

Hydronium Ion Batteries: A Sustainable Energy Storage Solution

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energy storage · hydronium ion batteries · intercalation · organic electrodes


Batteries have evolved with a history of more than two centuries, from the voltaic pile to the lead–acid battery to lithium ion batteries (LIBs). The functionality facilitated by advanced batteries has transformed our everyday life with dispatchable power sources in communications and recently in electrified transportation. Batteries represent an indispensable technology to propel the green economy; this would be true if the energy used to manufacture batteries is coming from renewable sources and the energy that is to charge the batteries is renewable as well. Right now, with the rapid growth of the market for electric vehicles, there could be tens of thousands of cars being charged during nights in one city, which would create a significant demand for power. If such power comes from power plants that rely on burning fossil fuels, this would not be able to solve the problems of environment pollution and lack of sustainability. Therefore, grid-scale storage must be realized to enable an energy ecosystem, which can store the energy from renewable-but-intermittent sources (sun and wind).

Inspired by the tremendous demand, battery scientists have started to shift their attention to batteries beyond lithium. While lithium is an ideal charge carrier for rechargeable ion batteries, LIBs are ill-suited for large-scale stationary storage owing to the Earth rarity of lithium (17 ppm in the Earth's crust) and the geopolitical challenge to mine lithium minerals at low cost. Recently, the focus of the community has been put on other metal ion carriers for post-LIBs; great progress has been made on batteries that operate on Earth-abundant elements, such as Na, K, Mg, and Al, of which the crust is three orders of magnitude richer than of lithium.^[1–4] In contrast, attention has rarely been given to non-metal ions. Compared with the heavy mass and large radius of metal ions, the proton is an ideal candidate as charge carrier for rechargeable batteries owing to small size, wide availability, and negligible cost. In fact, the proton has been used as a charge carrier for electrodes that form metal hydride alloys

in the conventional nickel hydride batteries.^[5] Intercalation of protons is also reported for porous graphitic carbon materials.^[6] Unfortunately, owing to the part of proton consumption associated with the hydrogen evolution reaction, most of these devices exhibit extremely low coulombic efficiency. Furthermore, almost all of these devices employ an alkaline electrolyte, where it is the dissociation of water that provides incoming protons. In comparison, protonic acids can directly produce protons by themselves when placed in an aqueous solution. However, owing to the very high dehydration energy of hydronium ions (11 eV) in protonic acids, the cations in protonic acid electrolytes are hydronium ions, rather than protons. Thus, can batteries employ hydronium ions as charge carriers in acidic electrolytes? Herein, we briefly describe latest approaches to answer this question.

Recently, Ji and co-workers have demonstrated, for the first time, hydronium ions can be reversibly stored in an electrode of crystalline 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA).^[7] In that study, they observed a highly reversible discharge–charge behavior of PTCDA in an aqueous acidic electrolyte of 1M H₂SO₄ after an initial conditioning process (Figure 1 a). The capacity and the operation potentials are comparable to that of Na-ion storage in the same electrode.^[8] They also discovered three pairs of redox peaks in the cyclic voltammogram (CV) curve of PTCDA in their system, thus suggesting that multiple redox reactions occurred during the charge–discharge process (Figure 1 b). They tentatively proposed that the H₃'/O₃' process corresponded to the H₃O⁺ intercalated into the structures, while the H₁'/O₁' redox reaction was assigned to the insertion/extraction of H₅O₂⁺ ions. It is worth noting that PTCDA has served as a very good model compound for hosting large ions. It has a long-range ordered molecular crystal structure, which contains large interstitial sites for ion storage. To clearly unravel a hydronium storage mechanism in the host structure, the authors employed *ex situ* X-ray diffraction (XRD) to investigate the structural evolution of the PTCDA electrodes at different stages of the electrochemical reaction. Interestingly, the results they observed provided substantial evidence that the structure of PTCDA had experienced dramatic but reversible dilation during cycling, as shown in Figure 2 b. Such a scale of structural change could not possibly be caused by proton intercalation owing to the extremely small size of protons. The authors attributed the structural change to the intercalation of hydronium ions into the structure as the size

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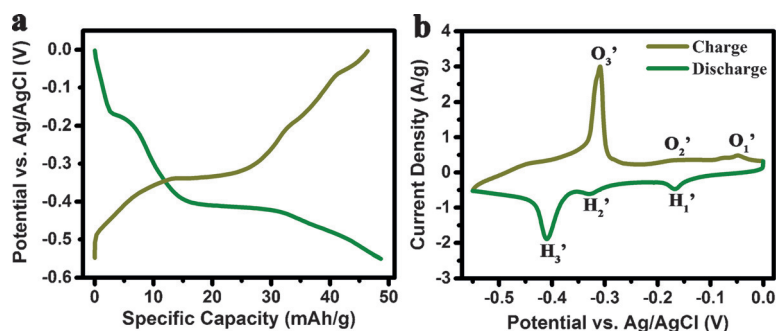


Figure 1. a) Galvanostatic charge–discharge profiles of the 10th cycle of the PTCDA electrode in 1 M H_2SO_4 . b) CVs curves at a scan rate of 1 mVs^{-1} after 50 galvanostatic charge–discharge cycles at 1 Ag^{-1} .

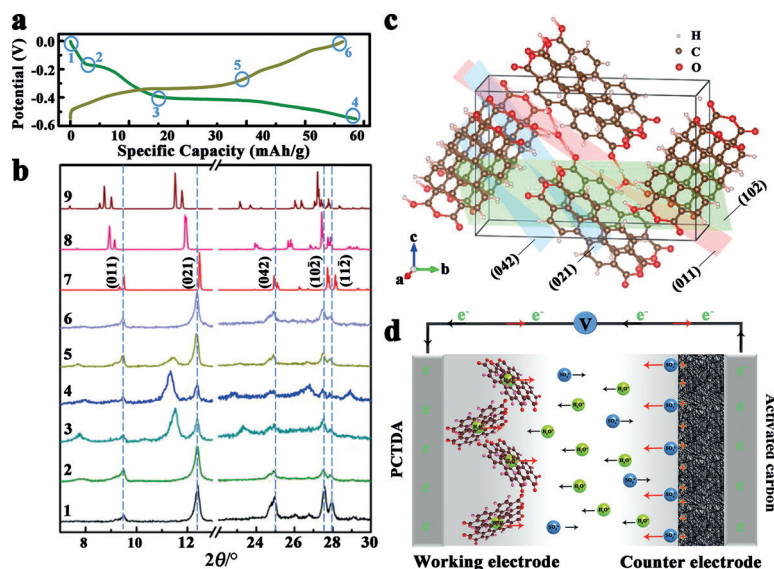


Figure 2. a) Charge–discharge (reduction/oxidation) profiles of the PTCDA electrode in the 50th cycle. b) XRD patterns (no. 1 to 6) of the PTCDA electrode corresponding to different stages of charge (points 1 to 6 in (a)). The patterns 7, 8, and 9 are simulated XRD patterns from pristine PTCDA, PTCDA with one H_3O^+ inserted per unit cell, and PTCDA with two H_3O^+ ions intercalated per unit cell, respectively. c) Simulated PTCDA unit cell incorporating two H_3O^+ . d) An illustration of the working principles of the hydronium ion battery.

of hydronium ions is very similar to that of Na-ions (ca. 102 pm).

Based on the result of the first-principles density functional theory (DFT) calculation, the authors further confirmed the change of XRD patterns was due to the hydronium ion insertion in PTCDA. And they also identified the sites of inserted hydronium ions in the unit cell of the PTCDA crystal, where the two hydronium ions were coordinated by three and two carbonyl groups, respectively (Figure 2c). On the other hand, to maintain the charge balance in the electrolyte, activated carbon serves as the positive electrode, electrostatically absorbing/desorbing SO_4^{2-} from/into the electrolyte in an electrical-double-layer manner (Figure 2d). The evidence is compelling that hydronium ions serve as the charge carrier in this system, thus providing the perspective for the future hydronium ion batteries.

Besides the sustainability benefit owing to the lack of reliance on any metal ion carriers, there may exist unique advantages of hydronium ion batteries, particularly regarding the power performance. The hydration in H_3O^+ may provide

a shielding effect for the proton, which may lower the activation energy for its migration in the host structure. This is evident in this reported results, where at 1 Ag^{-1} , a very large current density for battery electrodes, hydronium intercalates in PTCDA with very small polarization in contrast to the behavior of Na- and K-ions in PTCDA. It is reasonable to believe that the fast kinetics of hydronium in aqueous electrolytes may render the hydronium ion batteries high power capability.

The work of the Ji group is both of fundamental value as well as potentially large practical impact. As mentioned in the paper, it is likely that additional to H_3O^+ , H_5O_2^+ , or other higher-order-hydrated hydronium ions may be intercalated into the structure. This provides a unique opportunity to investigate the hydration of protons—one of the most fundamental phenomena in a confined environment. With respect to battery materials, to store hydronium ions presents a new paradigm for materials chemistry to design new materials, which will not only meet the needs of this area but possibly bring unexpected discoveries in the future. In

terms of the applications, even though the Ji paper focuses on one electrode, there could be ample room of scientific endeavor for future full cells. As already demonstrated by Ji et al., the PTCDA electrode can be coupled with a capacitive counter electrode as the cathode, thus forming a hybrid device. It is also possible that new high-potential materials will be discovered or identified for hydronium ion storage, where these materials may be of inorganic nature, such as metal oxides and phosphates, or open-framework structures like Prussian blue. There is a great chance that other intercalation electrodes will be identified so that a full-cell hydronium ion battery can be investigated.

This new direction promises remarkable opportunities, but of course there may also be some caveats. When exploring the functions of organic materials, attention should be paid to their solubility in the electrolyte; indeed the Ji paper has shown that the PTCDA electrode when being reduced does dissolve in the aqueous electrolyte to some extent. The structural stability of hydronium-insertion electrodes and their consequent long-term cycling stability should receive great attention for future studies. Furthermore, water does have a narrower stable voltage window compared to a non-aqueous electrolyte; therefore, it is also important to push the potential of the hydrogen evolution reaction and of the oxygen evolution reaction by introducing overpotential.

In summary, the work of Ji et al. indeed pushes the boundaries of the intercalation chemistry for battery purposes. There are significant opportunities in both fundamental and applied research, where this work serves as a good starting point.

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Conflict of interest

The authors declare no conflict of interest.

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