

Interface Concentrated-Confinement Suppressing Cathode Dissolution in Water-in-Salt Electrolyte

Jinming Yue, Liangdong Lin, Liwei Jiang, Qiangqiang Zhang, Yuxin Tong, Liumin Suo,* Yong-sheng Hu, Hong Li, Xuejie Huang, and Liquan Chen

Mass dissolution is one main problems for cathodes in aqueous electrolytes due to the strong polarity of water molecules. In principle, mass dissolution is a thermodynamically favorable process as determined by the Gibbs free energy. However, in real situations, dissolution kinetics, which include viscosity, dissolving mass mobility, and interface properties, are also a critical factor influencing the dissolution rate. Both thermodynamic and kinetic dissolving factors can be regulated by the ratio of salt to solvent in the electrolyte. In this study, concentration-controlled cathode dissolution is investigated in a susceptible Na₃V₂(PO₄)₃ cathode whose time-, cycle-, and state-of-charge-dependent dissolubility are evaluated by multiple electrochemical and chemical methods. It is verified that the super-highly concentrated water-in-salt electrolyte has a high viscosity, low vanadium ion diffusion, low polarity of solvated water, and scarce solute-water dissolving surfaces. These factors significantly lower the thermodynamic-controlled solubility and the dissolving kinetics via time and physical space local mass interfacial confinement, thereby inducing a new mechanism of interface concentrated-confinement which improves the cycling stability in real aqueous rechargeable sodium-ion batteries.

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1. Introduction

Traditional rechargeable batteries comprise a solid-liquid mixing system involving two solid electronic electrodes (cathode and anode), and one liquid ionic conductor (electrolyte), the properties of electrochemical liquid-solid interfaces are critical to the electrochemical performance of batteries.^[1] However, those solid-liquid interfaces are not always stable due to the high electrochemical and chemical activities of the electrolyte. For instance, in nonaqueous electrolytes, some electrodes such as transition metal-based oxide (TMBO) cathodes, Prussian blue analog (PBA) cathodes, sulfur cathodes, and organic electrodes suffer from interfacial degradation and cathode dissolution, resulting in active material loss and high interface resistance finally leading to short battery life.^[2] Because the dissolution phenomenon occurs at the solid-liquid interface, it is highly dependent on the properties of the electrode and the electrolyte, and the

dissolving degradation mechanisms are usually complicated and diverse. Generally, the available strategies for suppressing dissolution are categorized as follows: on the liquid electrolyte side and the solid electrode side. Compared to the strategies on solid electrodes, the enhancement of salt concentration in the liquid electrolyte is a more widely used strategy to suppress dissolution. Specifically, for TMBO cathodes, highly concentrated nonaqueous electrolytes suppress the particle disintegration due to crack propagation and participate in the formation of a compact cathode-electrode interface layer.^[3] For PBA cathodes, aqueous and highly concentrated electrolytes lower the dissolution because of the low water activity at the high salt concentration.^[4] For sulfur cathodes, organic and super-highly concentrated electrolytes reduce not only polysulfide dissolution and the shuttle effect, but also stabilize Li metal anodes owing to the high viscosity and high Li-ion transference number of the solvent-in-salt electrolyte.^[5] For organic-based batteries, the nonaqueous and highly concentrated electrolyte mitigates the dissolution of the discharge intermediate and final product.^[6]

Up to now, aqueous batteries have made breakthroughs in expanding the electrochemical window and improving energy density as well as prolonging work life,^[7] when compared with the abovementioned cases involving nonaqueous electrolytes.

Dr. J. M. Yue, Dr. L. D. Lin, Dr. L. W. Jiang, Dr. Q. Q. Zhang, Dr. Y. X. Tong, Prof. L. M. Suo, Prof. Y. S. Hu, Prof. H. Li, Prof. X. J. Huang, Prof. L. Q. Chen Beijing Advanced Innovation Center for Materials Genome Engineering Key Laboratory for Renewable Energy Beijing Key Laboratory for New Energy Materials and Devices Beijing National Laboratory for Condensed Matter Physics Institute of Physics Chinese Academy of Sciences Beijing 100190, China E-mail: suoliumin@iphy.ac.cn Dr. J. M. Yue, Dr. L. W. Jiang, Dr. Q. Q. Zhang, Dr. Y. X. Tong, Prof. L. M. Suo Center of Materials Science and Optoelectronics Engineering University of Chinese Academy of Sciences Beijing 100049, China Prof. L. M. Suo Yangtze River Delta Physics Research Center Co. Ltd Liyang 213300, China

It is still more challenging to address the cathode dissolution of vanadium-based (VBO) cathodes in aqueous solution^[8] due to the strong polarity of water easily attacking the VBO crystal structure to form dissolving vanadium species.^[9,10] For example, Na₃V₂(PO₄)₃ has a very high chemical and electrochemical stability in nonaqueous organic electrolytes,^[11] but exhibits inferior cycling stability in aqueous electrolytes^[12] because the thermodynamic dissolving equilibrium of VBO cathodes is highly dependent on the pH value of the solution and various oxidation states (III, IV, and V).^[10,13,14]

Thus far, it has been widely demonstrated that the increase in the salt concentration has a positive effect on the inhibition of vanadium dissolution,^[10,14] however, unfortunately, its concentration-controlled cathode dissolution mechanism has not been clarified yet. In this study, the concentration is set as the core variation to investigate the concentration-dependent dissolving phenomena deeply. Primarily, three different concentrated electrolytes are selected as the control samples including 1 m (mol kg⁻¹) sodium trifluoromethane sulfonate (NaOTf) (salt-in-water, 1 m SIW), 9 m NaOTf (water-in-salt, 9 m WIS), 22 m tetraethylammonium triflate (TEAOTf) + 9 m NaOTf (water-in-bisalt, 31 m WIBS), where TEAOTf with the same anion is introduced to achieve a higher salt concentration beyond the NaOTf saturation. Here, the time-, cycle- and state-of-charge (SOC) dependent dissolubility of Na₃V₂(PO₄)₃ cathode with varying concentrations is evaluated through multiple electrochemical and chemical methods. Combining the Noves-Whitney relationship with the Bockris-Devanathan-Muller (BDM) double electric layer model, the dissolution rate is quantified, and the kinetic and thermodynamic process of the vanadium dissolution in a super-highly concentrated electrolyte is described qualitatively. For the first time, the interface concentrated-confinement mechanism is proposed to give a full picture of the inhibition of cathode dissolution in the WIS electrolyte.

2. Results and Discussion

In order to observe vanadium dissolution in different concentrated electrolytes, the visual glass cells were assembled using $Na_3V_2(PO_4)_3/NaTi_2(PO_4)_3$ with an excessive amount of electrolytes. Before that, the stable electrochemical windows of three electrolytes were evaluated by the linear sweep voltammetry (LSV), they showed an increasing tendency with the increased concentration (31 m > 9 m >1 m) (Figure S1, Supporting Information), in addition, the cyclic voltammogram (CV) curves of Na₃V₂(PO₄)₃ and NaTi₂(PO₄)₃ in 1 m SIW electrolyte were also investigated (Figure S1, Supporting Information), obviously, it is wide enough to support the electrochemical couple of Na₃V₂(PO₄)₃ and NaTi₂(PO₄)₃, since 9 m WIS and 31 m WIBS electrolytes have wider stable electrochemical window than that of 1 m SIW, which could exclude the negative influence due to hydrogen and oxygen evolution in all three conditions. As Figure 1a shows, electrochemical reversibility is highly dependent on the salt concentration whose discrepancy is magnified by the flooding of the electrolyte due to the high mass ratio of electrolyte to the electrode. By raising the concentration from dilute (1 m SIW), to concentrated (9 m WIS), and to superconcentrated (31 m WIBS), the issue of severe overcharging

resulting from vanadium dissolution was addressed gradually. The electrochemical couple of $Na_3V_2(PO_4)_3/NaTi_2(PO_4)_3$ in 31 m WIBS exhibits a typical charge-discharge profile at 0.2 C, delivering the highest discharge capacity of 105 mAh g⁻¹ with the initial Coulombic efficiency (CE) of 88%. Moreover, along with the charge-discharge process, the WIBS electrolyte remained colorless from beginning to end (Figure 1a) (Figure S2, Supporting Information), further proving the absence of vanadium dissolution (inductively coupled plasma mass spectrometry (ICP-MS) results in Figure 1b). On the contrary, it was observed that the 1 m SIW electrolyte colors from clear to green indicating the severe dissolution of the Na₃V₂(PO₄)₃ electrode and 15 µg mL⁻¹ of vanadium ions were detected in the 9 m WIS electrolyte despite having no visible color change (Figure 1a). Meanwhile, Ti was not detected by the ICP-MS, confirming the chemical and electrochemical stability of NaTi₂(PO₄)₃ anode in aqueous media (Table S1, Supporting Information). All the abovementioned results indicate that the concentrated 31 m WIBS electrolyte can improve the electrochemical performance of the aqueous sodium-ion battery (ASIB) due to the inhibition of Na₃V₂(PO₄)₃ dissolution.

The full cell was constructed by $Na_3V_2(PO_4)_3$ as the cathode and $NaTi_2(PO_4)_3$ as the anode with a negative/positive (N/P) mass ratio of 1.5:1 where the cathode was excessive to compensate the deteriorated mass loss of the active $Na_3V_2(PO_4)_3$ and the sodium consumption due to the solid-electrolyte interface formation during cycling. Figure 1c-e shows the first cycle electrochemical behaviors of full cells with different concentrated electrolytes. The initial CV in Figure 1c shows two sharp redox peaks at 1.2 and 1.3 V corresponding to sodium extraction and insertion, respectively. Aside from the reversible redox pair of V^{4+}/V^{3+} in Na₃V₂(PO₄)₃ in the 1 m SIW electrolyte, the reduced peak of dissolved vanadium emerged at approximately 0.95 V,^[15] indicating that vanadium dissolution indeed occurred in the dilute aqueous electrolyte. Considering that the CE can directly index the cathode loss per cycle resulting from vanadium dissolution, the first cycle CE (1st-CE) in different concentrated electrolytes were tested at various charge-discharge rates to evaluate the impact of time, applied current density, and concentration (Figure S3-S5, Supporting Information). It is clearly shown that, besides the influence of concentration, the 1st-CEs tend to increase with the charge-discharge rate. It is revealed that cathode dissolution has the characteristics of salt concentration determination and time-dependent, listing as solubility ($\mu g m L^{-1}$) and dissolution rate ($\mu g m L^{-1}$ per day), respectively. The former reflects the vanadium dissolving capability and the mass capacity of electrolyte, and the latter represents the cumulative effect that is dependent on time and not on cycling life. It can also reasonably explain why the batteries suffering from cathode dissolution issues can achieve a satisfying cycle life at an extremely high rate. However, it should be emphasized that the high rate setting is not the final solution but a palliative that only hides the essence of the time-dependent vanadium dissolution. Figure 1e indicated that the 31 m WIBS electrolyte has all-sided advantages in the whole range of rates, particularly apparent at the low rate of 0.2 C. Compared with the CE at a high rate, the low rate is supposed to be the critical index for the cathode dissolution. The ASIB with the 1 m SIW electrolyte has a low 1st-CE at low (0.2 C, <10%) as well as a high rate







Figure 1. Salt concentration-dependent vanadium dissolution of $Na_3V_2(PO_4)_3$ cathode in aqueous solution. a) First charge–discharge profiles at 0.2 C with the corresponding color change photos. b) Corresponding content of dissolved vanadium after the first cycle. c–e) The first cycle electrochemical behaviors of aqueous $Na_3V_2(PO_4)_3/NaTi_2(PO_4)_3$ full cell with different concentrated electrolytes. c) The initial CV curves at the scanning rate of 0.1 mV s⁻¹. d) The charge–discharge profiles at 0.2 C in soft-packed batteries. e) The comparison of the 1st cycle Coulombic efficiencies at different rates.

(5 C, <60%) (Figure 1e) (Figure S6, Supporting Information) due to the strong vanadium solubility of the diluted aqueous solution. As displayed in Figure 1e, the 1^{st} -CE increased above 70% in the 9 m WIS and further enhanced to 88% in 31 m WIBS at a low rate of 0.2 C.

Figure 2a,b illustrated the electrochemical performance of the ASIB in three different concentrated electrolytes. The ASIB supported by the 31 m WIBS electrolyte had the highest 1^{st} -CE of 89.4% and much superior cycle stability with the highest capacity retention of 78% after 100 cycles. On the contrary, the

other two relatively less concentrated electrolytes (1 m SIW and 9 m WIS) presented a rapid capacity decay in the several initial cycles because the severe vanadium dissolution deteriorated $Na_3V_2(PO_4)_3$. Meanwhile, the rate performance in the 31 m WIBS electrolyte had an excellent capacity recovery, regaining nearly 100% of its first capacity at 1 C (Figure S7, Supporting Information). It is noted that the dissolution of vanadium is very sensitive to the charge–discharge rate due to the time-dependent character of cathode dissolution. As Figure 2c,d shows, the capacity retentions reported in the previous literature and obtained from





Figure 2. The electrochemical performance of aqueous $Na_3V_2(PO_4)_3/NaTi_2(PO_4)_3$ full cell. a) The cycle life at 1 C and b) the Coulombic efficiency at 1 C. The cycling stability comparison of available aqueous $Na_3V_2(PO_4)_3$ batteries (full cell and half-cell). c) Capacity loss per cycle and d) per hour.

our experiment are converted into rate-dependent capacity losses (capacity loss per cycle, %) and rate-independent capacity losses (capacity loss per hour, %). It clearly shows that our super-highly concentrated WIBS electrolyte has not only the highest capacity (\approx 97 mAh g⁻¹) but also the lowest capacity loss per cycle (0.22%). Besides, more impressively, our ASIB has the lowest capacity loss per hour (0.11%), indicating its intrinsic cathode stabilization in WIBS electrolyte (Table S2, Supporting Information).

The structural and chemical stability of the cycled $Na_3V_2(PO_4)_3$ electrodes in different concentrated electrolytes were further evaluated via CV, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and electrochemical impedance spectroscopy (EIS) (**Figure 3**). In the 9 m WIS electrolyte, the intrinsic redox peaks broadened after 25 cycles (the initial CV curve is shown in Figure S8, Supporting Information) accompanied by new reversible redox peaks of dissolved vanadium (0.95, 1.05 V), consistent with the constant charge–discharge results (Figure S9, Supporting Information). In the dilute 1 m SIW electrolyte, an irreversible dissolved vanadium peak appeared at the beginning of the initial cycle (Figure 1c). Subsequently,

the intrinsic redox peaks almost disappeared, however, a pair of broader dissolved vanadium peaks remaining after 25 cycles, indicating the severe vanadium dissolution and the instability of the Na₃V₂(PO₄)₃ electrode (Figure S10 and S11, Supporting Information). Furthermore, when the concentration reaches 31 m WIBS, the dissolved vanadium peak did not appear after 25 cycles (Figure 3a) and was confirmed by the constant current charge-discharge profiles after 100 cycles (Figure S12 and S13, Supporting Information). In order to confirm the positive effect of the WIBS electrolyte on the inhibition of vanadium dissolution, the longer cycled electrodes in WIBS electrolyte (150 cycles for XRD and 100 cycles for XPS) are chosen to compare with the 25 cycled electrodes in 1 m SIW and 9 m WIS. Figure 3b shows the XRD to check the structure change of the $Na_3V_2(PO_4)_3$ electrodes before and after cycles. In the 1 m SIW electrolyte, after 25 cycles, there is only one weak peak at $\approx 23.5^{\circ}$ remaining, with a very low-intensity, in contrast, in the 9 m WIS electrolyte after 25 cycles and in the 31 m WIBS electrolyte after 150 cycles still maintain the three identified peaks. It manifests that the structure deterioration of Na₃V₂(PO₄)₃ material in a dilute solution is



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Figure 3. The evolution of cycled $Na_3V_2(PO_4)_3$ electrodes in different concentrated electrolytes (25 cycles in 1 m SIW, 25 cycles in 9 m WIS, and ≥ 100 cycles in 31 m WIBS). a) The CV curves of aqueous full cells at the scanning rate of 0.1 mV s⁻¹ after 25 cycles. b) The XRD patterns of cycled electrodes. c) The Nyquist plots of the aqueous full cell with various cycles, d) XPS spectra of cycled $Na_3V_2(PO_4)_3$ (marked as NVP in the figure) electrodes. e) The degradation mechanism of $Na_3V_2(PO_4)_3$.

much more severe than that in higher concentrated electrolytes. The vanadium spectrum of XPS further confirms the existence of only the V³⁺ state in the Na₃V₂(PO₄)₃ electrode after cycled in the WIBS electrolyte for longer time (100 cycles) as opposed to that of 1 m SIW and 9 m WIS with a shorter time (25 cycles) which have an extra V⁴⁺ state corresponding to the irreversible product VO₂^[16]

Based on the above observations, we give the degradation mechanism of $Na_3V_2(PO_4)_3$ (Figure 3e). Firstly, the vanadium dissolution in aqueous electrolyte results in the capacity loss and structural damage of $Na_3V_2(PO_4)_3$ cathode that is just the beginning. Subsequently, the dissolved V^{3+} firstly adsorbed the electrode surface and then was oxidized into VO^{2+} . With the increasing of time, the dissociative VO^{2+} will be further electrochemically deposited into the solid VO_2 on the electrode surface and finally formed the passivation film that blocks the ionic and electronic transportation. The EIS further confirms our claims, the Nyquist plots in Figure 3c show the interfacial resistance under low concentration electrolytes (1 m SIW and 9 m WIS) continuously increased with the cycles due to the formation of an irreversible surface layer of VO_2 . Based on the above results,

we think the degradation mechanism of Na₃V₂(PO₄)₃ possibly originates from the capacity loss resulting from vanadium dissolution and the poor electronic/ionic transportation causing by the formation of the VO₂ passivation film (Figure 3e).^[17]

Figure 4 shows the solubility of the $Na_3V_2(PO_4)_3$ cathode at room temperature varied with SOCs (0%, 50%, and 100%), and the standing time. Because Na₃V₂(PO₄)₃ is involved in a two-phase electrochemical reaction during charging, the SOC represents the relative ratio of Na₃V₂(PO₄)₃ to NaV₂(PO₄)₃ (SOC 0%: 100% Na₃V₂(PO₄)₃, SOC 50%: 50% Na₃V₂(PO₄)₃-50% NaV₂(PO₄)₃, and SOC 100%: 100% NaV₂(PO₄)₃). ICP-MS was used to quantify the equilibrium concentration of vanadium ions in the immersion solutions. The proportion of dissolved vanadium was given in the pie charts (top part of Figure 4a). It revealed that the dissolubility of Na₃V₂(PO₄)₃ was more susceptible to the concentration than the SOC. After 15 days of soaking, more than 17% of the cathode was dissolved into the 1 m SIW electrolyte (SOC 0%: 18%, SOC 50%: 20%, and SOC 100%: 17%). The charge profile of $Na_3V_2(PO_4)_3$ in the nonaqueous electrolyte was shown in Figure 4b. However, the cathode loss was significantly reduced to less than 1.7% in the 9 m WIS electrolyte



Figure 4. $Na_3V_2(PO_4)_3$ dissolution experiment in different concentrated electrolytes. a) The state-of-charge (SOC) dependence dissolution experiment. The $Na_3V_2(PO_4)_3$ electrodes are charged into different SOCs (0%, 50%, and 100%) in the nonaqueous electrolyte, then soaked in the 1 m SIW, 9 m WIS, and 31 m WIBS electrolytes respectively, whose corresponding color changes (bottom) are recorded by the photo with the sanding of time (the initial, 8 days and 15 days) and the proportion of dissolved vanadium to total mass after soaked for 15 days is quantified by ICP-MS (top). b) The charge profile of $Na_3V_2(PO_4)_3$ in the nonaqueous electrolyte. c) The time-dependence vanadium dissolubility of pristine $Na_3V_2(PO_4)_3$ in 1 m SIW, 9 m WIS, and 31 m WIBS along with the linear fitting results according to the Noyes–Whitney equation.

and 0.09% in the 31 m WIBS electrolyte (Table S3, Supporting Information). In view of the color change, the WIBS electrolyte remained clear, signifying negligible dissolution, in comparison with the 1 m SIW electrolyte, whose color changed into green. In order to evaluate the dissolution rate of $Na_3V_2(PO_4)_3$, the Noyes-Whitney equation was applied to fit the time-dissolution relationship (Figure 4c). A mass of 4 mg of pristine $Na_3V_2(PO_4)_3$ powder was immersed in the same volume of the different electrolytes (4 mL). The amount of dissolved vanadium with soaking time was measured using the ICP-MS. As Figure 4c shows, the data were linearly fitted according to the Noyes-Whitney equation, whose slope was the dissolution rate of different concentrated electrolytes (K_{SIW} : 12.861 µg mL⁻¹ per day, K_{WIS} : 0.793 μ g mL⁻¹ per day, and K_{WIBS}: 0.021 μ g mL⁻¹ per day). It was clearly demonstrated that the WIBS electrolyte positively affects the inhibition of vanadium dissolution of $Na_3V_2(PO_4)_3$ (Table S4, Supporting Information).

The concentration-controlled dissolution experiments successfully demonstrated the ability of the 31 m WIBS electrolyte to suppress cathode dissolution at various testing conditions (charging rate, SOC, and resting time). Based on the abovementioned results, the possible mechanism of the cathode dissolution inhibition is proposed, including the unfavorable thermodynamic solubility and the kinetic limitable dissolution.

In the aspect of thermodynamics, the amount of water involving the dissolving process at the electrode interface and the dissolubility of the electrolyte are the two determining factors. On the one hand, the positive electrode surface is normally in a water depletion state as the molecular dynamics simulation results proved,^[18] resulting in low water content along the $Na_3V_2(PO_4)_3$ surface. On the other hand, in the electrolyte, the hydrated sodium, TEA cation, and free anion would form an electrical double layer (EDL) due to electrostatic interactions (Figure 5a). In an electrochemical and chemical dissolution, a reactant must cross the EDL to reach the electrode surface, thus, the structure and physical properties of the EDL determine the stability of the electrode. As the BDM model shows, the electrode-electrolyte interface has three regions, including the inner Helmholtz plane (IHP), the outer Helmholtz plane (OHP), and the diffusion layer. Meanwhile, since we are concerned about the interface properties of the positive electrode, thus the IHP layer would be mainly composed of the OTf anion by the formation of the negative-charge anion plane. Because the OTf anion is free without hydrating with water, so the IHP reduces the chance of water to be directly in contact with the cathode electrode; reasonably, the cation would be on the OHP layer correspondingly, specifically, in the 31 m WIBS system, both hydrated sodium and TEA cation have chance to

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Figure 5. The solid electrode–liquid electrolyte interfacial structure and corresponding kinetics performance near the interface of dissolved vanadium in three electrolytes. a) The BDM electric double layer model in different concentrated electrolytes. b) The Raman spectrum of the electrolytes. c) The viscosity comparison of 1 m SIW, 9 m WIS, and 31 m WIBS electrolytes. d) The thickness of the dissolution-diffusion layer (*d*) and concentration gradient (C_s-C_b) with the variation of the different viscous electrolytes.

be found in the OHP layer, however, as the concentration of TEA cation is much higher than that of sodium cation, so the free TEA cation, instead of hydrated Na cation, would occupy the OHP possibly and lower the water content in the region of the Helmholtz plane. It could also be supported by the results of molecular dynamics simulation along the positive electrode surface in the supercapacitor, in which the TEA cation shows a large probability to be found on the layer that behind of the negative-charge anion plane.^[19] In addition, since highly concentrated electrolytes (Na concentration \geq 9 m) are regarded as an all hydration system (Na(H₂O)₆) without free water existence,^[20] as shown in Figure 5b, the water activity goes down dramatically with the rise of concentration. Compared with the other two lower concentrated electrolytes, the 31 m WIBS electrolyte shows only one peak of the bound water,

indicating the low polarity of solvated water.^[21] Besides, the extremely high ratio of salt to water in the 31 m WIBS electrolyte physically lowers the chance of water-electrode contact, thereby significantly reducing the effective dissolving surface (A), which could also be qualitatively reflected by the Raman spectra of three electrolytes, a large solute–water dissolving surface would cause a high peak intensity of water. Obviously, the spectrum obtained from the 31 m WIBS electrolyte shows the weakest peak under the normalized intensity (Figure S14, Supporting Information), the strong solvated structure, combined with cation–anion aggregation, strengthens the bonding of water resulting in the low dissolubility of the cathode in the WIBS.^[20,22] Also, theoretically, a large radius TEA cation is difficult to form a hydrated ion with water due to its weak charge localization.^[23] On the contrary, the sodium hydration



of Na(H₂O)₆ can be easily realized. In the 9 m WIS system, the concentration of Na cation is relatively high to 9 m, which can bound almost all of the water to form $Na(H_2O)_6$, thereby reducing water activity. It is noted that TEA cation-rich 9 m WIS (1 m NaOTf+8 m TEAOTf) instead of 9 m WIS at the same salt concentration where a large amount of free water still exists probably resulting in severe vanadium dissolution leading to the fast capacity fading and low CE of the battery (Figure S15 and S16, Supporting Information). It is interesting that when the TEAOTf concentration continuously raises to the saturation (1 m NaOTf + 23 m TEAOTf), the cycle life seems to no noticeable improvement, but the CE increased significantly (Figure S17 and S18, Supporting Information). It indicated the super-high TEA salt concentration brings out the low effective contact area between water and the cathode and the high viscosity, also influencing the dissolving kinetic remarkably.

From the view of dissolving kinetics, the 31 m WIBS electrolyte has a much higher viscosity (30.2 mPa·S) than 1 m SIW (1.16 mPa-s) and 9 m WIS (4.66 mPa-s) (Table S5, Supporting Information). According to the Stokes-Einstein equation $(D = kT/6\pi \eta r, \text{ where } k \text{ is the Boltzmann constant, } T \text{ is the abso$ lute temperature, η is the viscosity of the electrolyte, and *r* is the radius of the solute molecule), the diffusion coefficient (D) of the dissolved vanadium is inversely proportional to viscosity due to hindering of the mobility of the dissolved vanadium. Thus, the highly viscous 31 m WIBS electrolyte should have the minimum D of vanadium (Figure 5c). Taking into account the concentration gradient near the surface based on the this given dissolution-diffusion layer (DDL) model (Figure 5d), the dissolution rate conforms to the Noves-Whitney equation in that the time-dissolving vanadium mass follows a linear relation (Figure 4c).^[24]

As shown in **Figure 6**, the physicochemical properties of the electrolyte linked with the parameters of the Noyes–Whitney equation and DDL models show the distribution of dissolved

vanadium on both interface and bulk electrolyte in SIW and WIS system, respectively. As previously explained, the effective contact area (A) is defined a parameter to index the amount of water involved in dissolving reaction and the water activity. In the WIBS electrolyte, water is barely involved in the dissolving process, and the weak dissolubility of the bonding water further reduces its dissolubility, thereby remarkably reducing the active surface area (A) (Figure 5b) (Figure S14, Supporting Information); meanwhile, the mobility of the dissolved vanadium is restricted by the high viscosity and the low diffusion coefficient (D). As discussed earlier, the $Na_3V_2(PO_4)_3$ cathode is much more stable in a highly concentrated electrolyte, so the surface concentration (C_s) for the dissolved vanadium along the electrode should be quite small. Due to an extremely low diffusion coefficient and the finite dissolved vanadium, the dissolving vanadium probably prefers to localize on the surface of the electrode resulting in a low concentration gradient of C_s-C_b and a thin dissolving vanadium diffusion layer (d). The dissolution rate in Figure 4c is used to evaluate the ability of dissolution.^[25] Although the denominator (d) decreases, the WIBS electrolyte still has the lowest dissolution rate (dm/dt) of 0.021 μ g mL⁻¹ per day, which indicates the other parameters might be the main factors whose positive effect overwhelming the negative effect along with the reduction of the dissolving vanadium diffusion layer. All in all, the WIBS electrolyte has extremely low cathode solubility and a relatively slow dissolution rate with the largely limited vanadium diffusion. We presume that the dissolved vanadium is very likely to be confined on the local surface of the cathode resulting in its enrichment on the surface which is called the interface concentrated-confinement. Because the dissolved mass is confined to the surface, it further lowers the concentration gradient and possibly allows the reversible electrochemical activity of the little dissolved vanadium on the surface of the electrode during the cycles (Figure 5c).



Figure 6. Schematic illustration of vanadium dissolution according the Noyes–Whitney equation. (dm/dt: cathode dissolution rate, *m*: the mass of dissolved material, *t*: time, *A*: the active water contract area, *D*: diffusion coefficient of dissolving vanadium in the electrolyte, *C*_s: the saturation concentration of cathode surface, *C*_b: the concentration of dissolving vanadium in the electrolyte, *d*: the thickness of dissolution-diffusion layer).



3. Conclusion

In summary, the determined concentration relationship between the electrochemical behavior and the cathode dissolution is investigated in a typical Na₃V₂(PO₄)₃ cathode. It is found that the full cell (Na₃V₂(PO₄)₃/NaTi₂(PO₄)₃) exhibits a high initial discharge capacity (\approx 97 mAh g⁻¹), the highest 1st-CE (>89%), and the lowest capacity fading (capacity loss per cycle (0.22%) and per hour (0.11%)) in a super-highly concentrated WIBS electrolyte at 1C. Based on the BDM electric double layer model and the Noyes-Whitney equation, the physicochemical properties of the WIBS electrolyte are linked with the parameters of the equation as follows. (1) The active contact area (A) is remarkably reduced due to water being barely involved in the dissolving process and the weak dissolubility of the bonding water; (2) the low diffusion coefficient (D) and the high viscosity mostly restricted the mobility of the dissolved vanadium; and (3) the finite dissolved vanadium possibly prefers to localize on the surface of the electrode resulting in a very low concentration gradient $(C_s - C_b)$ due to weak dissolubility and limited vanadium diffusion. It is concluded that the WIBS electrolyte remarkably lowers the thermodynamically controlled solubility and the dissolving kinetic by time- and physical space-local mass confinement, thereby inducing the interface concentrated-confinement mechanism which suppresses cathode dissolution and stabilizes the cathode during cycling.

4. Experimental Section

Material Synthesis: Na₃V₂(PO₄)₃/C was synthesized through the solidstate method as follows: the stoichiometric ratios of NaH₂PO₄·2H₂O (99.9%, Alpha), V₂O₃ (99.9%, Alpha) powders, and the corresponding amounts of sugar were put into an agate jar as precursors, and then the precursors were milled in a planetary ball mill (PM 200) at 400 rpm in a stainless-steel vessel for 8 h. After ball milling, the mixture was pressed into a pellet and then heated at 800 °C for 24 h in Ar atmosphere. NaTi2(PO4)3 was synthesized through the sol-gel method. $NaH_2PO_4 \cdot 2H_2O$ and $NH_4H_2PO_4$, in a stoichiometric ratio, were dissolved in deionized water. $C_{12}H_{28}O_4Ti$, which was dissolved in absolute ethanol, was then added to the initial solution under vigorous stirring. After evaporating the solvent in an oil bath, the obtained gel precursor was annealed at 800 °C for 6 h in Ar. With an intermediate grinding, the sample was annealed at 600 °C for 8 h in a quartz tube furnace with toluene vapor carried by Ar gas to obtain the $NaTi_2(PO_4)_3/C$ sample. Sodium trifluoromethanesulfonate (NaOTf) (>98%, TCI), the TEAOTF salt (99%) (Shanghai Fujie Chemical Co., Ltd), and water (HPLC grade, Alfa) were used as received. According to the molality (mol-salt in kg-solvent), five different kinds of aqueous electrolytes were prepared, which were recorded as the abbreviated concentrations (1 m, 9 m, 9 m + 22 m, 1 m + 8 m, and 1 m + 23 m).

Material Characterizations: Structural characterization was performed using an X'Pert Pro MPD X-ray diffractometer (XRD) (Philips, Netherlands) with Cu K α radiation (1.5405 Å) from 10 to 80 (2 θ). SEM images were acquired using a Hitachi S-4700 operating at 10 kV. The TEM images of Na₃V₂(PO₄)₃/C and NaTi₂(PO₄)₃/C were examined using a JEOL 2100 F field emission. XPS analysis was carried out on a high-resolution Kratos AXIS 165 X-ray photoelectron-spectrometer with monochromic Al K α radiation source. The content of dissolved vanadium in the cycled electrolyte was measured using an ICP-MS. The Raman spectra for electrolytes were collected with an NRS-5100 spectrometer (JASCO) between 4000 and 400 cm⁻¹.

Electrochemical Measurements: $NaTi_2(PO_4)_3$ and $Na_3V_2(PO_4)_3$ electrodes were prepared by compressing the active material, carbon

black, and PTFE at the weight ratio of 8:1:1. Titanium mesh (80 mesh) was used as collectors for both electrodes, which was covered by a carbon paper on both sides before used. The full cell was assembled in a soft-packed battery with the $Na_3V_2(PO_4)_3$ electrode (area of 5 mg cm⁻²) as the cathode, NaTi₂(PO₄)₃ (area of 3.2 mg cm⁻²) as the anode, and a Whatman glass fiber as the separator. The mass ratio of the cathode/ anode is 1.5/1 (1 C = 0.13 A g⁻¹). Cyclic voltammetry (CV) of aqueous full cell was measured using a CHI 600E electrochemical workstation on a soft-packed battery at a scan rate of 0.1 mV s⁻¹; CV of Na₃V₂(PO₄)₃ or NaTi₂(PO₄)₃ electrode in 1 m WIS electrolyte were measured using a CHI 600E electrochemical workstation on a three-electrode device at a scan rate of 2 mV s⁻¹, detailly, the work electrode is $Na_3V_2(PO_4)_3$ or NaTi₂(PO₄)₃ electrode, the counter electrode is Ti net, Ag/AgCl electrode is used as reference electrode, and LSV of electrolytes were also measured using a CHI 600E electrochemical workstation on a three-electrode device at a scan rate of 10 mV s^{-1} , the work electrode and counter electrode are both Ti net, and Ag/AgCl working as reference electrode. Viscosity was measured using an MCR 502 Anton Paar with a controlled shear rate and shear stress at 25 °C. EIS was performed on an electrochemical workstation (Zahner IM6, Germany) with AC signals of 5 mV in a frequency range of 1 Hz-6.0 MHz. Discharge and charge measurements were performed using a NEWARE (STS 7.6.x) battery test system (Shenzhen, China) at room temperature.

Dissolution Analysis: Three different cycled aqueous electrolytes were prepared in a full cell by using a visual glass cell which was cycled for one time at 0.2 C. As for the compound with different sodium contents, after charging to different capacities in a nonaqueous (1 м NaClO₄ in ethylene carbonate (EC)/diethyl carbonate (DEC), EC:DEC = 1:1 in volume) half coin cell, we disassembled the cycled cell and washed the cathode with dimethyl carbonate for several times. The two mentioned processes were performed in the glove box to eliminate the effect of moisture in the air. After the electrode was drained in the glove box, the cycled $Na_3V_2(PO_4)_3$ electrodes were immersed in 4 mL of the corresponding electrolytes. All the cathodes contained the same active material (4 mg). The obtained solutions were tested for the content of dissolved vanadium using the ICP-MS. As for the initial Na₃V₂(PO₄)₃ sample, 4 mg Na₃V₂(PO₄)₃ powder was immersed in 4 mL of the electrolyte solutions under atmospheric conditions and ambient temperature, fully mixed, and put in a stable place, with different soaking times. ICP-MS was employed to measure the content of dissolved vanadium in the clear upper solution.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

aqueous batteries, interfaces, sodium-ion batteries, vanadium dissolution, water-in-salt electrolytes

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