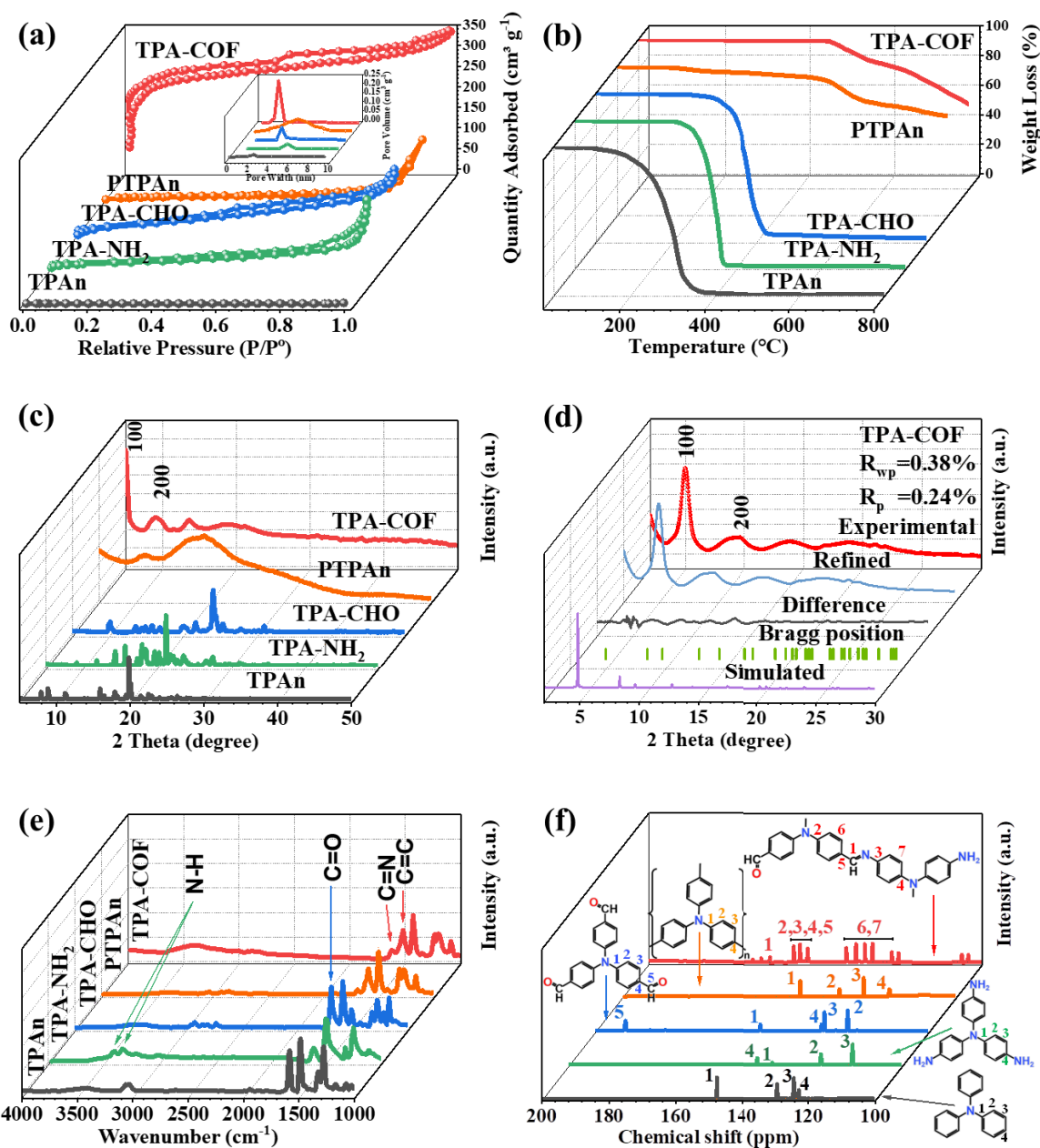


Fig. 4. Structure characterization results of TPAAn, TPA-NH₂, TPA-CHO, PTPAn and TPA-COF samples: (a) N₂ sorption isotherms, inset pore size distribution; (b) TG curves (N₂ atmosphere, 10 °C min⁻¹); (c) XRD patterns; (d) PXRD, refine and calculation of TPA-COF; (e) FTIR spectra and (f) ¹³C MAS-NMR spectra.

178

179 *2.3. Electrochemical Performances of TPA-samples as cathode*

180 The successful synthesis of TPA-COF and TPA-derivants was validated by a variety of physicochemical
181 results, while different electrochemical tests were employed to further distinguish the electrode performance.
182 It can be observed from the cyclic voltammetry (CV) curve in Fig. 5a that there are two pairs of obvious REDOX
183 peaks around 1.4-1.5 V and 0.6-0.7 V for TPA-COF, respectively, which correspond to the voltage plateau of
184 the typical charge-discharge curve in Fig. 5b. It is worth noting that the shape of CV curve of TPA-COF and
185 the plateau of charge-discharge curve are not consistent with typical pure battery performance, which suggests
186 that the Pseudo-capacitance might also make a nonnegligible contribution to the entire electrochemical process,
187 which is consistent with its macro-ring structure and the high specific surface area of N₂ absorption and
188 desorption curve. So as improved battery performance could be expected.

189 The results of EIS (Nyquist plots) tests and the data fitted to an equivalent circuit are shown in Fig. 5c. In
190 the figure, the ohmic resistance (R_s) of TPA_n, TPA-NH₂, TPA-CHO, PTPAn and TPA-COF is 2.23, 2.44, 2.31,
191 1.93 and 0.87 Ω , shows that the lowest system internal resistance of TPA-COF. In a similar trend, the R_{ct} values
192 corresponding to these five materials are respectively 44.15, 34.28, 26.42, 1.68, and 1.35 Ω , which reflects the
193 faster reaction rate of TPA-COF for ion transport through the SEI membrane and a constant phase element. R_s
194 represents the intrinsic resistance of the cathode material, including electronic and ionic resistances, as well as
195 contact resistances between particles and current collectors. A low R_s could implies a high electronic/ionic
196 conductivity, optimized crystal structure and improved morphology of the cathode. R_{ct} is the resistance
197 associated with the electrochemical reaction at the electrode-electrolyte interface, where charge transfer occurs
198 (e.g., AlCl₂⁺ intercalation/deintercalation). A low R_{ct} could implies the active surface area by using
199 nanostructured or porous materials to enhance the reaction sites and the application of electrolyte with high
200 ionic conductivity and good wettability to ensure efficient ion transport to the electrode surface. Combining

these two resistance values, TPA-COF is likely to have eligible conductivity as cathode material. This is also validated by the conductivity tests of Fig. 5e, the conductivity of TPA_n, TPA-NH₂ and TPA-CHO, PTPAn and TPA-COF are 0.21, 0.31, 0.34, 0.81 and 1.43 s cm⁻¹, respectively. The rising potential of conductivity is also the same with the pressure conductivity results. According to these results, the strategy of adding functional groups, polymerization and building COF structure could offer an ability to decrease the resistance and increase the electrochemical property of organic materials, in other words, a good rate performance could be expected for TPA-COF cathode.

As speculated above, the rate performance of TPA_n and derivants do continuously improve with the complexity of the structure increases. As can be seen in in Fig. 5d, they exhibit an average discharge specific capacities of about 56.3, 65.3, 82.1, 145.9 and 168.5 mAh g⁻¹ (51.2, 61.1, 77.3, 140.8 and 164.7 mAh g⁻¹ after a cycling of 120 at extremely changed rates, with a retention rate of 90.8%, 93.6%, 94.1%, 96.5% and 97.7%, respectively). And at a high current density of 5 A g⁻¹, TPA-COF is exhibiting an average discharge specific capacity 108.2 mAh g⁻¹, more than four times of TPA_n and two times of PTPAn. Thanks to the introduction of multiple reaction functional groups, the high conductivity COF product not only improves the rate performance for the cathode, but also realizes the long-term stability of its cycle performance due to the stable macro-ring structure obtained by condensation polymerization. The long-term cycling data in Fig. 5f demonstrates that the cycle life of TPA_n, TPA-NH₂, TPA-CHO and PTPAn could only maintain at a level of about 500 cycles with a maximum discharge specific capacity of 41.1, 51.6, 67.9 and 121.1 mAh g⁻¹, respectively. While TPA-COF shows a stable long-term cycle of more than 3000 cycles with a maximum discharge specific capacity of 161.2 mAh g⁻¹, and a capacity retention rate of about 84.8%.

As can be seen in Fig. 5g, a combination of these results will be clearer to demonstrate the improvement of TPA-COF, compared with other candidates. TPA-COF has an extraordinary evaluation in the performance at low and high current densities, long-term cycling and stability, while an unsatisfying expenditure in

production. This, together with the temporarily high preparation cost of ionic liquid electrolyte, has become a major economic barrier limiting the large-scale commercial applications of RAIBs.

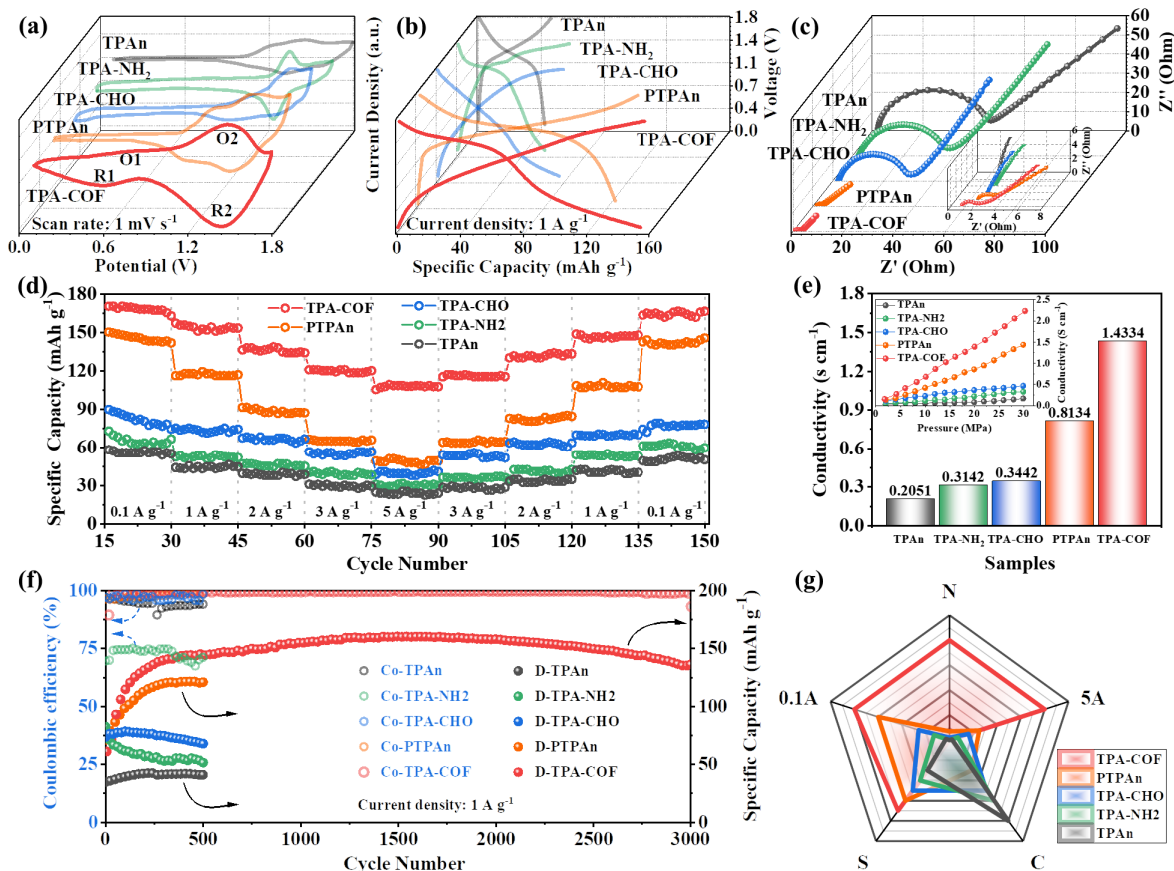


Fig. 5. Electrochemical analysis results of TPAAn, TPA-NH₂, TPA-CHO, PTPAn and TPA-COF: (a) Typical CV curves within 0.1–1.8 V; (b) Charge–discharge curves at current density of 1 A g⁻¹ in the voltage range of 0.1–1.8 V; (c) EIS data (Nyquist plots) after the 50th cycling at current density of 1 A g⁻¹ (d) Rate performance under current density from 0.1 to 5 A g⁻¹; (e) Conductivity data of samples; (f) Long-term cycling performance at current density of 1 A g⁻¹ in the voltage range of 0.1–2.4 V and (g) Evaluation on specific capacity at a current density of 0.1 A g⁻¹ (0.1A) and 5 A g⁻¹ (5A), number of cycling (N), stability after long cycling (S) and cost efficiency of production (C) for five cathode materials as RAIBs in this report.

234

235 2.4. Energy Storage Mechanisms of TPA-COF

236 The *ex-situ* EDX-mapping in Fig. 6a, 6c and 6e could offer a preliminary understanding of the working
237 mechanism of TPA-COF cathodes through direct visual presentation. The changes in the signals of dominating
238 elements, such as C and O, were not well-observed, suggesting that the basic structure exists continuously and
239 could be considered not effected during the charge and discharge process. While the electrical signals of Al
240 (red) and Cl (green) elements were strongly observed and uniformly distributed on the surface of the cathode
241 material after discharged to 0.1 V and charged to 2.1 V, while significantly weakened and could hardly be
242 noticed at the pristine stage. This change trend of elements is subsequently confirmed by EDX-Spectra results.
243 As later be seen from the peak changes in Fig. 6b, 6d and 6f, the peak values of Al and Cl of TPA-COF are
244 higher after discharging and charging, while the peak values of the two elements decrease to very low values
245 for pristine cathode, and the peak values of C and O elements remain almost unchanged[27]. Gaussian
246 simulations suggest that the COF spontaneously adsorbs Al-Cl species from the electrolyte, forming a COF-Al-
247 Cl complex. During cycling, the COF undergoes repeated combination and separation with Al-Cl species.
248 Assuming all sites perfectly combined with Al-Cl species, the calculated theoretical specific capacity of TPA-
249 COF is yielding a value of 183.89 mAh g⁻¹. The experimental capacity reached only ~87.55% of this value,
250 which, apart from pseudocapacitive contributions, could be attributed to certain proportion of reaction sites
251 being occupied by spontaneously adsorbed Al-Cl species, limiting the achievable capacity. These could predict
252 that during the working process of TPA-COF, the Al₂Cl₇⁻ and AlCl₄⁻ groups in the ionic liquid decompose to
253 form positive charge carriers consisting of Al and Cl elements and then inserted into the host of the cathode
254 material and gradually react with the active sites (mainly to be inferred as the N sites in the centre of TPAⁿ
255 structure in TPA-COF, cause it is observed that the signal and peak of N element become more notable during
256 reaction) to form new complexes of coordination.

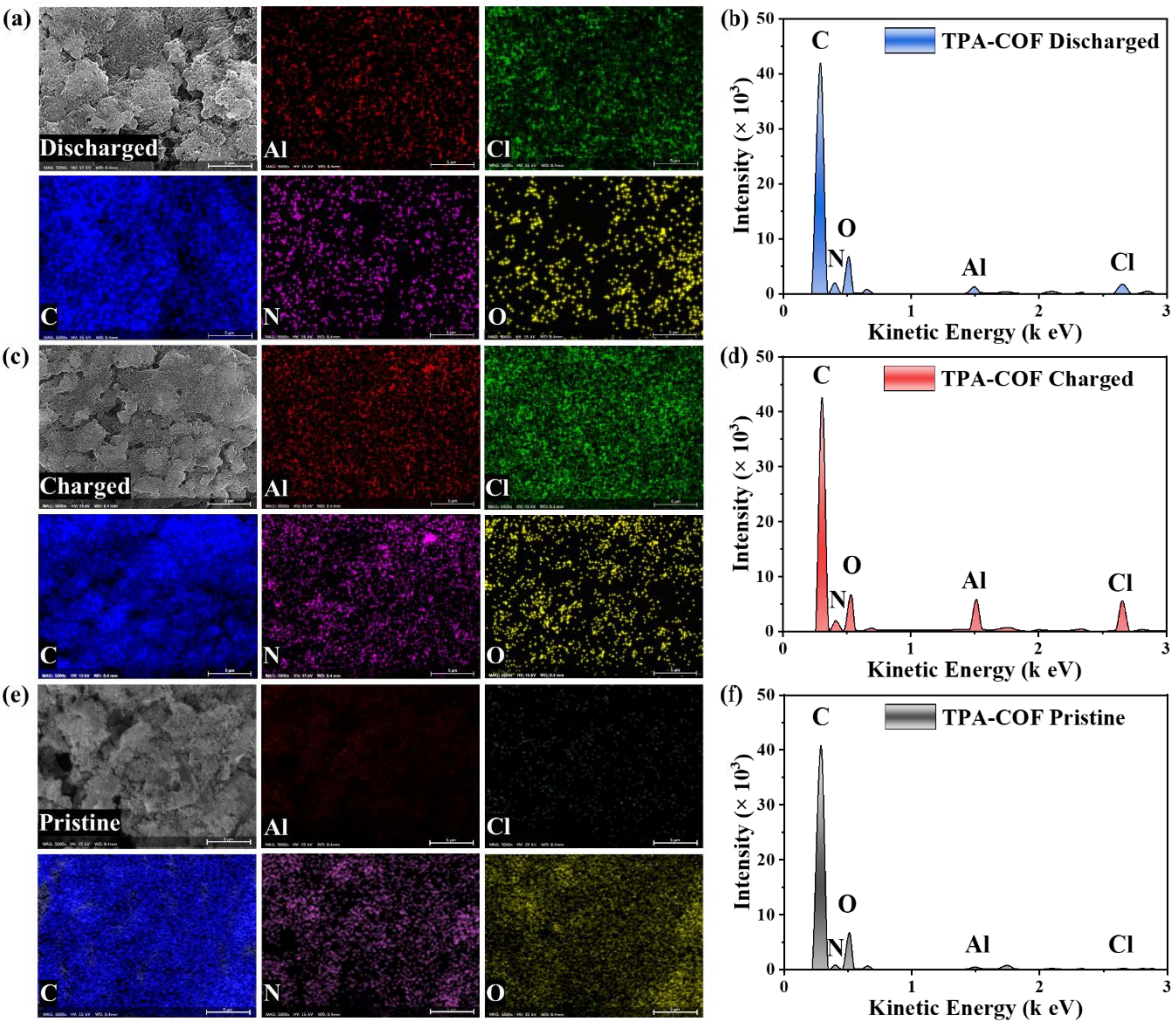


Fig. 6. EDX mapping images for C, N, O, Al and Cl of TPA-COF in different states (a) Discharged to 0.1 V, (c) Charged to 1.8 V and (e) Pristine; EDX spectra of TPA-COF in different states (b) Discharged to 0.1 V, (d) Charged to 2.1 V and (f) Pristine.

Although the elemental composition of the Al-Cl complexes as the charge carrier ions for TPA-COF has been confirmed, the reported mainstream generally believes that the charge carriers in RAIBs are divided into AlCl_4^- and AlCl_2^+ , and the reaction sites interacting with them also have two possibilities of N and O element[31]. Therefore, the working mechanism of TPA-COF should be determined through further detections.

As can be seen in Fig. 7a, TPA-COF cathode at different working states were demonstrated by solid-state ^{27}Al MAS NMR measurement. The signals of Al_2Cl_7^- (around 95 ppm) and AlCl_4^- (around 101 ppm) could be detected in both the electrolyte and initial TPA-COF cathode at the open-circuit voltage which are consistent with the performance of typical RAIBs system. While during the working process, the signal of AlCl_4^- remains and the signal of AlCl_2^+ (around 81 ppm) show no presence during charging but strong presence during discharging, manifesting that AlCl_2^+ should be the inserted Al (Al-Cl) species for the charged TPA-COF.

The ion species transferred between electrolyte and TPA-COF cathode could be further distinguished by 2D ^{27}Al ^1H HETCOR experiment in Fig. 7b. The aromatic ^1H spins in TPA-COF at about 6 ppm show strong signal and are correlated with both AlCl_4^- and AlCl_2^+ for ^{27}Al signals. As easily observed in the spectrum of cross-polarization HECTOR, the signal of AlCl_2^+ present a broader and much more significant peak than AlCl_4^- . The strong immobilization of AlCl_2^+ with TPA-COF framework could be the reason for the heightening and broadening of its peak line since the data are corresponding with the dipole-dipole coupling of heteronuclear ^1H - ^{27}Al .

The result of spin-echo experiment is exhibited in Fig. 7c since strengthening binding between Al species and cathode enhances the immobilization degree. The T_2 time (a time that the total magnetic flux is reduced by 63%) of AlCl_2^+ (around 1.9ms) is obviously shorter than Al_2Cl_7^- (around 2.2ms) and AlCl_4^- (around 4.6ms), revealing a stronger binding of Al (Al-Cl) species to TPA-COF cathode. The short T_2 time of AlCl_2^+ is inferred to be caused by the charge-compensated role played by the AlCl_2^+ ions. The combination of AlCl_2^+ and the cathode is reported different from AlCl_4^- and not stable enough that excessive cleaning of the samples during the test could significantly remove or even destroy it. Therefore, it is necessary to measure for several times

and retain a certain amount of electrolyte to ensure that it is accurately observed, and the extra Al_2Cl_7^- and AlCl_4^- detected from TPA-COF might be due to the adsorption from electrolyte under this circumstance.

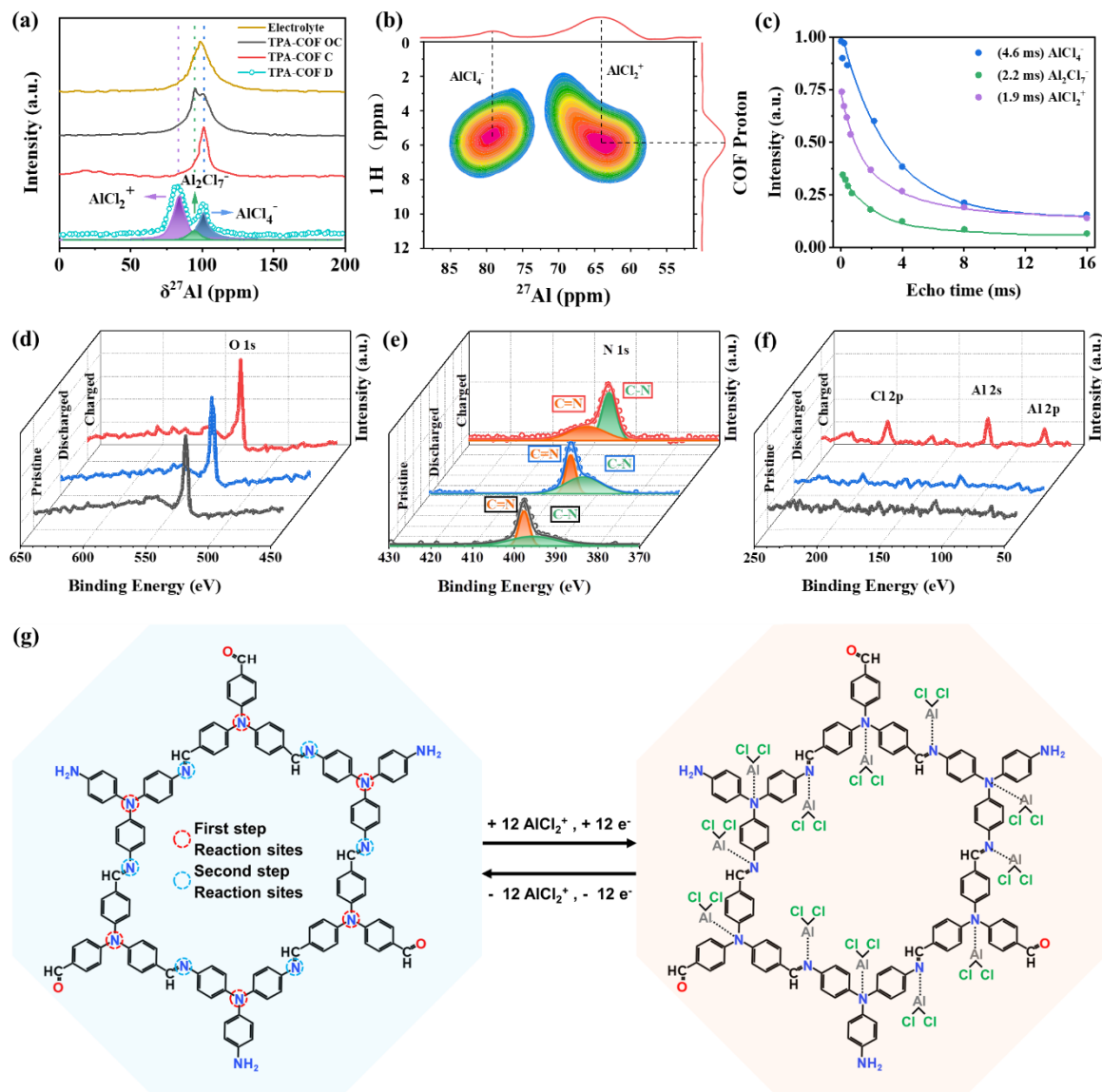
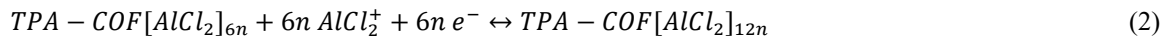


Fig. 7. (a) Solid-state ^{27}Al MAS NMR spectra of the electrolyte, open-circuit voltage, charged and discharged cathodes; (b) 2D ^{27}Al ^1H HETCOR experiment with contact time of 1 ms for discharged TPA-COF cathode; (c)

Spin echo derived time of different signals from the discharge TPA-COF electrode; XPS spectra of (d) O, (e) Detailed N 1s and (f) Al and Cl for pristine, charged and discharged cathodes; (g) Schematic diagram of charge-discharge mechanism of TPA-COF in RAIBs.

The reaction sites of TPA-COF are further confirmed by the *ex-situ* XPS data in Fig. 7d-f, the value and intensity of O 1s at three states remain almost unchanged, while the peaks of Al 2p, Al 2s and Cl 2p are observed, and one of N 1s at charged and discharged states change in the range of around 392-400 eV, implying that the N element is the main reaction site for the combination/separation with AlCl_2^+ . This is also mutually verified with the MESP and other simulation results in Fig. 2b and c, since the N sites coordination energy with AlCl_2^+ at top five stage is below zero. Regarding Fig. 7e and f, the presence of AlCl species and the corresponding reaction sites can be further confirmed. The pristine TPA-COF exhibits distinct peaks corresponding to C=N and C-N bonds, which represent the binding linkage formed between TPA-NH₂ and TPA-CHO, as well as the nitrogen in the central position of the TPAn structure. During charge and discharge process, significant changes in C=N and C-N are observed, indicating the involvement of imine nitrogen sites in the cathode material. These sites undergo coordination with AlCl_2^+ species during battery operation, which is consistent with the proposed storage mechanism of ions.

Based on all discussion above, it is proposed that the working mechanism of TPA-COF cathodes in RAIBs could be described as shown in Fig. 7g. In the ideal case for a typical TPA-COF macro-ring, there are twelve N sites would take combination/separation of AlCl_2^+ at two different situations: (1) six N sites in the center of six TPAn-like structure at low voltage, (2) six N sites at the binding bond of -NH₂ and -CHO groups between every two adjacent TPAn-like structure at high voltage. This two-step process at different voltage could be respectively depicted in **Equation 1 and 2**. Correspondingly, the reaction occurring in the negative electrode is mainly the mutual transformation from Al and AlCl_4^- to Al_2Cl_7^- , involving the interconversion between Al_2Cl_7^- and AlCl_4^- to generate AlCl_2^+ (**Equation 3 and 4**).



3. Conclusion

In summary, our work introduces a possible routing to polymerize small molecules into COF materials with adding functional groups. TPA here is tactically engineered through NH₂ and CHO bindings and orderly polymerized into TPA-COF as macro-ring structure. The well-defined TPA-COF cathode with multiple N active sites exhibits a high capacity of 161.2 mAh g⁻¹ at 1 A g⁻¹, and a stable cycling of 3000 cycles with a retention rate of 84.8% in RAIBs. The electrochemical characteristic of TPA-COF is much better than not only TPA monomer or further added TPA-NH₂ and TPA-CHO functional groups, but also the conventional polymerized production as PTPAn. This superior advantage comes from the enhanced structural stability through molecular level regulatory design, complex environmental tolerance guaranteed by the macro-ring structure and high conductivity due to its high porosity, as well as the high REDOX activity thanks to the introduction of multiple reaction sites. The successful synthesis and preparation of TPA-COF and its excellent application prove that the strengthening strategy of introducing designable active functional groups into small molecular monomers and polymerization into macro units COF structure is feasible and effective. In addition, this strategy of COFs containing REDOX-active groups might be enlightening for designable high-performance organic cathode in RAIBs for devices in large-scale energy storage systems.

333 **CRedit authorship contribution**

334 Guokang Wei: Conceptualization, Data curation, Investigation, Writing-Original draft preparation.
335 Jia Qiao: Conceptualization, Writing-reviewing and editing, Supervision, Project administration.
336 Xin Li: Formal analysis, Methodology.
337 Aichun Dou: Formal analysis, Investigation.
338 Sijiang Hu: Data curation, Methodology.
339 Wei Xie: Resources, Validation.
340 Zhenhua Luo: Supervision, Writing-reviewing and editing.
341 Jianhong Yang: Supervision, Writing-reviewing and editing.

342 **Declaration of competing interest**

343 The authors declare that they have no known competing financial interests or personal relationships that
344 could have appeared to influence the work reported in this paper.

345 **Data availability**

346 Data will be made available on request.

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