Universal quinone electrodes for long cycle life aqueous rechargeable batteries

Yanliang Liang1, Yan Jing1, Saman Gheytani1, Kuan-Yi Lee1, Ping Liu2, Antonio Facchetti3* and Yan Yao1,4*

Aqueous rechargeable batteries provide the safety, robustness, affordability, and environmental friendliness necessary for grid storage and electric vehicle operations, but their adoption is plagued by poor cycle life due to the structural and chemical instability of the anode materials. Here we report quinones as stable anode materials by exploiting their structurally stable ion-coordination charge storage mechanism and chemical inertness towards aqueous electrolytes. Upon rational selection/design of quinone structures, we demonstrate three systems that coupled with industrially established cathodes and electrolytes exhibit long cycle life (up to 3,000 cycles/3,500 h), fast kinetics (≥20C), high anode specific capacity (up to 200–395 mAh g−1), and several examples of state-of-the-art specific energy/energy density (up to 76–92 Wh kg−1 / 161–208 Wh l−1) for several operational pH values (~1 to 15), charge carrier species (H+, Li+, Na+, K+, Mg2+), temperature (~35 to 25 °C), and atmosphere (with/without O2), making them a universal anode approach for any aqueous battery technology.

The increasing demand for integration of electricity generated from renewable energies into the grid and electrification of transportation vehicles call for batteries that are environmentally friendly, safe, inexpensive, and long lasting. Aqueous rechargeable batteries featuring low-cost and nonflammable water-based electrolytes are intrinsically safe and do not rely heavily on the protection from complex battery management systems, thereby providing robustness and cost advantages over competing lithium-ion batteries that use volatile organic electrolytes and are responsible for recent catastrophic explosions. However, state-of-the-art aqueous rechargeable batteries show short cycle life and fall short of meeting large-scale applications where frequent replacement of batteries is undesirable.

The anode materials have been the cycle-life-limiting component for most, if not all, aqueous rechargeable batteries. For example, lead-based acidic batteries are inexpensive and reliable but have poor cycle life (200 cycles for deep cycling) due to the premature ageing of the lead (Pb) anode into a thick PbSO4 passivation layer. No other faradaic electrode material has been discovered to work as anode for acid batteries. Recent efforts to substitute Pb with non-faradaic activated carbon (AC) extend cycle life at the cost of ~60% reduction in specific energy. Another established family of aqueous rechargeable batteries is nickel-based alkaline batteries, including nickel–iron, nickel–cadmium, nickel–zinc, and nickel–metal hydride (MmH) batteries, which consist of the same nickel hydroxide (Ni(OH)2) cathode but varying anodes. However, iron, cadmium, and zinc anodes undergo dissolution–precipitation, while MmH volume expansion–contraction during battery charge–discharge cycling negatively impacts cycle life. The comparatively most stable MmH is made of rare earth metals and the expensive cobalt, with the latter accounting for one-half of the total material cost for a nickel–MmH battery. The emerging aqueous lithium-ion batteries (ALIBs) use less corrosive, near-neutral electrolytes and store charge via an ion intercalation mechanism where the structure of the electrode material does not alter significantly. Therefore, ALIBs could achieve a much longer cycle life than those of their commercial acidic and alkaline siblings. However, the only two practical anodes for ALIBs, lithium metal phosphates and polyimides, are unstable to oxygen and alkalis, respectively, severely restricting applications. Finally, recent developments of aqueous sodium-ion batteries highlight the use of low-cost and highly stable AC and Prussian Blue anodes; however, both approaches exhibit very low capacities (~50 mAh g−1) and with the lack of anode materials meeting all requirements, the application of aqueous rechargeable batteries for large-scale energy storage has been stagnant. The major challenges for aqueous anodes lie in the search for materials that are chemically robust towards aqueous electrolytes, easily accessible and inexpensive, have high specific capacity, store charge via a structurally reversible/stable mechanism, and fit in the electrochemical stability window of the electrolyte solvent, thus water.

Quinones, of which the most common motif comprises the 1,2-benzoquinone or 1,4-benzoquinone units (Fig. 1), have been considered for nonaqueous metal-ion batteries and aqueous flow batteries. These compounds store charge via an ‘ion-coordination’ mechanism where the cations coordinate to the negatively charged oxygen atoms upon electrochemical reduction of the carbonyl groups, and uncoordinate reversibly during the reverse oxidation (Fig. 1; not to be confused with quinone derivatives where the carbonyls are converted to redox-inactive groups). Properly functionalized quinones have shown excellent chemical stability and their reduction potentials can be readily tuned from 1.7 to 3.2 V versus Li on molecular engineering. Despite these advantages, there are only very few pioneering reports on their use in aqueous batteries. Alt et al. investigated tetrachloro-1,4-benzoquinone (TCBQ) in 2 M sulfuric acid and demonstrated...
We first report on the selection of suitable quinone structures using an acidic medium and then demonstrate that three quinones are excellent candidates for broad applicability. Details of quinone synthesis are reported in the Supplementary Information (see Synthesis of quinones and Supplementary Figs 1–13 for quinone structural characterization). Briefly, the synthesized quinones (~5 µm in size, Supplementary Fig. 14) were mixed with conductive carbons and pressed into disk electrodes with an active mass ranging from 2.2 to 37 mg cm⁻². Electrode/cell fabrication and measurements are described in the Methods section. Coin cells are typically used for both three-electrode half-cell and two-electrode full-cell measurements. Table 1 collects the major performance parameters for the optimal quinones fabricated here as well as those of reference materials operating in acidic (Entries 1–3), slightly acidic (Entry 4), neutral (Entries 5–8), slightly alkaline (Entry 9), and alkaline (Entry 10–12) electrolyte solutions.

**Quinone-based acidic batteries**

In preliminary experiments the electrochemical reaction of several simple quinones in 4.4 M sulfuric acid (a close approximation of the ‘battery acid’ used in commercial Pb-acid batteries) was studied. The molecular structures and the potential–capacity data for the more promising quinones are shown in Fig. 2a. Most quinones show a reduction potential within 0.15–0.53 V versus SHE, and theoretical specific capacities of 250–400 mAh g⁻¹. Because the cell voltage is determined by the potential difference between the anode and the cathode, these quinone anodes will enable full-cell voltages of 1.25–1.63 V when coupled with a PbO₂ cathode (1.78 V versus SHE). Such voltages are comparable to the 1.30 V for the AC–PbO₂ hybrid and 25–45% lower than the 2.1 V for Pb–PbO₂. From the plots of Fig. 2b and Supplementary Fig. 15 the plateau-shaped voltage profiles for these quinones clearly provide a stable voltage output, which is far more desirable than the sloping profile for the non-faradaic AC. Among these candidates, pyrene-4,5,9,10-tetrae (PTO, red structure in Fig. 2a) stands out due to the combination of high anode specific capacity (up to 200–250 mAh g⁻¹), fast kinetics (67–84% charge/discharge capacity at 10C), and state-of-the-art specific energy/energy densities (up to 76–92 Wh kg⁻¹/161–208 Wh l⁻¹) for several pH conditions (pH 1 to 15), charge carrier species (H⁺, Li⁺, Na⁺, K⁺, Mg²⁺), temperature (−35 to 25 °C), and atmosphere (with/without O₂).

**Figure 1 | Schematics of aqueous rechargeable batteries based on quinone anodes operating at different pH values with the indicated corresponding redox chemistries.** On the anode side (left panel) is shown the redox/ion-coordination reaction of 1,2-benzoquinone (left) and 1,4-benzoquinone (right) structures. Quinone anodes can be used in acid, neutral, and alkaline electrolytes (middle panel). Depending on the choice of the electrolyte, a wide range of cathode materials including the industrially mature PbO₂ (acidic), LiMn₂O₄ (neutral), and Ni(OH)₂ (alkaline) can be used to complete a battery. The corresponding cathode reactions are shown in the right panel.
redox potential than that of Pb, resulting in uncompromised specific energy. According to the reactions for PTO–PbO (equation (1)) and Pb–PbO₂ (equation (2)) batteries:

\[
\text{PTO} + 0.5\text{PbO}_2 + \text{H}_2\text{SO}_4 \rightleftharpoons \text{PbSO}_4 + 0.5\text{PTO} + 2\text{H}_2\text{O} \quad (1)
\]

\[
\text{PbO}_2 + \text{Pb} + 2\text{H}_2\text{SO}_4 \rightleftharpoons 2\text{PbSO}_4 + 2\text{H}_2\text{O} \quad (2)
\]

a PTO–PbO₂ battery requires 50% less sulfuric acid and Pb to store the same amount of charge. The specific energy/energy density of a PTO–PbO₂ battery is 76 Wh kg⁻¹/161 Wh l⁻¹ based on active electrode materials and electrolyte (including both sulțe H₂SO₄ and solvent H₂O). These values are virtually identical to the 78 Wh kg⁻¹/171 Wh l⁻¹ for Pb–PbO₂ and much higher than the 38 Wh kg⁻¹/37 Wh l⁻¹ for AC–PbO₂. Note that the significantly lower compacted density of PTO than that of Pb (1.65 versus 4.35 g cm⁻³) does not compromise energy density significantly because PTO, due to its very high specific capacity, constitutes only a considerably small weight fraction (15 wt%) in the battery (compare with 28 wt% for Pb in Pb–PbO₂; the weight fraction breakdown of all battery configurations involved in this work is summarized in Supplementary Table 1). The reduced H₂SO₄ consumption also contributes to the substantial energy density.

A PTO–PbO₂ cell cycle at 100% depth of discharge at 2C charge–discharge rate (1C = 400 mA g⁻¹) for more than 1,500 cycles (>1,200 h) without obvious decrease in capacity and voltage (Fig. 2c and Supplementary Fig. 16). The average coulombic efficiency for the 1,000th–1,500th cycles is 99.8%. The cell is also stable during a longer-term cycling at a low current density of C/5, with 88% capacity retention after 200 cycles (>1,700 h, Supplementary Fig. 17). The stable cycling performance is attributed to three properties of PTO. First, the solubility of PTO in the electrolyte is low (4.7 × 10⁻⁴ M; compare with 1.5 × 10⁻³ M for PbSO₄); quinones with higher solubility in acid, for example, 2,5-dihydroxy-1,4-benzooquinone (DHBQ), suffer from fast capacity decay (Supplementary Fig. 18). Second, PTO shows an appreciably high proton diffusivity of 2.32 × 10⁻⁹ cm² s⁻¹ (Supplementary Fig. 19), and therefore does not form ionically insulating layers like PbSO₄ does. Third, the electrochemical activity for the charge–transfer reaction of PTO is much higher than that for Pb, as characterized by the much higher exchange current density for a PTO electrode (516.6 mA g⁻¹) than that for Pb (1.41 mA g⁻¹) (ref. 35) (Supplementary Fig. 20). The PTO cell retains 84% of the maximum capacity at a very high charge/discharge rate of 20C (Fig. 2d), sufficient for the demanding scenarios for vehicle batteries such as engine starting (up to 18C pulse discharge) and regenerative breaking (up to 3C pulse charge)⁷⁻⁸. Therefore, we have demonstrated that the PTO anode overcomes the passivation and kinetic problems for Pb without sacrificing specific energy/energy density like AC does.

**Quinone-based neutral batteries**

The results above prompted us to explore quinone anodes for batteries with neutral electrolytes, in particular ALIBs. We found that PTO is soluble in neutral electrolytes and undergoes fast capacity decay (Supplementary Fig. 21), therefore we have designed a polymerized version of PTO, namely PPTO (Fig. 3a), to achieve sufficient insolubility (Entry 5). The electrochemical performance of PPTO is compared with lithium titanium phosphate (Li₅Ti₃(PO₄)₄), which is the state-of-the-art anode material for ALIBs (Entry 7). PPTO shows more than double the specific capacity of Li₅Ti₃(PO₄)₄ (229 versus 103 mA g⁻¹) albeit 0.46 V higher reduction potential (Fig. 3a). A PPTO–LiMnO₂ cell shows an average voltage of 1.13 V with a specific energy/energy density of 92 Wh kg⁻¹/208 Wh l⁻¹, which are comparable to those for Li₅Ti₃(PO₄)₄–LiMnO₂ (90 Wh kg⁻¹/243 Wh l⁻¹). Remarkably, PPTO retains 80% of the initial capacity and shows no obvious change in voltage profile after 3,000 deep cycles at 1C (280 mA g⁻¹, Fig. 3c and Supplementary Fig. 22), making it amongst the most stable anode materials for ALIBs discovered to date. Like PTO, PPTO delivers fast electrode kinetics, with 60% of the maximum capacity delivered at 20C charge/discharge (Supplementary Fig. 23a). It is noteworthy that the difference between charge and discharge potentials does not increase with increasing current density, translating into consistently high energy efficiency even during fast charging (Supplementary Fig. 23b).

An important advantage of PPTO over Li₅Ti₃(PO₄)₄ and other anode materials reported for ALIBs is its ability to support the ‘oxygen cycle’, a common phenomenon for all commercial aqueous rechargeable batteries. The oxygen cycle is a built-in safety mechanism where oxygen evolves from water oxidation by the cathode at high charge states, diffuses across the electrolyte, and is reduced by the charged anode (Fig. 3c). Note, the pH of the electrolyte medium decreases/increases near the cathode/anode due to H²⁺/OH⁻ formation, respectively. This mechanism spontaneously protects this type of cells from overcharge and helps to synchronize the charge state of all cells in a battery pack. Previously reported ALIBs do not have a proper anode to support the oxygen cycle. Li₅Ti₃(PO₄)₄ quickly decays in the presence of oxygen in the electrolyte⁹. Although polyimides are compatible with oxygen

| Table 1 | Electrochemical characteristics, battery configuration and performance parameters of quinones versus other materials. |
|---|---|---|---|---|---|---|---|
| Entry | pH | Anode | Charge carrier* | Reduction potential† (V versus SHE) | Specific capacity‡ (mAh g⁻¹) | Cathode | Specific energy† (Wh kg⁻¹) | Energy density† (Wh l⁻¹) | Cycling stability (capacity%@cycle number (cycled time)) |
| 1 | –1 | PTO | H⁺ | 0.51 | 395 | PbO₂ | 76 | 161 | 96%@1,500 (1,200 h) This work |
| 2 | –1 | Pb | SO₄²⁻ | –0.34 | 129 | PbO₂ | 78 | 171 | 80%@240 (4,500 h)³ | 7 |
| 3 | –1 | AC | H⁺ | 0.48 | 50 | PbO₂ | 83 | 37 | 83%@3,000 (5,500 h) 13 |
| 4 | 3–4 | PPTO | Mg²⁺ | 0.04 | 144 | CuHCF | 25 | 45 | 66%@1,000 (1,600 h) This work |
| 5 | 7 | PPTO | Li⁺ | –0.06 | 229 | Li₂MnO₄ | 92 | 208 | 80%@3,000 (3,500 h) This work |
| 6 | 7 | PPTO | Na⁺ | –0.07 | 201 | NaₓV₂(PO₄)₃ | 30 | 80 | 79%@80 (150 h) This work |
| 7 | 7 | Li₅Ti₃(PO₄)₄ | Li⁺ | –0.52 | 103 | Li₂MnO₄ | 90 | 243 | 89%@1,200 (160 h) 20 |
| 8 | 7 | Polyimide | Li⁺ | –0.19 | 160 | Li₂MnO₄ | 89 | 186 | 76%@50,000 (950 h) 22 |
| 9 | 13 | PPTO | Li⁺ | –0.06 | 195 | LiCoO₂ | 66 | 180 | 83%@700 (1,200 h) This work |
| 10 | 15 | PAQS | K⁺ | –0.60 | 200 | Ni(OH)₂ | 79 | 138 | 88%@1,350 (2,300 h) This work |
| 11 | 15 | MnM | H⁺ | –0.81 | 300 | Ni(OH)₂ | 180 | 597 | 80%@300 (n/a) 45 |
| 12 | 15 | Zn | OH⁻ | –1.19 | 500 | Ni(OH)₂ | 290 | 714 | 84%@300 (800 h) 7 |

*For the anode material. † Determined from three-electrode galvanostatic charge–discharge measurements. ‡ For a battery consisting of anode/cathode materials and (if involved in the reaction) electrolyte. The unusually long time for the small cycle number is due to the slow discharge (C/5) and charge (C/16) required for sustaining cycle life.
Figure 2 | Quinone-based acidic batteries. a. Chemical structure of selected quinones investigated in this study and their reduction potential and theoretical capacity based on one-carbonyl one-electron reduction. The practical specific capacities of AC and Pb are shown for comparison. Dashed line indicates the reduction potential of PbO$_2$. b. Galvanostatic charge–discharge profiles for PTO (40 mA g$^{-1}$), AC (50 mA g$^{-1}$), Pb (10 mA g$^{-1}$), and PbO$_2$ (20 mA g$^{-1}$). c. Capacity retention of a PTO–PbO$_2$ cell during galvanostatic cycling at 2C. d. Capacity of a PTO–PbO$_2$ cell charged/discharged at C/10–20C. Inset shows the voltage profiles at selected C rates. All data were collected in 4.4 M H$_2$SO$_4$. | VOL 16 | AUGUST 2017 | www.nature.com/naturematerials

(Entry 8) (ref. 37) they are prone to rapid hydrolysis in the locally alkaline environment resulting from oxygen reduction: naphthalene diimides have half-lives of seconds in moderately alkaline solutions (for example, pH 12) (ref. 38). In contrast, quinones have been reported to show excellent stability in both oxygen$^{27}$ and alkaline solutions (for example, 5 M KOH) (ref. 30). PPTO in particular proves to be sufficiently stable in a fairly alkaline electrolyte (pH 13), where it is cycled for more than 1,200 h with a 83% capacity retention (vide infra). Such cycling stability originates from the combination of quinone core chemical inertness, PPTO poor solubility, and amide linkage resistance towards hydrolysis in these conditions. Amides of aliphatic acids, which are analogous to PPTO, have half-lives of 240–270 years at neutral pH and about 2–3 years at a pH of 12 (ref. 39). Note that these half-lives are for amides dissolved in solutions (homogeneous reactions), which is a physical state completely different than that of our insoluble PPTO (solid state). Heterogeneous reactions (and hydrolysis in this case) can be orders of magnitude less efficient, if negligible at all. Furthermore, it is reasonable that an anode spends less than 10% of its lifetime under basic conditions, considering that the oxygen cycle takes place only during the high-voltage charging process, thus one can expect a further lifetime extension. If desired, even higher stability may be possible by substituting the intrinsically base-sensitive amide linkage with more stable bridge units/groups via alternative polymerization methods. Reduced (charged) PPTO is reversibly oxidized by oxygen to regenerate PPTO at its discharged state with both the voltage profile and capacity preserved (Fig. 3d). In fact, this oxygen compatibility is a general property of all quinones featured in this work regardless of the pH of the electrolytes (−1 to 15; Supplementary Fig. 24). The oxygen consumption capability of quinones makes it possible to use high-voltage cathode materials$^{46}$ that approach the potential for the oxygen evolution reaction (OER), enabling high voltages and specific capacities (Supplementary Fig. 25). An ALIB combining the high-capacity PPTO anode and a high-voltage cathode will yield up to 63% higher specific energy than those of the state-of-the-art ALIBs.

Other aqueous metal-ion batteries enabled by PPTO
In addition to the neutral ALIB described above, we were able to prototype several other interesting aqueous metal-ion batteries based on a PPTO anode and near-neutral electrolytes. This is possible due to the high tolerance of PPTO for electrolytes with different pH and cationic species. Thus, an alkaline ALIB featuring an alkaline Li$_2$SO$_4$ electrolyte (pH = 13), PPTO anode, and LiCoO$_2$ cathode (Entry 9) exhibits a high anode specific capacity of 200 mAh g$^{-1}$, an energy density of 180 Wh l$^{-1}$, and retains 83% of the initial capacity for more than 700 cycles/1,200 h (Supplementary Fig. 26). Being able to use relatively alkaline electrolytes significantly expands the choice of cathode materials which would otherwise suffer from proton-induced dysfunction in neutral electrolytes$^{41}$. Furthermore,
we replaced lithium in ALIBs with the low-cost and Earth-abundant sodium to construct aqueous sodium-ion batteries (ASIBs). This technology may find application in areas where cost and stability, and not energy density, may be of primary importance. A prototype quinone-based ASIB with the PPTO–sodium vanadium phosphate (Na3V2(PO4)3) configuration shows high anode specific capacity (201 mAh g−1) and 79% retention after 80 cycles in a neutral sodium nitrate electrolyte (Entry 6, Supplementary Fig. 27), although the energy density (80 Wh l−1) is modest as limited by the low specific capacity and potential of Na3V2(PO4)3 (52 mAh g−1 at 0.65 V versus SHE). Finally, we have explored for the first time the feasibility of an aqueous magnesium-ion battery (AMIB). The success of an AMIB relies on the acid compatibility of PPTO (Entry 4 and Supplementary Fig. 28) considering that all aqueous magnesium electrolytes are noticeably acidic due to partial Mg2+ hydrolysis. We have assembled an AMIB using PPTO as the anode and a Prussian blue analogue/magnesiated copper hexacyanoferrate (MgCuHCF) (ref. 43) as the cathode which shows stable cycling performance (66% retention after 1,000 cycles) and uncommonly fast kinetics for a rechargeable magnesium battery (85% of maximum capacity at 2C; 1C = 140 mAh g−1; Supplementary Fig. 29).

Quinone-based alkaline batteries

We further expanded quinone anodes in even more alkaline electrolytes (pH > 14) in conjunction with the highly industrially mature Ni(OH)2/nickel oxyhydroxide (NiOOH) cathode (Entry 10). Since alkaline electrolytes have low-lying HER potentials, our quinone of choice for an alkaline battery is an anthraquinone-based polymer, poly(anthraquinonyl sulfide)44 (PAQS), which has a 0.54 V more negative reduction potential than that of PPTO. The reactions for PAQS–Ni(OH)2 (equation (3)) and MmH–Ni(OH)2 (equation (4)) are:

\[
\text{Ni(OH)}_2 + (0.5/n)\text{PAQS} + \text{KOH} \rightleftharpoons \text{NiOOH} + (0.5/n)\text{PAQS-K}_2 + 2\text{H}_2\text{O} \tag{3}
\]

\[
\text{Ni(OH)}_2 + \text{Mm} \rightleftharpoons \text{NiOOH} + \text{MmH} \tag{4}
\]

where \(n\) is the degree of polymerization of PAQS. At room temperature, PAQS shows a specific capacity of 200 mAh g−1 in 10 M potassium hydroxide (KOH) (Fig. 4a). Because of the consumption of the KOH electrolyte, the specific energy/energy density of PAQS–Ni(OH)2 (79 Wh kg−1/138 Wh l−1) are not as high as those of MmH–Ni(OH)2 (∼180 Wh kg−1/597 Wh l−1; Entry 11) but comparable to those of PTO–PbO2. By comparing the voltage profiles of PAQS and MmH electrodes it is clear that there is much room for further lowering the reduction potential of the quinone anode before hydrogen would evolve. For example, a quinone with the capacity of PTO but a reduction potential 0.2 V lower than that of PAQS would yield much higher specific energy/energy density of 115 Wh kg−1/203 Wh l−1. A PAQS–Ni(OH)2 cell cycled at 100% depth of discharge for 1,350 cycles at 1C (200 mAh g−1) with an 88% capacity retention (Fig. 4b).

The absence of noticeable change in the charge–discharge profile (Supplementary Fig. 30) after prolonged cycling reflects the excellent stability of the electrode in these extreme conditions. Such stability
outperforms those of the most optimized metal hydrides (80% retention after 1,300 cycles)\(^6\). Like PPTO, PAQS also functions with various metal cations. Sodium hydroxide and lithium hydroxide are both plausible electrolytes for a PAQS–Ni(OH)\(_2\) battery in addition to KOH (Supplementary Fig. 31). Such a tolerance allows the use of mixed hydroxide electrolytes to customize battery performance, a common practice for the nickel–metal hydride battery technology\(^46\).

PAQS also addresses one of the major disadvantages of nickel–MmH batteries—that is, drastic reduction in electrochemical performance at low temperatures. Most commercial MmH–Ni(OH)\(_2\) batteries deliver only ∼50% of the nominal energy and can rarely discharge beyond C/2 at −25 °C (ref. 47). This performance reduction originates from the large charge-transfer resistance for the redox reaction of MmH, which increases by 100× as temperature decreases from 25 to −40 °C (ref. 48). In comparison, the charge-transfer resistance for PAQS only doubles from 25 to −25 °C (Fig. 4d and Supplementary Fig. 33). The activation energy for the redox reaction of PAQS, calculated from the Arrhenius equation of the charge-transfer resistance versus temperature dependence, is as low as 8 kJ mol\(^{-1}\) (compare with 39 kJ mol\(^{-1}\) for MmH), implying little performance dependence on temperature. The exchange current density of the two electrodes reiterates the different dependence of the electrochemical activity on temperature for the two materials (Fig. 4c and Supplementary Fig. 32b). Consequently, PAQS experiences a mere 7% reduction in capacity as the temperature decreases from 25 to −25 °C, and the voltage gap between charge and discharge at C/2 (1C = 225 mA g\(^{-1}\)) increases only slightly from 101 to 127 mV (Fig. 4d). Importantly, the rate capability of PAQS is consistently high regardless of temperature, with 93 and 86% capacity remaining at 10C charge/discharge at 25 and −25 °C, respectively (Fig. 4d and Supplementary Fig. 33).

**Challenges and opportunities of quinone anodes**

Figure 3a summarizes the reduction potential versus pH of PTO, PPTO, and PAQS electrodes in a Pourbaix diagram. The media at which our quinones operate span a very wide pH range, from strongly acidic through neutral to strongly alkaline. From the plot it is clear that at every pH value these quinones approach the HER potential and still have room for further improvement. For −1 < pH < 1, the reduction potentials of all three quinones are pH-dependent and decrease by 59 mV per pH increment, indicating a proton storage mechanism where one proton is stored for every injected electron and vice versa. As the pH increases above 3, the concentration of proton decreases to such an extent that metal-ion storage becomes dominant and the reduction potential becomes pH-independent. Indeed, compositional analysis via inductively coupled plasma method for a PPTO electrode charged (electrochemically reduced) in a LiSO\(_4\) (pH 7) electrolyte solution was performed and confirmed that virtually all (∼97%) of the injected charge was balanced by lithium ions instead of protons (see details in Methods).

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**Figure 4 | Quinone-based alkaline batteries.** a. Galvanostatic charge–discharge profiles of PAQS (100 mA g\(^{-1}\)), MmH (150 mA g\(^{-1}\)), and Ni(OH)\(_2\) (40 mA g\(^{-1}\)). b. Capacity retention of a PAQS-Ni(OH)\(_2\) cell during galvanostatic cycling at 1C. c. Exchange current density and charge-transfer resistance of PAQS and MmH electrodes as a function of temperature (data for MmH retrieved from ref. 48). d. Capacity of a PAQS-Ni(OH)\(_2\) cell charged/discharged at C/2–20C at 25 °C and C/2-10C at −25 °C. Inset shows the voltage profiles at C/2. All data here were collected in 10 M KOH.
Finally, Fig. 5b and Supplementary Table 2 compare some of the most important electrode parameters for quinones and competing commercial and emerging anode materials, including Pb, AC (both for acidic batteries), LiTi$_2$(PO$_4$)$_3$, polyimide (both for ALIBs), MmH, and Zn (Entry 12) (both for alkaline batteries). Quinone anodes deliver specific capacity and energy density values that can match or exceed those of several existing anode materials (Supplementary Fig. 34a). However, structural modification of these quinoid cores/structures with, for instance, simple electron-donating organic functionalities can overcome one of the major limitations of the three examples reported here, which is the relatively high reduction potential. Thus, optimized quinones retaining PTO specific capacity but with lower reduction potentials combined with reasonably improved cathodes may further increase the specific energy/energy density of quinone-based batteries to 115–228 Wh kg$^{-1}$/203–522 Wh l$^{-1}$, most of which values are unachievable with other existing anodes (Supplementary Fig. 34b). Furthermore, polymerization protocols affording macromolecules with even higher molecular weights, thus lower solubility, as well as different quinone unit connectivities could further enhance cell stability. However, our quinones already clearly demonstrate excellent cycle life and without availability/cost/environmental issues that some heavy metals and phosphates experience$^{49,50}$. Their fast electrode kinetics and efficient charge transport ensure high power and fast chargeability even at low temperatures; hence, overcoming some of the major obstacles for existing acid and alkaline batteries. Their support for the oxygen cycle further adds the critically important reliability to neutral aqueous rechargeable batteries, paving the way towards their practical application.

In conclusion, this work demonstrates that regardless of the pH of the medium, charge carrier species, temperature, and atmosphere, quinones can be designed to operate as stable anode materials. Quinone anodes can be coupled with any cathode/electrolyte combinations for aqueous rechargeable batteries. They enable batteries with long cycle life, high capacity, fast kinetics, as well as several examples of excellent energy density values, rendering them viable contenders for large-scale energy storage. Furthermore, the possibility of structural modifications of quinone cores with electron-withdrawing and/or electron-donating substituents and variation of the polymerization protocols provides an opportunity to improve cell performance and stability further.

**Methods**

Methods, including statements of data availability and any associated accession codes and references, are available in the online version of this paper.
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Author contributions

Y.Y. and Y.L. conceived this work; Y.L., P.L., and Y.Y. designed the experiments; Y.L., Y.J., and S.G. synthesized the materials; Y.L., Y.J., S.G. and K.-Y.L. carried out the electrochemical measurements; A.F. and Y.L. performed the battery material cost analysis; Y.Y. and A.F. directed the project; Y.L., A.F. and Y.Y. co-wrote the paper; all authors analysed the results and commented on the manuscript.

Additional information

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Competing financial interests

Y.Y. and Y.L. are inventors of patent applications (US/2014/0308581, US/2016/0049659) on the neutral and alkaline batteries described herein. Y.Y., Y.L., S.G. and Y.J. are inventors of a patent application (US/62/165,377) on the acid batteries. A.E. has no competing interests.
Methods

Fabrication of quinone electrodes. Quinones shown in Fig. 2a were mixed with hydrophilic multi-walled carbon nanotubes (COOH-functionalized, 10–30 μm in length, 2.5nm inner diameter, US Research Nanomaterials) in a 1:1 ratio (all ratios are reported by weight unless specified otherwise) with the aid of H₂O₂, dried under vacuum, and pressed to form disk electrodes with the areal mass loading being 16 mg cm⁻². PPTO, Super P carbon (TIMCAL), and polytetrafluoroethylene (MTI) were mixed in a 6:3:1 ratio with the aid of ethanol, pressed into a stainless steel mesh disk (type 316), and dried in vacuum. The areal mass loading of PPTO in the electrode is 2.2 mg cm⁻². PAQS, Super P carbon, and polytetrafluoroethylene were mixed in a 7:2:1 ratio with the aid of H₂O and resulting mixture was pressed and dried under vacuum to form electrodes. The areal mass loading of PAQS in the electrode is 37 mg cm⁻². The Pb electrode was cut from a commercial Pb-acid battery. Activated carbon (AC) cloth (KYNON) was used as the electrode as received. Carbon-coated LiTi₄(PO₄)₃ was synthesized as previously reported⁴. The LiTi₄(PO₄)₃ electrode was fabricated via a procedure similar to that for PPTO but with a 7:2:1 ratio. The Mischmetal electrode was fabricated by sputtering a slurry of MnNi₃Co₃.₆Mn₀.₄Al₂₋X(N(CXTC), Ni (Ts255), carboxymethyl cellulose, polyacrylate sodium, and styrene-butadiene rubber (10:1:0.009:0.012:0.525) in H₂O onto nickel foam followed by drying and pressing. The electrode was activated by galvanostatically charging-discharging at 75 mA g⁻¹ for 10 cycles and then 150 mA g⁻¹ for 5 cycles in 8 M KOH.

Half-cell measurements. Three-electrode half-cell measurements were performed to determine the dependence of reduction potentials of quinones on pH and the voltage profiles of individual electrode materials. In particular, the former was measured by cyclic voltammetry and the latter by galvanostatic charge discharge. Coin cells (CR2032) were used to perform the three-electrode measurements. The electrodes of interest were placed at the positive side as the working electrode. Activated carbon cloth served as the counter electrode at the negative side. For pH 1 to 13, Ag/AgCl (0.197 V versus SHE) was used instead. The reference electrodes connected to the electrolyte via a hole at the negative side. For pH > 13, Ag/AgCl (0.197 V versus SHE) served as the reference electrode. For more alkaline electrolytes, Hg/HgO (0.098 V versus SHE) served as the reference electrode. In particular, the former was used for acid batteries; 2.5 M LiNO₃ was used instead. The reference electrodes connected to the electrolyte via a hole at the negative case. For pH > 13, Ag/AgCl (0.197 V versus SHE) served as the reference electrode. For more alkaline electrolytes, Hg/HgO (0.098 V versus SHE) served as the reference electrode. For pH > 13, Ag/AgCl (0.197 V versus SHE) served as the reference electrode. For more alkaline electrolytes, Hg/HgO (0.098 V versus SHE) served as the reference electrode. For more alkaline electrolytes, Hg/HgO (0.098 V versus SHE) served as the reference electrode. For more alkaline electrolytes, Hg/HgO (0.098 V versus SHE) served as the reference electrode.

Full-cell measurements. The cycling performance, rate capability, and temperature-dependent properties were measured with two-electrode full-cell set-ups. The quinone anode is the capacity-limiting component in each of the full cells. The cathodes were brought to 50% state of charge (SOC) at room temperature. The cycled PAQS–AC cell was brought to 50% SOC at room temperature. The cell was then brought to the desired temperature and left to rest for 30 min prior to measurements. Electrochemical impedance measurements were performed from 100 kHz to 5 mHz with a perturbation voltage of 3 mV. The charge-transfer resistance was fitted from the semicircle at mid frequency. The activation energy was calculated from either exchange current density or charge-transfer resistance using the Arrhenius equation.

Electrode composition analysis. The intercalating ion species in PPTO charged in 2.5 M Li₂SO₄ was analysed with the inductively coupled plasma (ICP) technique. The fabrication of electrode and cell followed the typical procedure described above, except that 5 wt% of carbon black was added to the electrode mixture as an inert internal reference. The cell was disassembled at the fully charged (liithiated) state. The electrolyte on the surface of the PPTO electrode was briefly absorbed with weighing paper. The mixture was scraped from the stainless steel mesh current collector, dried, and digested for analysis. There are two types of lithium ions in the electrode: the lithium ions coordinated to PPTO and those from residual Li₂SO₄. The latter is subtracted by measuring the concentration of sulfur: Li₂SO₄ is the only species in the cell that contains sulfur, and the atomic ratio of Li₂ is 2:1. The ratio of coordinated lithium to the host PPTO cannot be directly determined because none of the elements in PPTO (carbon, hydrogen, oxygen, and nitrogen) is measurable with ICP. The internal reference calcium carbonate is therefore used to indicate the PPTO concentration in the sample solution. The use of an internal reference ensures accurate measurement of lithium content despite incomplete transfer of the electrode material from the current collector.

Energy and power calculations. The specific energy of a cell configuration (Eₛ) is calculated as the product of the cell voltage (V₉₉) and cell specific capacity (Cₛₚ) following the recent review paper ‘Polymer-based organic batteries’ from U.S. Schubert’s group⁴. Eₛ = Cₛₚ × V₉₉ (5)

Cₛₚ is typically calculated from the specific capacities of cathode (C₉₉) and anode (Cₐ₉₉):

Cₛₚ = (C₉₉⁻¹ + Cₐ₉₉⁻¹)⁻¹ \quad (6)

where C₉₉ is calculated based on the weight of active materials—that is, the weight of inert components such as packaging materials, separator, conductive agent, current collectors, and so on is not included. Therefore Eₛ is the maximum specific energy that can be delivered by a cell configuration. A rough estimation of actual specific energy is to consider that the inert components add ~100% weight to active materials, thus halving the specific energy from the maximum. The weight of electrolytes needed to be included for calculation when the electrolyte is consumed in the battery reaction (that is, acid batteries of all forms and quinone–nickel batteries), thus Cₛₚ = (C₉₉⁻¹ + C₉₉⁻¹ + Cₐ₉₉⁻¹)⁻¹ \quad (7)

where Cₛₚ is the ‘apparent specific capacity of the electrolyte, which is defined as Cₛₚ = z × F/(Mₐ × c₋) \quad (8)

where Mₐ is the molecular weight of the solute that participates in the reaction (for example, H₂SO₄ and KOH), z is the mole number of electrons transferred with the consumption of one mole of electrolyte solute molecule (for example, z = 1 for Pb–PbO₂ and z = 2 for PPTO–PbO₂), F is the Faraday constant, and c₋ is the mass concentration of the electrolyte. V₉₉ is theoretically the difference between the potential of cathode (E₉₉) and anode (Eₐ₉₉):

V₉₉ = E₉₉ − Eₐ₉₉ \quad (9)

Experimentally, V₉₉ is usually obtained as the average voltage between charge and discharge. Specifically for plotting the Ragone plot (Supplementary Fig. 14a), the cell voltage is defined as the discharge voltage so as to reflect the change of output voltage as the current density changes. Because of the lack of current density-dependent voltage data for some cell configurations reported in literature, up to 10% overestimation of specific energy should be expected in the Ragone plot for non-quinone-based batteries. In the end, the universal equation for Eₛ is expressed as

Eₛ = (Cₛₚ⁻¹ + Cₛₚ⁻¹ + Cₛₚ⁻¹)⁻¹ × V₉₉ \quad (10)

Energy density (Eₑ) is defined as energy per total volume of cathode/anode materials and, if involved in the reaction, electrolytes:

Eₑ = | V₉₉ / (Vₗ + Vₐ + Vₑ) | \quad (11)

Eₑ = | (Cₛₚ × (Wₗ + Wₐ + Wₑ)) / (Vₗ/ρₗ + Vₐ/ρₐ + Vₑ/ρₑ) | \quad (12)

Eₑ = | (Cₛₚ × (Wₗ + Wₐ + Wₑ)) / (Vₗ/ρₗ + Vₐ/ρₐ + Vₑ/ρₑ) | \quad (13)
Equation (13) can be written as

$$W_{\text{v,cell}} = Q/C_{\text{v,cell}}$$  \hspace{1cm} (14)

The compacted density of the electrode materials is used where possible: PbO$_2$, 4.2 (ref. 55); Pb, 4.35 (ref. 55); Cu, 8.96 (ref. 56); PTO 1.65; 4.4 M KOH 1.255; LiMn$_2$O$_4$, 2.8 (ref. 57); LiCoO$_2$, 4.0 (ref. 57); LiTi$_2$(PO$_4$)$_3$, 2.6 (ref. 58); polyimide 1.58; PPTO 1.68; Ni(OH)$_2$, 2.6 (refs 59,60); MnH$_4$ 4.75 (ref. 60); PAQS 1.69; ZnO 2.25 (ref. 61); 10 M KOH 1.445. The theoretical density is used for CuHCF (1.8 (ref. 62)) because the compacted density is not found in the literature. The theoretical density of Na$_x$V$_2$(PO$_4$)$_3$F$_2$ (3.2 (ref. 63)) is used for Na$_x$V$_2$(PO$_4$)$_3$ because the lack of data for the latter. Specific power is the quotient of specific energy divided by the time it takes to discharge a cell completely. To demonstrate the potentially achievable specific energy in a cell configuration, several hypothetically plausible electrode materials are considered. ‘PbO$_2$ (90%)’ denotes PbO$_2$ with a utilization of 90% (ref. 64) instead of the typical 50–70% in commercial Pb-acid batteries. ‘Quinone’ refers to quinones with the specific capacity of PTO (395 mAh g$^{-1}$) and the reduction potential of anthraquinone (AQ) in acid (0.16 V versus SHE), LiTi$_2$(PO$_4$)$_3$ in neutral (−0.52 V versus SHE), and 200 mV lower than PAQS in alkaline (−0.80 V versus SHE). ‘LiCoO$_2$’ differs from the LiCoO$_2$ in Fig. 3 in that half a lithium is extracted from the latter (corresponding theoretically to 140 mAh g$^{-1}$ and experimentally to 100 mAh g$^{-1}$) while more is extracted from the former (leading to ≥ 200 mAh g$^{-1}$). LiCoO$_2$ can only couple with quinone anodes because OER will inevitably occur towards the end of charge much like the situation for PbO$_2$ and Ni(OH)$_2$, and only quinones support the oxygen cycle among anodes for near-neutral conditions.

**Cost analysis.** Some of the chemicals used in the synthesis procedure reported herein were replaced with equivalents used in larger scales for a more realistic scaled-up cost estimation. PTO can be synthesized via either Ru- or Cr/Mn-based methods where pyrene ($1 kg^{-1}$) and oxidation procedures scaled-up cost estimation. PTO can be synthesized via either Ru- or Cr/Mn-based methods where pyrene ($1 kg^{-1}$) and oxidation procedures (ref. 65) is oxidized by 4 eq. of CrCl$_3$ ($2 kg^{-1}$) to afford the product in 85–90% yields. The synthesis of PPTO considers the same procedure as reported herein except for replacing the reducing SnCl$_2$ and oxidant DDQ with Na$_2$S ($0.5 kg^{-1}$) and FeCl$_3$ ($0.25 kg^{-1}$), respectively, during the conversion of 2 to 3 (65–70% yield), and replacing DMAP with pyridine ($2.5 kg^{-1}$) for the polymerization (80–85% yield). PAQS is synthesized by the reaction between equimolar 1,5-dichloroanthraquinone ($2 kg^{-1}$) and Na$_2$S ($0.5 kg^{-1}$). The cost of pyrrole is calculated based on polyN,N’-(ethane-1,2-diyl)-1,4,5,8-naphthalenetetracarboximide$^{59}$, which is synthesized by the reaction between equimolar 1,4,5,8-naphthalenetetracarboxylic dianhydride ($52 kg^{-1}$) and ethylenediamine ($52 kg^{-1}$) (80–85% yield). Miscellaneous costs such as waste disposal, personnel, analytics, transportation, and so on will add ~10–15% to the cost at a $100-kg scale (~1000-kg scale could be even lower). The cost for PTO, PPTO, PAQS, and polyimide is thus estimated at $4–6, $10–15, $3–4, and $3–4 per kg, respectively. The price for existing anode materials is available from various sources: Pb ($2.3 kg^{-1}$) (ref. 66), AC ($14–18 kg^{-1}$) (ref. 69), LiTi$_2$(PO$_4$)$_3$ ($22–25 kg^{-1}$) (ref. 70), MnH$_4$ ($15–18 kg^{-1}$) (ref. 71), and ZnO ($3–5 kg^{-1}$) (ref. 68). A fixed price for commercially available cathode materials is used for battery cost estimation: PbO$_2$ ($2 kg^{-1}$) (ref. 68), LiMn$_2$O$_4$ ($7.4 kg^{-1}$) (ref. 72), Ni(OH)$_2$ ($9 kg^{-1}$) (ref. 71). The battery cost reported in $kWh^{-1}$ is calculated based on cathode and anode active materials.

**Data availability.** The data that support the findings of this study are available within the article and its Supplementary Information or from the authors, see author contributions for specific data sets.

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