

INTEGRATION OF REDOX-ACTIVE CATECHOL PENDANTS INTO POLY(IONIC LIQUID) FOR THE DESIGN OF HIGH-PERFORMANCE LITHIUM-ION BATTERY CATHODES

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The quest to build safe, low-cost, high-energy and largescale rechargeable lithium-ion batteries (LIBs) feeds an ever-growing interest in pursuit of novel redox-active polymer (RAP)-based electrodes,^{1–6} which can potentially pave the path toward sustainable electrochemical energy storage (EES) technologies.^{7–9} In this context, batteries that employ quinonebased RAPs have demonstrated suitability as robust organic electrode materials (OEMs) owing to their high theoretical specific capacity (low molecular weight associated with a $2e^-/2Li^+$ process per quinone unit), structural diversity, tunable redox potential, fast kinetics as well as potential compatibility with post-LIB chemistries.^{1–6,10,11} In particular, ortho-quinone RAPs have recently emerged as more attractive than their paracounterparts: exhibiting improved life cycle (3400 cycles with 98% capacity retention), higher discharge potential (as high as 3.1 V vs Li^+/Li), higher specific energy (1200 Wh kg^{-1}) and enhanced rate capability (working at a high C-rate of 600C).^{12–16} Although those pioneering works represent an important advent in organic EES in terms of lithium storage performance for the quinone-RAP family, further increase of output voltage while maintaining a high energy and power capabilities, and long service life is still an imperative task.¹⁷

There exist several molecular engineering approaches to increase the voltage of small organic electroactive compounds; the most widely used consists in introducing electronwithdrawing groups (EWG).^{18,19} In the case of quinone derivatives, the introduction of EWG on benzoquinones increased the discharge potential from 2.5 to 3.1 V.¹⁸ This trend was also validated by theoretical calculations.^{20,21} However, these strategies were reported for small OEMs only, which demonstrated limited cyclability owing to their high solubility in organic electrolytes.²⁰

In light of this, we propose the use of catechols bound to a polymer backbone bearing ionically charged electron-withdrawing groups (of N-vinylimidazolium-type) to provide OEM combining a high discharge potential (due to the electronegative substituent) with an enhanced rate capability (due to the ionic nature of the polymer). We note here that the catechol polymeric pendants serve dual functions, acting both as the active-material (in situ generation of ortho-quinones that undergo reversible $2e^-/2Li^+$ redox process; Figure 1a) and as the binder (mussel-inspired adhesion onto high-surface energy substrates, CNTs here; Figure 1b,c).^{6,13,15} Excluding the use of an external binder is

always an extra advantage to increase the energy density of the device and to ensure long cycle life, by avoiding spurious reactions arising from the binder.²²

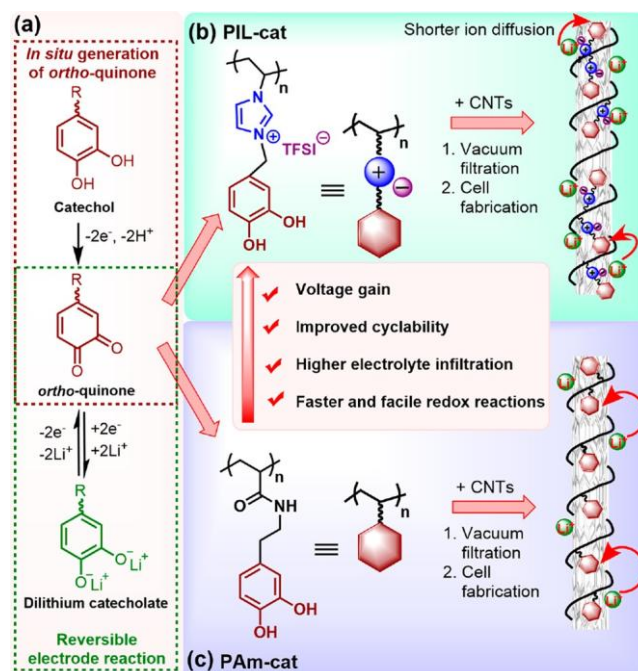


Figure 1. Construction of catechol-based PIL/CNTs buckypaper for LIBs. (a) ortho-Quinone/dilithium catecholate redox reaction. (b,c) Enhancement in the electrochemical performance of cationic PIL-cat (b) compared to its neutral counterpart PAm-cat (c).

We thus report the preparation and the evaluation of the electrochemical performances of a novel self-standing, binder-, and metal current collector-free LIB cathode that consists in a buckypaper composed of a multifunctional surface- and redoxactive poly(ionic liquid) (PIL) bearing catechol pendants and multiwalled carbon nanotubes (CNTs). The integration of catechol moieties into a poly(*N*-vinylimidazolium) backbone having bis(trifluoromethanesulfonyl)imide (TFSI⁻) counteranion²³ (abbreviated as PIL-cat, Figure 1b) is anticipated to impart the following enhancement in Li-storage performances, compared to the catechol units in the polyacrylamide neutral version (abbreviated as PAm-cat, Figure 1c):²⁴ (i) improved binding between cationic RAP and CNTs via their well-known cation- π ²⁵ and π - π ²⁶ interactions for the fabrication of a binder-free electrode, (ii) superior cyclability due to that binding ability, resulting in minimal/no leaching of RAP from the buckypaper into the organic electrolyte,^{13,15,26} (iii) increase in the discharge potential due to electron-deficient PIL building block,²⁷ (iv) enhanced rate capability owing to facilitated Li⁺ and TFSI⁻ counteranion mobility both at the electrode-electrolyte interface and in the bulk of the electrode,²⁸ which is often a limiting factor at high C-rates. It is worth to mention here that to the best of our knowledge, only two articles by Mecerreyes²⁹ and Nishide³⁰ have demonstrated the application of redox-active PILs as OEMs in LIB, but the former work was limited by short-term cyclability (losing 60% of the initial capacity over 100 charge-discharge cycles), and the latter by the capacity (20 mAh g⁻¹).

Fundamental electrochemical evaluation of the RAP/buckypaper (containing 20 wt % RAP) composite working electrode (WE) was carried out in a 2032 coin-type half-cell fabricated with Li metal

as the reference and counter electrodes, and 1.5 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in a mixture of tetraglyme (G4) and ethyl methyl carbonate (EMC) (G4:EMC = 1:2, v/v) as the electrolyte. This RAPsupported buckypaper WE is prepared by dispersing CNTs and RAPs (PIL-cat or PAm-cat) in iso-propanol, followed by vacuum filtration and rinsing steps to remove unbound polymer (see experimental section for details). Transmission electron microscopy images consolidate the PIL-cat's binder propensity onto the CNTs (Figure S2). The aforementioned optimized electrolyte was chosen based on superior electrochemical performance of PAm-cat in LiTFSI/G4+EMC compared to other conventional electrolyte systems owing to G4-mediated strong coordination ability to the Li^+ ions, that can be doped into ortho-quinone (discharging cycle) and undoped from the catechol dianion smoothly by sufficiently reducing catecholate–dilithium ion pair complex interactions during the subsequent charging cycles (see Figure S3a for the Li^+ transport mechanism, and section S1 for detailed discussion).³¹ RAPs/buckypaper approach has been adapted for all our electrochemical testing because this electrode configuration was demonstrated to significantly improve the half-cell performance compared to the tradition electrode architecture (electrode ink deposited on Aluminum foil current collector) due to enhanced electronic/ionic conductivity in the buckypaper (see section S2 for detailed discussion).³² Note that, unless specifically mentioned, the capacity of the WE was always calculated based on the total weight of the polymer, as is usually the case for comparing the specific capacities of polymer-based electrodes.²

Figure 2a shows cyclic voltammograms (CV) recorded at different scan rates from 0.25–100 mV s^{-1} in the voltage range between 2.0 and 4.0 V (vs Li^+/Li). The CV profile of PAm-cat displays a pair of broad redox peaks centered at $E_{p,a} \approx 3.3 \text{ V}$ and $E_{p,c} \approx 3.05 \text{ V}$,¹⁵ whereas the same quasi-reversible delithiation/lithiation reactions (Figure 1a) occur at much higher anodic ($E_{p,a} \approx 3.54 \text{ V}$)/cathodic ($E_{p,c} \approx 3.4 \text{ V}$) potentials in the case of PIL-cat (Figure 2a and Figure S7). Importantly, when electron-withdrawing imidazolium moieties are incorporated with the ortho-quinones (PIL-cat), a 350 mV reduction (discharge) potential gain is noted compared to PAm-cat, which is also evident from differential capacity–voltage curves (Figure S8). A high reduction potential of 3.4 V is thus measured for PIL-cat, which largely exceeds the value measured for the best reported polyelectrolyte bearing orthoquinone pendants (3.05 V).¹⁵

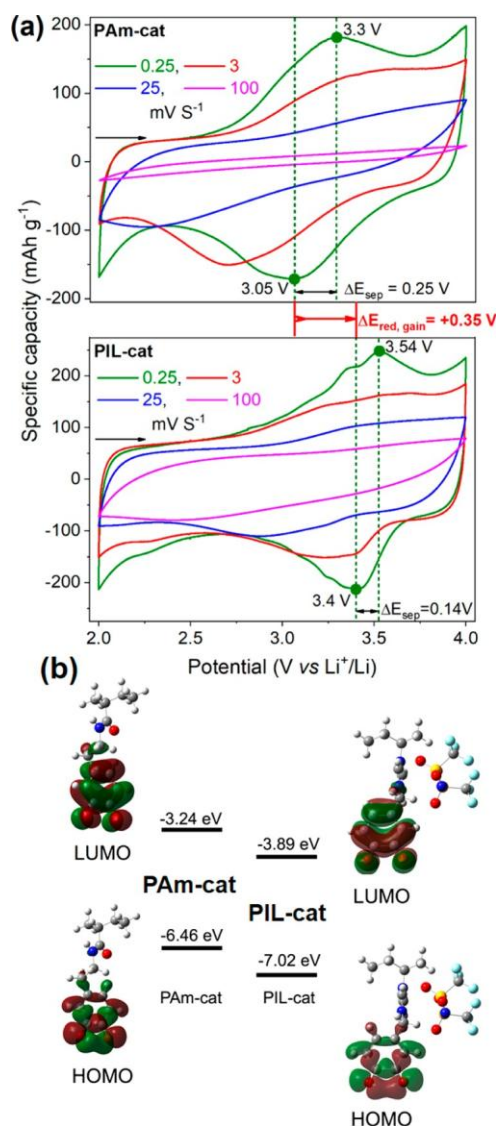


Figure 2. (a) Representative cyclic voltammograms of PAm-cat¹⁵ and PIL-cat/buckypaper electrodes in Li-ion half-cell. (For sake of comparison with PIL-cat, the data for PAm-cat are reproduced with permission from ref 15. Copyright (2017) John Wiley and Sons.) (b) HOMO and LUMO energy levels of PAm-cat and PIL-cat in their quinone form.

Quantum-chemical calculations were then performed to get additional insights into the electronic structure of PAm-cat and PIL-cat. The molecular geometries, charge density distributions, and energies of the electronic levels were calculated for molecular model systems for both polymers in the quinone form using a density functional theory (DFT) method at the B3LYP/6-31g** level of theory (Figure 2b, see SI for calculation protocol). The energy of the lowest unoccupied molecular orbital (LUMO) of a redox molecule is qualitatively related to the reduction potential: the lower the LUMO level, the higher the reduction potential.^{20,21,33} As presented in Figure 2b, the LUMO is localized on the quinone unit in both systems and the computed LUMO energy of PIL-cat is 0.65 eV lower (i.e., more stable) than that of PAm-cat. The stabilization of the LUMO in PIL-cat is related to the electron-withdrawing effect of the imidazolium ring on the ortho-quinone unit. A more relevant approach to compare the

electrochemical behavior of the two polymers is to calculate their electron affinity (EA), defined as the total energy difference between the reduced (i.e., negatively charged) and neutral molecule. The EA value for PIL-cat is significantly larger than that of PAm-cat: 2.4 vs 1.6 eV; this clearly indicates that an extra negative charge is more stable on PIL-cat, due to the proximity of the positively charged imidazolium group. The calculations also indicate that the TFSI[−] counterion does not play a significant role in the electronic behavior of PIL-cat. The trends from these theoretical calculations are thus in very good agreement with the CV measurements and rationalize the beneficial effect of imidazolium on raising the discharge potential of PIL-cat compared to PAm-cat.^{20,21,33}

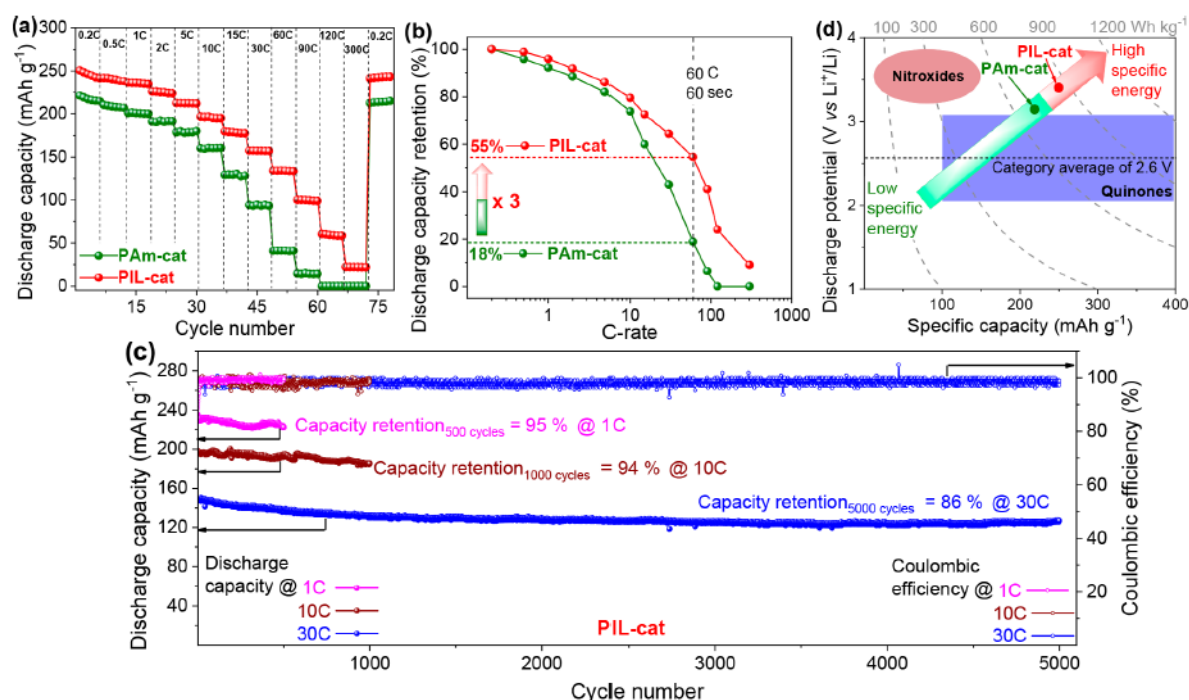


Figure 3. Comparative electrochemical performances of PAm-cat and PIL-cat/buckypaper electrodes in Li-ion half-cells. (a,b) Rate capability: discharge capacity vs cycle number (a), and discharge capacity retention at different C-rates (b), the capacities at higher C-rates are normalized with respect to the capacity at 0.2C (1C = 250 mA g^{−1} for PAm-cat and 1C = 106 mA g^{−1} for PIL-cat). (c) Long-term cyclability and Coulombic efficiencies measured at 1, 10 and 30C for PIL-cat. (d) Comparison of the average discharge potential, specific capacity and energy of poly(orthoquinone)s reported in this work with the state-of-the-art nitroxide and quinone polymers. The capacities were measured based on the total weight of polymer. (For sake of comparison with PIL-cat, the data for PAm-cat are reproduced with permission from ref 15. Copyright (2017) John Wiley and Sons.)

The CV curves of PIL-cat are also characterized by a smaller peak-to-peak voltage separation than that of PAm-cat at the given scan rate (Figure 2a), demonstrating faster kinetics in PIL-cat.³⁴ Quantitatively, the heterogeneous reaction rate constant (k^0), determined from the scan rate dependence of the peak potential using the Laviron method, is found to be 1 order of magnitude higher for PIL-cat than PAm-cat (1.5×10^{-3} vs 1.4×10^{-4} cm s^{−1}, Figure S9 and related discussion).

Additionally, power-law analyses of peak currents as a function of the scan rate reveal more surface-controlled and/or less diffusion-limited redox processes in PIL-cat than in PAm-cat (Figure S10 and

related discussion). Furthermore, electrochemical impedance spectroscopy (EIS) technique was employed to understand the difference in the kinetic aspects of electro-ionic reactions between PAm-cat and PIL-cat composite electrodes.^{15,35} Figure S11 shows the Nyquist plots and the equivalent circuit used to fit the EIS data, and fitted elements are collected in Table S2 and discussed in the associated text. In brief, PIL-cat/buckypaper demonstrated a lower charge-transfer resistance (R_{ct} ; 77 ± 0.32 vs $105 \pm 0.41 \Omega$) and a higher apparent diffusion coefficient (D_{app} ; 0.28×10^{-12} vs $0.05 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$), in addition to a higher electrolyte uptake up to 500 wt % compared to only 132 wt % for the PAm-cat/buckypaper. The PIL-mediated improved electrode wettability and the facile, faster transportation of the electrolyte ions into the bulk reaction sites are therefore anticipated to deliver a superior rate performance for PIL-cat over its neutral counterpart.

Figure 3a,b and Figure S12 show the comparative rate performance studies by galvanostatic charge-discharge (GCD) experiments at progressively increasing C-rates of 0.2 to 300C in the potential window of 2.0–4.5 V for the PAm-cat and PIL-cat/buckypapers. At low C-rate of 0.2C, PAm-cat reaches a reversible capacity of 218 mAh g^{-1} (theoretical capacity, C_{th} , of 250 mAh g^{-1}) with an initial Coulombic efficiency of 87%. Interestingly, PIL-cat shows a higher capacity of 247 mAh g^{-1} , which is 230% of the theoretical value ($C_{th} = 106 \text{ mAh g}^{-1}$), with a higher Coulombic efficiency (90%). This capacity excess is attributed to significant doublelayer capacitance contributions to the total stored charge, as expected for ionically charged polymer-wrapped high surfacearea CNTs in addition to their faradaic contributions (see detailed discussion in Figures S13 and S14).^{15,28,36} This is fully consistent with previous results on polyelectrolytes bearing catechols/buckypapers used as cathodes.¹⁵

The discharge capacities monotonically decrease with increase in the C-rates, but more drastically in the case of PAm-cat (Figure 3a). For instance, PIL-cat demonstrates high reversible capacities (and also their retention) of 236 (96%), 197 (80%) and 59 (24%) mAh g^{-1} at 1, 10 and 120C, respectively (Figure 3b). At a high C-rate of 60C, PIL-cat still delivers 134 mAh g^{-1} , which is more than three times higher than that of PAm-cat (41 mAh g^{-1}) at the same C-rate (Figure 3a). When the C-rate is shifted back from 300C to 0.2C, nearly quantitative recovery of the initial capacities is observed in both the cases, signifying a strong tolerance to the rapid Li^+ ions (de)doping.

Furthermore, the rate capability of PAm-cat and PIL-cat/ buckypapers are compared for different active-material mass loadings, ≈ 10 , ≈ 20 and $\approx 40 \text{ wt } \%$ (Figure S15). With the increase of mass loading, both the discharge capacity (at 0.2C) and the rate capability of PAm-cat are dramatically decreased compared to PIL-cat. At 40 wt % mass loading and 60C (1 min charge/discharge), the capacity delivered by the PIL-cat electrode is ≈ 3 times higher than that of PAm-cat. The combined CV, EIS and rate capability studies reveal that PIL backbone not only facilitates Faradaic reactions, but also allows a facile and rapid ion-transport along shortened diffusion paths both at the electrode-electrolyte interface and in the bulk of the electrode, leading to enhanced utilization of redox-sites and hence higher capacity, especially at high C-rates and mass loading, which is crucial for achieving superior rate capability.^{28,36} Long-term cyclability is another vital requisite for the development of “next-generation” high-performance OEMs. We thus evaluated the cycling stability of PIL-cat/ buckypaper by repeated GCD experiments between charge and discharge potential limits of 4.5 and 2.0 V, respectively. The half-cells attain stable capacities of 230 and 198 mAh g^{-1} after few initial catechol-to-quinone activation cycles (<5) and retain 95% and 94% of their initial capacity over 500 and 1000 full cycles at 1 and 10C, respectively (Figure 3c and Figure S16a). Remarkably, the reversible capacity of the PIL-cat/ buckypaper

is maintained at 127 mAh g⁻¹ after prolonged testing (5000 cycles), with 86% capacity retention, losing a minute 0.004 mAh g⁻¹/cycle at 30C (Figure 3c and Figure S16b).

Moreover, the Coulombic efficiency is close to 100% during the whole cycling tests. This ultralong cyclability is assumed to be the result of: (i) negligible side-reactions during the reversible quinone/catecholate redox reaction, (ii) the high binding ability of PIL-cat to CNTs, which restricts the dissolution of RAP into the nonaqueous electrolyte and, (iii) the sufficiently weakened Li⁺-catecholate ion pair complexes (which would otherwise lead to Li⁺ accumulation at the quinone sites during the subsequent charging cycles) due to the electron-withdrawing imidazolium cations.^{12,15}

In summary, we have demonstrated that CNT buckypapers containing PIL with pendant surface- and redox-active catechols (PIL-cat) are promising cathode materials for LIBs. The electron-withdrawing and ion conducting nature of PIL backbone not only enhanced discharge potential (+350 mV) of quinones but also improved performance metrics: delivered a high reversible capacity of 247 mAh g⁻¹ at 0.2C, with a remarkable capacity of 134 mAh g⁻¹ at 60C, and impressively retained 86% of its initial capacity during the prolonged cycling test (5000 cycles) compared to neutral polymer chain (PAmcat). Moreover, this reduction potential gain imparted by the PIL backbone offers a promising practical high voltage (and thus, specific energy of 850 Wh kg⁻¹) organic cathode (3.4 V vs Li⁺/Li), whose value is higher than that of state-of-the-art quinone-RAPs (3.05 V), and close to that of nitroxide-bearing polymers (Figure 3d). We postulate that our approach paves ways toward the design of sustainable and high-performance EES technologies. Current works deal with simplifying the polymer backbone to improve the specific capacities.

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