

Regulating Solvent Co-Intercalation in Bi-Layered Vanadium Oxides for Zinc Batteries by Nanoconfinement Chemistry

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ABSTRACT

Electrochemical intercalation typically involves ion desolvation at the electrolyte-electrode interface, incurring kinetic limitations and strong ion-host interactions. The emerging mechanism of solvent co-intercalation, where ions intercalate together with a (partially) intact solvation shell, can mitigate these drawbacks, but has thus far been primarily explored from the viewpoint of electrolyte design. Herein, we demonstrate the feasibility of regulating solvent co-intercalation by electrode nanoconfinement design. By tuning the nanoconfining interlayer environment of bi-layered vanadium oxides from hydrophilic to hydrophobic, the Zn^{2+} intercalation properties in aqueous electrolyte are modified. Comprehensive experiments and simulations reveal progressively reduced solvation/hydration of intercalating Zn^{2+} with decreasing interlayer hydrophilicity, affecting maximum capacity, redox potential, and kinetics of the electrochemical intercalation reactions. Similar electrochemical trends are observed in non-aqueous electrolytes, indicating the potential of nanoconfinement design as a universal strategy for regulating ion-solvent (co-)intercalation in various battery chemistries.

INTRODUCTION

Electrochemically-driven ion intercalation is the fundamental charge storage mechanism for many modern rechargeable batteries.¹⁻⁵ The intercalation reactions typically consist of three main steps: Solvated ion migration through a liquid electrolyte to the electrolyte/electrode interface, interfacial charge transfer, and subsequent solid-state diffusion of the intercalant within the electrode host lattice.⁶ For a typical charge transfer process, the coordinating solvent molecules of the liquid electrolyte are stripped off from the surface-adsorbed ions (*i.e.*, desolvation), before the naked ion can then be inserted into the host lattice. From a simplified point of view, this step can be seen as a ligand exchange reaction as known from the field of inorganic coordination chemistry. Although the overall reaction is supported by entropy, the desolvation step is inevitably associated with an energy barrier presenting a kinetic limitation.⁷ An emerging strategy to overcome the disadvantages associated with desolvation is the intercalation of ions together with a (partially) intact solvation shell. This is also referred to as solvent co-intercalation.^{6,8} Such reactions have gained momentum since the discovery of highly reversible co-intercalation of solvated Na⁺ into graphite, a process that is thermodynamically prohibited for naked Na⁺.⁹ Co-intercalation phenomena are also encountered in other post-lithium energy storage like magnesium batteries,^{10,11} and aqueous zinc- or proton-batteries.^{12,13} Studies into the origins and the working mechanism are emerging.¹⁵⁻¹⁷ Current strategies to regulate the feasibility and extent of solvent co-intercalation are, however, strongly focused on utilizing specialized electrolytes in both aqueous and organic systems.

The lack of consideration for regulating the co-intercalation properties of electrode materials presents a severe bottleneck, particularly for emerging multivalent battery chemistries where electrolytes are designed towards interfacial stability and whose electrolyte salts normally have low solubility, thus significantly reducing their tunability. Isolated reports of two-dimensional titanium carbide MXenes indicate that their surface chemistry can influence the extent of solvation of adsorbing or intercalating ions,^{18,19} leading us to hypothesize that electrode design can be an alternative lever for tuning solvation. Consequently, there is an urgent need for exploring and understanding electrode materials design principles aimed at either promoting or inhibiting solvent co-intercalation, particularly regarding electrode materials commonly

employed in state-of-the-art batteries, *i.e.*, layered transition metal oxides.

Pillaring approaches generally target the regulation of electrode materials' interlayer space, where intercalating species are hosted. They have been explored to modify the nanoconfining interlayer environment of host materials such as bi-layered vanadium oxides. However, these works mostly focus on the geometric aspect of nanoconfinement, *e.g.*, manipulating the interlayer spacing with spacer pillars of different dimensions,²⁰⁻²³ neglecting the chemical environment of nanoconfined species. Capitalizing on the wide chemical diversity offered by organic molecules, we herein explore their capability as functional pillars to control the solvophilicity of the host's interlayer environment and thus, introduce a paradigm-shift for regulating the extent of solvent co-intercalation as a function of nanoconfinement chemistry.

The proposed materials design principle is investigated using a series of bi-layered V₂O₅ hosts with modified nanoconfinement chemistries based on pillar molecules of varying hydrophilicity. Adopting established Zn²⁺ intercalation from aqueous electrolytes as a model reaction, comprehensive analyses disclose a clear trend of progressively reduced hydration of intercalating Zn²⁺(H₂O)_n upon decreased interlayer hydrophilicity of the host materials. The concept is also extended to organic electrolytes, confirming that the strategy of tuning nanoconfinement chemistry holds potential for diverse battery chemistries including those employing non-aqueous electrolytes.

RESULTS & DISCUSSIONS

Materials synthesis and characterization

A series of bi-layered V₂O₅ materials incorporating three different pillar molecules with varying polarity is synthesized by a bottom-up approach. Such variations in pillar functionality are hypothesized to affect the hydrophilic characteristics of the hosts' interlayer environments. These pillars are water (H₂O, the most hydrophilic inorganic pillar), 2,2'-(Ethylenedioxy)bis(ethylamine) (C₆H₁₆N₂O₂, "EBEA", a hydrophilic organic pillar) and 1,8-Diaminooctane (C₈H₂₀N₂, "DOA", a hydrophobic organic pillar). The choice is motivated by their varying lone electron pair density, which is investigated through electron localization function (ELF) analysis. It is highest for H₂O, followed by EBEA, while DOA possesses the

least accessible lone pairs (**Figure 1a**, **Note S1**). We hypothesize this as a general design principle to tune the hydrophilicity of the resulting nanoconfined interlayer environments of the host materials, which is validated by a combination of sorption experiments (**Figure 1b**). First, nitrogen sorption isotherms are analyzed. They indicate mostly macroporous samples with moderate specific surface areas (SSA) of around 25, 20 and 31 m² g⁻¹ for V₂O₅-H₂O, V₂O₅-EBEA and V₂O₅-DOA, respectively. These SSA values and the increase of gas uptake at high relative pressures are indicative of N₂ sorption taking place mostly on the external surface. Water vapor sorption isotherms show different trends. The sorption values far exceed the uptakes of N₂ at 100 % humidity. V₂O₅-H₂O exhibits the highest sorption capacity up to 516 cm³ g⁻¹, followed by V₂O₅-EBEA (326 cm³ g⁻¹) and then V₂O₅-DOA (164 cm³ g⁻¹). The large water sorption capacities suggest the involvement of the interlayer space in sorption.²⁴ Specifically, the high uptake of V₂O₅-H₂O at low humidity reveals a particularly strong interaction of this sample with water. Moreover, the progressively reduced sorption volumes with decreasing hydrophilic interlayer chemistries confirm the effectiveness of nanoconfinement manipulation in tuning solvophilicity.

Electron microscopy characterization shows a nano-ribbon morphology of all samples (**Figure S1-2**). The crystal structure of the materials is analyzed by powder X-ray diffraction (XRD, **Figure 1c**), confirming the characteristic bi-layered V₂O₅ structure model.²⁵ All samples present lamellar ordering (though turbostratic) as indicated by the prominent (001) reflections with 2θ values of 6.39°, 7.28° and 6.15°. These correspond to similar d-spacings of 13.82 Å (V₂O₅-H₂O), 12.13 Å (V₂O₅-EBEA), and 14.37 Å (V₂O₅-DOA), respectively. Moreover, differences in intensity counts and peak width indicate a decreasing trend of crystalline domain size, which is validated by microstructural analysis via transmission electron microscopy (**Figure S2**). X-ray absorption spectroscopy (XAS, **Figure S3**) at the V K-edge reveals similar bulk chemical environments across the material series, closely resembling the reference α-V₂O₅ while exhibiting strong deviations from the centrosymmetric coordination. This aligns with the structure characteristics of bi-layered V₂O₅.²⁵

X-ray photoelectron spectroscopy (XPS) verifies consistent vanadium valence states across all materials (**Figure S4**), and further discloses the presence of ionic components from protonated

alkylammonium pillars (**Figure 1d**).²² This suggests ionic interaction between pillars and bi-layered vanadium oxides, where $\text{V}_2\text{O}_5\text{-H}_2\text{O}$ is reported to confine hydroniums inside the interlayer.²⁶ Thermogravimetric analysis (**Figure S5**) quantifies the chemical compositions of the three samples as $\text{V}_2\text{O}_5 \cdot 1.168\text{H}_2\text{O}$ (“ $\text{V}_2\text{O}_5\text{-H}_2\text{O}$ ”, $M_w=202.92 \text{ g mol}^{-1}$), $(\text{C}_6\text{H}_{16}\text{N}_2\text{O}_2)_{0.271}\text{V}_2\text{O}_5 \cdot 0.362\text{H}_2\text{O}$ (“ $\text{V}_2\text{O}_5\text{-EBEA}$ ”, $M_w=228.57 \text{ g mol}^{-1}$), and $(\text{C}_8\text{H}_{20}\text{N}_2)_{0.259}\text{V}_2\text{O}_5 \cdot 0.184\text{H}_2\text{O}$ (“ $\text{V}_2\text{O}_5\text{-DOA}$ ”, $M_w=222.56 \text{ g mol}^{-1}$), respectively.

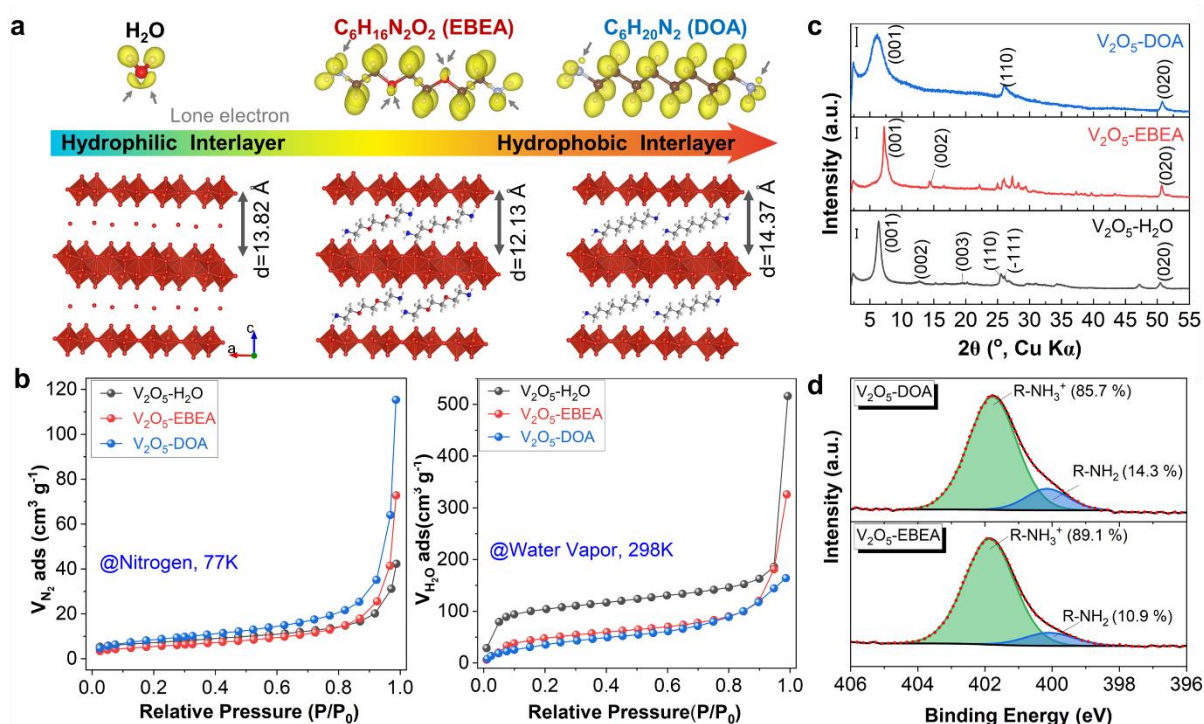


Figure 1. Physicochemical properties of the bi-layered vanadium oxide series. (a) Electron localization function computed from first-principle simulation (iso-value of 0.7) and the correlated material modification strategy. A grey arrow indicates one lone-electron-pair. (b) Gas sorption isotherms of the materials, using nitrogen at 77 K (left) and water vapor at 298 K (right). (c) Powder X-ray diffraction (XRD) patterns of the vanadium oxide series obtained in transmission geometry. The scale bars indicate the same intensity count. (d) X-ray photoelectron spectroscopy (XPS) analysis of N 1s spectra for V₂O₅-DOA and V₂O₅-EBEA powders.

Electrochemical characterization

The electrochemical Zn^{2+} intercalation properties of the V_2O_5 -based electrode materials series are tested as positive electrodes in a two-electrode setup (2032-type coin cells) versus zinc metal negative electrodes in aqueous electrolytes of 3 M zinc trifluoromethanesulfonate ($\text{Zn}(\text{OTf})_2$). Zinc salts based on the OTf^- anion are chosen to minimize the potential influence from ion association (e.g., formation of ion pairs) in the electrolyte,²⁷ because lower cation-anion interactions can be expected due to the reduced charge density with bulky anion size, facilitating Zn^{2+} dissociation. The highly hydrophobic nature of OTf^- helps to limit side reactions involving water molecules,²⁸ and also prevents a possible anion incorporation into the host's interlayer space. Furthermore, the electrolyte concentration was set as 3 M following previous reports,^{12, 29} to restrict the free solvent (water) activity and ensure the expected electrochemical performance. All samples exhibit highly symmetric and repeating discharge-charge profiles across the initial cycles, indicating little structural/chemical irreversibility in all three electrodes during the initial electrochemical reduction (**Figure 2a-c**). This is further underlined by the high initial Coulombic efficiencies (CEs) approaching 100 %. Additionally, slight capacity increases are observed in their initial cycles, possibly due to an interface optimization of the V_2O_5 electrode leading to reduced impedances (**Figure S6**) and/or the zinc metal anode (with a native insulating oxide layer).

Tuning the nanoconfinement chemistry reveals a gradual capacity increase for decreasingly hydrophilic samples from H_2O - to EBEO- and DOA-pillared V_2O_5 . Their cathodic capacities reach 339, 364, and 401 mAh g^{-1} at the 3rd cycle, corresponding to an electron transfer number per V_2O_5 of $2.57e^-$ ($\text{V}_2\text{O}_5\text{-H}_2\text{O}$), $3.10e^-$ ($\text{V}_2\text{O}_5\text{-EBEO}$) and $3.33e^-$ ($\text{V}_2\text{O}_5\text{-DOA}$), respectively. This underlines the dependence of the capacity on the nanoconfinement chemistry. While concurrent H^+ intercalation across the whole potential range has been reported in vanadium oxides,³⁰ the contribution in our case is found to be limited (maximum protonation capacity is found in $\text{V}_2\text{O}_5\text{-H}_2\text{O}$, below ca. 40 mAh g^{-1}) in each sample when testing in dilute H_2SO_4 that matches the pH of 3 M $\text{Zn}(\text{OTf})_2$ (**Figure S7**, **Table S1** and **Note S2**).

Rate handling measurements (**Figure 2d**) reveal that $\text{V}_2\text{O}_5\text{-H}_2\text{O}$ surpasses $\text{V}_2\text{O}_5\text{-EBEO}$ in capacity at higher specific currents, while $\text{V}_2\text{O}_5\text{-DOA}$ maintains the highest capacity across all

current densities. All samples show high CEs across various current densities, confirming the high chemical reversibility of the charge storage processes. Long-term cycling performances are compared in **Figure 2e**. The hydrophobic sample V_2O_5 -DOA shows the best stability, with an overall capacity retention of 77 % after 3,500 cycles. In contrast, V_2O_5 -EBEA experiences a fast capacity drop at the beginning, before gradually stabilizing (44 % retention). V_2O_5 -H₂O displays an initial capacity increase but rapid cell degradation after about 1,600 cycles.

Differences in redox properties are further investigated in the cyclic voltammetry (CV) profiles (**Figure 2f**). Signals for V_2O_5 -H₂O are generally characterized by two pairs of broad and symmetric peaks, where the low-potential pair appears more significant accounting for higher amount of charge storage. The redox signature of V_2O_5 -EBEA and V_2O_5 -DOA becomes sharper and less symmetric, accompanied with noticeable shifts in anodic/cathodic electrode potential compared to V_2O_5 -H₂O. The first/high potential reduction (R1) peak of both V_2O_5 -DOA and V_2O_5 -EBEA samples shifts towards lower potentials compared to V_2O_5 -H₂O. Notably, a slight peak split is observed across all samples at the first reduction zone, which merge together at increased sweeping rates. The high-potential redox peaks of the organically-pillared samples also become more pronounced, leading to increased capacities at elevated voltages. Contrarily, the second/low potential reduction (R2) peak of both V_2O_5 -DOA and V_2O_5 -EBEA samples shifts towards higher potentials compared to V_2O_5 -H₂O. The shifts of redox peaks in different directions, as well as the significant change in CV shape between the samples are indicative of a variation in the intercalation mechanism. CV measurements at varying sweep rates (“*b*-value” analysis,³¹ **Figure 2g-i**) suggest a trend towards more surface-limited kinetics for V_2O_5 -H₂O, whereas a mixed control and/or finite-length diffusion control is revealed for both V_2O_5 -EBEA and V_2O_5 -DOA samples.

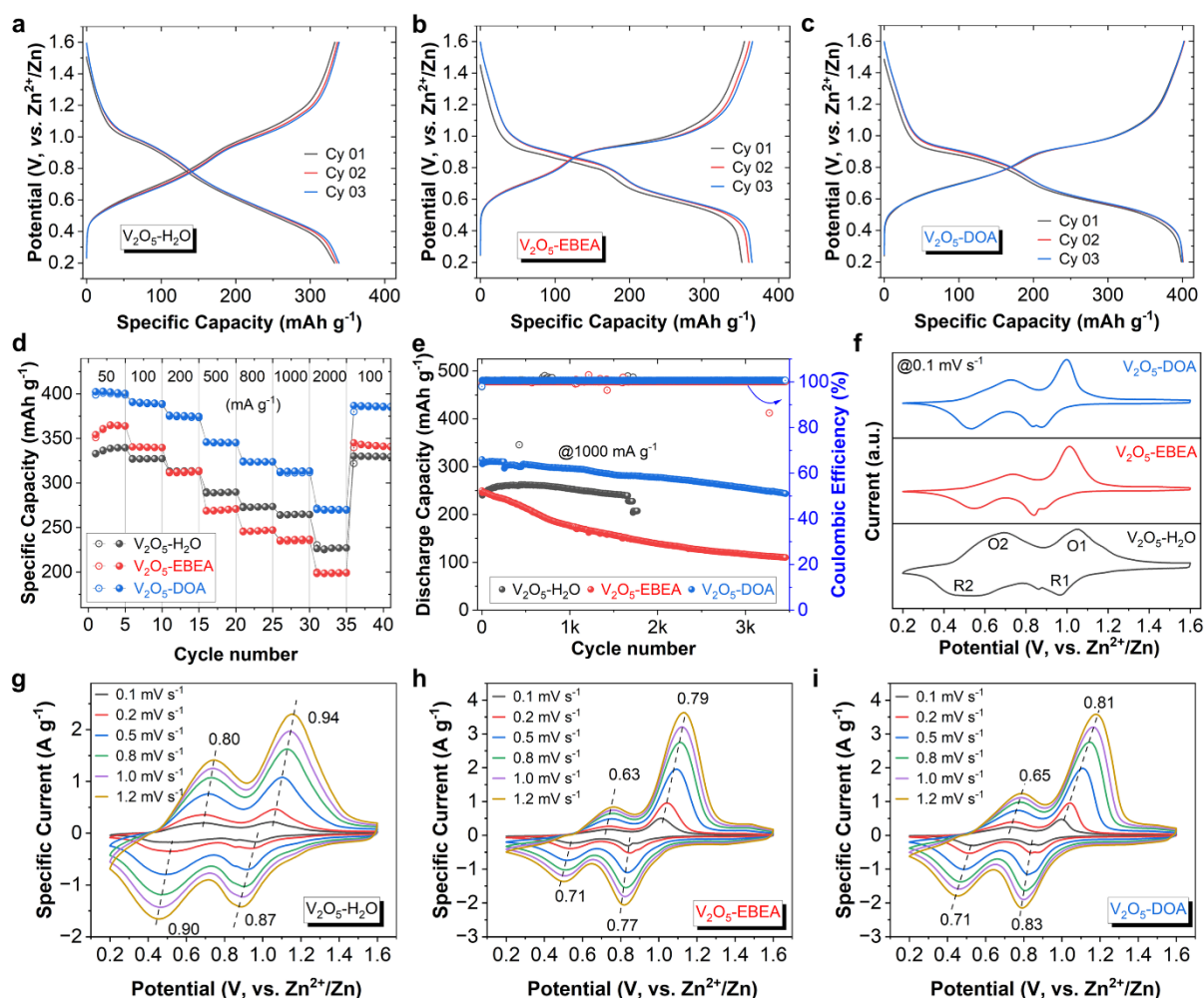


Figure 2. Electrochemical properties of V_2O_5 with varying interlayer chemistry in 3 M $\text{Zn}(\text{OTf})_2$ electrolyte. Galvanostatic discharge-charge profiles of the initial three cycles for (a) $\text{V}_2\text{O}_5\text{-H}_2\text{O}$, (b) $\text{V}_2\text{O}_5\text{-EBEA}$, and (c) $\text{V}_2\text{O}_5\text{-DOA}$ at a specific current of 50 mA g^{-1} . (d) Rate performance of the different electrode materials. Hollow and solid cycles correspond to discharge and charge processes, respectively. (e) Long-term cycling performances of the materials series. Each cell was pre-cycled at 50 mA g^{-1} for 5 times before switching to 1 A g^{-1} current, and only the latter is shown for clarity. (f) The CV profiles of the three materials at 0.1 mV s^{-1} . CV measurements of (g) $\text{V}_2\text{O}_5\text{-H}_2\text{O}$, (h) $\text{V}_2\text{O}_5\text{-EBEA}$, and (i) $\text{V}_2\text{O}_5\text{-DOA}$ electrodes at varying sweeping rates.

Analysis of solvent co-intercalation behavior

Basic electrochemical characterization, discussed above, reveal differences in Zn^{2+} intercalation capacity, redox potentials, and kinetics among the different electrodes. We hypothesize that these differences arise from changes in the extent of solvent (water) co-intercalation, caused by the variations in nanoconfinement chemistry. To verify, first, the electrochemical properties of the three electrode materials are evaluated in a non-aqueous electrolyte (**Figure 3a-c**) of saturated anhydrous $\text{Zn}(\text{OTf})_2$ in acetonitrile (ACN), *i.e.*, in an environment where water co-intercalation can be ruled out. The salt dissociation ability, or solvating power of a solvent can be empirically correlated with its donor number (DN) and dielectric constant (ϵ).³² In this context, ACN exhibits a weaker solvating power compared to water, evidenced by their respective DN (14.1 vs. 18.0) and ϵ (38.0 vs. 81.0).³³ Moreover, $\text{Zn}(\text{OTf})_2$ shows substantially lower solubility in ACN (less than 1 M). Consequently, the resulting Zn^{2+} solvation complexes likely require reduced energy for desolvation, thereby significantly decreasing the potential/extent of solvent co-intercalation.

This effect is reflected in a reduced capacity observed in the ACN-based electrolyte across all samples (**Figure 3a, b**) compared to the aqueous electrolyte. Furthermore, the ability of the materials series to enable non-hydrated Zn^{2+} intercalation can also be readily compared. Hydrophobic V_2O_5 -DOA can host the highest number of non-hydrated Zn^{2+} (**Figure 3b**). This is followed by the intermediate sample V_2O_5 -EBEA, while the most hydrophilic V_2O_5 - H_2O sample shows very limited charge storage in non-aqueous electrolyte. This demonstrates the essential role of solvent (water) co-intercalation particularly in the hydrophilic V_2O_5 - H_2O . Notably, redox profiles after 50 cycles (**Figure 3c**) reveal a distinct pair of redox peaks ($\text{R}_{2\text{A}}/\text{O}_{2\text{A}}$) in V_2O_5 -DOA and V_2O_5 -EBEA, which closely match the R_1/O_1 pair in aqueous electrolyte in both electrode potential and amplitude. In contrast, V_2O_5 - H_2O exhibits severe polarization and negligible capacity. This is a strong indication that these redox signals correspond to the (de)intercalation of desolvated Zn^{2+} in both aqueous and non-aqueous electrolytes. Further electrochemical analysis can be found in **Figure S8-11** and **Note S3**.

Back to aqueous electrolytes, the activation-controlled desolvation process during charge transfer is analyzed using varying temperature electrochemical impedance spectroscopy (VT-

EIS)³⁴ in three-electrode cells. Nyquist plots exhibit a small (not obvious in V₂O₅-H₂O) and a large semicircle from high to medium frequency ranges, and then a sloping tail at low frequencies attributed to Warburg impedance that correlates to the mass transport in the bulk electrode lattice (**Figure 3d-f**). The intercept and semicircles correspond to solution resistance (R_s), a passivation layer resistance (R_p), and a charge transfer resistance (R_{ct}), respectively.³⁵ Upon temperature increase, V₂O₅-H₂O displays almost unchanged Nyquist profiles, with even slightly increased R_{ct} at further elevated temperatures (**Figure S12**). This indicates an activation-less charge transfer, where no physically meaningful activation barrier can be extracted from the Arrhenius plot. This finding aligns with the H₂O sorption capability of V₂O₅-H₂O (**Figure 1b**) and more generally the water-swallowable nature of vanadium oxide xerogel,³⁶ thus providing again strong evidence for a desolvation-free water co-intercalation process in the hydrophilic sample. In sharp contrast, both V₂O₅-DOA and V₂O₅-EBEA are found to be associated with a typical temperature-dependent, activation-controlled process, where an activation energy (E_a) is required to achieve charge transfer. This is evident from the noticeable shrinkage of the second semicircle (R_{ct}) with rising temperatures. These findings with distinct differences between the samples demonstrate that varying nanoconfinement chemistry with associated changes in interlayer hydrophilicity can efficiently tune the desolvation-related charge transfer resistance and thus the extent of hydration of intercalating Zn²⁺.

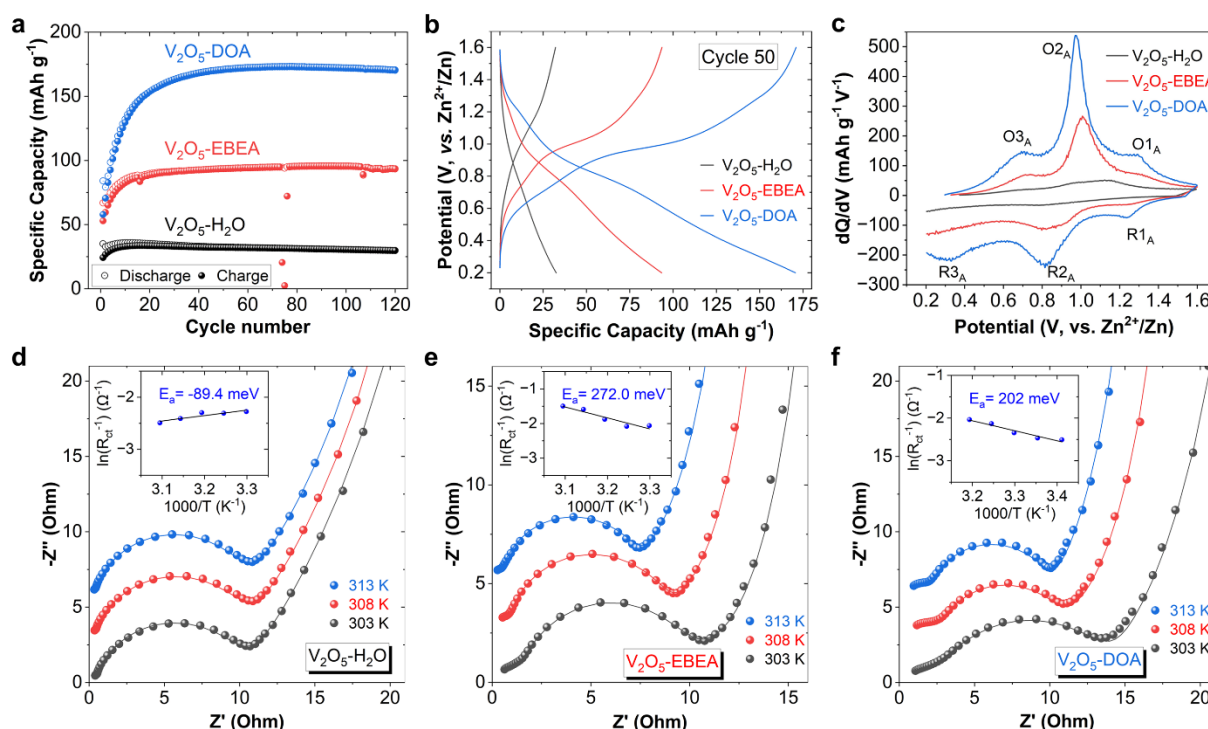


Figure 3. Validation of solvent co-intercalation in the V_2O_5 series. (a-c) Electrochemical properties of the various materials in a nonaqueous electrolyte ($\text{Zn}(\text{OTf})_2$ in ACN). (a) The cycling performances of the materials, (b) their galvanostatic discharge-charge profiles at the 50th cycle and the corresponding (c) differential capacity plots. (d-f) VT-EIS measurements for the material series in the aqueous electrolyte ($\text{Zn}(\text{OTf})_2$ in water). The Nyquist plots for (d) $\text{V}_2\text{O}_5\text{-H}_2\text{O}$, (e) $\text{V}_2\text{O}_5\text{-EBEA}$, and (f) $\text{V}_2\text{O}_5\text{-DOA}$ under selected steps of varying temperatures. The insets show the Arrhenius plots of inverse R_{ct} values as a function of $1000/T$, with the slope values representing the activation energy for charge transfer.

This central finding is further verified via *operando* mass monitoring using electrochemical quartz crystal microbalance (EQCM). Mass changes were tracked starting from the resting period, as presented in **Figure 4a-c**. Spontaneous water uptake is readily observed in $\text{V}_2\text{O}_5\text{-H}_2\text{O}$ even prior to electrochemical stimulation, by an increasing mass over time upon immersion in electrolytes. This aligns with the water sorption isotherms (**Figure 1b**) and is accordingly attributed to free solvent (water) flooding into electrodes' interlayer space.^{17, 37} This is further supported by XRD measurements (inset) where expanded d-spacing is detected. Interestingly, the opposite trend is observed in $\text{V}_2\text{O}_5\text{-DOA}$, with the electrode mass gradually decreasing until stabilizing after approximately 2 h. This can be mainly caused by partial desorption of

nanoconfined species from the electrode, evidenced by the XRD detection of a new peak at reduced d-spacing. An intermediate behavior is identified in V₂O₅-EBEA, presenting as a moderate mass increase lower than that of V₂O₅-H₂O. Notably, XRD results reveal more complicated structure changes with a minor reflection emerges at expanded d-spacing and the original (001) splits to generate another peak of lowered d-spacing. These suggest a dynamic mass exchange, involving both solvent uptake and confined species loss.

Figure 4d-f illustrate mass evolutions of the electrode series during CV measurements in real time. V₂O₅-H₂O and V₂O₅-EBEA show monotonic evolution trends with mass increase during the intercalation step and decrease during the de-intercalation process. Notably, V₂O₅-DOA shows a distinctly different evolution trend characterized by transient mass reversals during both scans. Specifically, during the cathodic scan (ion intercalation), the initial mass increase is followed by a decrease through the potential ranges for the 1st reduction peak (R1), after which the increasing trend resumes. Conversely, during the anodic scan, the decreasing mass trend reverses into a sharp increase approaching the peak potential of the major oxidation peak (O1), before eventually returning to a decreasing trend at the end of the redox peak. This phenomenon is attributed to interfacial desorption (during intercalation) or adsorption (during de-intercalation) of solvent(-water), which reflects significant (de-)solvation processes around the major peak potentials (R1/O1).^{13, 38} These mass change characteristics are highly reversible across multiple cycles (**Figure S13**). Higher impedances of V₂O₅-DOA than other groups are also disclosed in dynamic measurements (**Figure S14-15, Note S4**). Overall, the findings strongly support our hypothesis of reduced hydration extent of intercalating Zn²⁺ into hydrophobic V₂O₅-DOA.

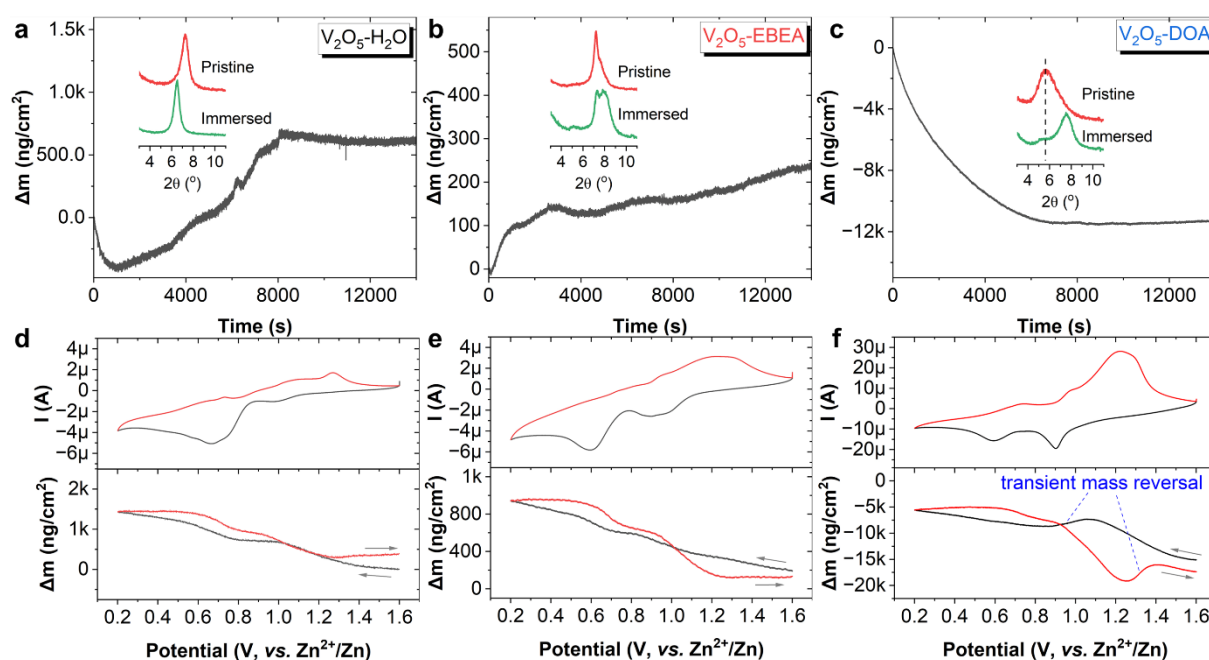


Figure 4. *Operando* observation of varying solvent co-intercalation. EQCM results for (a, d) $\text{V}_2\text{O}_5\text{-H}_2\text{O}$, (b, e) $\text{V}_2\text{O}_5\text{-EBEA}$, and (c, f) $\text{V}_2\text{O}_5\text{-DOA}$ in aqueous electrolytes. (a-c) Mass evolution profiles (vs. time) during the OCP step, and the insets show normalized XRD results highlighting the corresponding electrode structure changes. (d-f) CV curves at 0.5 mV s^{-1} (3rd cycle) with the corresponding mass change profiles.

Computational insights into atomistic ion intercalation processes

Ab initio molecular dynamics (AIMD) simulations are used to investigate the intercalation of Zn^{2+} ions into three types of V_2O_5 -based materials, focusing on how the host lattice and confined molecules dynamically respond to electrochemical intercalation. These simulations are complemented by *operando* XRD measurements, which reveal that all materials follow similar reaction pathways involving a mix of solid-solution intercalation and phase transitions (**Figure S16–21, Note S5**). The AIMD results focus on the initial solid-solution regime, which concludes following the first reduction peak (R1) in the CV curves.

Hydrophilic $\text{V}_2\text{O}_5\text{-H}_2\text{O}$ (**Figure 5a**) shows strong hydrogen bonding within the interlayer space due to the high density of water molecules and lone pairs. These water molecules stabilize the framework and facilitate Zn^{2+} coordination with both water and lattice oxygens, forming two configurations. While Zn^{2+} typically exhibits six-fold coordination in aqueous electrolytes ($\text{Zn}(\text{H}_2\text{O})_6^{2+}$),³⁹ simulations suggest rearranged coordination after intercalation in the lattice.

Radial distribution function (RDF) analysis (**Figure 5b**) confirms this, showing the first coordination shell of Zn–O around 2 Å with a reduced coordination number. At low Zn²⁺ concentration, no distortion of the V₂O₅ layer is observed, consistent with the *operando* XRD measurements (**Figure S17**). This indicates minimal ion-host-interaction due to strong Zn²⁺ hydration.⁴⁰ At higher Zn²⁺ concentration, minor structural disruptions of the local Zn–O coordination appear, reflected by a drop in RDF intensity. These changes correlate with the subsequent phase transition observed in *operando* XRD upon further Zn²⁺ intercalation. Solid-state diffusion of Zn²⁺ occurs via both the confined water layer and in close proximity to the V₂O₅ layer, where the latter is analogous to surface-like diffusion with fast kinetics.²²

In V₂O₅-EBEA, Zn²⁺ interact not only with water, but also with EBEA pillars, which contain oxygen atoms rich in lone pairs. They are part of the Zn²⁺-coordination environment, as illustrated in **Figure 5c**. Therefore, Zn²⁺ intercalation leads to little structural distortion of the V₂O₅ lattice, but the Zn²⁺ transport is restricted to the confined EBEA layer, thereby limiting ion mobility and slowing electrochemical kinetics. RDF analysis (**Figure 5d**) show weaker Zn–O coordination compared to V₂O₅-H₂O, but it becomes intensified at increased Zn²⁺ concentrations due to the interaction with EBEA molecules.

In the case of V₂O₅-DOA, Zn²⁺ predominantly coordinate with lattice oxygens, with no direct interaction with DOA molecules (**Figure 5e**). At low Zn²⁺ concentrations, ions reside close to the oxide layers rather than within the center of the interlayer. Despite the interaction with lattice oxygens, rapid Zn²⁺ mobility is observed through surface-like diffusion,²² owing to few water molecules in vicinity which effectively serve as ligands. However, the stronger ion-host interaction leads to structural distortions of the oxide framework, which aligns with increased structural changes observed by *operando* XRD (**Figure S17**). The RDF profiles (**Figure 5f**) reveal a decline in Zn–O coordination with increasing Zn²⁺ concentration, indicating weakened lattice interaction. A drop of the coordination number at higher Zn²⁺ levels is observed only in V₂O₅-DOA, likely due to excess Zn²⁺ accumulating near DOA molecules but without forming bonds (**Figure S22**).

The RDF analysis on the V–O pair (**Figure S23**) verifies a similar distorted but well-defined coordination environments across all materials, where V₂O₅-DOA presents the most rigid V–O

bonding network. Overall, AIMD simulations reveal how the nanoconfinement chemistry critically affects Zn^{2+} coordination, mobility and intercalation-induced lattice distortion. These insights clarify the atomistic origins of the electrochemical behavior observed experimentally.

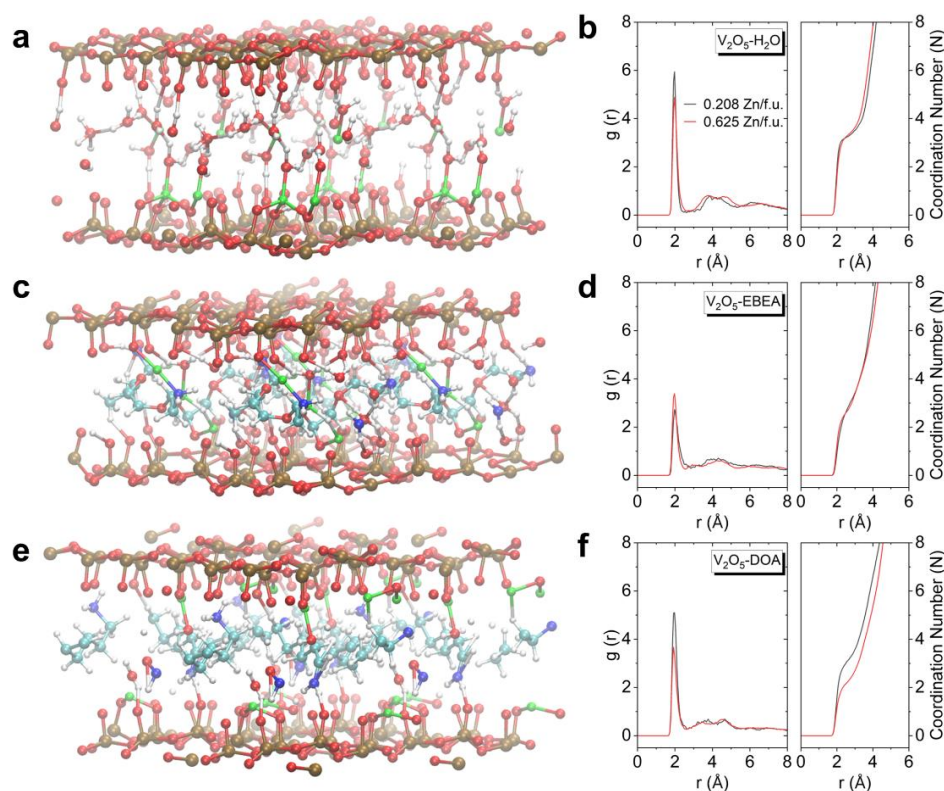


Figure 5. Ab initio molecular dynamics simulations. Simulated properties of (a, b) $\text{V}_2\text{O}_5\text{-H}_2\text{O}$, (c, d) $\text{V}_2\text{O}_5\text{-EBEA}$ and (e, f) $\text{V}_2\text{O}_5\text{-DOA}$, respectively. Side views of captured computation results for Zn^{2+} diffusion within (a) $\text{V}_2\text{O}_5\text{-H}_2\text{O}$, (c) $\text{V}_2\text{O}_5\text{-EBEA}$ and (e) $\text{V}_2\text{O}_5\text{-DOA}$ at a low ion loading. Zinc is shown in green, oxygen in red, vanadium in brown, hydrogen in white, nitrogen in blue and carbon in cyan. (b, d, f) Radial distribution function and the coordination number for the Zn-O pair of the electrode series.

CONCLUSIONS

In this work, we demonstrate that solvent co-intercalation can be effectively regulated by electrode nanoconfinement design. A series of bilayered vanadium oxides with tunable hydrophilicity of their interlayer space is synthesized to tailor the electrode-electrolyte interactions in an aqueous environment. Electrochemical Zn^{2+} intercalation from aqueous electrolytes shows strong dependence of the charge storage capacity, redox potentials and kinetics on the interlayer hydrophilicity. The most hydrophobic material, V_2O_5 -DOA, exhibits improved Zn^{2+} storage capacity and stronger ion-host interaction. Using a range of *operando* characterizations and *ab initio* molecular dynamics modeling, a varying degree of solvent(water) co-intercalation has been identified as the origin for the observed differences in electrochemical performance. Moreover, hydrophobic V_2O_5 -DOA also exhibits higher capacity in non-aqueous electrolytes than other samples, underlining its ability to accommodate anhydrous Zn^{2+} in varying electrolyte environments. These findings establish nanoconfinement chemistry as a powerful knob to tune solvent co-intercalation in layered transition metal oxide electrodes, opening new avenues to tailor electrochemical intercalation reactions and achieve novel batteries with efficient solvent co-intercalation.

Supporting Information

Experimental procedures, characterization and computational methods; supporting figures, tables and notes including materials characterization, electrochemical evaluations in dilute acidic electrolytes, non-aqueous electrolytes, temperature-dependent impedance spectra investigations, staircase potential electrochemical impedance spectroscopy measurements, *ex-situ* and *operando* X-ray diffraction investigations, simulation and X-ray absorption spectra results.

Author Contributions

H.G. and S.F. conceived and developed the study. H.G. performed materials synthesis, morphologic and thermogravimetric analysis, all diffraction and electrochemical experiments. M.S. conducted the computational study. S.R. and M.O. carried out the gas sorption measurements. Y.H. performed the X-ray absorption spectroscopic measurements and analysis. R.L. conducted the transmission electron microscopic measurements. J.W. performed X-ray photoelectron spectroscopic analysis. M.F., M.O., A.G. and S.F. supervised the project. All authors contributed to discussion of the results and writing of the manuscript.

Notes

The authors declare no competing interests.

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