Reversible Hydration Enabling High-Rate Aqueous Li-Ion Batteries

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ABSTRACT: Layered TiS$_2$ has been proposed as a versatile host material for various battery chemistries. Nevertheless, its compatibility with aqueous electrolytes has not been thoroughly understood. Herein, we report on a reversible hydration process to account for the electrochemical activity and structural evolution of TiS$_2$ in a relatively dilute electrolyte for sustainable aqueous Li-ion batteries. Solvated water molecules intercalate in TiS$_2$ layers together with Li$^+$ cations, forming a hydrated phase with a nominal formula unit of Li$_{0.38}$H$_2$O$_{2.5}$TiS$_2$ as the end-product. We unambiguously confirm the presence of two layers of intercalated water by complementary electrochemical cycling, operando structural characterization, and computational simulation. Such a process is fast and reversible, delivering 60 mAh g$^{-1}$ discharge capacity at a current density of 1250 mA g$^{-1}$. Our work provides further design principles for high-rate aqueous Li-ion batteries based on reversible water intercalation.

While batteries for electric vehicles have been dominated by Li-ion technology, alternative chemistries are regaining unprecedented attention to account for society’s colossal need for grid energy storage. By replacing toxic and flammable organic electrolyte solvents with water, the cost can be lowered and safety further enhanced.

However, the 1.23 V electrochemical stability window (ESW) of TiS$_2$ remains unclear. In particular, the TiS$_2$ partial intercalation, water electrolysis, and combined intercalation, and electrocatalytic activity of TiS$_2$ attention of the research community was rapidly switched to layered oxides, which led to the birth of modern Li-ion batteries.

In this work, we revisit the classic TiS$_2$ electrode in aqueous Li-ion batteries via electrochemical cycling, synchrotron-based operando X-ray diffraction (XRD), and molecular dynamics (MD) simulation. We unambiguously confirm a highly reversible TiS$_2$ hydration process as the main intercalation mechanism. Our findings provide timely insights into designing sustainable and high-rate aqueous batteries based on hydrated intercalants, in which the role of water should be critically assessed.

To evaluate the performance of TiS$_2$, LiFePO$_4$ (oversized) || TiS$_2$ cells were tested in both nonaqueous (1 mol L$^{-1}$ of LiPF$_6$ in ethylene carbonate/diethyl carbonate (1:1), denoted as LP40) and aqueous electrolyte (2 m of LiTFSI in water). When cycled at 50 mA g$^{-1}$, the nonaqueous cell delivered a reversible capacity of ca. 203 mAh g$^{-1}$, while that of the aqueous cell was ca. 88 mAh
g\(^{-1}\), as compared in Figure 1a. When having a closer look at the representative differential capacity (\(dQ/dV\)) curve of the aqueous cell in Figure 1b, three regions of interest can be identified. Region I and Region II are centered around 0.52 and 0.59 V (cell voltage, same as below unless otherwise specified), respectively, suggesting two sequential biphasic reactions. Region III spans between 0.70–1.20 V, showing a rectangular shape with solid-solution-like behavior. Minor irreversibility is observed close to the end of charge, which is attributed to the hydrogen evolution reaction (HER).

To evaluate the cycling stability of the biphasic and solid-solution regions of TiS\(_2\), two aqueous cells were assembled; one was cycled between 0.2–0.7 V (Regions I and II) and the other between 0.7–1.2 V (Region III). The cycling curves are compared in Figure 1c, while their corresponding \(dQ/dV\) curves are plotted in Figure S1 in the Supporting Information. Upon extended cycling, almost no capacity decay is observed in the high-voltage Region III, while performance degradation takes place first in Region I, then in Region II. In fact, when Region I is omitted from cycling (i.e., 0.43–1.2 V), an improved capacity retention can indeed be achieved (Figure S2).

The reaction kinetics of the three regions was also evaluated by rate capability tests. Specifically, aqueous cells were cycled under different current densities, ranging from 50 mA g\(^{-1}\) to 1250 mA g\(^{-1}\). As shown in Figure 1d, the cell was able to deliver 60 mAh g\(^{-1}\) reversible discharge capacity in less than 3 min, corresponding to a nominal rate of 20C. It is also worth noting that Region I is more sensitive to higher current densities, while the slope of Region III remains largely unchanged.

To deepen the understanding of the structure–property relationship, we investigated the dynamic structural change of TiS\(_2\) in aqueous electrolytes by synchrotron-based operando XRD (Figure 2), using a pouch-cell configuration. Owing to strong preferential orientation (see SEM image of the pristine electrode in Figure S3) and peak overlapping with the Al pouch, the (001) peak of the pristine TiS\(_2\) phase at 3.56° cannot be detected in transmission geometry (which is a known issue reported elsewhere\(^{14}\)), but can be readily seen in ex situ experiments performed in reflection geometry (Figure S4).

Overall, diffraction peaks can be indexed by a nonhydrated TiS\(_2\) phase (denoted \(p\)) and a dihydrate Li(H\(_2\)O)\(_2\)TiS\(_2\) phase (denoted \(d\)).\(^{21,22}\) Weak diffraction peaks at ca. 6.97°, 7.25°, and 12.13° can be qualitatively assigned to an intermediate monohydrate Li(H\(_2\)O)\(_x\)TiS\(_2\) phase (denoted \(m\)). The main difference among the three phases is the number of water layers between TiS\(_2\) layers (0, 1, and 2 for the \(p\), \(m\), and \(d\) phases, respectively). A qualitative comparison among the \(p\), \(m\), and \(d\) phases during cycling is provided in Figure S5.

Owing to the lack of detectable (00l) reflections of the \(p\) phase, as well as the very few reflections coming from the \(m\) phase, the structural model used to extract unit cell parameters was based on the dihydrate structure proposed by Whitting-
Attempts were made to fit more than one phase sequentially, but this led to unstable refinements. Since the $p$ phase and the $d$ phase share the same space group ($P-3m1$), one can essentially extract the $c$-axis of the $p$ phase from the $d$ phase by $c/2$. In addition, no broadening or splitting of the (100) or (110) reflections were observed in Figure 2b, which means the a

Figure 2. (a) Synchrotron-based operando XRD plot of a LiFePO$_4$ || TiS$_2$ aqueous pouch-cell. Stars refer to peaks stemming from the pouch. (b) Colormap of different $2\theta$ ranges of interest. (c) Evolution of refined lattice parameters $a$ and $c$ along cycling.
and b unit cell parameters are equal in both phases. Based on this, the a and c unit cell parameters obtained from sequential Pawley fits are plotted as a function of time in Figure 2c. It is evident that the refinements are still slightly unstable on the c-axis, which is due to (001) being the only (00l) reflection with observable intensity.

Peaks of the hydrated m and d phases are governed by the phase transitions discussed in Figure 1b. Specifically, the m phase only appears at the end of the first plateau, followed by another biphasic transition to form the d phase at the end of the second plateau. An interlayer spacing of ca. 11.34 Å is calculated based on the (001) peak position of the d phase as it emerges during Region II. As the charging continues in Region III, further intercalation of hydrated Li\(^+\) reduces the electrostatic repulsion between TiS\(_2\) layers, shortening the interlayer spacing along the crystallographic c-axis. The in-plane crystallographic a, b-axes expand during the charging in Region III, leading to a slightly distorted d' phase at the end of charge with an interlayer spacing of ca. 11.18 Å.

When indexing the m phase by the structural model proposed by Whittingham,\(^{16}\) we note that the relative intensity of (00l) reflections where l = 3n is much stronger. This is indicative of a change in stacking order from 1T to 3R of the Ti-S layers previously observed in LiTiS\(_2\) by neutron diffraction.\(^{23}\) We can therefore also index the m phase in the rhombohedral space group R-3m (166) with a = 3.477(1) Å and c = 17.452(7) Å at

Figure 3. Snapshot of the MD simulation cell (a) for an interlayer distance of 5.7 Å at OCV, with oxygen (red), hydrogen (white), Ti (purple), S (yellow) and Li (green). For TFSI\(^-\), only the N atom (blue) is shown. MD snapshots and atomic density profiles of the working electrode are plotted at 8.52 Å and −0.13 V vs SHE (b–c), 11.34 Å and −0.19 V vs SHE (d–e), 11.18 Å and −0.65 V vs SHE (f–g), corresponding to the m, d, and d' phases, respectively. The density profiles are computed along the direction of the interlayer spacing and averaged over all the interlayers of the electrode. The pore size, i.e. interlayer distance, is highlighted by the light blue background in (c), (e), and (g). The origin is set at the position of the Ti plane.
the end of the first plateau. Whether such a structural rearrangement occurs is, however, not feasible to extract from these data.

Molecular dynamics (MD) simulations were performed to provide more theoretical insight. The construction of the cell and simulation parameters are included in the Supporting Information. At open-circuit condition with an interlayer distance of 5.7 Å for the pristine TiS$_2$ (Figure 3a), no intercalation takes place. By increasing the interlayer distance and lowering the electrode potential, the kinetic barrier for Li$^+$ intercalation gets reduced and water also starts to intercalate, leading to Region I, where a monolayer of intercalated water molecules is observed in Figure 3b,c. The H$_2$O–TiS$_2$ molar ratio is calculated to be around 0.9, which agrees with the stoichiometry of the monohydrate phase. Li$^+$ ions are found out of the plane formed by the oxygen atoms of the water molecules. In Region II (Figure 3d,e), the intercalated water forms a bilayer, while Li$^+$ ions are found in the space between the two layers, with a very low probability within one of the layers. The H$_2$O–TiS$_2$ molar ratio is calculated to be around 1.6, indicative of an incomplete dihydrate phase. We also observe that this interlayer can accommodate a trace amount of TFSI$^-$ anions, with a ratio of ca. 10.47 TFSI$^-$ for 1 Li$^+$. The lower intensity of the oxygen density peak compared to the monolayer case is explained by the presence of the TFSI$^-$ anions, owing to the large space it occupies between TiS$_2$ layers. In Region III (Figure 3f,g, we still observe a bilayer of water with Li$^+$ intercalated in the space between the two layers, but with a narrower distribution. The H$_2$O–TiS$_2$ molar ratio is calculated to be around 1.8, suggesting that water cointercalation continues in Region III as well. Contrary to Region II, TFSI$^-$ anions are completely absent, because of a higher accumulated charge and sufficiently low potential of the electrode.

Based on the complementary electrochemical testing, operando structural characterization, and computational simulation, we propose a comprehensive intercalation mechanism in Scheme 1 to account for the reversible electrochemical hydration of TiS$_2$ in aqueous electrolytes. Owing to the large hydration energy of Li$^+$ (−128 kcal mol$^{-1}$) and small diameter of the hydration shell (4.0 Å),$^{24}$ cointercalation of hydrated Li$^+$ ions is thermodynamically favorable, resulting in an expansion of the interlayer distance. A defective monohydrate phase ($m$) will form in Region I with a nominal composition of Li$_{0.13}$(H$_2$O)$_{1-x}$TiS$_2$, deduced from the specific capacity of the first redox plateau. The biphasic transition agrees with the plateau observed in Region I of Figure 1b. Upon further intercalation, another layer of water can be accommodated by TiS$_2$, forming a dihydrate phase ($d$) in Region II with a nominal composition of Li$_{0.25}$(H$_2$O)$_{2-\gamma}$TiS$_2$. The biphasic transition results in another plateau observed in Region II of Figure 1b. The hydrated Li$^+$ should be homogeneously distributed between TiS$_2$ layers, taking into account the electrically conducting nature of TiS$_2$, thus delocalized negative charges.$^{17}$ In Region III, hydrated Li$^+$ will continuously fill up the space between TiS$_2$ layers, with lowered charge-transfer resistance, deduced from in situ electrochemical impedance spectroscopy (EIS) analysis (Figure S6). The gradual lithiation of the phase possesses a solid-solution behavior, which agrees with the sloping Region III of Figure 1b and the drifting d(001) reflection to higher 2$\theta$ values in Figure 2. A nominal composition of the end-of-charge

"Nominal compositions and structural evolutions are suggested for Regions I–III (not to scale)."
compound is deduced as Li$_{0.38}$(H$_2$O)$_{0.85}$TiS$_2$ with a H$_2$O:TiS$_2$ molar ratio close to 2. Our value agrees well with that reported by Schöllhorn and Meyer, who showed that a lithium composition $>$0.4 would trigger hydrogen evolution. On discharge, the reverse process takes place. Irreversibility is mainly observed in Region I, i.e. when removing all water from the monohydrate phase. A significant energy penalty is experienced, supported by the asymmetric dQ/dV curves of Region I in Figure 1b.

As previously discussed, TiS$_2$ is capable of accommodating various guest molecules in nonaqueous systems. For example, Alvarez Ferrero et al. recently reported that diglyme can be cointercalated in TiS$_2$, together with Na$^+$ ions, resulting in a potential downshift of 350 mV in a Na half-cell. In addition, the cointercalated diglyme molecules seem to permanently modify the TiS$_2$ structure, leading to irreversible change of the potential profile after 100 cycles. In contrast, water cointercalation is mostly reversible in this study, evidenced by the completely disappearing (001) peak of the water- intercalated phase at the end of discharge (Figure S5) and the retained voltage profile after 100 cycles (Figure 1c). We rationalize this unique feature by the large lithium hydration energy and small hydration shell radius—the resulting less expansion of the TiS$_2$ interlayer distance in our work, compared to the reference, also promotes long-term reversibility of the cointercalation process. Moreover, in nonaqueous systems, intercalated solvents remain intact and chemically inert, as is the case for diglymes. On the other hand, given the notoriously narrow water stability window, intercalated water may undergo electrochemical reduction, complicating the interfacial stability of the system under study. Therefore, all the features associated with water cointercalation suggest that this work is not a continuation from previous studies, but presents unique advantages for using layered TiS$_2$ in sustainable and high-rate aqueous batteries.

Apart from TiS$_2$, transition metal oxide electrodes are also known to form hydrates, such as vanadium oxide hydrates (V$_2$O$_5$·nH$_2$O). The structural water in the latter case is believed to effectively shield the charge density of Zn$^{2+}$ and facilitate fast ion diffusion. In the case of dichalcogenide, the O···H···S interaction is much weaker, facilitating the reversible water cointercalation into the bulk. To prove this, an aqueous cell was stopped at the charged state, the intercalated TiS$_2$ electrode was recovered and cycled in a nonaqueous cell after vacuum drying at 120 °C, as illustrated in Figure 4a. The charged electrode, denoted as 1c-dried, delivered ca. 78 mAh g$^{-1}$ capacity against Li in LP40 electrolyte, corresponding to 0.33 Li$^+$ release (based on its theoretical capacity of 238 mAh g$^{-1}$). Upon subsequent lithiation, almost full capacity can be regained. The dQ/dV profile in Figure 4b is in agreement with previous studies using nonaqueous electrolytes. It is therefore evident that intercalated water molecules have all been expelled by heating, while Li$^+$ ions remain in the restored TiS$_2$ phase.

Furthermore, there is a general consensus that a solid-electrolyte interphase (SEI) is critical to prevent HER from happening for aqueous batteries, hence the need for either intrinsic or artificial SEI. Recently, Droguet and co-workers have shown that inorganic artificial SEI is insufficient to prevent water reactivity for aqueous systems. Elastic polymer grafting and film-forming additives are possible strategies to stabilize the anode—electrolyte interface. However, in a system like TiS$_2$, drastic lattice expansion and contraction take place in each cycle, imposing a serious challenge to the mechanical stability of the surface passivation layer. We have previously shown, by operando gas analysis, that no SEI is formed on TiS$_2$. In fact, should there be a functioning SEI, hydrated Li$^+$ ions will have to dehydrate first, which would not result in water cointercalation. Therefore, we believe that for electrodes following reversible hydration mechanism, an SEI is not a prerequisite. Consequently, the electrolyte ESW will be compromised, as in our case only ca. 0.4 Li$^+$ can be stored per TiS$_2$, beyond which water reduction will inevitably proceed. We are now screening possible electrolyte cosolvents, which could effectively alter the solvation structure of Li$^+$ and thus the redox behavior.

Lastly, the universality of the proposed mechanism remains to be verified in other aqueous systems, i.e. when Li$^+$ is replaced by larger cations, such as Na$^+$ and K$^+$, bearing in mind that the latter may have different hydration structures. It would also be interesting to examine other layered materials, such as MoS$_2$ and MXenes, which have also been proposed as intercalation electrodes for aqueous batteries.

In summary, we report a fundamental understanding of the electrochemical activity and structural evolution of TiS$_2$ in aqueous Li-ion batteries. We demonstrate a cooperative Li$^+$ and water cointercalation process as the main intercalation mechanism. Up to two layers of water can be reversibly stored between TiS$_2$ layers. The resulting aqueous full-cell demonstrates excellent rate capability, delivering 60 mAh g$^{-1}$ reversible
capacity at a current density of 1250 mA g\(^{-1}\), which is ascribed to both fast Li transport kinetics in aqueous electrolytes and a sufficiently large interlayer distance of the host material modified by water. Our work reveals the complex nature of intercalation reactions in aqueous batteries, in which the reactivity of hydrated cations with the layered chalcogenide may lead to intriguing electrochemical and structural properties.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.4c00224.

Experimental and computational methods, cycling and electrochemical impedance spectroscopy data, additional operando/ex situ XRD plots, scanning electron microscopy image (PDF)

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Notes
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