Hydronium-Ion Batteries with Perylenetetracarboxylic Dianhydride Crystals as an Electrode

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Abstract: *We demonstrate for the first time that hydronium ions can be reversibly stored in an electrode of crystalline 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA). PTCDA exhibits a capacity of 85 mAh g^{-1} at 1 A g^{-1} after an initial conditioning process. Ex situ X-ray diffraction revealed reversible and significant structure dilation upon reduction of PTCDA in an acidic electrolyte, which can only be ascribed to hydronium-ion intercalation. The lattice expansion upon hydronium storage was theoretically explored by first-principles density functional theory (DFT) calculations, which confirmed the hydronium storage in PTCDA.*

Energy storage, as the currently missing enabler for the wide utilization of renewable energy, has remained the focus of knowledge production for the 21st century. The forefront of battery innovations has migrated from lithium-ion batteries (LIBs) to a variety of new solutions, such as Li–S batteries,[1] Li–O$_2$ batteries,[2] sodium-ion batteries (NIBs),[3] and potassium-ion batteries (KIBs).[4] To date, rechargeable batteries with metal ions as charge carriers occupy the primary attention. However, proton and hydronium ions, as analogues of Li$^+$, Na$^+$, and K$^+$, have been rarely explored as charge carriers for rechargeable batteries. Among batteries that rely on protons as charge carriers, one example is the metal alloy anode of nickel/metal hydride batteries (NiMH), which incorporates hydrogen in the form of metal hydrides during battery charging.[5] Another example is the adsorption of proton/hydrogen by high-surface-area electrode materials, such as carbon nanotubes[6] and activated carbon.[7] Qu investigated the important mechanism of proton intercalation in graphite electrodes, where hydrogen is predominantly stored in the galleries of graphitic domains, with small amounts stored by surface adsorption.[8] To date, most electrochemical hydrogen storage systems exhibit fairly low coulombic efficiency caused by the hydrogen evolution reaction (HER). Interestingly, all prior studies employed alkaline electrolytes, which rely on the dissociation of water molecules to provide protons/hydrogens for incorporation by the electrodes. Note that the dehydration energy of H$_3$O$^+$ is 11.66 eV,[9] which is so high that in aqueous Brønsted–Lowry acids as the electrolyte, the ions intercalating into electrode host structures will be hydronium ions, H$_3$O$^+$, or their hydrated forms, H$_{2x+1}$O$_x$$^+$, instead of protons. H$_3O^+$ exhibits an effective ionic radius of 100 ± 10 pm,[10] which is very close to that of Na$^+$, 102 pm,[11] and the ion is thus not too large to be considered. Surprisingly, to date, batteries based on the electrochemical storage of hydronium ions have never been reported.

To store hydronium ions, the interstitial sites in the electrode host structures should be relatively spacious, and the ion-insertion potential needs to be high enough to avoid HER. To this end, electrodes of organic solids may be suitable as their unique capability of storing large metal ions has been demonstrated.[12] Furthermore, the reduction potential of organic materials is essentially determined by their lowest unoccupied molecular orbital (LUMO), which is tunable. As an advantage over graphite electrodes, one can tether the edges of fused aromatic rings of organic molecules to electron-withdrawing groups to lower the energy level of the LUMO, thus increasing the cation-insertion potential. Therefore, their cation intercalation potential can be higher than that of graphite. Among solid organic electrodes, 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA), a well-known pigment that has been investigated for the storage of Li$^+$, Na$^+$, and K$^{+[12a,b,13,14]}$ ions, again caught our attention for this proof-of-concept study of hydronium ion battery (HIB) electrodes.

Herein, we report the first evidence for hydronium intercalation into a highly crystalline organic electrode of PTCDA, which exhibits a specific capacity of 85 mAh g^{-1}, reversible structural changes during cycling, and relatively stable cycling life. We characterized the structural change upon hydronium intercalation, and ex situ X-ray diffraction revealed significant but reversible lattice expansion. This finding confirmed that the intercalant ions are hydronium ions instead of naked protons.

To test the hydronium storage properties of PTCDA, we investigated the PTCDA electrode in a three-electrode cell setup with 1 M H$_2$SO$_4$ as the electrolyte. In this setup, the counter-electrode is composed of an excessive mass of activated carbon, which also serves as the positive electrode by operating in an electrical double layer manner by electrostatically absorbing/desorbing anions from/into the electrolyte, i.e., SO$_4$$^{2-}$. A Ag/AgCl electrode in saturated aqueous KCl solution, with a potential of 0.197 V versus the standard hydrogen electrode, acted as the reference electrode, and all potentials in this study are reported versus the Ag/AgCl

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reference electrode. The PTCDA electrode was tested as the working electrode and the negative electrode, where during cell charging, PTCDA is reduced while incorporating cations, which are hydronium ions.

We collected cyclic voltammograms (CVs) for the PTCDA electrode in the three-electrode cell. In the first cycle, the cathodic scan reveals two minor peaks at around -0.22 V (R_1) and -0.39 V (R_2), and a major peak beyond -0.49 V (R_3; Figure 1a). During the following anodic scan,

Figure 1. CVs recorded at a scan rate of 1 mVs^{-1} for a) the first cycle, and b) the cycle after 50 GCD cycles.

two peaks at -0.31 V and -0.27 V were observed, which were assigned to O_3 and O_2, respectively, corresponding to the R_3 and R_2 reduction reactions. The cell thus exhibits a polarization of approximately 0.2 V, and R_1 appears to be irreversible. Interestingly, after 50 galvanostatic charge–discharge (GCD) cycles at 1 Ag^{-1}, the CV curve (Figure 1b) displays three pairs of redox peaks at $-0.41/-0.31$ V (R_3'/O_3'), $-0.33/-0.17$ V (R_2'/O_2'), and $-0.17/-0.05$ V (R_1'/O_1'), which are quite reversible. Comparison of these two CV curves suggests that the redox behavior of PTCDA in the acidic electrolyte evolves significantly simply owing to the initial GCD cycling. The R_1'/O_1' pair appears only after GCD cycling; the R_3'/O_3' pair exhibits much smaller polarization compared with R_3/O_3, where, interestingly, the O_3' peak at -0.31 V does not shift at all. Overall, the extent of polarization decreases from about 0.2 to 0.1 V after GCD cycling, and the peak intensity of R_3'/O_3' increases slightly. The change in the CV behavior features a conditioning process that occurs over initial GCD cycling, which makes redox reactions of PTCDA more amenable. The occurrence of multiple redox reactions, and the emergence of the new R_1'/O_1' redox pair, is suggestive of an interesting phenomenon that hydrated hydronium and hydronium ions may sequentially serve as intercalants. The R_1'/O_1' process occurs at a fairly high potential, where we postulate that hydrated hydronium ions, such as $H_5O_2^+$, may be reversibly intercalated into the structures only after the initial conditioning process owing to their large size. The difference in the proton hydration free energy between one hydration (H_3O^+) and two hydration ($H_5O_2^+$) was reported to be approximately 0.25 eV,[15] corresponding to an energy penalty of about 0.25 V for dehydration from $H_5O_2^+$ to H_3O^+, which is rather close to the potential difference of about 0.24 V between R_1' and R_3'. We tentatively attribute the R_3'/O_3' and R_1'/O_1' redox reactions to the insertion/extraction of H_3O^+ and $H_5O_2^+$ ions, respectively.

In the first GCD cycle at 1 Ag^{-1}, the PTCDA electrode exhibits a large polarization (Figure 2a), which is consistent with the gaps between the redox peaks in the initial CV curves (Figure 1a). Interestingly, the capacity of 70 mAhg^{-1} obtained in the first reduction sweep is close to the theoretical

Figure 2. GCD profiles of a) the first cycle, b) the fifth cycle, and c) the tenth cycle. d) A comparison of the GCD profiles for the storage of Na ions at 1 Ag^{-1}, K ions at 0.5 Ag^{-1}, and hydronium ions (10th cycle) at 1 Ag^{-1} in PTCDA. Adapted from Ref. [14] with permission from John Wiley and Sons.

capacity of 68 mAhg^{-1} when every PTCDA molecule stores one electron/monovalent cation. In the fifth cycle, the polarization is much lower, and the reduction of PTCDA occurs at higher potentials while the capacity increases to 85 mAhg^{-1} (Figure 2b), corresponding to the incorporation of 1.3 monovalent cations per PTCDA molecule. Similar to the CV results, the potentials for the oxidation sweeps remain nearly the same. Clearly, the initial polarization of the PTCDA electrode mainly comes from the conditioning "effort" of the cation incorporation during PTCDA reduction. Moreover, in the tenth cycle, the potential of the charging (reduction) process is eventually transformed into sequential plateaus mainly at -0.17 V and -0.41 V aside from some sloping regions, and correspondingly, there are plateaus at -0.34 V and -0.05 V (minor) during the discharging (oxidation) process, which is generally consistent with the CV results in Figure 1b.

PTCDA has demonstrated its unique storage capability towards large metal ions, namely Na$^+$ and K$^+$, and its structure can reversibly dilate and contract when hosting/extracting Na$^+$ ions[14] while it turns amorphous upon initial cycling by incorporating large K$^+$ ions.[12a] It is quite intriguing that the operation potential for the hydronium intercalation is significantly higher than that for sodium- and potassium-ion intercalation by approximately 0.3 V and 0.8 V, respectively, on average. The polarization for hydronium storage is also significantly smaller than for both sodium- and potassium-ion storage. The much higher insertion potential indicates that it

is thermodynamically and kinetically more facile for the PTCDA framework to host hydronium ions. The favorable energetics may have to do with the smaller desolvation energy of hydronium compared to Na^+ or K^+ ions in their non-aqueous electrolyte based on ethylene carbonate (EC) and diethyl carbonate (DEC). The minimal polarization may be related to the fast migration of hydronium ions through the PTCDA structure. Of course, the higher conductivity of the aqueous acidic electrolyte may play a role as well.

It is critical to learn the structural response of PTCDA towards hosting hydronium ions. If the structure does dilate upon PTCDA reduction, proton intercalation in the structure would be trivial. Thus we investigated the evolution of the PTCDA crystal structure during cycling by ex situ X-ray diffraction (XRD) measurements conducted at different states of charge (SOCs) in the 50th cycle. Figure 3b depicts specific angle regions where primary peak shifts and new peaks were observed. The full XRD patterns are shown in the Supporting Information, Figure S1. Upon charging (reduction) to −0.17 V (pattern 2), a minor peak appears at 7.8°,

which was later assigned as the (001) peak by simulation, and the (011) peak turned asymmetric, being slightly left-shifted. Upon further charging to −0.40 V (pattern 3), the new (001) peak at about 7.7° became more intense. Furthermore, a strong peak appeared at 11.6° to the left of the weakened (021) peak, and a relatively weak peak appeared at 23.4° to the left of the weakened (042) peak. We attribute the above two peak shifts to the diffraction of dilated (021) and (042) planes, respectively, where the d spacings increase from 0.72 to 0.77 nm, and from 0.36 to 0.38 nm, respectively. Such a large-scale structural expansion could not possibly originate from the intercalation of naked protons, and so we were left to conclude that the reduction of the PTCDA electrode in an acidic electrolyte corresponds to the intercalation of hydronium ions. As the PTCDA electrode was further charged to −0.55 V (pattern 4), the new peaks derived from the (021) and (042) peaks continued to shift to lower angles, and their intensities were further enhanced. Moreover, at −0.55 V, the (10$\bar{2}$) peak was also shifted from 27.6° to a lower angle of 26.7° in response to the intercalation of hydronium ions. A new peak also appeared at 28.9°, which was assigned as the (130) peak by comparison with the simulation results.

Aside from the emergence of new peaks, the peak shifts are incomplete as both the original peaks and the shifted peaks are present in the charged states, which indicates that portions of the pristine PTCDA domains, most likely the cores of large particles, remain intact. During the following discharge (oxidation), all peaks gradually shift back to their original positions. Upon discharging to −0.3 V (pattern 5), the intensities of the new (001) peak and the shifted (021) and (042) peaks all decreased. Upon discharging to 0 V (pattern 6), all new peaks disappeared, and the intensities of the original peaks were recovered, so that patterns 1 and 6 are almost identical, demonstrating the excellent structural reversibility of PTCDA upon intercalation/deintercalation of hydronium ions.

We also explored the mechanism of hydronium insertion in PTCDA by theoretical ab initio structural calculations using density functional theory (DFT) with the Vienna ab initio simulation package (VASP). Note that hydronium ions could have higher hydration numbers; however, detailed theoretical investigations of the hydration numbers are beyond the scope of this paper. Therefore, H_3O^+, the smallest hydrated proton with the least steric hindrance, was chosen as the intercalation species in the simulation experiment. In Figure 4, we computed the incorporation of two hydronium ions into one PTCDA unit cell that comprises two equivalent PTCDA molecules, where the theoretical capacity is 68 mAh g^{-1}.

As shown in Figure 4, when two hydronium ions (H_3O^+) are intercalated into the unit cell, they stay in the interstitial space between stacked PTCDA molecules along the (011) planes, and are stabilized by adjacent carbonyl groups. The simulated diffraction patterns are shown as patterns 7, 8, and 9 for the pristine compound, the unit cell with one hydronium ion, and the unit cell with two hydronium ions, respectively (Figure 3b). When hydronium ions are intercalated into the PTCDA lattice, new (001) and (130) diffraction peaks appear at about 7.7° and 28.9°, respectively, which generally matches

Figure 3. a) Charge/discharge (reduction/oxidation) profiles of the PTCDA electrode in the 50th cycle. b) XRD patterns (1–6) of the PTCDA electrode corresponding to the SOC points 1 to 6 in (a). For the full XRD patterns, see Figure S1. Patterns 7 to 9 are simulated XRD patterns for pristine PTCDA, PTCDA with one H_3O^+ ion inserted per unit cell, and PTCDA with two H_3O^+ ions intercalated per unit cell.

Figure 4. Simulated PTCDA unit cell incorporating two H_3O^+ ions.

the experimental results. The (021), (042), and (10$\bar{2}$) peaks are all increasingly shifted to the left from the situation with one hydronium ion inserted per unit cell to two hydronium ions accommodated per unit cell, which is in agreement with the experimental XRD results.

The well-matched experimental and simulation patterns provide a solid ground for looking at the simulation-derived parameters. Figure 4 clearly shows the specific positions of the hydronium ions in the host lattice, which are along one body diagonal in the (011) plane, resulting in interlayer expansion of the (021), (042), (10$\bar{2}$), and (11$\bar{2}$) planes. Table 1 summa-

Table 1: Simulated PTCDA unit-cell parameters.

Compound	a [Å]	b [Å]	c [Å]	α [°]	β [°]	γ [°]	V [Å^3]
pristine	3.74	18.95	10.75	90.00	96.00	90.00	757.71
one H_3O^+	3.54	19.35	11.71	89.61	100.20	90.84	790.46
two H_3O^+	3.46	19.64	12.33	88.22	103.56	92.01	813.01

rizes the cell parameters of pristine and hydronium-interca-lated PTCDA unit cells. The unit cell expands along the b and c axes after hydronium-ion intercalation, which is consistent with the shifts in the peaks corresponding to the (021) and (042) planes, and leads to an expansion of the unit cell volume from 757.71 to 813.01 Å^3 (expansion by 7.3%) when two hydronium ions are intercalated into one unit cell. Surprisingly, the unit cell slightly contracts along the a axis, even though the two hydronium ions are stored close to the body diagonal in the (011) plane. This result can be explained by considering Figure 4, where one hydronium ion interacts with three carbonyl groups, and the two of them oriented in parallel along the a direction are pulled closer by the H_3O^+ ion. Another unit cell parameter showing a prominent change after intercalation is the β angle, expanding from 96.00° to 103.56° when accommodating two H_3O^+ ions, which is in good agreement with the shift in the (10$\bar{2}$) peak according to XRD (Figure 3b).

We used Fourier transform infrared (FTIR) spectroscopy to investigate possible bonding variations, particularly for the

carbonyl groups in the anhydrides, upon hydronium interca-lation. To understand the impact of ion intercalation on the chemical bonding, we compared spectra of hydroniated and potassiated PTCDA (Figure S3). In Figure S3b, after potas-siation, the peak at 1788 cm^{-1}, which is due to carbonyl stretching, shifts to 1773 cm^{-1}, indicating a weakened C=O double bond; a new peak at 1824 cm^{-1} is also observed, which was attributed to the formation of potassium enolate groups. However, for hydronium intercalation, the peaks from 1730 to 1769 cm^{-1} only slightly decrease in intensity, suggesting that no new chemical bonds are formed. The disparity between hydroniation and potassiation in terms of the changes in the chemical bonds in PTCDA is quite intriguing, and we postulate that the protons are screened by the hydration, which weakens the enolization process, thus being different from the case with "naked" K$^+$ ions. Other than the slightly diminished anhydride peaks, all other peaks remained the same as for pristine PTCDA, indicating that the structure is perfectly preserved after cycling.

We tested the cycling stability of PTCDA, which was found to be relatively stable (Figure S2). Indeed, as an anhydride, PTCDA may undergo hydration, thus forming perylenetetracarboxylic acid. To investigate this matter, we soaked a pristine PTCDA electrode with the 1M H_2SO_4 electrolyte for five days, but the color of the electrolyte did not change, and it also did not fluoresce (Figure S4a). Note that when molecules with perylene rings dissolve, the solution fluoresces. However, the fact that the pristine PTCDA electrode does not dissolve cannot warrant that reduced PTCDA would not dissolve. To further investigate this, we collected the electrolyte from cells after 120 cycles; the electrolyte exhibited a brown color, as shown in Figure S4a, which indicates a certain level of solubility of the reduced PTCDA. Interestingly, the color of the electrolyte turned light green after the cycled electrolyte had been left in air for four hours (Figure S4b). To further confirm that the light green color is from PTCDA, a UV/Vis spectrum was recorded. As shown in Figure S5, the cycled electrolyte shows a broad absorption peak around 460 nm, which is consistent with the two peaks at 438 and 467 nm from the standard PTCDA/KOH solution, confirming the presence of PTCDA in the electrolyte.

In summary, we have shown that hydronium ions can be reversibly electrochemically stored in PTCDA with a capacity of 85 mAh g^{-1}. The amenable redox reactivity of PTCDA in 1M H_2SO_4 solution requires an initial conditioning process, as demonstrated by cyclic voltammetry and galvanostatic charge/discharge cycles, and this process increases the specific capacity and lowers the polarization. Ex situ XRD revealed the reversible dilation of the PTCDA structure upon hydro-nium intercalation, which was supported by first-principles DFT calculations. The calculations revealed the structural changes of PTCDA upon hydronium incorporation and the specific sites of the inserted hydronium ions in the PTCDA structure. We have thus developed a proof-of-concept inser-tion electrode material for hydronium-ion batteries, which may potentially provide new solutions for energy storage.

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