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SUMMARY

Metal or metal-ion based battery represents the mainstream battery technology, in which metal-ion either participates in electrode redox or acts as the charge carrier in electrolyte. The principle guides the battery designs and leads to the most widely adopted battery construction of metal-ion acceptor/metal salt in appropriate solvent/metal-ion donor. Though with significant progress, many issues have been incurred, including dendrite growth, SEI corruption, and safety concerns. In this paper, the intercalation/deintercalation of organic cations other than metal ions is revealed and has been fulfilled in an all-organic battery composing of organic anode/cathode, and pure ionic liquid electrolyte. The metal-free and solvent-free concept has been demonstrated by polyimide/EMITFSI/polytriphenylamine full-cell, through which
capacity approaching theoretical value, rate capability up to 200 C, cycling life longer than 5000 cycles, and remarkable low-temperature performance has been achieved. Our pioneer work provides an alternate way of developing future efficient, safe, green, and versatile rechargeable batteries.

**KEYWORDS**: metal-free, organic cation intercalation, ionic liquid, organic electrode material, green battery

**INTRODUCTION**

Over the past decades, we are seeing the biggest changes in energy storage industry, in which renewable energy becomes a rising role and has earned increased attention. Electrochemical energy storage and conversion, especially batteries, as an important member in the emerging energy field, made tremendous progress. From early lead-acid, nickel-cadmium, and nickel-hydrogen batteries, to current lithium, sodium, and magnesium batteries, a variety of batteries have been developed, with different charge/discharge mechanisms and anode/electrolyte/cathode constructions summarized in Figure 1A. Among them, aprotic metal battery (e.g., Li/S and Li/air) and aprotic metal-ion battery (e.g., graphite/LiCoO₂ and hard carbon/Na₃V₂(PO₄)₃) undoubtedly are the mainstream of current research. In addition, aqueous metal-ion battery (e.g., polyimide (PI)/LiNO₃/LiCoO₂) has becoming increasingly attractive in recent years due to its prominent safety and potential application in grid energy. The above batteries have one thing in common that metal cation (M⁺) is the only charge carrier in ion
conduction and charge balancer in electrode redox. Beside this typical battery concept, the battery involving metal cation (M⁺) participating the anode reaction and anion (A⁻) participating the cathode reaction was proposed recently, and typical examples are dual-graphite battery (also called dual-ion battery by some authors⁹,¹⁰) and all-organic battery (e.g., poly(anthraquinonyl sulfide) (PAQS)/polytriphenylamine(PTPAn)¹¹ and PI/PTPAn¹²). All the above batteries, with either inorganic or organic electrode materials, have two indispensable components. One is the metal element (e.g., Li, Na, K, Mg), apart from a major participant in anode electrochemical redox (e.g., Li⁺/Li, Mg²⁺/Mg, ...), it is also an important charge carrier within electrolyte or electrode material. The other is the solvent (either aprotic ester and ether, or water) in the electrolyte, which functions as the medium dissolving electrolyte salt and maintaining ionic conductivity. However, these two primary components bring some issues, such as unforeseen metal dendrite growth, volatility and flammability of aprotic solvent, and less reliable stability of electrolyte toward electrode. In addition, the annoying SEI issues and even concerns on metal resource can be generated. All these hampers the further improvement and practical application of existing battery systems.

Actually, current research already provides some clues to the solution. On one hand, organic electrode materials¹³–¹⁶ can help to wean from the dependence on transition metal-based inorganic electrode, and provide more space on performance improvement. Generally, the organic electrode materials can be divided into n-type (reduced to negatively-charged species and neutralized by receiving cations) and p-type (oxidized to positively-charged species and neutralized by receiving anion), and applied as anode
or/and cathode in various battery types (Figure 1A). Within the n-type family, carbonyl-based organics such as quinone polymers and polyimides, have been widely studied and demonstrated high capacity and reliable stability. More importantly, owing to its unique cation-independent redox character, this type of organics, for example, PAQS$^{17-20}$, is capable of reacting with different metal cations including Li$^+$, Na$^+$, K$^+$, and Mg$^{2+}$ without crystalline limitation. On the other hand, in the last few years, the safety advantage of room temperature ionic liquid (RTIL)$^{21,22}$ has been extensively reported and its application in battery has been frequently mentioned, because of the merits of non-volatility, non-flammability, as well as chemical, electrochemical, and thermal stability. Other than improving battery safety,$^{23}$ its effect in regulating the electrode/electrolyte interface$^{24}$ and suppressing the dissolution and shuttle of sulfur cathode has also been revealed.$^{25}$ Nevertheless, when using ionic liquid, there is usually a trade-off between the viscosity, ionic conductivity and safety. Hence, in practical case, adding aprotic solvent to form binary, ternary and even quaternary electrolyte is necessary, and then it certainly reduce the advantage of ionic liquid. Virtually, the ionic conductivity of many pure ionic liquids fully satisfies the requirement of rechargeable batteries ($>10^{-3}$ S cm$^{-1}$ at room temperature),$^{26}$ it alone can well fulfill the ion transfer within the electrolyte and then single-component electrolyte totally composing of ionic liquid is feasible. Unfortunately, the current battery design all required metal-ion as charge carrier, which is absent in pure ionic liquid. Up to today, reversible organic cation (C$^+$) intercalation/de-intercalation into electrode material has been hardly reported. The pioneer work attempting to use pure ionic liquid electrolyte in dual-
graphite battery was not that successful,\textsuperscript{10} the results as well as many other literatures\textsuperscript{27,28} indicated that graphite was not an appropriate anode for C\textsuperscript{+} intercalation because it will be gradually exfoliated by the large C\textsuperscript{+}, leading to low cycling stability and low coulombic efficiency.

Herein, for the first time, we discovered that n-type organic electrode materials showed unique redox reversibility with organic cation (C\textsuperscript{+}) in ionic liquid, and thus realized a novel, totally metal-free and solvent-free battery constructing by n-type organic anode, p-type organic cathode, and pure ionic liquid electrolyte. It distinguished from previously reported batteries by the real metal-free character and organic-cation based redox. The pure ionic liquid electrolyte makes the battery intrinsically safe, while the solvent-free electrolyte together with the all-organic electrode design well resolves the issues produced by solvation effect or the unwanted interaction between solvent and electrode, and further supply a possible new strategy for energy density improvement.

In addition, the metal-free character enhances the battery’s resource sustainability, environmental friendliness, and simplifies battery disposal. In this paper, the battery was mainly demonstrated by the full-cell comprising of polyimide (PI\textsubscript{5}) anode, polytriphenylamine (PTPAn) cathode, and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI) electrolyte (Figure 1C). The PI\textsubscript{5}/EMITFSI/PTPAn full-cell exhibited super-fast reaction kinetics, capacity close to 111 mAh g\textsuperscript{-1} based on PTPAn, and very stable cycling performance. In addition, it showed distinctive temperature adaptability and promising application in wide-temperature-range operation. We believe, the metal-free battery proposed in this work
Figure 1. Cell Configurations and Related Information of Various Rechargeable Batteries

(A) The cell configurations and charge transfer processes of five conventional rechargeable batteries, including aprotic metal battery, aprotic metal-ion battery, aqueous metal-ion battery, dual-graphite battery, and all-organic battery, as well as the totally metal-free battery proposed in this work. For electrode materials, M means alkali or alkaline earth metal such as Li, Na, K, or Mg; inorganics are intercalation materials represented by the transition metal oxide as LiCoO₂, LiFePO₄, etc.; n-type organics are mostly carbonyl polymers, such as polyimides (e.g., PI5) and quinone polymers; p-type organics are usually conjugated amine-based polymers such as polytriphenylamine.
(PTPAn). For electrolytes, the brown color represents conventional, non-aqueous electrolyte consisting of aprotic solvent, metal cation M+, and anion A− such as bis(trifluoromethylsulfonyl)imide (TFSI−), bis(fluorosulfonyl)imide (FSI−), and hexafluorophosphate (PF6−); the green color represents aqueous electrolyte consisting of H2O, M+, and anion B− such as NO3−, ClO4−, and SO42−. The novel solvent-free electrolyte only contains pure ionic liquid, typically are composed of anion A− and organic cation C+ such as 1-ethyl-3-methylimidazolium (EMI+), 1-butyl-1-methylpyrrolidinium (BMP+), and amyltriethylammonium (ATEA+).

(B) The structure and ionic radius (in nm)29–33 of the aforementioned cations (M+ and C+) and anions (A− and B−).

(C) Electrochemical redox mechanism of the metal-free battery illustrated by PI5/pure ionic liquid/PTPAn full cell.

RESULTS

Material Selection and Half-Cell Performance

To construct the metal-free battery, appropriate n-type organic anode, p-type organic cathode, and pure ionic liquid electrolyte needed to be selected first. Though many organic electrode materials had been studied before, only few polymers showed reliable redox reversibility and cycling stability. We scanned the literatures,16 and summarized the candidate pool in Figure S1. The n-type anode could include polyimide (PI2 and PI5) and polyanthraquinone (PAQ), possessing relatively high specific capacity (200–300 mAh g−1) and low redox potential (2.0–2.7 V vs. Li+/Li); the p-type cathode could
be polytriphenylamine (PTPAn), polyaniline (PAn), and poly(2,2,6,6-tetramethylpiperidine-1-oxyl-4-yl methacrylate) (PTMA), with relatively low specific capacity (100–150 mAh g\(^{-1}\)) and high redox potential (3.0–4.0 V vs. Li\(^+\)/Li). After considering the cycling stability, cell voltage as well as capacity, PI5 was chosen as the anode while PTPAn was used as the cathode. On the other hand, we mainly focused on ionic liquids with TFSI\(^-\) anion due to their low viscosity and high conductivity feature (TFSI\(^-\) salt usually had higher ionic conductivity than PF\(_6^-\), and lower melting point than BF\(_4^-\) series\(^{36,34}\)). Among the analogues, EMITFSI was finally picked for the reason that EMI\(^+\) had smaller ionic radius than BMP\(^+\) and ATEA\(^+\) (Figure 1B). However, in the later, BMPTFSI and ATEATFSI were still used to demonstrate the universality of the metal-free battery.
Figure 2. Comparison of PI5 and PTPAn electrode in Conventional Ester Electrolyte and Novel Ionic Liquid Electrolyte.

(A and B) The cycling performance of PI5 and PTPAn at 1 C rate in 1 M LiTFSI/EC+DEC electrolyte and EMITFSI+0.01 M LiTFSI electrolyte (0.01 M LiTFSI was added into pure ionic liquid to establish the Li⁺/Li redox couple on Li reference
electrode, see the Method part).

(C and D) The typical voltage profiles (from the 10th cycle) of PI5 and PTPAn in the two electrolytes.

(E and F) The rate performance of PI5 and PTPAn in the two electrolytes, the current rate changed in step-wise mode from 1 C to 200 C.

(G–J) The typical CV curves of PI5 and PTPAn in the two electrolytes at different scan rates from 0.1 mV s\(^{-1}\) to 1 mV s\(^{-1}\). Corresponding data analysis of the redox peaks labeled from 1# to 8# could be found in Figure S5.

Before testing the full-cell performance, it was necessary to investigate the electrochemical behavior of PI5 anode and PTPAn cathode separately in EMITFSI electrolyte, since it was a brand-new electrolyte for rechargeable batteries. In order to accurately measure the potential of PI5 and PTPAn in EMITFSI electrolyte, three-electrode cell was used in either galvanostatic charge/discharge test or cyclic voltammogram (CV) test. PI5 was the working electrode while excess PTPAn was the counter electrode, and vice versa if PTPAn was studied. Li foil was used as the quasi-reference electrode for both of them, and 0.01 M LiTFSI was added into EMITFSI to establish a Li\(^{+}\)/Li redox couple, leading to 0.12 V lower potential than standard Li\(^{+}\)/Li potential according to Nernst equation (see the method part). The possible competing reaction between EMI\(^{+}\) and Li\(^{+}\) with the n-type PI5 electrode barely happened due to the very low Li\(^{+}\)/EMI\(^{+}\) molar ratio (1/391). For convenience, EMITFSI electrolyte hereinafter referred to EMITFSI+0.01 M LiTFSI for half-cell and pure EMITFSI for
full-cell.

The results of galvanostatic charge/discharge test of PI5 and PTPAn in EMITFSI electrolyte and 1 M LiTFSI/EC+DEC electrolyte was compared in Figure 2A–2D (results in 1 M LiPF6/EC+DEC were presented in Figure S3). Generally, in either electrolytes, PI5 and PTPAn showed quite similar capacity and cycling performance (Figure 2A and 2B). They all exhibited high redox reversibility with maximum capacity of 206 mAh g⁻¹ (PI) and 111 mAh g⁻¹ (PTPAn), and stable cycling with little capacity fading during 200 cycles (10% for PI5 and 5.7% for PTPAn, respectively). If comparing with 1 M LiTFSI/EC+DEC electrolyte, EMITFSI electrolyte actually brought even higher coulombic efficiency (stable value of 98.6% to 100.0% for PI5, and 96.5% to 99.6% for PTPAn, respectively). Moreover, for PI5 anode, lower average charge voltage was obtained in EMITFSI electrolyte (2.46 V) than in 1 M LiTFSI/EC+DEC (2.58 V, Figure 2C); while for PTPAn cathode, little higher average discharge voltage (from 3.75 to 3.77 V, Figure 2D) was observed in EMITFSI electrolyte. The difference in charge/discharge voltage together implied higher working voltage of PI5/PTPAn full-cell with EMITFSI electrolyte.

The rate capability of the organic electrode was examined. Previously, ionic liquid electrolyte was usually criticized for increasing the viscosity, decreasing the ionic conductivity of the electrolyte, and further harming the high-rate performance. The result of charge/discharge tests under step-wise increasing current was shown in Figure 2E and 2F. PI5 and PTPAn both presented much superior rate capability in EMITFSI electrolyte than in 1 M LiTFSI/EC+DEC electrolyte. For instance, under 200 C, the
capacity of PI5 in EMITFSI electrolyte (84% retention) almost doubled that in 1 M LiTFSI/EC+DEC (48% retention); and for PTPAn, the 40% capacity retention at 200°C was achieved in EMITFSI electrolyte; while it mostly could not work in 1 M LiTFSI/EC+DEC. Similar trend was revealed in CV measurements (Figure 2G-2J). When the scan rate was increased from 0.1 to 1.0 mV s\(^{-1}\), highly symmetrical redox peaks were preserved in EMITFSI, while in 1 M LiTFSI/EC+DEC, the cathodic branches leaned to more negative voltage and the anodic ones leaned to more positive voltage, agreeing with previous reports\(^{35,36}\). The results suggested much better redox reversibility of PI5 and PTPAn in EMITFSI.

We tried to semi-quantitatively compare the electrochemical behavior of PI5 and PTPAn in different electrolytes. Either in EMITFSI or 1 M LiTFSI/EC+DEC electrolyte, the dependence of peak current \(i\) on scan rate \(v\) followed the power-law equation of \(i=av^b\), in which \(b\) could be indicative of the surface-controlled reaction \((b=1)\) or the bulk diffusion-controlled reaction \((b=0.5)\).\(^{37,38}\) The data analysis in Figure S5 showed that the \(b\) values for PI5 were significantly increased from 0.77–0.93 range in 1 M LiTFSI/EC+DEC to 0.95–0.99 in EMITFSI, while for PTPAn, they were slightly increased from 0.94–0.98 to 0.95–0.99. The \(b\) values of PI5 and PTPAn all being closed to 1 in EMITFSI electrolyte indicated that they mostly undergo a pseudocapacitive reaction, which might be the reason of the excellent high-rate performance and the faster reaction kinetics of PI5 and PTPAn in EMITFSI electrolyte. We thought the different electrochemical kinetics could be explained by the high ionic conductivity as well as the non-solvation nature of ionic liquid. EMITFSI electrolyte showed higher
ionic conductivity (10.8 mS cm\(^{-1}\), consistent with the reported value\(^{34}\)) than 1 M LiTFSI/EC+DEC (7.4 mS cm\(^{-1}\)) at room temperature (Figure S6). It was unexpected but still reasonable if the following points was taken into account. Firstly, the highly-ionized and solvent-free feature of EMITFSI could bring more available ion-conduction carriers (EMI\(^+\)/Li\(^+\)=TFSI\(^-\)/TFSI\(^-\)=3.9/1) in per unit volume of electrolyte; secondly, the much bigger ionic size of EMI\(^+\) (0.294 nm) than Li\(^+\) (0.076 nm) greatly weakened the coordination with solvent and the electrostatic interaction with anion (TFSI\(^-\)), and it could be evidenced by a supplementary test, in which the diluent electrolytes of 0.1 M EMITFSI/EC+DEC still showed high conductivity than 0.1 M LiTFSI/EC+DEC (Figure S6). Beside the ionic conductivity, the solvation effect might be another important factor affecting the reaction kinetics, which was rarely emphasized in the study of inorganic electrode materials due to the rate-controlling step of ion-diffusion within the lattice.\(^{39}\) However, since the electrochemical reaction of organic electrode material, like PI5, was pseudocapacitive in principle, it could be benefitted by the faster transportation of non-solvated EMI\(^+\), absence of solvation/de-solvation process, as well as the higher cation abundance. EMITFSI promoting the rate performance of PTPAn could be explained similarly. Despite the same doping anion of TFSI\(^-\) in the two different electrolytes, the higher TFSI\(^-\) concentration and weaker interaction within EMI\(^-\)–TFSI\(^-\) ion pair guarantee the immediate TFSI\(^-\) supply for the p-type reaction. In summary, ionic liquid electrolyte not only participates the electrochemical redox of n-type anode and p-type cathode, but also endows the ultrafast reaction kinetics of the metal-free battery.
Figure 3. Electrochemical Performance of PI5/PTPAn Full-Cell with pure EMITFSI

(A and B) The cycling performance and corresponding voltage profiles at 1 C rate.

(C) Comparison of the experimental and the calculated voltage profiles of PI5/PTPAn full cell (the calculated curve was obtained by subtracting the charging/discharging curve of PI5 anode from that of PTPAn cathode.

(D and E) The rate performance and corresponding voltage profiles, the rate was step-wise changed from 1 C to 200 C.

(F) The long-term cycling performance at 20 C within 5000 cycles.

Full-Cell Performance and Analysis
Hereinabove, the electrochemical property of PI5 and PTPAn was well investigated and their superior electrochemical property in EMITFSI electrolyte was revealed, next the PI5/PTPAn full-cell was examined. In the galvanostatic charge/discharge tests of the full-cell, the C rate and specific capacity were all based on the cathode. Figure 3A and 3B showed the cycling behavior and voltage profiles under 1 C rate, in which the specific capacity reached to 111 mAh g⁻¹ in 10 cycles and slowly faded to 93 mAh g⁻¹ after 200 cycles, accompanying with stable coulombic efficiency of 98%. The slightly lower efficiency indicated that there were minor side reactions between electrode and electrolyte, and it also led to the increase of charge transfer resistance (Rct) along with the cycle number (Figure S7). This might be the main reason of capacity decay since both anode and cathode were insoluble in the electrolyte. In Figure 3C, we tried to predict the full-cell charge/discharge curve by subtracting the voltage profile of anode from the cathode, and then found that the experimental curve completely coincided with the calculated one. The charge/discharge curve had two plateaus with equal specific capacity and small charge/discharge voltage gap of 0.11 V (Figure S8), indicating the low-polarization and highly-reversible character of PI5/EMITFSI/PTPAn full-cell. In Figure 3D and 3E, the strikingly excellent rate performance was exhibited. Even up to 200 C, 70% of the 1C capacity could be reserved (the charge or discharge process could be completed in 12.6 seconds). In addition, the capacity could fully recover with the current returning to 1C. Increasing coulombic efficiency was observed at higher current rate, mostly above 99% during the test. Obvious polarization increment was only observed at very high current rate of above 100 C (Figure 3E). The long-term cycling
was tested at 20 C (Figure 3F). After 5000 cycles, the specific capacity was maintained above 80 mAh g⁻¹, about 75% of its maximum value (107 mAh g⁻¹), accompanying with 100% coulombic efficiency. Now the conclusion could be made that owing to pure ionic liquid electrolyte, the PI5/EMITFSI/PTPAn metal-free battery had achieved breakthrough improvement on electrochemical performance.

**Figure 4. XPS Analysis of PI5 Anode and PTPAn Cathode at various Charge/Discharge state**

(A) C1s spectra of PI5 anode and (B) N1s spectra of PTPAn cathode in various state of fresh electrode, after the 1ˢᵗ charge and after the 1ˢᵗ discharge. Noted that PI5 and PTPAn was removed from the PI5/EMITFSI/PTPAn full cell after the 1ˢᵗ charge or discharge. The bands at 292.4 eV for –CF₂ and 292.9 eV for –CF₃ in Fig 4A should be ascribed to PTFE binder and the residual TFSI⁻, respectively. In Fig 4B, the energy band of –C₃N at around 399.5 eV in charged PTPAn should be attributed to TFSI⁻ ⁴⁰ doping accompanying with PTPAn oxidation.

The redox mechanism of the full-cell was investigated in term of X-ray photo-electron spectroscopy (XPS) by tracing the evolvement of energy bands of some characteristic
groups. For PI5 anode, the energy band of –C=O group at 289.4 eV could be observed in the fresh electrode and discharged electrode, while PI5 being charged in the full-cell, another energy band of –C–O bond at 287.1 eV appeared instead, indicating the reversible reduction/oxidation of carbonyl group. For PTPAn cathode, reversible transformation between tertiary amine and tertiary ammonium cation could be monitored by the appearance/disappearance of the energy band at 402.5 eV (–C3N+). Thus, the XPS analysis verified that ion-doping reaction reversibly happened in PI5 and PTPAn as reported previously41,42 even in pure and metal-ion-absent ionic liquid (Figure 1C).

Figure 5. Low-Temperature Performance of PI5/PTPAn Full-Cell with pure EMITFSI Electrolyte

(A and B) The cycling performance and the voltage profiles (from the 50th cycle) under 1 C rate at different temperatures of 30°C, 10°C, and –10°C.
(C and D) The rate performance and the voltage profiles at −10°C under step-wise increasing the current rate from 1 C to 200 C.

The low-temperature property was always a bottleneck as regards the application of ionic liquid, hence we evaluated the PI5/EMITFSI/PTPAn full-cell again under different temperature. For conventional Li-ion batteries, the reaction kinetics at low-temperature was more impacted by the slow solid ion-diffusion and/or high solid-electrolyte interface (SEI) resistance, and poor capacity retention was thus usually observed.\textsuperscript{43,44} Whereas for our metal-free battery, the pseudocapacitive reaction nature of PI5 and PTPAn as well as the still-high ionic conductivity of EMITFSI at −10°C (Figure S6) implied that the low-temperature performance of PI5/PTPAn cell could be expected. In Figure 5A, the discharge capacity and coulombic efficiency of the full-cell was plotted against cycle number at 30, 10, and −10°C (lower-temperature test was not conducted because the freezing point of EMITFSI was −12°C)\textsuperscript{34}. At −10°C, increased electrochemical impedance (Figure S9) brought lower discharge capacity in the initial cycle, but the capacity could be reached to 107 mAh g\textsuperscript{−1} after some “activation” cycles, after which super flat cycling curve also could be observed (99.8% capacity retention after 200 cycles). The results indicated that the low temperature had two effect on the cell performance. On one hand, lower temperature caused higher viscosity and further incurred a longer activation process to get the electrode sufficiently infiltrated. On the other hand, low temperature greatly reduced the occurrence of side reactions, and we thus saw improved cycling stability and coulombic efficiency at −10°C than 30°C. The
low temperature led to very insignificant change in the charge/discharge curves (Figure 5B), suggesting that the high redox reversibility was well maintained at low temperature. Moreover, the fast reaction kinetics was also preserved at low temperature, and the PI5/PTPAn full-cell presented decent rate capability under –10°C and delivered appreciable capacity of 79 mAh g⁻¹ at 50 C (Figure 5C), accompanying with acceptable voltage polarization (Figure 5D).

Figure 6. Flammability Test of the Three Types of Electrolytes

A piece of glass fiber disc was wetted by 0.3 mL (A) conventional 1 M LiTFSI/EC+DEC (1:1, v/v), (B) hybrid electrolyte of 1 M LiTFSI/EC+DEC+EMITFSI (1:1:2, v/v/v), and (C) pure EMITFSI, and then ignited by an alcohol burner. The combustion phenomena were recorded by a camera and typical pictures at different time (in second) after igniting were presented to show the combustion process. The images in the rightmost two rows showed the glass fiber disc before and after burning.

Non-Flammability of Pure Ionic Liquid Electrolyte

Ionic liquid had been known for the non-volatility, non-flammability, and thermal
stability and it was thus widely used as additive or co-solvent for safety enhancement of the aprotic electrolyte. In Figure 6, we compared the flammability of three kinds of electrolytes including conventional 1 M LiTFSI/EC+DEC electrolyte, pure EMITFSI, and their 1:1(volume ratio) mixture which was typically used in the report about non-flammable electrolyte\textsuperscript{23}. The combustion experiment was conducted following the protocol used in previous study\textsuperscript{45}. A piece of glass fiber disc soaked with electrolyte was ignited, and pictures were taken after different time interval to record the burning process. As anticipated, the conventional ester electrolyte burned immediately and kept burning for 22 seconds. The hybrid electrolyte was less flammable and extinguished after 16 seconds, with some black ashes left on the disc. Among them, the pure EMITFSI electrolyte was totally non-flammable during a test time of 25 seconds, suggesting the distinct safety advantage of the PI5/EMITFS/PTPAn cell.

**Universality of Metal-Free Battery Concept**

Inspired by the above results, we thought the reversible interaction of organic cations other than EMI\textsuperscript{+} could also happen on n-type organic anode, and thus many other ionic liquids might be applied in metal-free battery. To prove it, another two kinds of ionic liquids, pure BMPTFSI and ATEATFSI, were used as the electrolyte in the PI5/PTPAn full-cell. Despite the bigger ionic size of BMP\textsuperscript{+} (0.339 nm) and ATEA\textsuperscript{+}, it exhibited similar capacity performance and cycling stability at 1 C rate to that in EMITFSI (Figure S10A), except the initial several “activation” cycles. The charge/discharge curves in BMPTFSI and ATEATFSI electrolyte were also quite similar to that in
EMITFSI, with slightly increased voltage polarization (Figure S10B). The results could be explained by the higher viscosity and lower ionic conductivity of BMPTFSI and ATEATFSI than EMITFSI (Figure S11), which caused increased electrolyte resistance ($R_s$) and charge transfer resistance ($R_{ct}$) in EIS tests (Figure S12). In spite of the slower reaction kinetics, the successful application of BMPTFSI and ATEATFSI suggested the wide range of electrolyte options when building the metal-free battery.

Not merely the electrolyte, the n-type anode was also not necessarily limited to PI5. In view of the lower redox potential of anode being preferred for the full-cell, PI2 and PAQ anode was studied. Unfortunately, they turned out to be unsuitable anode in EMITFSI, probably due to some compatibility issues with the electrolyte. The results in Figure S13 indicated that PI2 and PAQ both had better utilization and cycling stability in ether electrolyte of 1 M LiTFSI/DOL+DME. While in pure EMITFSI, the performance of PI2 and PAQ was far from expectation, they either showed poorer capacity retention (47% after 50 cycles for PI2) or lower capacity (95 mAh g$^{-1}$ for PAQ). The compatibility issues might be generated by the poor wettability of the electrode, the side reactions, and even the altered reaction kinetics, which needed to be further investigated. We also evaluated the performance of the full-cell with PI or PAQ anode. In Figure S14, the lower capacity of PAQ accordingly decreased the capacity release of PAQ/PTPAn full-cell, while the worse capacity retention of PI2 deteriorated the cycling stability of PI2/PTPAn full-cell. However, the remarkably elevated discharge voltage (1.67 V) of PI2/PTPAn full-cell still should be mentioned, because it implied that for the foreseeable future, the energy density of the metal-free battery was very likely be
improved by using the n-type organic anode with much lower redox potential and good compatibility with ionic liquid. For instance, di-lithium terephthalate showed so far the lowest redox potential of 1.0 V vs. Li+/Li in the organic electrode family.\textsuperscript{46}

**DISCUSSION**

In conclusion, highly reversible intercalation/deintercalation reaction of organic cation with n-type organic electrode was first revealed. The metal-free battery was thus constructed by connecting n-type organic anode and p-type organic cathode using pure ionic liquid electrolyte. The PI5/EMITFSI/PTPan full battery demonstrated the good specific capacity release, strikingly high rate performance of 70% capacity reserved at 200 C, outstanding long-term cycling stability of 75% capacity retention after 5000 cycles, and remarkable low-temperature performance. The pseudocapacitive electrochemical redox of PI5 and PTPAn in EMITFSI was facilitated by the high ionic conductivity, highly available unpaired cation/anion, and non-solvation character of pure ionic liquid electrolyte. In addition, the novel, metal-free battery was intrinsically non-flammable, resource-sustainable, environmentally friendly, and potentially recyclable. Our pioneer work revealed alternative strategy for future energy storage. Firstly, the energy density still has huge margin of improvement because of the wide electrochemical window of ionic liquid (up to 6 V)\textsuperscript{47}, the structure diversity of organic electrode materials and thus tunable cell voltage and capacity; Secondly, wide-temperature-range battery can be readily fulfilled by adjusting the electrolyte recipe as required, and the ionic liquid with lower freezing point and higher
stability/compatibility with organic electrode will being perused. Thirdly, the flexibility of polymer electrode and inherent safety of ionic liquid endow it with the potential application in flexible and wearable batteries. Therefore, the metal-free battery is not only a conceptional innovation, but also a competitive candidate in future sustainable and versatile energy storage applications, whether small electronic components or electric vehicle batteries or even grid energy storage.

**EXPERIMENTAL PROCEDURES**

**Electrode Material Synthesis**

PI5 was synthesized by a polycondensation reaction using 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTCDA, 98.0%, TCI) and hydrazine (98.0%, J&K) according to our previous work.36 PI2 was synthesized by a similar polycondensation reaction using pyromellitic dianhydride (PMDA, 99.5%, J&K) and ethylene diamine (EDA, 99.0%, Sigma-Aldrich) following the same literature.36 PAQ was synthesized through a coupling polymerization reaction using 1,4-dichloroanthraquinone (DCAQ, 98.0%, TCI) as monomer and bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)₂, 98.0%, J&K) as dehalogenation agent, following our previous report.48 PTPAn was synthesized by an oxidative polymerization reaction using triphenylamine (TPAn, 99.0%, J&K) as monomer and FeCl₃ (99.99%, Aldrich) as oxidant in accordance with previous report.11

**Electrolyte Preparation**
All the electrolytes were made in argon filled glove box by mixing the electrolyte salt and solvent in fixed proportion. The salt included lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 99.9%, J&K), lithium hexafluorophosphate (LiPF₆, 99.99%, Aldrich), and the solvent was ethylene carbonate (EC, 99.0%, TCI), diethyl carbonate (DEC, 99.5%, J&K), 1,3-dioxacyclopentane (DOL, 99.8%, J&K), and 1,2-dimethoxyethane (DME, 99.5%, J&K). Conventional electrolyte recipe of 1M LiTFSI/EC+DEC or 1M LiPF₆/DOL+DME (volume ratio of the binary solvent was 1:1) was used in the study. All the ionic liquids, including 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI, 99.0%, J&K), 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMPTFSI, 99.0%, J&K), and amyltriethylammonium bis(trifluoromethanesulfonyl)imide (ATEATFSI, 98.0%, TCI) were commercially purchased and used as electrolyte without further purification.

**Material Characterizations**

Fourier transform infrared spectroscopy (FTIR) of the above polymer materials were conducted using KBr pellets on a NICOLET 5700 FTIR spectrometer within wave number range of 400–4000 cm⁻¹ (Figure S2). X-ray photoelectron spectroscopy (XPS) measurement of the electrode in different states was carried out on an ESCALAB 250Xi spectrometer (Thermo Fisher) equipped with a monochromatized Al Kα source (1486.6 eV) for excitation.
**Electrochemical Measurements**

The cathode or anode was composed of 60 wt% active material (PTPAn, PI5, PI2, PAQ), 30 wt% Ketjenblack ECP-600JD carbon and 10 wt% polytetrafluoroethylene (PTFE) binder. The mixture was pressed on a disk of stainless steel mesh with typical active material loading of 0.7–1.2 mg cm\(^{-2}\) for anode (PI5, PI2, PAQ) or 1.2–2.0 mg cm\(^{-2}\) for cathode (PTPAn). CR2016 coin-cell was used in the half-cell with conventional electrolytes of 1 M LiTFSI/EC+DEC, 1 M LiPF\(_6\)/EC+DEC, or 1 M LiTFSI/DOL+DME, and it contained the fore-mentioned electrode as cathode and lithium anode, separated by a Celgard 2400 separator. Swagelok three-electrode cells was used in the study of the electrochemical property of the organic electrode in ionic liquid electrolyte. EMITFSI+0.01 M LiTFSI was the electrolyte and a piece of Whatman GF/D glass fiber acted as the separator. PTPAn or PI5, PI2, PAQ was the working electrode and the counter electrode was PI5 or PTPAn as required, more detailed electrode information could be found in the relative discussion. lithium foil was the reference electrode. CR2016 coin-cell was also used in the full-cell tests. It consisted of PTPAn cathode, PI5, PI2, or PAQ anode as required and pure ionic liquid electrolyte (EMITFSI, BMPTFSI, or ATEATFSI). The mass ratio of cathode to anode was determined by the rule of anode having 10% excess capacity, and the cathode and anode was separated by a disc of glass fiber. The galvanostatic charge/discharge tests were carried out on LANHE CT2001A battery test system (Wuhan, China) or Autolab PGSTAT302 electrochemical workstation (for high current rate tests). The cyclic voltammetry (CV) tests were performed on CHI660A electrochemical workstation using the above three-
electrode cells. Different cutoff voltages were used depending on the cell configuration. More specifically, the voltage limit was 1.5–3.5 V for Li/PI5, 1.5–3.0 V for Li/PI2 and Li/PAQ, 3.0–4.2 V for Li/PTPAn, and 0–2.7 V for all full-cells (PI5/PTPAn, PI2/PTPAn, PAQ/PTPAn). It should be pointed out that, when testing the three-electrode cell containing EMITFSI+0.01 M LiTFSI electrolyte, the actual potential of Li+/Li reference electrode is 0.12 V lower than the standard Li+/Li electrode potential (−3.04 V vs. SHE) according to the Nernst equation, $\Delta \varphi_{\text{Li}^+/\text{Li}} = \varphi_{\text{Li}^+/\text{Li}} - \varphi_{\text{Li}^+/\text{Li}}^\Theta = \frac{(RT)}{(nF)} \ln \frac{[\text{Li}^+]}{[\text{Li}]} = -0.12$ V (T = 303.15 K, [Li+] = 0.01 M). Thus, to keep the voltage consistency, the voltage range was adjusted accordingly (e.g., 1.38–3.38 V for Li/PI5, and 2.88–4.08 V for Li/PTPAn when using EMITFSI+0.01 M LiTFSI electrolyte). In addition, for the convenience of comparison, the CV or voltage profiles were all plotted versus standard Li+/Li electrode. The current rate was determined by the theoretical capacity of the electrode material, such as 1C rate is 203 mA g$^{-1}$ for PI5, and so on, 221 mA g$^{-1}$ for PI2, 260 mA g$^{-1}$ for PAQ, and 111 mA g$^{-1}$ for PTPAn. The electrochemical impedance spectroscopy (EIS) of full-cells was collected at different state on Autolab PGSTAT302 electrochemical workstation with frequency range of $10^5$–$10^{-2}$ Hz and potential amplitude of 10 mV. Unless specified, all the cells were fabricated in an argon filled glove box and tested at room temperature of 30°C.

**Other Measurements**

The dependence of ionic conductivity on temperature of electrolytes was measured on Leichi DDB 303A conductivity meter (Shanghai, China) from −10°C to 40°C.
flammability of the electrolytes was evaluated by the combustion experiment following the protocol in the reference.\textsuperscript{23,45} A piece of Whatman GF/B glass fiber soaked with 0.3 mL electrolyte was ignited and pictures were taken after different time interval to record the burning process.

**SUPPLEMENTAL INFORMATION**

Supplemental Information includes 14 figures and 1 table.

**AUTHOR CONTRIBUTIONS**

J.Q., Z.S. and H.Z. conceived the idea and co-wrote the manuscript. J.Q. carried out the experiments. F.M. offered a lot of useful suggestions throughout the experiment. N.L. helped with part of material preparation and physical characterization. Q.L. helped with part of flammability test and ionic conductivity test.

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**DECLARATION OF INTERESTS**
The authors declare no competing interests.

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**Figure S1.** The voltage, capacity, and structure of p-type organic cathode candidates and n-type organic anode candidates for metal-free batteries: polytriphenylamine (PTPan), polyaniline (PAn), poly(2,2,6,6-tetramethylpiperidine-1-oxyl-4-yl methacrylate) (PTMA), polyimide (PI2 and PI5), and polyanthraquinone (PAQ).
Figure S2. FTIR spectra (KBr pellets) of the polymers involved in this paper, including PTPAn, PI5, PI2, and PAQ. All the characteristic peaks were consistent with the literature values: for PTPAn, $^{11}$ 1597, 1489, 1319, 1269, 816 cm$^{-1}$; for PI5, $^{36}$ 1705, 1583, 1317, 1117, 760 cm$^{-1}$; for PI2, $^{36}$ 1774, 1724, 1392, 726 cm$^{-1}$; for PAQ, $^{17}$ 1670, 1591, 1541, 1379, 1326, 1309, 1248, 1174, 1115, 843, 798, 727, 596 cm$^{-1}$. 
Figure S3. The cycling performance (A, B) and typical voltage profiles (C, D) (from the 10th cycle) of PI5 and PTPAn half-cell with conventional ester electrolytes containing different salts (1 M LiPF₆ or LiTFSI in EC+DEC) at 1 C rate. Compared to TFSI⁻, PF₆⁻ could obviously improve the stable Coulombic efficiency of PTPAn from 96.6% to 99.6%, probably due to its higher oxidative stability than TFSI⁻ at high charging potential. However, PF₆⁻ was not suitable to compose a pure ion liquid electrolyte due to the high melting point or low ionic conductivity at room temperature.²⁶
Figure S4. Comparison of the typical voltage profiles (from the 10th cycle) of PI5/PTPAn full-cell with conventional ester electrolyte of 1 M LiTFSI/EC+DEC and novel pure ion liquid electrolyte of EMITFSI at 1 C. The average discharge voltage of the latter (1.31 V) was obviously higher than that of the former (1.17 V), highly agreeing with the corresponding PI5 and PTPAn half-cell voltage profiles shown in Figure 2C and 2D.
Figure S5. Anodic and cathodic peak current dependence on the scan rate derived from CV curves of PI5 (A) and PTPAn (B) in Figure 2G-2J. The data represented the slope of each fitted line which could explain the intercalation and capacitance contribution to the charge/discharge capacity (slope of 0.5 indicated complete intercalation reaction, while slope of 1 indicated complete capacitance reaction) in the two electrolytes of 1 M LiTFSI/EC+DEC (dash line) and EMITFSI+0.01 M LiTFSI (solid line). (pa: anodic peak, pc: cathodic peak)
Figure S6. Ionic conductivity profiles of different electrolytes (EMITFSI, 1 M LiTFSI/EC+DEC, 0.1 M EMITFSI/EC+DEC, and 0.1 M LiTFSI/EC+DEC) measured at temperature from 40°C to −10°C. For the diluent electrolyte of 0.1 M EMITFSI or 0.1 M LiTFSI in the same mixed solvent (EC+DEC), the former showed even higher ionic conductivity than the latter, although the ionic size of EMI+ (0.294 nm) was much larger than nude Li+ (0.076 nm). This was probably because the unsolvated EMI+ processes higher diffusion coefficient ($D$) than solvated Li+, according to the ionic conductivity formula, $\sigma=nq^2D/KT$ ($\sigma$: ionic conductivity; $n$: ionic concentration; $q$: ionic electrical charge; $D$: diffusion constant; $K$: Boltzmann's constant; $T$: absolute temperature).
Figure S7. Nyquist plots of the PI5/PTPAn full-cell with EMITFSI electrolyte after 1st, 2nd, 10th, and 100th discharge process. The inset was the equivalent circuit used to fit the EIS data, where $R_s$, $R_{ct}$, CPE, and $W$ represented solution resistance, charge transfer resistance, constant phase element, and Warburg impedance, respectively. The $R_{ct}$ increased gradually from $13.8 \, \Omega$ to $23.9 \, \Omega$ during 100 cycles, indicating that the side reaction was not serious and the electrode status was relatively stable to sustain long-term cycling tests.
Figure S8. The differential (dQ/dV) curve calculated from the typical charge/discharge voltage profile of PI5/PTPAn full-cell with EMITFSI electrolyte (Figure 3B). The curve showed two pairs of symmetric redox peaks located at 1.02/0.91 V (a/c) and 1.72/1.61 V (b/d), respectively, with only a small gap of 0.11 V for both pairs. This was reasonable because either PI5 anode or PTPAn cathode undergone a highly reversible two-step redox process in the EMITFSI electrolyte (Fig. 2I and 2J).
Figure S9. Nyquist plots of the PI5/PTPAn full-cell with EMITFSI electrolyte after the 10th discharge process at different temperatures and the corresponding equivalent circuit pattern. As the temperature was decreased from 30°C to 10°C and −10°C, the $R_s$ grew from 4.09 Ω to 6.29 Ω and 14.2 Ω, while the $R_{ct}$ grew from 18.9 Ω to 25.3 Ω and 47.7 Ω, indicating the lowering of electrolyte ionic conductivity and slowing of electrochemical reaction kinetics at lower temperature.
Figure S10. The cycling performance (A) and typical voltage profiles (B, from the 50th cycle) of P15/PTPAn full-cell with different pure ion liquid electrolytes of EMITFSI, BMPTFSI, and ATEATFSI, respectively. Despite the appearance of initial cycles of “activation process” and the slight shape differences in voltage curves, the full-cell showed similar electrochemical behavior with BMPTFSI or ATEATFSI, as with EMITFSI electrolyte, indicating that the concept of metal-free battery was applicable for different pure ion liquid electrolytes.
**Figure S11.** The ionic conductivity profiles of different pure ion liquid electrolytes (EMITFSI, BMPTFSI, and ATEATFSI) at temperature from 40°C to −10°C. Among the three kinds of ion liquids, EMITFSI showed the highest ionic conductivity, which was about one order of magnitude higher than that of ATEATFSI. This could explain the battery performance difference shown in Figure S10 and why we chose EMITFSI as the representative pure ion liquid electrolyte to demonstrate our metal-free battery concept.
Figure S12. Nyquist plots of the PI5/PTPAn full-cell with different pure ion liquid electrolytes after the 10th discharge process and the corresponding equivalent circuit pattern. As EMITFSI was replaced by BMPTFSI and ATEATFSI, the $R_s$ was obviously increased from 4.09 $\Omega$ to 10.3 $\Omega$ and 22.9 $\Omega$, while the $R_{ct}$ was increased from 18.9 $\Omega$ to 34.4 $\Omega$ and 91.4 $\Omega$. This tendency was quite consisted with the battery performance shown in Figure S10 and the ionic conductivity shown in Figure S11, which could be probably ascribed to the tendency of increasing ionic radius from EMI$^+$ to BMP$^+$ and ATEA$^+$ (Fig. 1B).
Figure S13. The cycling performance (A, B) and typical voltage profiles (C, from the 3rd cycle; D, from the 30th cycle) of PI2 and PAQ half-cell with different electrolytes of 1 M LiTFSI/DOL+DME, 1 M LiTFSI/EC+DEC, and EMITFSI+0.01 M LiTFSI. The results indicated that PI2 also showed high electrochemical activity in pure ion liquid electrolyte, with even lower redox potential to elevate the voltage of the full-cell, but the cycling stability needed to be significantly improved. However, the reversible capacity of PAQ was much lower in pure ion liquid electrolyte than in conventional ether electrolyte, which might be related to the poor infiltration of EMITFSI with this polymer.
Figure S14. The cycling performance (A) and typical voltage profiles (B, from the 10th cycle) of PI2/PTPAn and PAQ/PTPAn full-cell with EMITFSI electrolyte. The average discharge voltage of PI2/PTPAn (1.67 V) and PAQ/PTPAn (1.40 V) were obviously improved compared to PI5/PTPAn system (1.31 V).
Table S1. Fitted values of elements in the equivalent circuit for EIS data of PI5/PTPAn full-cell in different status (Figure S7, S9, and S12).

| cycles  | Status temperature | electrolyte | $R_s$  | $R_{ct}$ | CPE-T   | CPE-P   | W-R | W-T | W-P |
|---------|--------------------|-------------|--------|----------|---------|---------|-----|-----|-----|
| 1st     | 30°C               | EMITFSI     | 4.16   | 13.8     | $6.59 \times 10^{-6}$ | 0.924  | 23.3 | 0.192 | 0.436 |
| 2nd     | 30°C               | EMITFSI     | 4.16   | 16.3     | $8.94 \times 10^{-6}$ | 0.898  | 28.1 | 0.382 | 0.451 |
| 10th    | 30°C               | EMITFSI     | 4.09   | 18.9     | $1.11 \times 10^{-5}$ | 0.883  | 30.0 | 0.462 | 0.454 |
| 100th   | 30°C               | EMITFSI     | 4.01   | 23.9     | $7.58 \times 10^{-6}$ | 0.916  | 40.4 | 0.335 | 0.433 |
| 10th    | 10°C               | EMITFSI     | 6.29   | 25.3     | $2.70 \times 10^{-5}$ | 0.809  | 45.3 | 0.845 | 0.452 |
| 10th    | -10°C              | EMITFSI     | 14.2   | 47.7     | $6.43 \times 10^{-6}$ | 0.893  | 26.2 | 0.0611 | 0.299 |
| 10th    | 30°C               | BMPTFSI     | 10.3   | 33.4     | $7.46 \times 10^{-6}$ | 0.893  | 32.4 | 0.161 | 0.361 |
| 10th    | 30°C               | ATEATFSI    | 22.9   | 91.4     | $8.13 \times 10^{-6}$ | 0.879  | 127  | 1.27  | 0.415 |