Converting a Low-Cost Industrial Polymer into Organic Cathodes for Practical Aqueous Zinc-Ion Batteries

Nanduni S. W. Gamage,^{†a} Yanlin Shi,^{†a} Chanaka, J. Mudugamuwa,^a Jesús Santos-Peña,^{*b} David A. Lewis,^a Justin M. Chalker,^a Zhongfan Jia^{*a}

 ^a Institute for Nanoscale Science and Technology, College of Science and Engineering, Flinders University, Sturt Road, Bedford Park, SA 5042, Australia
 ^b Université Paris Est Creteil, CNRS, ICMPE, UMR 7182, 2 rue Henri Dunant, 94320 Thiais, France

[†] These authors contribute equally.

Corresponding author: Jesús Santos-Peña Email: jesus.santos-pena@cnrs.fr Zhongfan Jia E-mail: zhongfan.jia@flinders.edu.au

ABSTRACT:

Aqueous zinc-ion batteries (AZIBs) using organic cathodes have emerged as a sustainable energy storage technology benefitting from high safety, low cost and abundant feedstocks. However, most organic cathodes are n-type polyaromatic compounds and conjugated polymers, which require sophisticated synthesis and provide a low operational voltage and slow Zn²⁺ diffusion kinetics. Herein, we report access to p-type radical polymer cathodes from a commercially available poly(methyl vinyl ether-alt-maleic anhydride) (poly(MVE-alt-MA)) polymer. The modification of poly(MVE-alt-MA) with 4-amino-TEMPO produces radical polymers (PTEMPO) that are easily scalable to tens of grams. The corresponding polymer AZIBs deliver a capacity of 92 mAh g⁻¹ at 10 C with 95% capacity retention over 1000 cycles. Importantly, the electrode composites and battery assembly procedure are optimised so that no fluoro-containing electrolytes and binders are needed, and cheap carbon additives can be used. We assemble the Swagelok batteries, small pouch and large pouch batteries with mass loading of 7.8 to 50 mg cm⁻², demonstrating nearly 100% coulombic efficiency. The pouch battery with 0.8-0.9 g of active polymer displayed a 60-mAh capacity with 1.5 V operational voltage. This work paves the way for simple and practical implementation of polymer AZIBs for real-world applications.

INTRODUCTION

The development of rechargeable batteries has been one of the most important inventions that have changed human life in recent decades.¹ The necessity and importance of such energy storage technologies are evident in the ubiquity of portable electronic devices and the increasing prevalence of electric vehicles. Lithium-ion batteries (LIBs) are at the front of these technologies and will continue leading the market for years.² However, ever-increasing demand and consumption of LIBs have led to resource shortages and supply-chain issues of strategic metals like lithium and cobalt.³ Meanwhile, millions of spent batteries, most of which are not properly recycled, have caused enormous waste and environmental risk.4-5 Therefore, sustainable energy storage technologies are urgently needed to relieve the challenges associated with LIBs.⁶ The new technologies will require abundant elements and safe battery construction with minimum risk from production to operation. Among many emerging non-LIBs, aqueous zinc-ion batteries (AZIBs) stand out because of the much higher abundance of zinc in the earth's crust (ten times more than lithium), and its low toxicity and high safety. As such, AZIBs have gained tremendous attention and significant progress in recent years.⁷

AZIBs usually use zinc metal as an anode and inorganic or organic compounds as a cathode. While substantial work has been devoted to the improved stability of zinc anode,⁸⁻¹¹ high-performing cathodes are needed and remain a major challenge for AZIBs. When inorganic cathodes containing Mn and V are used, Zn²⁺ intercalation in a significant change in the crystal structure and an ambiguous charge storage mechanism.¹²⁻¹⁶ Such a process could lead to low energy efficiency and power performance. Although non-metal cathode AZIBs such as Zn-Br₂ or Zn-I₂ batteries have also been developed, their shuttle issue has yet to be fully overcome.¹⁷⁻¹⁹ On the contrary, using organic compounds as cathodes allows a much faster charge/discharge rate, and the batteries only consist of zinc metal and zinc ions as the metal components.²⁰ Thus far, organic cathodes are mostly polyaromatic molecules consisting of N, O or S atoms, such as imine, imine-carbonyl, and carbonyl compounds, which, under reduction, allow coordination with Zn²⁺ ions.²¹⁻²² Their polymer counterparts, mostly conjugated polymers²³⁻²⁶ or covalent organic frameworks,²⁷⁻²⁸ have been explored extensively as cathodes in AZIBs to reduce unwanted dissolution.²⁹⁻³⁰ However, these conjugated materials are mostly n-type and still

require Zn²⁺ ion coordination. They are also brittle inorganic structures due to their rigid polyaromatic and crystalline structures, requiring polymer binders for electrode preparation. Despite some of these materials possessing high specific capacities, the corresponding organic AZIBs using conjugated polymers or polyaromatic molecules often display a slope charge/discharge profile or low voltage output of 1V or below, which varies with the extent of electrochemical doping.^{31,32}

For two decades, non-conjugated redox-active polymers (RAPs) have been recognized as highly versatile organic cathodes for energy storage.³³⁻³⁴ RAPs consist of redox-active groups covalently linked to an aliphatic polymer backbone, in which electron transfer is achieved through a hopping mechanism between pendant groups.³⁵ With the aid of carbon additives, RAPs have been widely employed in polymer/metal hybrid batteries³⁶ and fully organic polymer batteries.³⁷⁻³⁸ The most RAPs include redox-active in quinone, phenothiazine, popular groups tetrathiafulvalene, and nitroxide radicals,³⁹ in which nitroxide radical polymers (NRPs) showed a relatively high redox potential (i.e., 0.76 V vs Ag/AgCI) and excellent reversibility in both organic and aqueous media.⁴⁰ As such, NRPs, mostly consisting of pendant TEMPO (i.e., 2,2,6,6-tetramethylpiperidiyl-1-oxyl) radicals, are attractive polymer cathode materials for organic AZIBs to achieve the high output voltage (i.e., >1.5 V). Nishide et al. reported a promising first example of NRPs in AZIBs and showed that poly(TEMPO-vinyl ether) thin film (100 nm to 1 μ m) could deliver an initial capacity of 131 mAh g⁻¹ but only maintained 65% after 500 cycles.⁴¹ Luo et al. later demonstrated that AZIB performance with this polymer strongly depended on the electrolytes.⁴² Their best coin cell delivered 70-80 mAh g⁻¹ stable capacity at 1 A g⁻¹ current with a capacity fade of 23% over 1000 cycles. Recently, a peptide-based block copolymer consisting of NRP blocks was used in AZIBs, reporting a capacity of about 80 mAh g⁻¹ from two-electron storage when discharged to 0.7 V.⁴³ Their copolymer design diminished the storage capability, which would make the practical implementation challenging. Although NRPs have been extensively studied later in Zn/polymer redox flow batteries,⁴⁴⁻⁴⁵ the effort to further promote their practical applications in solid AZIBs remains limited. Challenges in practical organic AZIBs mainly include developing robust and simple chemistry to produce high-performing cathodes at scale and exploring more cost-effective procedures to fabricate the battery with satisfactory performance. For these reasons, NRPs are still promising candidates

for AZIBs. Still, limited effort⁴²⁻⁴³ has been devoted to implementing practical batteries since the early report of the concept.^{41, 46} Therefore, we considered it prudent to reassess NRP-based cathodes in AZIBs to realise their practical utility in energy storage.

Herein, we aim to advance the real-life implementation of NRP in organic AZIBs. Specifically, we use industrially sourced poly(methyl vinyl ether-alt-maleic anhydride) (poly(MVE-alt-MA)) as a low-cost polymer and, through a one-pot, two-step modification process, synthesize NRP cathodes. Two pathways are proposed by using H₂N-TEMPO (Approach I) or triacetonediamine (Approach II) to react with maleic anhydride on poly(MVE-alt-MA) (Figure 1a). The carboxylic acid groups resulting from the anhydride-amine reaction can further react with excess amine compounds using a carbodiimide coupling agent to increase the radical contents in final polymers. NRPs were characterized by NMR, IR and EPR to confirm their structures and radical content prior to testing in AZIBs. Various carbon additives and electrolyte conditions were explored to fabricate the batteries, targeting optimal performance while minimizing cost. We also conducted multiple-batch syntheses with scales up to 18 g achievable. Multiple battery tests were carried out to demonstrate the reproducibility. The Swagelok batteries assembled with a high areal loading of 7.8 mg cm⁻² provided a capacity of 92 mAh g⁻¹ over 1000 cycles with a capacity loss of 0.007 % per cycle. Finally, several large pouch batteries were assembled with capacities of 50 to 75 mAh, demonstrating an easy and highly practical fabrication of NRP-based AZIBs (Figure 1b and c).

Results and discussion

NRPs used in AZIBs should be hydrophilic but water-insoluble, ensuring good ion conductivity but no dissolution in the electrolyte. Previous reports demonstrated such a design by incorporating TEMPO radicals onto either poly(vinyl ether) or an amphiphilic copolymer backbone.^{43, 46} Synthesis of these polymers requires noble metal catalysts or multiple-step reactions. Copolymerization with non-radical monomers further reduced the theoretical capacity of the NRP.⁴³ Moreover, complex synthesis could be a hurdle for practical implementation and scale-up. Simple chemical modification of commercially available polymers could be a feasible approach to address this issue at the outset. Here, we modified an industrially produced polymer, poly(methyl vinyl ether-alt-maleic anhydride) (poly(MVE-alt-MA), ~US\$20/kg), to provide PTEMPO through two approaches (Figure 1a). Notably, another commercially available polymer, poly(ethylene-alt-maleic anhydride) (poly(Ealt-MA)), has been employed for radical modification and applied for radical/lithium batteries.⁴⁷ We chose poly(MVE-alt-MA) for its methoxy group, which could provide extra hydrophilicity. In approach I, poly(MVE-alt-MA) was directly modified with NH2-TEMPO to provide PTEMPO. Approach II involved the synthesis of 2,2,6,6tetramethylpiperidine (TEMP) functional polymers (i.e., PTEMP) through the modification of poly(MVE-alt-MA) with triacetonediamine, a commercially available intermediate produced from ammonia and acetone. PTEMP was then oxidised to PTEMPO. Poly(MVE-alt-MA) with an average molecular weight (Mw) of 1080 kDa and dispersity Đ of 3.47 was first used. Although we successfully obtained high molecular weight PTEMPO-1 and PTEMPO-2 through both approaches, this reaction could sometimes fail to produce soluble polymers and result in polymer ionogels. The gelation is primarily due to the extremely high molecular weights and thus high viscosity of poly(MVE-alt-MA) solution, as previously found for poly(E-alt-MA) modification.⁴⁸ When using a lower molecular weight poly(MVE-*alt*-MA) (M_w=216 KDa, Đ=2.70), we repeatedly produced soluble PTEMPO through both approaches. In both approaches, anhydrous DMF was used to dissolve poly(MVE-alt-MA). NH₂-TEMPO or triacetonediamine readily reacts with maleic anhydride groups, resulting in amide and carboxylic acid. The latter can further react with NH₂-TEMPO or triacetonediamine by adding a condensation reagent (Figure 1a). We have successfully synthesized six batches of PTEMPO polymers at various scales (Table S1) and characterized them before testing in batteries (Figure 1b).





Figure 2a shows typical ¹H NMR spectra of PTEMPO-3 and PTEMP. Compared to poly(MVE-*alt*-MA), new peaks at 1.2-1.5 ppm and 4.1 ppm for PTEMP and PTEMPO were ascribed to methyl and methine protons from the piperidine ring. The calculation of reaction efficiency was 65% by NMR (assuming two radicals per anhydride as 100%). This value was close to that obtained from the electron paramagnetic resonance (EPR) spectra (Table S1). PTEMPO was also characterized by ATR-IR and compared to the precursor poly(MVE-*alt*-MA), a small model radical 4-acetyl-TEMPO (ACT), as shown in Figure 2b. Poly(MVE-*alt*-MA) showed a strong C=O stretching peak from anhydride at 1750 cm⁻¹, a C-O stretching peak from methyl ether at 1050 cm⁻¹, and a small CH₃- from the methoxy group at 2950 cm⁻¹. ACT showed the typical C=O stretching for amide at 1640 cm⁻¹ and N-O at 1550 cm⁻¹. PTEMPO, consisting of TEMPO radical with amide linkage, showed similar peaks at 1645 cm⁻¹, 1545 cm⁻¹,

and 2950 cm⁻¹ as found in ACT, peaks at 3400 cm⁻¹ and 1710 cm⁻¹ corresponding to carboxylic acid, and a peak at 1050 cm⁻¹ for methoxy groups, which is consistent with the proposed structure in Figure 1a. Finally, we characterized all PTEMPO polymers by EPR to obtain their radical contents. The typical EPR spectra with broad signals suggest the radical-radical coupling along the polymer chain (Figure 2c). Here, we used ACT as a standard to elaborate a calibration curve (Figure S1), from which we calculated radical contents, theoretical capacities, and reaction efficiencies of all PTEMPO synthesized through approaches I and II from two polymer precursors (Table S1). It can be found that PTEMPO synthesized from poly(MVE-*alt*-MA) with a lower molecular weight resulted in higher modification efficiencies and theoretical capacities. For the low molecular weight poly(MVE-alt-MA), two separate reactions at a threegram scale produced PTEMPO-3 and PTEMPO-4 with similar theoretical capacities of 93 and 85 mAh g⁻¹. The scaled-up reaction (PTEMPO-5, 18 g, Figure 1c) led to a lower efficiency and, thus, a lower capacity of 63 mAh g⁻¹. We introduced approach II by using triacetonediamine instead of NH₂-TEMPO to explore the possibility of maximising the utilisation of commercially available materials. Notably, the obtained PTEMPO polymers (PTEMPO-2 and PTEMPO-6) showed capacities of 50-57 mAh g⁻ ¹, presumably due to the overall low efficiency of two-step reactions (i.e., conjugation and oxidation). These PTEMPO polymers were then used as cathode materials and tested in AZIBs.



Figure 2. Characterizations of PTEMPO: (a) ¹H NMR (dosy) of poly(MVE-*alt*-MA) precursor, (i) PTEMP and (ii) PTEMPO-3 after reduction by Pd/C and ammonium formate in MeOD-*d*₄. (b) ATR-IR spectra of poly(MVE-*alt*-MA), ACT and PTEMPO-3. (c) EPR spectra of PTEMPO-3 to PTEMPO-6 in ethanol.

The polymers were well soluble in acetone, ethanol or water depending on their radical contents, as the amount of unreacted carboxylic acid rendered them with different solubility. Notably, all polymers were not soluble in 2.0 M Zn(OTf)₂, a predominant electrolyte for AZIBs (Figure S2). We selected PTEMPO-3 as the first candidate due to its high theoretical capacity. An initial attempt was to use multiwall carbon nanotubes (MWCNTs) as conductive additives. Owing to the high molecular weights of PTEMPO polymers, we prepared the slurry without using a PVdF binder. Moreover, the slurry was initially prepared in NMP, but ethanol or water was later used. The slurry was spread on carbon felt and, after drying, paired with zinc foil to assemble Swagelok batteries. The battery was tested immediately at 5-10 C after assembly. We usually observed a gradual capacity increase over 20 cycles and reached its stable capacity (Figure S3) before formal testing. The initial test helped activate the zinc foil and thoroughly wet the polymer electrode. Figure 3 illustrates the battery performance using PTEMPO-3 at a PTEMPO:MWCNTs ratio of 1:1 (w/w) in 2.0 M Zn(OTf)₂ with areal mass loading of 4.5 mg cm⁻². The battery delivered 92 mAh g⁻¹ discharge capacity at 5C and 76 mAh g⁻¹ at 30 C (Figure 3a). The voltage profile showed no obvious polarization until 13 C, indicating excellent rate performance (Figure 3b). The battery was then charged/discharged at 10 C to evaluate its long-term cyclability at a high rate (Figure 3c). Remarkably, the discharge capacity retained 90 mAh g⁻¹, 93% of its highest value, with an average Coulombic efficiency of 99.93%. The voltage profile over 1000 cycles showed no polarization developed (Figure 3d) and extremely stable charge and discharge middle voltage (Figure S4). To further evaluate the reproducibility, we tested the long-term cyclability of multiple batteries (Figure S5). In general, all batteries provided discharge capacities close to their theoretical value. Notably, increasing the mass loading to 7.8 mg cm⁻² did not compromise its capacity and cycling performance.



Figure 3. Performance of AZIBs using PTEMPO-3 as cathode. (a) Rate performance, (b) Charge/discharge voltage profile at various C-rate, (c) Long cycling of the battery at 10 C, and (d) Charge/discharge voltage profile at different cycles. Battery configuration: PTEMPO-3/MWCNTs=1/1, electrolyte: 2 M Zn(OTf)₂, mass loading: 4.5 mg cm⁻².

To further increase the mass loading, we prepared the electrode at a PTEMPO:MWCNTs ratio of 3:1. The batteries delivered approximately 60 mAh g⁻¹ capacity at 5C when the mass loading was up to 19.7 mg cm⁻² (Figure S6). The morphological characterization by SEM showed the MWCNT network (Figure 4a) uniformly filled with PTEMPO polymers at a PTEMPO-3/MWCNTs ratio of 1/1 (Figure 4b). Increasing the ratio to 3/1 resulted in a large amount of polymer aggregated around MWCNTs (Figure 4c). The EDX from the composites showed increased N and O signals (Figure 4d). Although the specific capacities decreased when increasing the ratio to 3/1 (Figure 56), the cells can provide a much higher capacity of 1.2 mAh cm⁻² based on four replicates (Figure 4e). The cells delivered an energy density greater than 100 Wh kg⁻¹ with a power density of up to 2600 W kg⁻¹ (Figure 4f).



Figure 4. Properties and performance PTEMPO AZIBs at different polymer/MWCNT ratios. (a-c) The SEM morphologies of MWCNTs, electrode composites at PTEMPO-3/MWCNT=1/1, and PTEMPO-3/MWCNTs=3/1, (d) EDX of electrode composites, (e) Capacity and (f) Rangon plots of AZIBs at two PTEMPO/MWCNTs ratios.

We also tested other PTEMPO polymers (Table S1 and Figure S7), and it was found that the PTEMPO synthesized through approach II delivered lower discharge capacities than their theoretical values, whereas those synthesized through approach I provided discharge capacities very close to their theoretical values. Therefore, the Approach I directly using NH₂-TEMPO is preferable for higher radical content and fewer synthetic steps. Approach II could be further optimised in the future. Interestingly, those PTEMPO polymers with different radical contents can all facilitate fast charge/discharge, i.e., up to 50 C (Figure S7). This phenomenon indicates that the charge self-exchange rate constant (k_{ex}) must be high even with the decreasing radical content. Previous theoretical considerations and computations evidence indicate the major contribution to k_{ex} of TEMPO radicals on polymers is from the radicals between the polymer chain segments rather than the two neighbour radicals.⁴⁹ As such, it is expected that the slight decrease in radical content should not lead to a significant decrease in k_{ex} . To provide evidence for such a process in our system, we chose PTEMPO-2 (1.86 mmol g⁻¹) and PTEMPO-3 (3.46 mmol g⁻¹) for comparison, as these two polymers have the largest difference in radical content. Electrochemistry studies of PTEMPO-2 and PTEMPO-3 films coated on the glassy carbon electrode were conducted in 2 M Zn(OTf)₂ (Figure S8). Through the Cottrell plot, we found the apparent charge diffusion coefficients (D_{app}) for PTEMPO-2 and PTEMPO-3 were 8.35x10⁻¹³ and 1.79x10⁻¹² cm² s⁻¹. Assuming $D_{et}\sim D_{app}$ in a solid-state battery, k_{ex} values estimated from the Dhams-Ruff equation were 4.06 x 10² and 3.38 x 10² M⁻¹s⁻¹(Table S2). The data were close to previous reports of NRPs with different radical content.⁵⁰

Since the redox reaction of TEMPO radicals always accompanies anion uptake, we next attempted to replace $Zn(OTf)_2$ with a non-fluorinated electrolyte, $Zn(CIO_4)_2$. By comparing the cyclic voltammograms of both PTEMPO-3 redox reactions and the plating/stripping of zinc foil, it was found that PTEMPO-3 and zinc exhibited similar redox reaction behaviour in both electrolytes with potential gaps greater than 1.5 V (Figure 5a). Using PTEMPO-3 as a cathode, both cells demonstrated similar rates and cycling performance. A slightly lower capacity of 71 mAh g⁻¹ when using Zn(OTf)₂ as electrolytes compared to 78 mAh g^{-1} when using $Zn(CIO_4)_2$ (Figure 5b). We also observed similar polarization for both electrolytes, and the batteries remain at a plateau capacity of greater than 70 mAh g⁻¹ at a C-rate of 43 to 49 C (Figures 5c and 5d). The batteries were then charged and discharged to various states of charge (SOC), and their electrochemical impedance spectroscopy (EIS) spectra were recorded. At the charge plateau voltage of 1.64 V, the electron transfer resistance R_{ct} were 33.3 and 30.0 Ω , and at the discharge voltage of 1.45 V, the R_{ct} were 26.7 and 25.3 Ω for Zn(OTf)₂ and Zn(ClO₄)₂, respectively (Figure S9 and S10). The low but similar R_{ct} indicates the fast charge transfer kinetics in both electrolytes. Oxidation of the TEMPO radical forms an oxoammonium cation, which requires an ion to balance it. Therefore, we also extracted the ion diffusion coefficient Dion for the PTEMPO electrode at various SOC from EIS spectra. At the charge plateau, *D*_{ion,CIO4}⁻ was 1.29 x10⁻⁹ cm² s⁻¹ and D_{ion,OTf} 8.12 x10⁻¹⁰ cm² s⁻¹, which were two-order of magnitude higher than those observed for the batteries at fully charged or discharged states (Figures 5e and 5f), consistent with previous reports.⁵¹ The discrepancy of *D*_{ion} values in two

electrolytes may explain the aforementioned higher capacities and rate performance of AZIBs using $Zn(CIO_4)_2$. Taken together, $Zn(OTf)_2$ could be replaced by $Zn(CIO_4)_2$ without compromising the performance of the PTEMPO cathode.



Figure 5. (a) CV curves of zinc plating/stripping and redox reaction of PTEMPO-3 in aqueous electrolytes (i) $2M Zn(OTf)_2$ and (ii) $2M Zn(CIO_4)_2$, (b) Cycling performance and (c, d) charge/discharge voltage profile of batteries in two electrolytes, (e, f) Ion diffusion coefficient of batteries at different SOC. Battery configuration: PTEMPO-3/MWCNTs=1/1 (w/w), mass loading for $Zn(OTf)_2$ 3.2 mg cm⁻² and (b) 3 mg cm⁻².

MWCNTs are commonly used conductive additives in various battery systems, demonstrating excellent performance in NRP/metal hybrid batteries, as shown in our previous work⁵²⁻⁵³ and this work. Nevertheless, utilizing cheaper conductive additives can reduce the overall cost if the battery performance is not significantly compromised. To this end, we selected PTEMPO-3 as the active material to form electrode composites with four conductive carbon additives. Figure 6 illustrates the voltage profile of PTEMPO-3 AZIBs using MWCNTs, BP2000, N234 and YP-50F as conductive additives in 2M Zn(ClO₄)₂ electrolyte. N234 showed very similar rate performance as MWCNTs but with obvious polarization when increased current to 6C. While YP-50F showed poor rate performance and low capacity, BP2000 demonstrated excellent rate performance, as when the C-rate increased from 2 C to 11 C, the capacities were very close, and no polarization was observed (Figure 6). Notably, BP2000 and N234 are nanosized carbon additives like MWCNTs (insets in Figure 6, Figure S11) and could form a much larger interface with PTEMPO, the poor performance using YP-50F was likely due to its large particle size (i.e., $>5 \mu m$). The cost for MWCNTs could be greater than US\$500/kg, whereas N234 and BP2000 are much cheaper at less than US\$1/kg and US\$1.6/kg, respectively. Therefore, the cost of PTEMPO AZIBs could be drastically reduced by using either N234 or BP200 carbon.



Figure 6. A comparison of battery performance for AZIBs using PTEMPO-3 as cathode, 2M Zn(ClO₄)₂ as electrolytes and different carbons as conductive additives (a)

MWCNTs, (b) N234, (c) BP2000, and (d) YP-50F. Battery configuration: PTEMPO-3/carbon=1/1 (w/w).

To demonstrate the simplicity of pouch battery fabrication and the battery performance, we first assembled small pouch batteries using PTEMPO-4/MWCNTs composite as cathode and 2M Zn(OTf)₂ as an electrolyte. With an areal mass loading of 8 mg cm⁻², the cell can deliver a capacity of 70 mAh g⁻¹ at a 5C rate. After 300 cycles, the cell retained 91% initial capacity (Figure 7a). This small pouch cell also showed excellent rate performance, such as 40 mAh g⁻¹ at 80 C, i.e., fully charged in 45 seconds (Figure 7b). These cells can easily power an LED light (Figure 7c) and an electric fan (Supporting video I). Since we have shown that the fluorinated electrolytes Zn(OTf)₂ and expensive MWCNTs could be replaced by Zn(ClO₄)₂ and BP2000, respectively, we finally decided to use PTEMPO-5/BP-2000 composite as cathode and Zn(CIO₄)₂ as the electrolyte to fabricate a large pouch battery. The slurry was prepared using a probe Sonicator to disperse BP-2000 in a PTEMPO-5 ethanol solution. No fluorocontaining electrolyte and binder were used and the toxic NMP solvent was also avoided. The slurry was pasted on the carbon felt with a mass loading of about 50 mg cm⁻², the highest reported to date for organic AZIBs. We achieved 0.8-0.9 g PTEMPO-5 in each pouch battery at 18 cm². A typical battery displayed stable charge/discharge over 80 cycles with an average Coulombic efficiency of 99.8% (Figure 7d). The voltage profile showed increased polarization when the current increased from 100 to 300 mA, presumably due to the loose pack of the pouch resulting in high internal resistance (Figure 7e). This could be addressed with a more professional pouch battery production line. Nevertheless, the battery remained a decent charge and discharge plateaus and the performance was reproducible (Figure S12). One typical battery provided an average open-circuit voltage (VOC) of 1.57 V (Figure 7g), and a series of two batteries can be charged and discharged from 2.0 to 3.8 V with a VOC of 3.3 V, which remains greater than 3.05 V over 96 h (Figure 7f). The battery series can also power an electric fan (Figure 7h) and a model car (Supporting video II), which usually requires two 1.5 V primary batteries. Four pouch batteries in a series can deliver a VOC of 6.12 V with an average of 1.53 V (Figure 7i), again demonstrating excellent reproducibility. Finally, we compared our battery performance with previous polymer AZIBs that displayed a satisfactory discharge plateau (Table S3). Cathodes made from

NRPs can deliver high operational voltage, stable cyclability and superior rate performance. Specifically, for NRP-based AZIBs, a comparison with previous work shows that our system significantly lifted the areal mass loading of active materials by 17-50 times while maintaining excellent capacities and stability at various C-rate (Figure 7j). These results and real battery demonstrations suggest that the PTEMPO cathode composite developed in this work is a practical means towards implementing organic AZIBs.



Figure 7. Pouch battery performance: (a-c) Small pouch batteries using PTEMPO-4 with PTEMPO/MWCNT ratio of 1/1 and an aerial loading of 8 mg cm⁻², 2M Zn(OTf)₂ as an electrolyte. (a) Cyclability and the Coulombic efficiency at 5 C for 300 cycles, (b)Voltage profiles at various C-rates, and (c) Two pouch batteries (5 mAh each) lighting an LED. (d-i) Large pouch batteries using PTEMPO-5 with PTEMPO/BP 2000 ratio of 1/1 and an aerial loading of 50 mg cm⁻², and 2M Zn(ClO₄)₂ as an electrolyte. (d) Cyclability and the Coulombic efficiency of the pouch battery for 80 cycles, (e) Voltage profile at different charge/discharge currents, (f) Voltage profile of two pouch battery with 60 mAh capacity and 1.576 V VOC, (h) Two pouch batteries powering an electric fan,

(i) Four pouch cells showing 6.120 V voltage output, (j) Radar chart to compare previous NRP-based AZIBs with this work. This work-1, Swagelok batteries; This work-2, small pouch batteries; This work-3, large pouch batteries.

Conclusion

Chemical modification of a commercially available poly(MVE-alt-MA) with 4-amino-TEMPO radical led to TEMPO-containing NRPs, PTEMPO. These polymers consisting of amide, methoxy, and carboxylic acid functionalities showed good hydrophilicity but insolubility in aqueous electrolytes, suitable being organic cathodes for AZIBs. The syntheses at gram to tens of grams scale result in PTEMPO polymers with theoretical capacities up to 93 mAh g⁻¹. For a typical Swagelok AZIB with 50% active material and 50% of MWCNT using Zn(OTf)₂ as an electrolyte, the battery with mass loading of 4.5 mg cm² delivered a discharge capacity of 92 mAh g⁻¹ at 10C and an operational voltage of 1.45 V. The battery retained 93% of its highest capacity after cycling 1000 times and maintained 99.93% Coulombic efficiency. Furthermore, Zn(ClO₄)₂ electrolyte and cheaper carbon additives were used to achieve optimised battery performance and reduced cost. Particularly, the mass loading of active polymers was increased to 18 mg cm⁻² and the battery still delivered greater than 70 mAh g⁻¹ capacity at 5C. A lab-made pouch battery using scaled-up PTEMPO polymer, a non-fluoro Zn(ClO₄)₂ electrolyte and BP 2000 carbon black without binder provided a capacity of nearly 70 mAh g⁻¹ and a middle discharge voltage of 1.4 V. With a mass loading of 50 mg cm⁻², the pouch battery had a capacity of 60 mAh. This work developed easy access to scaled-up NRPs from a cheap commercial polymer and optimised its battery performance using low-cost additives with, so far, the highest mass loading. Our work reevaluated the utilization of high redox potential NRP cathodes in AZIBs, showing the promise of its real-world application.

Supporting Information

Full experimental and characterization data and videos of battery-operated electronic devices are supplied in Supporting Information.

Acknowledgements

The authors thank the Australian Research Council (DP230100587, DP230100642, LE230100168) and the French-Australian International Research Network on Conversion and Energy Storage (IRN-FACES) for financial support. The authors also acknowledge the Australian National Fabrication Facility (ANFF) SA node for supporting the electroanalytical and electrochemical synthesis labs at Flinders University.

Author contributions

Conceptualization: ZJ, JSP, DAL; Data curation: NSWG, YS, CJM; Formal analysis: NSWG, YS, CJM, JSP, ZJ; Resources: ZJ, JMC, Funding acquisition: ZJ, JSP, DAL, JMC, Supervision: ZJ, JMC; Writing – original draft: ZJ; Writing – review and editing: all authors. NSWG and YS contributed equally.

Competing interests

The authors declare no competing interests.

Reference

[1]. Whittingham, M. S., History, Evolution, and Future Status of Energy Storage. *Proc. IEEE* **2012**, *100*, 1518-1534.

[2]. Choi, J. W.; Aurbach, D., Promise and reality of post-lithium-ion batteries with high energy densities. *Nat. Rev. Mater.* **2016**, *1* (4), 1-16.

[3]. Gu, S.; Zhang, L.; Fu, B.; Wang, X.; Ahn, J. W., Feasible route for the recovery of strategic metals from mixed lithium-ion batteries cathode materials by precipitation and carbonation. *Chem. Eng. J.* **2021**, *420*, 127561.

[4]. Mrozik, W.; Rajaeifar, M. A.; Heidrich, O.; Christensen, P., Environmental impacts, pollution sources and pathways of spent lithium-ion batteries. *Energy Environ. Sci.* **2021**, *14* (12), 6099-6121.

[5]. Melchor-Martínez, E. M.; Macias-Garbett, R.; Malacara-Becerra, A.; Iqbal, H. M. N.; Sosa-Hernández, J. E.; Parra-Saldívar, R., Environmental impact of emerging contaminants from battery waste: A mini review. *Case Stud. Chem. Environ. Eng.* **2021**, *3*, 100104.

[6]. Larcher, D.; Tarascon, J. M., Towards greener and more sustainable batteries for electrical energy storage. *Nat. Chem.* **2015**, *7*(1), 19-29.

[7]. Li, C.; Jin, S.; Archer, L. A.; Nazar, L. F., Toward practical aqueous zinc-ion batteries for electrochemical energy storage. *Joule* **2022**, 6 (8), 1733-1738.

[8]. Wang, T.; Li, C.; Xie, X.; Lu, B.; He, Z.; Liang, S.; Zhou, J., Anode Materials for Aqueous Zinc Ion Batteries: Mechanisms, Properties, and Perspectives. *ACS Nano* **2020**.

[9]. Ming, F.; Zhu, Y.; Huang, G.; Emwas, A. H.; Liang, H.; Cui, Y.; Alshareef, H. N., Co-Solvent Electrolyte Engineering for Stable Anode-Free Zinc Metal Batteries. *J. Am. Chem. Soc.* **2022**, *144* (16), 7160-7170.

[10]. Yang, K.; Fu, H.; Duan, Y.; Ma, Z.; Wang, D.; Li, B.; Park, H. S.; Ho, D., Poloxamer Pre-solvation Sheath Ion Encapsulation Strategy for Zinc Anode–Electrolyte Interfaces. *ACS Energy Lett.* **2024**, 9 (1), 209-217.

[11]. Na, Z.; Qi, H.; Li, S.; Wu, Y.; Wang, Q.; Huang, G., Stable Zinc Metal Anode by Nanosecond Pulsed Laser Enabled Gradient Design. *ACS Energy Lett.* **2023**, *8* (8), 3297-3306.

[12]. Han, D.; Cui, C.; Zhang, K.; Wang, Z.; Gao, J.; Guo, Y.; Zhang, Z.; Wu, S.; Yin, L.; Weng, Z.; Kang, F.; Yang, Q.-H., A non-flammable hydrous organic electrolyte for sustainable zinc batteries. *Nat. Sustain.* **2022**, *5* (3), 205-213.

[13]. Cao, L.; Li, D.; Pollard, T.; Deng, T.; Zhang, B.; Yang, C.; Chen, L.; Vatamanu, J.; Hu, E.; Hourwitz, M. J.; Ma, L.; Ding, M.; Li, Q.; Hou, S.; Gaskell, K.; Fourkas, J. T.; Yang, X. Q.; Xu, K.; Borodin, O.; Wang, C., Fluorinated interphase enables reversible aqueous zinc battery chemistries. *Nat. Nanotechnol.* **2021**, *1*6 (8), 902-910.

[14]. Zhong, C.; Liu, B.; Ding, J.; Liu, X.; Zhong, Y.; Li, Y.; Sun, C.; Han, X.; Deng, Y.; Zhao, N.; Hu, W., Decoupling electrolytes towards stable and high-energy rechargeable aqueous zinc–manganese dioxide batteries. *Nat. Energy* **2020**, *5* (6), 440-449.

[15]. Zhang, N.; Cheng, F.; Liu, J.; Wang, L.; Long, X.; Liu, X.; Li, F.; Chen, J., Rechargeable aqueous zinc-manganese dioxide batteries with high energy and power densities. *Nat. Commun.* **2017**, *8* (1), 405.

[16]. Zhang, N.; Dong, Y.; Jia, M.; Bian, X.; Wang, Y.; Qiu, M.; Xu, J.; Liu, Y.; Jiao, L.; Cheng, F., Rechargeable Aqueous Zn–V2O5 Battery with High Energy Density and Long Cycle Life. *ACS Energy Lett.* **2018**, *3* (6), 1366-1372.

[17]. Zhang, S. J.; Hao, J.; Li, H.; Zhang, P. F.; Yin, Z. W.; Li, Y. Y.; Zhang, B.; Lin, Z.; Qiao, S. Z., Polyiodide Confinement by Starch Enables Shuttle-Free Zn-Iodine Batteries. *Adv. Mater.* **2022**, *34* (23), e2201716.

[18]. Bai, Z.; Wang, G.; Liu, H.; Lou, Y.; Wang, N.; Liu, H.; Dou, S., Advancements in aqueous zinc-iodine batteries: a review. *Chem. Sci.* **2024**, *15* (9), 3071-3092.

[19]. Alghamdi, N. S.; Rana, M.; Peng, X.; Huang, Y.; Lee, J.; Hou, J.; Gentle, I. R.; Wang, L.; Luo, B., Zinc-Bromine Rechargeable Batteries: From Device Configuration, Electrochemistry, Material to Performance Evaluation. *Nanomicro. Lett.* **2023**, *15* (1), 209.
[20]. Cui, H.; Ma, L.; Huang, Z.; Chen, Z.; Zhi, C., Organic materials-based cathode for zinc ion battery. *SmartMat* **2022**, *3* (4), 565-581.

[21]. Cui, J.; Guo, Z.; Yi, J.; Liu, X.; Wu, K.; Liang, P.; Li, Q.; Liu, Y.; Wang, Y.; Xia, Y.; Zhang, J., Organic Cathode Materials for Rechargeable Zinc Batteries: Mechanisms, Challenges, and Perspectives. *ChemSusChem* **2020**, *13* (9), 2160-2185.

[22]. Grignon, E.; Battaglia, A. M.; Schon, T. B.; Seferos, D. S., Aqueous zinc batteries: Design principles toward organic cathodes for grid applications. *iScience* **2022**, *25* (5), 104204.

[23]. Sun, T.; Zhang, W.; Nian, Q.; Tao, Z., Proton-insertion dominated polymer cathode for high-performance aqueous zinc-ion battery. *Chem. Eng. J.* **2023**, *452*.

[24]. Sun, T.; Li, Z. J.; Zhi, Y. F.; Huang, Y. J.; Fan, H. J.; Zhang, Q., Poly(2,5-Dihydroxy-1,4-Benzoquinonyl Sulfide) As an Efficient Cathode for High-Performance Aqueous Zinc–Organic Batteries. *Adv. Funct. Mater.* **2021**, *31* (16).

[25]. Shi, H. Y.; Ye, Y. J.; Liu, K.; Song, Y.; Sun, X., A Long-Cycle-Life Self-Doped Polyaniline Cathode for Rechargeable Aqueous Zinc Batteries. *Angew. Chem. Int. Ed.* **2018**, *57* (50), 16359-16363.

[26]. Häupler, B.; Rössel, C.; Schwenke, A. M.; Winsberg, J.; Schmidt, D.; Wild, A.; Schubert, U. S., Aqueous zinc-organic polymer battery with a high rate performance and long lifetime. *NPG Asia Mater.* **2016**, *8* (7), e283-e283.

[27]. Yin, C.; Chen, J.; Pan, C.-L.; Pan, Y.; Hu, J., MOF-Derived Mn3O4@C Hierarchical Nanospheres as Cathodes for Aqueous Zinc-Ion Batteries. *ACS Appl. Energy Mater.* **2022**, 5 (11), 14144-14154.

[28]. Wang, W.; Kale, V. S.; Cao, Z.; Kandambeth, S.; Zhang, W.; Ming, J.; Parvatkar, P. T.; Abou-Hamad, E.; Shekhah, O.; Cavallo, L.; Eddaoudi, M.; Alshareef, H. N., Phenanthroline Covalent Organic Framework Electrodes for High-Performance Zinc-Ion Supercapattery. *ACS Energy Lett.* **2020**, *5* (7), 2256-2264.

[29]. Wang, H.-g.; Wu, Q.; Cheng, L.; Zhu, G., The emerging aqueous zinc-organic battery. *Coordin Chem Rev* **2022**, *472*.

[30]. Li, Z.; Tan, J.; Wang, Y.; Gao, C.; Wang, Y.; Ye, M.; Shen, J., Building better aqueous Zn-organic batteries. *Energy Environ. Sci.* **2023**, *1*6 (6), 2398-2431.

[31]. Wang, Q.; Liu, Y.; Chen, P., Phenazine-based organic cathode for aqueous zinc secondary batteries. *J. Power Sources* **2020**, *4*68.

[32]. Menart, S.; Pirnat, K.; Pahovnik, D.; Dominko, R., Triquinoxalinediol as organic cathode material for rechargeable aqueous zinc-ion batteries. *J. Mater. Chem. A* **2023**, *11* (20), 10874-10882.

[33]. Kim, J.; Kim, J. H.; Ariga, K., Redox-Active Polymers for Energy Storage Nanoarchitectonics. *Joule* **2017**, *1* (4), 739-768.

[34]. Tan, S. T. M.; Quill, T. J.; Moser, M.; LeCroy, G.; Chen, X.; Wu, Y.; Takacs, C. J.; Salleo, A.; Giovannitti, A., Redox-Active Polymers Designed for the Circular Economy of Energy Storage Devices. *ACS Energy Lett.* **2021**, 6 (10), 3450-3457.

[35]. Sato, K.; Ichinoi, R.; Mizukami, R.; Serikawa, T.; Sasaki, Y.; Lutkenhaus, J.; Nishide, H.; Oyaizu, K., Diffusion-Cooperative Model for Charge Transport by Redox-Active Nonconjugated Polymers. *J. Am. Chem. Soc.* **2018**, *140* (3), 1049-1056.

[36]. Muench, S.; Wild, A.; Friebe, C.; Häupler, B.; Janoschka, T.; Schubert, U. S., Polymer-Based Organic Batteries. *Chem. Rev.* **2016**, *11*6 (16), 9438-9484.

[37]. Nguyen, T. P.; Easley, A. D.; Kang, N.; Khan, S.; Lim, S. M.; Rezenom, Y. H.; Wang, S.; Tran, D. K.; Fan, J.; Letteri, R. A.; He, X.; Su, L.; Yu, C. H.; Lutkenhaus, J. L.; Wooley, K. L., Polypeptide organic radical batteries. *Nature* **2021**, *593* (7857), 61-66.

[38]. Suga, T.; Ohshiro, H.; Sugita, S.; Oyaizu, K.; Nishide, H., Emerging N-Type Redox-Active Radical Polymer for a Totally Organic Polymer-Based Rechargeable Battery. *Adv. Mater.* **2009**, *21* (16), 1627-1631.

[39]. Shi, Y.; Monteiro, M. J.; Jia, Z., Chapter 2 Synthetic Strategies and Methods for Redox Polymers. In *Redox Polymers for Energy and Nanomedicine*, The Royal Society of Chemistry: 2021; pp 27-92.

[40]. Xie, Y.; Zhang, K.; Yamauchi, Y.; Oyaizu, K.; Jia, Z., Nitroxide radical polymers for emerging plastic energy storage and organic electronics: fundamentals, materials, and applications. *Mater. Horiz.* **2021**, *8* (3), 803-829.

[41]. Koshika, K.; Sano, N.; Oyaizu, K.; Nishide, H., An Aqueous, Electrolyte-Type, Rechargeable Device Utilizing a Hydrophilic Radical Polymer-Cathode. *Macromol. Chem. Phys.* **2009**, *210* (22), 1989-1995.

[42]. Luo, Y.; Zheng, F.; Liu, L.; Lei, K.; Hou, X.; Xu, G.; Meng, H.; Shi, J.; Li, F., A High-Power Aqueous Zinc–Organic Radical Battery with Tunable Operating Voltage Triggered by Selected Anions. *ChemSusChem* **2020**, *13* (9), 2239-2244.

[43]. Deng, Y.; Teng, C.; Wu, Y.; Zhang, K.; Yan, L., Polypeptide Radical Cathode for Aqueous Zn-Ion Battery with Two-Electron Storage and Faster Charging Rate. *ChemSusChem* **2022**, *15* (7), e202102710.

[44]. Winsberg, J.; Janoschka, T.; Morgenstern, S.; Hagemann, T.; Muench, S.; Hauffman, G.; Gohy, J. F.; Hager, M. D.; Schubert, U. S., Poly(TEMPO)/Zinc Hybrid-Flow Battery: A Novel, "Green," High Voltage, and Safe Energy Storage System. *Adv. Mater.* **2016**, *28* (11), 2238-2243.

[45]. Winsberg, J.; Muench, S.; Hagemann, T.; Morgenstern, S.; Janoschka, T.; Billing, M.; Schacher, F. H.; Hauffman, G.; Gohy, J. F.; Hoeppener, S.; Hager, M. D.; Schubert, U. S., Polymer/zinc hybrid-flow battery using block copolymer micelles featuring a TEMPO corona as catholyte. *Polym. Chem.* **2016**, *7* (9), 1711-1718.

[46]. Koshika, K.; Chikushi, N.; Sano, N.; Oyaizu, K.; Nishide, H., A TEMPO-substituted polyacrylamide as a new cathode material: an organic rechargeable device composed of polymer electrodes and aqueous electrolyte. *Green Chem.* **2010**, *12* (9), 1573-1575.

[47]. Chen, Y. G.; Zhang, Y. F.; Liu, X.; Fan, X. L.; Bai, B.; Yang, K.; Liang, Z. X.; Zhang, Z. S.; Mai, K. C., Long-Life and High-Power Binder-Free Cathode Based on One-Step Synthesis of Radical Polymers with Multi-Pendant Groups. *Macromol. Rapid Commun.* **2018**, 39 (12), 6.

[48]. Johnson, D. W. New Applications for Poly(ethylene-alt-maleic anhydride). Durham University, 2010.

[49]. Kemper, T. W.; Larsen, R. E.; Gennett, T., Relationship between Molecular Structure and Electron Transfer in a Polymeric Nitroxyl-Radical Energy Storage Material. *J. Phys. Chem. C* **2014**, *118* (31), 17213-17220.

[50]. Ma, T.; Fox, E.; Qi, M.; Li, C. H.; Sachithani, K. A. N.; Mohanty, K.; Tabor, D. P.; Pentzer, E. B.; Lutkenhaus, J. L., Charge Transfer in Spatially Defined Organic Radical Polymers. *Chem Mater* **2023**, *35* (21), 9346-9351.

[51]. Wang, S.; Li, F.; Easley, A. D.; Lutkenhaus, J. L., Real-Time Insight into the Doping Mechanism of Redox-Active Organic Radical Polymers. *Nat. Mater.* **2019**, *18* (1), 69-75.

[52]. Hu, Y. X.; Zhang, K.; Hu, H.; Wang, S. C.; Ye, D. L.; Monteiro, M. J.; Jia, Z. F.; Wang, L. Z., Molecular-level anchoring of polymer cathodes on carbon nanotubes towards rapid-rate and long-cycle sodium-ion storage. *Mater. Chem. Front.* **2018**, *2* (10), 1805-1810.

[53]. Kim, J. K.; Kim, Y.; Park, S.; Ko, H.; Kim, Y., Encapsulation of organic active materials in carbon nanotubes for application to high-electrochemical-performance sodium batteries. *Energy Environ. Sci.* **2016**, *9* (4), 1264-1269.