

Perspective

2D Materials with Nanoconfined Fluids for Electrochemical Energy Storage

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In the quest to develop energy storage with both high power and high energy densities, while maintaining high volumetric capacity, recent results show that a variety of 2D and layered materials exhibit rapid kinetics of ion transport by the incorporation of nanoconfined fluids.

Recent Developments

With the portable electronics revolution and advent of large-scale electric vehicle penetration, electrochemical energy storage (EES) is utilized in more devices than ever before.¹ These devices are popular because they perform both the conversion and storage of energy, unlike fuel-based technologies, which decouple those functions. This allows EES to be adaptable to the limited space or weight requirements needed for most applications. However, as a result of the fact that energy storage and conversion co-exist in one EES device, there is a coupling between the stored energy (energy density) and the rate of storage (power density). In redox-active systems, such as batteries and pseudocapacitors, the power density is limited by ion transport if sufficient electronic conductivity is assumed.^{2,3} While fast electron transport can be obtained by a variety of methods, including the addition of highly conductive and high-surface-area carbon,⁴ or using metallically conductive active materials,⁵ obtaining fast ion transport has proved more challenging. The primary technique to improve ion transport of EES has been to increase the surface area and particle size in order to decrease the ion-diffusion distance. However, this comes at the expense of the volumetric energy density and typically leads to increased side reactions.⁶ This Perspective highlights the foundational research and emerging strategies to characterize and improve ion transport in EES based upon intercalation reactions by the use of confined fluids in layered and two-dimensional (2D) densely packed solid-state materials.

Within the field of EES, 2D and layered materials represent some of the most successful electrodes. They enable the reversible intercalation of ions and involve minimal structural changes, thus allowing for the use of micron-sized particles and leading to high volumetric energy densities. These materials include layered lithium metal oxides (LiMO₂) and graphite.⁷ Over the past decade, the EES community has focused on the unique properties of nanomaterials and the nanoscale control of materials. In the case of 2D materials, this includes the manufacture of nanosheets, either by exfoliation of the bulk layered materials⁸ or by direct synthesis.⁹ These nanosheets often exhibit improved kinetics and more facile volume expansion compared with their bulk counterparts.¹⁰ While current batteries are limited by solid-state ion diffusion in the electrodes, nanosheets have smaller ion-diffusion distances and more surfaces exposed to the electrolyte. The increased spacing between the nanosheets accommodates the volume expansion/contraction and minimizes macroscopic volume change upon intercalation/deintercalation.¹¹ The benefits of nanosheets and other nanostructured materials in improving rate

Context & Scale

There is a growing need to develop thinner, lighter, and faster electrochemical energy storage solutions to meet the increasing demands in applications ranging from storage of renewable energy to powering electric cars and enabling the Internet of Things. In the quest to develop energy storage with both high power and high energy densities, while maintaining high volumetric capacity, recent results show that a variety of 2D and layered materials exhibit rapid kinetics of ion transport by the incorporation of nanoconfined fluids. Examples of such materials include the hydrated layered oxides of tungsten, vanadium, and manganese, as well as carbides and nitrides of transition metals (MXenes) with layers of water confined between 2D sheets. In these materials, water or other solvent molecules reside in interlayer spacing on the order of Ångströms to a few nanometers. Such materials are of particular interest in high-power electrochemical capacitors and for batteries utilizing multivalent cations. Relatively little is known about the mechanism of ion charge transfer and transport in nanoconfined fluids, and which features would lead to the optimal nanoconfined fluid structure for energy storage. As a result, this field presents significant

capability of energy storage devices have now been widely demonstrated.¹² The remaining challenges in nanostructured energy storage materials are to mitigate the detrimental effects that arise from high surface areas: increased parasitic side reactions with the electrolyte, first cycle irreversibility, and low volumetric capacity.⁶

An intriguing concept has emerged in energy storage over the past few years whereby the interlayer of 2D materials is “functionalized” with fluid molecules to improve ion transport. These molecules are usually present during low-temperature liquid-phase soft chemistry synthesis. Classic examples of the synthesis of 2D and layered materials with nanoconfined fluid molecules are the sol-gel synthesis of $V_2O_5 \cdot nH_2O$ xerogels and co-precipitation synthesis of birnessite MnO_2 . In an aqueous environment, the hydrolysis and condensation reactions leading to the formation of $V_2O_5 \cdot nH_2O$ xerogels result in a bilayered structure of VO_5 square pyramids, with water molecules intercalated between the bilayers.¹³ In these xerogels, the typical water content (n) is ~ 1.6 – 2 , which results in an interlayer spacing of ~ 11.5 Å.¹⁴ Birnessite MnO_2 can be synthesized by co-precipitation of potassium permanganate and manganese sulfate in water.¹⁵ Despite the typical formula for birnessite as “ δ - MnO_2 ,” the resulting material contains both cations and interlayer water, and is better represented as $X_m MnO_2 \cdot nH_2O$, where X is a cation present during the synthesis, such as K^+ . In $V_2O_5 \cdot nH_2O$ xerogels and δ - MnO_2 , water is critical to the stability of the layered structure. Dehydration of $V_2O_5 \cdot nH_2O$ xerogels leads to the formation of orthorhombic V_2O_5 .¹⁶ In the case of δ - MnO_2 , it was determined that the bond strength between water and cations in the interlayer determines the temperature at which the birnessite structure dehydrates and collapses.¹⁷ Nanoconfined fluids can also be introduced upon exposure of a dry 2D material to a reducing or oxidizing agent in the presence of a solvent or by electrochemical co-intercalation of electrolyte solution (solvent with ions). In these materials, the layered structure is already stable and the successful incorporation of nanoconfined fluids depends upon the ability of the 2D material to accommodate the solvent molecules in the interlayer. An example of this type of layered material is α - MoO_3 , which can intercalate hydrated cations in aqueous electrolytes in the presence of a reducing agent, as reported by Schöllhorn et al.¹⁸ Another method for incorporating nanoconfined fluids is by the use of low-temperature, liquid-phase exfoliation of bulk layered materials. For example, the selective etching of layered ternary transition metal carbides and nitrides leads to the formation of MXenes. The 2D layers of MXene are hydrophilic, and as a result they spontaneously intercalate water from the atmosphere or solution in between the layers.¹⁹ In all of these examples, the obtained 2D materials become pillared by nanoconfined solvent molecules, but the behavior of these nanoconfined fluids is not very well understood. However, their presence typically leads to increased ion storage kinetics, *vide infra*. To illustrate this point, Figure 1 shows the potential benefits and drawbacks of three types of 2D/layered materials: a bulk (micron-sized) layered material, a 2D material with confined fluid, and exfoliated nanosheets.

While the concept of interlayer solvation has recently engendered interest, some of the earliest examples of this strategy for improving energy storage were observed in the 1980s and 1990s. These include studies by Livage and co-workers on Li^+ intercalation in hydrated V_2O_5 xerogels¹⁴ and electrochromism in $WO_3 \cdot nH_2O$ thin films.²⁰ It was also found that interlayer water was necessary to intercalate Mg^{2+} into the layers of vanadium bronzes; no intercalation was observed when no interlayer water was present.²¹ Structural water was also found to be critical for the function of rechargeable Ni-MH and Ni-Cd batteries. $Ni(OH)_2$ is a layered material used as a cathode for these batteries, and comes in two polymorphs, α - $Ni(OH)_2$ and

opportunities to understand the fundamentals of ion behavior in nanoconfined fluids and for these understandings to be applied to future electrochemical energy storage.

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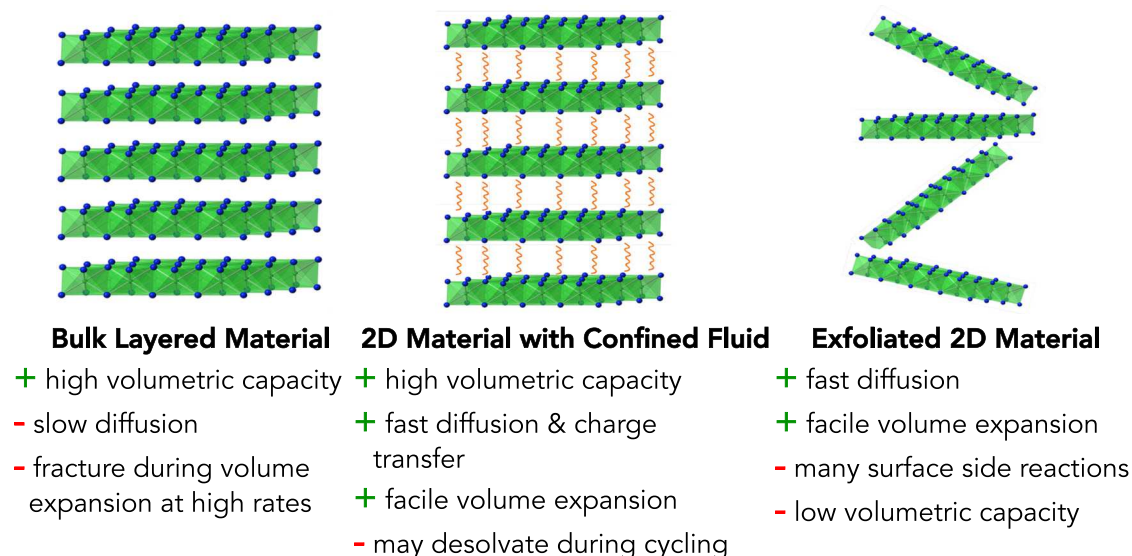


Figure 1. Benefits and Drawbacks of Three Types of Material Structures

Benefits and drawbacks of three types of material structures: bulk layered material, a 2D material with a confined fluid, and exfoliated (or nanosheet) 2D material. 2D materials with nanoconfined fluids represent an intermediate material structure for high power and high energy density storage that may exhibit the benefits of bulk layered and exfoliated 2D materials.

β -Ni(OH)₂. β -Ni(OH)₂ exhibits a layered structure of edge-sharing octahedra, and α -Ni(OH)₂ (Ni(OH)₂·nH₂O; 0.4 < n < 0.7) is its hydrated polymorph.²² The electrochemically active form of β -Ni(OH)₂ contains between 0.1 and 0.4 moles of structural water,²² and its presence has been linked with fast proton diffusion and high electrochemical activity.²³ Although α -Ni(OH)₂ has a higher capacity than β -Ni(OH)₂, it is unstable in highly alkaline electrolytes and transforms to β -Ni(OH)₂ over time.²⁴ Likely due to the fact that these early studies found that interlayer water could be unstable or removed after electrochemical cycling in highly alkaline or aprotic electrolytes, the concept of utilizing interlayer solvation and the nanoscale confinement of fluids for improving ion transport remained underexplored in the coming decades.

More recently, many more studies have reported the benefits of incorporating interlayer solvent molecules within 2D materials. While vanadium oxides are representative of the numerous layered materials that are likely to incorporate interlayer solvent molecules upon exposure to a liquid environment, some materials can be synthesized with more strongly bound structural water. Examples include layered and hydrated tungsten and molybdenum oxides: WO₃·2H₂O, WO₃·H₂O, MoO₃·2H₂O, and MoO₃·H₂O. These crystalline materials exhibit both secondary-bound interlayer water as well as covalently bound structural water that forms MO₅(OH₂) octahedra (M = W or Mo). The layered structure of these hydrated materials can be visualized with low-temperature high-resolution transmission electron microscopy (HRTEM), as shown in Figure 2A for WO₃·2H₂O. Recently, one of our groups found that WO₃·2H₂O exhibits almost ideal pseudocapacitive behavior for proton storage (Figure 2B), whereas the anhydrous WO₃ exhibits battery-type behavior.²⁵ The ability to compare a hydrated and anhydrous form of the same redox-active materials with similar surface areas leads to the direct observation of the improvement in kinetics with structural water. It should be noted that, initially, the anhydrous oxide exhibits higher capacity than the hydrated material, which may indicate that interlayer molecules can also act as redox-site “blocking” species.

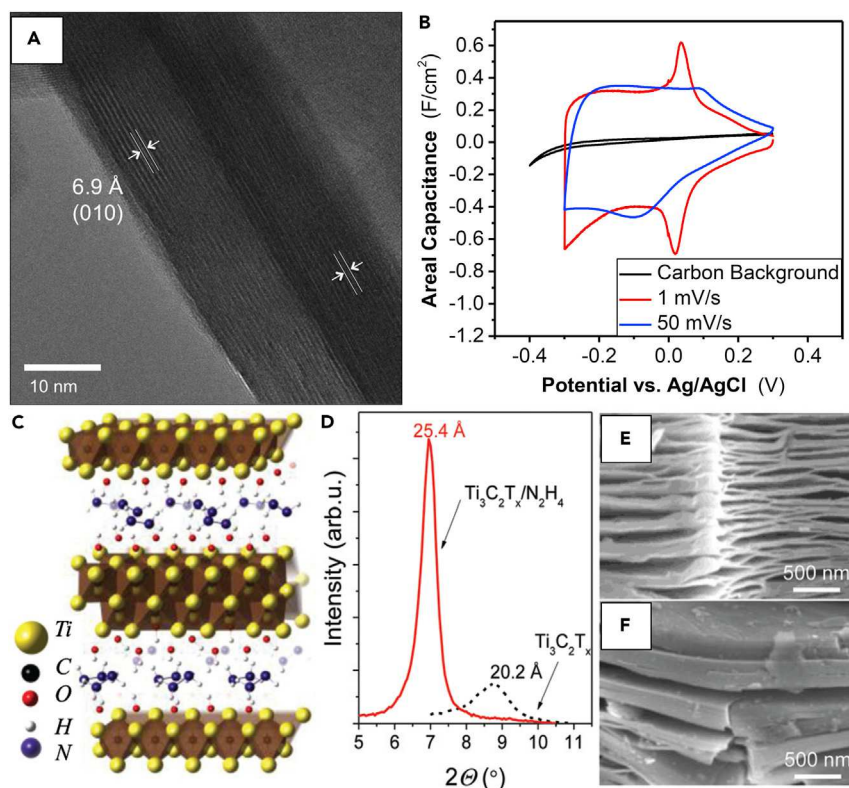


Figure 2. The Structure and Properties of 2D Materials with Nanoconfined Fluids

(A and B) The structure and properties of 2D materials with nanoconfined fluids. (A) Low-temperature HRTEM of a platelet of $\text{WO}_3 \cdot 2\text{H}_2\text{O}$; two types of structural water molecules reside in the 6.9-Å interlayer region. (B) Cyclic voltammograms of $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ at charge/discharge times of 10 min (1 mV s^{-1}) and 12 s (50 mV s^{-1}) show its capacitive behavior. Reprinted from Mitchell et al.,²⁵ with permission. Copyright 2017, American Chemical Society.

(C–F) Structure of $\text{Ti}_3\text{C}_2\text{T}_x$ -based MXene intercalated with hydrazine (C), X-ray diffraction patterns of the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene before and after hydrazine intercalation showing increased interlayer spacing (D), and cross-sectional scanning EM images before (E) and after (F) hydrazine intercalation. Reproduced from Mashtalir et al.,²⁶ with permission from The Royal Society of Chemistry.

Confined fluid molecules lead to improvement in energy storage kinetics in layered materials other than just oxides. For example, 2D carbides, nitrides, and carbonitrides known as MXenes also show a rich chemistry of intercalating polar solvents. In a recent example, one of our groups modified the interlayer of $\text{Ti}_3\text{C}_2\text{T}_x$ (T is a surface termination indicating O, OH, or F) with hydrazine monohydrate (Figure 2C).²⁶ Upon intercalation of this solvent, the interlayer spacing increased by 5 Å (Figures 2D–2F) and led to an increase in both gravimetric and volumetric capacitance across all cyclic voltammetry sweep rates tested ($2\text{--}100 \text{ mV s}^{-1}$). A MXene with a nanoconfined fluid has also demonstrated that pseudocapacitive materials can surpass the high-power performance of double-layer capacitor carbon materials, storing more than 200 F g^{-1} in a protic electrolyte in 0.01 s.²⁷

Since the early pioneering work by Novák et al.²¹ there has been significant interest in interlayer solvation for multivalent cation intercalation. A recent study investigated the effect of strongly bound structural water (water that is removed at $T \geq 300^\circ\text{C}$) in electrodeposited, nanostructured $\text{V}_2\text{O}_5 \cdot 0.6\text{H}_2\text{O}$ on Mg^{2+} intercalation from a non-aqueous electrolyte.²⁸ With this material an Mg^{2+} capacity of $\sim 240 \text{ mAh g}^{-1}$ was obtained, and it was found that the structural water was

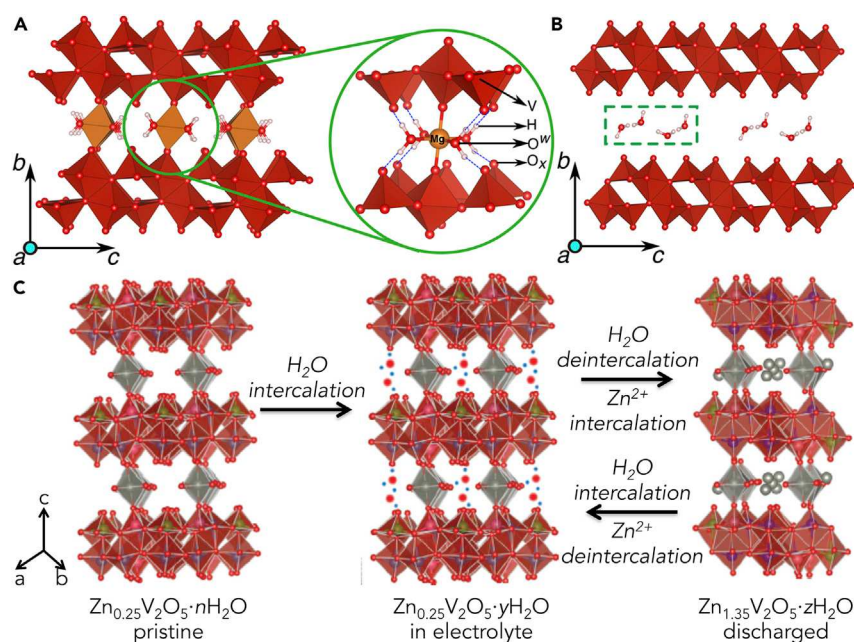


Figure 3. Recent Developments in the Use of Hydrated Layered Oxides for Multivalent Cation Energy Storage

(A and B) Recent developments in the use of hydrated layered oxides for multivalent cation energy storage. (A) Structure of $\text{Mg}_x\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ xerogels showing bonding between the intercalated Mg^{2+} , terminal oxygen of the V_2O_5 , and oxygen of the interlayer water. (B) Structure of the hydrated V_2O_5 xerogel showing hydrogen bonding within the water layer. Reprinted from Sai Gautam et al.,²⁹ with permission. Copyright 2016, American Chemical Society.

(C) Structure and Zn^{2+} energy storage mechanism of $\text{Zn}_{0.25}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ nanobelts in an aqueous electrolyte. Reprinted from Kundu et al.³² with permission from Macmillan Publishers Ltd.

necessary for electrochemical activity. Moreover, this strongly bound structural water was stable during cycling, and it was further hypothesized that the interlayer water molecules “act as a lubricant for reversible (de)intercalation of solvated Mg^{2+} ions....”²⁸ A combined theoretical-computational study of V_2O_5 xerogels²⁹ found that Mg^{2+} /water co-intercalation within the layers led to higher intercalation voltages compared with a dry electrolyte, particularly when the Mg content was <0.5 per metal oxide. Moreover, it was found that the interlayer water is an active participant within the V_2O_5 interlayer. The structure of the $\text{Mg}_x\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ (Figure 3A), as calculated from density functional theory, shows that within the layer the Mg^{2+} is coordinated by the oxygens of the interlayer water molecules while the hydrogens from the interlayer water form hydrogen bonds to the V_2O_5 oxygens. Upon Mg^{2+} deintercalation, the interlayer water molecules form a hydrogen-bonded network within the layer (Figure 3B). Another strategy to increase the kinetics of Mg^{2+} intercalation in non-aqueous electrolytes is to first electrochemically cycle the material in an aqueous electrolyte to drive the formation of a hydrated layered structure, as exemplified by recent studies with birnessite MnO_2 .^{30,31} These studies showed that the water-containing MnO_2 exhibited improved kinetics for Mg^{2+} intercalation, which was attributed to the ability of structural water to “shield” the intercalating cation.

The use of interlayer hydration is particularly beneficial for aqueous rechargeable batteries, where there is no concern over the contamination of the electrolyte with water molecules. In a recent example, $\text{Zn}_{0.25}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ nanobelts were used as

cathodes for aqueous rechargeable zinc batteries.³² In this materials system, additional structural water is incorporated upon immersion in an aqueous electrolyte. Upon electrochemical reduction, Zn^{2+} enter the interlayer, leading to a decrease in the vanadium oxidation state and the removal of some structural water (Figure 3C). An analogous water-free material was not compared, but the good electrochemical kinetics of the hydrated material were attributed to the presence of structural water. It was concluded that the structural water led to “Coulombic shielding” of the intercalated Zn^{2+} from the oxide lattice during solid-state diffusion, lower charge transfer at the interface, and improved flexibility of the structure during intercalation/deintercalation. Water molecules within bilayered, nanostructured, and hydrated V_2O_5 were also identified as enabling fast Zn^{2+} intercalation in a non-aqueous electrolyte.³³

Besides oxides and MXenes, interlayer solvation has enhanced the kinetics of energy storage of few-layer graphene.³⁴ In this case, the interlayer solvent (diglyme) was introduced via electrochemical co-intercalation with Na^+ , and the increase in kinetics was attributed to decreased charge-transfer resistance from lack of a desolvation process at the interface. Recently, it was also found that ether/ Li^+ co-intercalation in graphite can lead to high power capability due to the lack of an interfacial desolvation step and solid-electrolyte interphase formation.³⁵ It should be noted that interlayer solvation in transition metal sulfides has been studied for several decades³⁶ but most of these materials have not been characterized for energy storage, or the function of interlayer solvation has not been fully understood. The fact that interlayer solvation exists in fairly diverse classes of materials means that it is likely to be a universal mechanism for tuning the ion transport of EES devices, particularly for high power densities or intercalation of multivalent ions.

Key Opportunities and Potential Challenges

The studies mentioned above demonstrate that there can be significant improvements in the rate capability of layered and 2D materials upon incorporation of confined fluid molecules into the interlayer. In some cases, there is even a transition from battery to capacitor response without increasing the material surface area: a good indication that materials with nanoconfined fluids may be able to exhibit volumetric energy densities that approach those of bulk materials. While layered compounds with intercalated water will not be able to reach the theoretical volumetric capacity of ideal 100% dense materials, they may actually offer the same or even higher volumetric capacity than conventional porous electrode films due to a decrease in volume of micropores and more complete utilization of active material. There is significant opportunity to understand the detailed mechanisms of energy storage within redox-active materials with nanoconfined fluids. As shown in Figure 4, the potential benefits of these materials derive from the effects of nanoconfined fluids on interfacial charge transfer and ion diffusion.

The typical ion intercalation mechanism from a liquid electrolyte to an anhydrous solid-state electrode proceeds via several stages. In the case of cation intercalation, there is diffusion within the electrolyte toward the electrochemical interface, surface diffusion along the electrode to the intercalation site, desolvation of the cation, and ion transfer from the electrolyte to the electrode at the same time as an electron moves from the external circuit toward the interface.³⁷ Such a description may not apply to layered and 2D materials with confined fluids, as interlayer solvation may lead to more surface-like charge transfer and diffusion mechanisms. Charge transfer at confined interfaces within may occur with either partial ion desolvation or solvent co-intercalation (due to the expanded interlayer); in either case, the potential effect would be a decrease in the charge-transfer activation energy, as compared with an

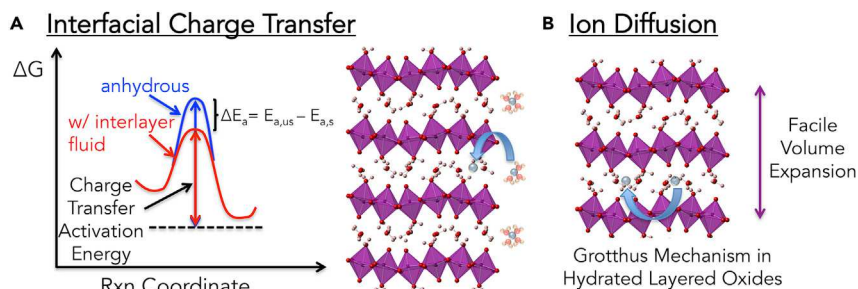


Figure 4. Potential Benefits of 2D Materials with Nanoconfined Fluids for EES

(A and B) Potential benefits of 2D materials with nanoconfined fluids for EES on (A) interfacial charge transfer and (B) ion diffusion.

anhydrous material (Figure 4A). In fundamental studies of Li^+ charge transfer at graphite interfaces in non-aqueous electrolytes, Abe et al.³⁸ found that the activation energy for the charge transfer of solvated Li^+ was about half that for desolvated Li^+ (25 versus 53–59 kJ mol^{-1}). Indeed, Xu and von Wald Cresce concluded that Li^+ desolvation is the primary contributor to the charge-transfer activation energy for Li^+ intercalation into $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and graphite in a non-aqueous electrolyte.³⁹ This is very significant because the charge-transfer process is assumed to follow an Arrhenius-type exponential relationship with the activation energy⁴⁰:

$$\frac{1}{R_{CT}} = A_0 \exp\left(\frac{-E_a}{RT}\right)$$

Here, R_{CT} is the charge-transfer resistance, A_0 is the pre-exponential constant, $-E_a$ is the activation energy, R is the gas constant, and T is the temperature. The solvation energies of salts in polar solvents (such as water or aprotic solvents, e.g., dimethyl carbonate used for non-aqueous electrolytes) are usually quite high, and tend to increase as the ionic charge to ionic radius ratio increases.⁴¹ Therefore, a decrease in the charge-transfer activation energy due to partial solvation or solvent co-intercalation should be detectable using techniques such as impedance spectroscopy.^{38,40} Another effect of nanoconfined fluids on interfacial charge transfer is the influence of frustrated solvation, that is, deviation from the preferred solvation of a cation by, for example, the sharing of some solvent molecules with a neighboring cation in the interlayer. In one recent simulation study, it was found that water molecules in the interlayer of hydrated birnessite MnO_2 experience frustrated hydration, and that this can increase the interfacial electron transfer rate.⁴² Experimental evidence further showed that the intercalation of electrocatalytically active cations into the hydrated interlayer of birnessite MnO_2 led to high activity for the oxygen evolution reaction.^{43,44}

Once the charge transfer occurs, the ion must diffuse within the electrode material due to the concentration gradient developed between the interface and the bulk of the material. In bulk materials, this is typically accomplished by hopping from vacancy to vacancy, with the activation energy determined by the highest energy transition state between the vacant sites.⁴⁵ Interlayer solvation has been hypothesized to enable decreased Coulombic interactions with the framework by a “shielding” action as well as by the fact that such layered materials have higher interlayer spacing.⁴⁶ Breaking of the Coulomb law was recently shown for organic ions in subnanometer confinement.⁴⁷ In the case of hydrated materials, it may be possible for the protons to move via the hydrogen-bonded network in a Grotthus mechanism (Figure 4B).⁴⁸ Such transport is much faster than typical vacancy-assisted diffusion in anhydrous materials.

In addition to the basic understanding of nanoconfined fluids on the energy storage process, there are many other interesting questions to answer. For example, the interlayer may be increased to large dimensions ($>40\text{ \AA}$) by the use of nanoconfined fluids⁴⁹: at which point do the walls of the material no longer “sense” each other, and how does this affect ion transport? Is there a tradeoff between capacity and kinetics when the interlayer contains a fluid? How does the chemistry of the nanoconfined fluid affect ion transport? How does the chemistry of the framework (e.g., oxide, sulfide, carbide, or carbon) affect transport within solvated layers? How do the number of fluid layers and their bonding to the framework affect the mechanical properties and, in turn, ion transport? Materials with both weakly bound and covalently bound interlayer fluids are possible. How does the stability of these fluid molecules vary with the type of electrolyte? What is the role of interlayer defects that distort the nanoconfined fluid? Interestingly, recent work on birnessite MnO_2 nanosheets showed that Mn Frenkel defects in the interlayer lead to increased pseudocapacitance.⁵⁰ The formation of an Mn vacancy in the transition metal layer (and the concomitant presence of Mn in the interlayer) was hypothesized to provide a new low-energy site for Na^+ intercalation.

To answer these questions and obtain a mechanistic understanding of energy storage in 2D and layered materials with nanoconfined fluids, advanced experimental techniques will be necessary to provide information on the structure of nanoconfined fluids and ion transport within these layers. These should be selected with care due to the sensitivity of the fluid molecules. For example, ultrahigh vacuum techniques, such as X-ray photoelectron spectroscopy, may lead to fluid loss. However, low-temperature analogs of such techniques (such as the low-temperature HRTEM in Figure 2A) may provide sufficient stability of the interlayer fluid for *in situ* studies. One example of an advanced characterization tool for studying the dynamics of confined water molecules is quasi-elastic neutron scattering. This was utilized by one of our groups to determine the diffusion coefficient of water confined between layers of MXene.¹⁹ Neutron and X-ray pair distribution function analysis¹³ and nuclear magnetic resonance⁵¹ are additional examples of techniques that can analyze fluids in nanoconfinement.

The primary challenge associated with 2D materials with nanoconfined fluids is that by increasing the interlayer spacing with these molecules, or just by the presence of an interlayer fluid, the materials are more likely to exfoliate or dissolve in a liquid electrolyte, unless constricted in packaged devices. As a result, their liquid-like properties thus make them vulnerable and may affect the electrochemical reversibility. For example, the increased structural water content in layered $\alpha\text{-Ni(OH)}_2$ makes it unstable, and this phase is known to convert to $\beta\text{-Ni(OH)}_2$ upon electrochemical cycling.⁵² While the $\alpha\text{-Ni(OH)}_2$ phase exhibits a higher capacity than $\beta\text{-Ni(OH)}_2$,²⁴ the phase transformation to $\beta\text{-Ni(OH)}_2$ leads to volume change of the electrode and decreased capacity, both of which are undesirable from an application standpoint.⁵³ Therefore, it will be necessary to study different types of electrolytes (aqueous, non-aqueous, and solid-state), electrode film morphologies and architectures, as well as electrochemical conditions to determine the most suitable environment for these solid/liquid hybrid materials.

How the Field Might Develop

Future development in EES will be aimed at enabling lighter, thinner, and faster batteries with a higher energy density. In layered and 2D materials, the presence of fluids in the interlayer provides a unique environment within which to study the effect of fluid nanoconfinement on ion transport. Replacing the vacant interlayer

with fluid molecules or a salt solution may provide an “internal electrolyte” for ion transport and charge storage in such materials. At present, research on these materials has primarily focused on the effect of nanoconfined fluids on the capacity retention as a function of rate. However, more detailed studies are needed to understand the mechanisms of ion transport in interlayer fluids as well as the potential drawbacks. There are obvious similarities between the redox-active, 2D materials with nanoconfined fluids studied for energy storage and the structure of clays and hydrated minerals. The question of ion transport in such systems is also under active study, and may provide an opportunity for collaboration between the energy storage and geology fields. For example, in a recent density functional theory study of the layered mineral mackinawite (FeS), it was found that proton transport within the hydrated layers retained the Grotthuss transport mechanism found in bulk water.⁵⁴

It will also be necessary to understand how to control the interlayer fluids by the composition of the interlayer species, the number of layers, their arrangement within the interlayer, and the chemistry of the framework. From the fundamental studies as well as pioneering work performed on sulfides in the late 1970s, it is clear that interlayer solvation occurs in virtually all layered materials including oxides, sulfides, polyanions, graphene, and MXenes. The large number of compositions within the layered and 2D materials coupled with the number of interlayer fluid species that could intercalate is likely to lead to a large library of tunable, hybrid solid/liquid 2D systems. Moreover, alternating layers of 2D materials can be used to further modify and control the behavior of ions and confined liquids.⁵⁵ The use of nanoconfined fluids is likely to extend beyond EES to applications such as solid lubricants, water desalination, and ion-selective membranes.

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