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Universal organic anodes enable safe low-cost aqueous rechargeable batteries with long cycle life, high capacity, and fast kinetics

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Future battery advances and economies of scale will help scrub CO_2 emissions from transportation and the grid. Economical energy storage lets battery-powered electric vehicles replace internal combustion engines in the transportation sector, which now accounts for the plurality of CO_2 emissions. For grid-scale applications, the benefits of adding storage are many and well documented [1–2]. Beyond increased penetration of intermittent renewable energy generated from such as solar panels and wind and tide turbines, battery storage also supplies previously stored power during times of high demand and mitigates the need for additional installed capacity on the grid. Over the long term, reducing the load allows utilities to avoid the cost of new substations and transmission lines and fundamentally transform the grid [3].

The relevant metric for life-cycle analyses of these larger-scale applications is the cost. The demands on energy, power, lifetime and safety characteristics will vary between storage applications, but the battery system will not be installed in the absence of a strong value proposition. A sophisticated technoeconomic analysis has many considerations to address [4]. Cost is minimized with design choices that favor abundant materials and scalable processing techniques. Energy density increases with higher-voltage and capacity materials, and more efficient cell architectures. Incident-free long life is achieved with materials that are mechanically, thermally and electrochemically stable, and aided by battery management systems [5].

Recent battery fires of smartphones and electric vehicles highlight the safety concerns of batteries using flammable non-aqueous electrolytes [6]. In contrast, aqueous electrolytes are low lost, easy to process and handle, and environmentally benign with minimal safety concerns [7]. They provide the high safety, robustness, affordability, and low environmental footprint that grid storage and electric vehicles critically desire. However, aqueous batteries generally show poor cycle life, limited by the structural and chemical instability of the anode materials. For example, lead-acid batteries have the infamous “sulfation” problem related to the rapid structural/chemical failure of lead anode. Alkaline batteries have seen many anode iterations over the past century including iron, cadmium, mischmetal alloys, and zinc, but all undergo severe structural degradation upon cycling along with chemical corrosion, high cost, and limited resource availability. Neutral aqueous metal-ion batteries, notably aqueous lithium-ion batteries (ALIBs), are still in their infancy stage of battling chemical corrosion of anode by oxygen and fluctuating pH. If this century-old anode stability limitation is overcome through material innovation, aqueous batteries will be freed from their current small-scale applications and become a major player in the future terawatt energy landscape.

In the attempt to develop a universal solution to all aqueous anode challenges, Yao and colleagues [8] have turned to organic quinone materials. Although the study of organic electrodes started as early as inorganic electrodes, the interest in searching for and developing better organic electrodes diminished with the tremendous success of intercalation compounds including both transition metal compounds and graphite. Recently there is a clear revitalized interest in organic electrodes [9], as the inorganic electrodes reached their nearly insurmountable limits. Organic electrode materials offer potentially low cost (no expensive elements involved and with mild synthesis approaches such as neutral reaction and polymerization under room-temperature or moderate tem-

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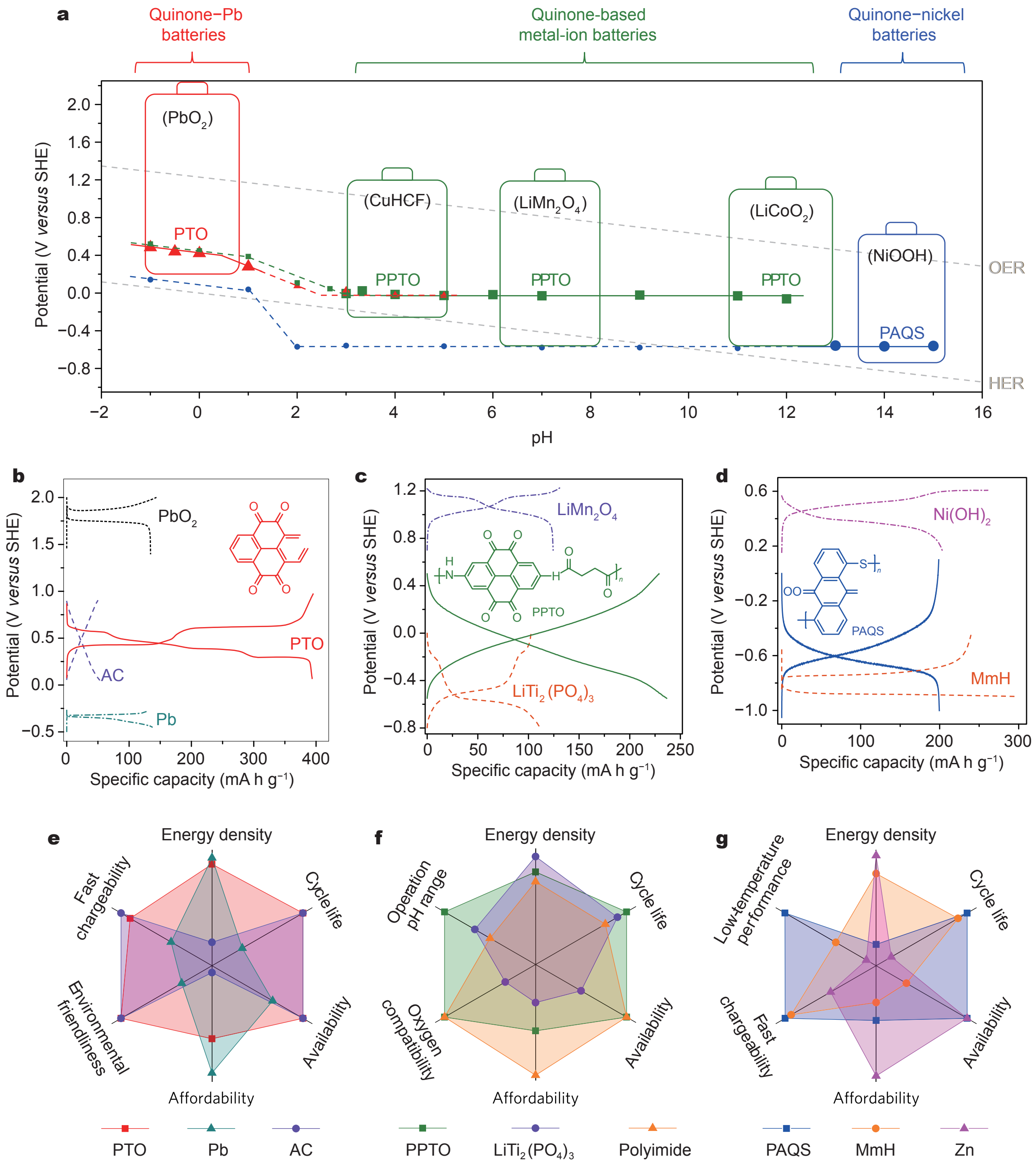

Figure 1 (a) Correlation between the reduction potentials of quinone electrodes measured with cyclic voltammetry and the pH value of aqueous electrolytes. The battery drawings depict plausible battery configurations based on quinone anodes and suitable cathodes. (b–d) Chemical structures of PTO, PPTO, and PAQS, and galvanostatic charge–discharge profiles for the related materials in the corresponding electrolytes. (e–g) Itemized comparison of quinones with existing anode materials for acidic batteries (activated carbon: AC, and Pb), ALIBs ($LiTi_2(PO_4)_3$ and imide), and alkaline batteries (nickel-metal hydride: MmH, and Zn). Reprinted with permission from Ref. [8], Copyright 2017, Nature Publishing Group.

perature), recyclability (containing no heavy and transition metals), more adaptability to different design constraints to fabricate functional devices, low size limitation of insertion ions, and a high theoretical capacity close to 500 mA h g^{-1} [9].

Specifically quinones possess readily tunable reduction potentials ranging from −0.7 to 0.8 V *vs.* standard hydrogen electrode (SHE), which match well with the hydrogen evolutionreaction (HER) potential of water (−0.9 to 0.1 V *vs.* SHE depending on pH) and therefore can fit into the electrochemical stability window of any given aqueous electrolytes. Two particular features of quinones help them tackle the persistent stability problems for aqueous anodes: (1) quinones store charge *via* a host structure-preserving ion-coordination mechanism, thus fundamentally avoiding structural degradation; and (2) quinones can be made chemically inert towards highly corrosive aqueous electrolytes and oxygen, hence are immune to chemical corrosion. In addition, quinones are made of low-cost, Earth-abundant, and readily recyclable elements and can be synthesized from inexpensive precursors *via* low-energy processes, which are considerable advantages over traditional electrode materials.

Upon rational selection/design of quinone structures, Yao and his co-workers [8] have identified three quinones, named pyrene-4,5,9,10-tetraone (PTO), polymerized PTO (PPTO), and poly(anthraquinonyl sulfide) (PAQS) (molecular structures shown in Fig. 1), as aqueous anode materials that work optimally regardless of operational pH values (−1 to 15), charge carrier species (H^+, Li^+, Na^+, K^+, Mg^{2+}), temperature (−35 to 25°C), and atmosphere (with/without O_2). Pourbaix diagram of the quinones shows that their reduction potentials approach the HER potential at every pH value, with room possible for further lowering (Fig. 1a). Consequently, three battery systems with the quinone anodes coupling with industrially established cathodes and electrolytes have been demonstrated: (1) acidic battery with PTO anode and PbO_2 cathode (Fig. 1b), (2) neutral lithium-ion battery with PPTO anode and $LiMn_2O_4$ cathode (Fig. 1c), and (3) alkaline battery with PAQS anode and $Ni(OH)_2$ cathode (Fig. 1d). These batteries exhibit state-of-the-art specific energy/energy density of up to 76–92 $W\ h\ kg^{-1}$/161–208 $W\ h\ L^{-1}$ while providing unprecedented long cycle life of up to 3,000 cycles/3,500 h. Additional advantages for quinones over currently available anode materials include virtually infinite raw material abundance, comparatively low cost, low CO_2 footprint, fast charging-discharging at over 20 C, and excellent low temperature (down to −25°C) performance (Fig. 1e–g). These results establish quinones as a universal anode approach for any aqueous battery technology.

Aqueous rechargeable batteries featuring low-cost and nonflammable water-based electrolytes and long-proven reliability have long been attractive candidates for large-scale energy storage but are plagued by unacceptably short cycle life. The quinone anodes developed by Yao's group [8] boost the cycle life of these batteries along with other benefits, rendering them viable contenders for large-scale energy storage. There are still plenty of possibilities of structurally modifying the quinone cores and varying the polymerization protocols to further improve cell performance and stability.

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