Tuning the interlayer of transition metal oxides for electrochemical energy storage

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Layered transition metal oxides are some of the most important materials for high energy and power density electrochemical energy storage, such as batteries and electrochemical capacitors. These oxides can efficiently store charge via intercalation of ions into the interlayer vacant sites of the bulk material. The interlayer can be tuned to modify the electrochemical environment of the intercalating species to allow improved interfacial charge transfer and/or solid-state diffusion. The ability to fine-tune the solid-state environment for energy storage is highly beneficial for the design of layered oxides for specific mechanisms, including multivalent ion intercalation. This review focuses on the benefits as well as the methods for interlayer modification of layered oxides, which include the presence of structural water, solvent cointercalation and exchange, cation exchange, polymers, and small molecules, exfoliation, and exfoliated heterostructures. These methods are an important design tool for further development of layered oxides for electrochemical energy storage applications.

I. INTRODUCTION & BACKGROUND

According to the U.S. National Air and Space Administration (NASA), the level of CO$_2$ in the atmosphere has exceeded 400 ppm, the highest it has been in over 400,000 years. At the same time, over 1 billion people, primarily in sub-Saharan Africa and Asia, do not have access to electricity. These environmental and human development factors lead to a pressing need for grid energy storage to enable the integration of sustainable energy conversion devices, which are typically intermittent in nature. In addition, portable electronics and electric vehicles continue to proliferate and push the performance of lightweight, high-volumetric energy density storage devices. For these diverse applications, electrochemical energy storage is the primary energy storage technology due to the large number of chemistries, their scalability, and efficiency. In addition to the large application demand, the constantly evolving capability to understand phenomena at electrochemical interfaces is leading to significant improvements in the fundamental understanding of electrochemical processes. Electrochemical measurements have now been coupled with such advanced materials characterization techniques as transmission electron microscopy (TEM), x-ray diffraction (XRD), x-ray absorption (XAS), atomic force microscopy (AFM), and Raman microscopy, to name just a few. This pairing has enabled in situ and in operando characterization of materials for electrochemical technologies leading to advancements in the mechanistic understanding of interfacial phenomena. Lastly, advancements in materials synthesis are leading to the control of materials at the atomic scale so that electrochemical energy storage electrodes can be highly tailored for diverse applications, from small sensors to grid energy storage. With this congruence of societal need, improved understanding of interfaces, and control over material...
synthesis, it is no wonder that the present time is being hailed as the ‘golden age’ for electrochemistry.\(^\text{22}\)

Within this dynamic research and application landscape, layered transition metal oxides are a highly important class of materials for electrochemical energy storage due to their use in lithium ion battery cathodes,\(^\text{23}\) sodium ion battery cathodes,\(^\text{24}\) and electrochemical capacitors.\(^\text{25}\) The unique feature of these materials is the presence of an interlayer region that serves as the host for ion intercalation. The purpose of this review is to describe methods by which the interlayer of layered metal oxides can be tuned to achieve improvements in electrochemical performance or for new mechanisms of energy storage. The interlayer modifications discussed are the presence of structural water, solvent co-intercalation and exchange, cation exchange, polymers, and small molecules, exfoliation, and synthesis of exfoliated metal oxide heterostructures.

II. STRUCTURE OF LAYERED TRANSITION METAL OXIDES

The wide interlayer spacing and weak interlayer bonding of layered oxide materials allows for the intercalation of a large variety of guest species, including cations, anions, and polymers. These layered structures are built up of transition metal–oxygen clusters, with the transition metal typically in octahedral, or 6-fold, coordination by oxygen ligands.\(^\text{26}\) In layered oxides, the strong interaction between the transition metal cation and the electrons of the oxygen ligand means that oxygens will bond weakly to transition metals in adjacent layers.\(^\text{26}\) The octahedra are assembled into extended structures by sharing corners, edges, and rarely, faces. The critical feature of layered transition metal oxides is that the intralayer bonding is significantly stronger than the interlayer bonding. The layered oxides are typically formed by transition metals in high oxidation states—+4, +5, and +6. Figure 1 illustrates the layered structure of several different redox-active layered oxides: (a) layered bimessite MnO\(_2\) (δ-MnO\(_2\)), (b) orthorhombic V\(_2\)O\(_5\), and (c) monoclinic WO\(_3\)-2H\(_2\)O. These represent the variety of layered structures built up from MO\(_x\) octahedra sharing edges and corners. Layered oxide structures are extremely versatile and allow for modification of both the inorganic framework (via substitutional doping\(^\text{27}\) or vacancy formation)\(^\text{28}\) and the interlayer; the latter is the focus of this review.

III. MECHANISMS OF ELECTROCHEMICAL ENERGY STORAGE IN LAYERED TRANSITION METAL OXIDES

The development of high energy density electrochemical storage is in large part due to the properties of layered transition metal oxides. These include high ionic and electronic conductivity, capability of undergoing redox reactions, and the availability of interlayer sites for the intercalation of cations from the electrolyte. In general, when a layered metal oxide is placed in contact with an electrolyte, several different mechanisms are possible. In order of increased capacity and structural disorder, these are: (i) double-layer capacitance,\(^\text{29}\) (ii) pseudocapacitance,\(^\text{25}\) (iii) intercalation,\(^\text{30}\) (iv) decomposition,\(^\text{31}\) and (v) conversion,\(^\text{32}\) as illustrated in Fig. 2. Double-layer capacitance is the only mechanism that is purely electrostatic and therefore does not contain a charge transfer step.\(^\text{33}\) As a result, this mechanism provides lifetimes of over 1 million cycles, which are orders of magnitude greater than with mechanisms that involve a redox process. The highest capacitances of ~150 F/g are obtained with high surface area (>1000 m\(^2\)/g) carbon materials.\(^\text{34}\) Two different types of Faradaic capacitance (pseudocapacitance) can occur in transition metal oxides: redox pseudocapacitance and intercalation pseudocapacitance.\(^\text{35}\) Redox pseudocapacitance occurs due to surface or near-surface redox reactions; materials that exhibit this
phenomenon include RuO$_2$·0.5H$_2$O (Ref. 36) as well as most nanostructured transition metal oxides. Intercalation pseudocapacitance occurs due to redox reactions at the surface as well as the bulk that are not kinetically limited by solid-state diffusion or phase transitions, as in Nb$_2$O$_5$. When present, both pseudocapacitive mechanisms will exhibit capacitive, or surface-limited, kinetics, with capacitance values between ~300 and 1000 F/g. Intercalation reactions encompass a more general mechanism than intercalation pseudocapacitance, in that kinetics can be limited by solid-state diffusion and nucleation of a new phase can occur. Intercalation reactions provide capacities of up to 400 mA h/g in the case of multi-electron intercalation. Decomposition and conversion reactions destroy the layered transition metal oxide structure during the 1st cycle, and require the nucleation of Li$_2$O and suboxides or metal nanoparticles. These reactions provide the highest capacities for energy storage with metal oxides, typically >500 mA h/g. The reversibility and rate capability of decomposition and conversion reactions is high after the first cycle, but due to the variation in reaction pathways between the lithiation/delithiation processes, the overall energy efficiency is low (typically, ~1 V hysteresis occurs even at low rates in oxides). Despite many years of intense effort to overcome this issue by designing highly advanced electrode architectures, it has been extremely challenging to improve the energy efficiency sufficiently for application in commercial devices.

Intercalation is the best mechanism for energy storage in metal oxides when considering the optimization of capacity, rate capability, efficiency, and lifetime. The general intercalation equation is:

$$\text{MO} + x\text{A}^+ + xe^- \leftrightarrow \text{A}_x\text{MO}$$  

where MO is a layered transition metal oxide and A$^+$ is a cation (typically H$^+$, Li$^+$, and Na$^+$ but multivalent ions such as Mg$^{2+}$ and Al$^{3+}$ can also intercalate). As a result of the beneficial properties of intercalation, the mechanism has been successfully utilized for high energy density electrochemical energy storage in commercially-available lithium-ion and nickel-metal hydride batteries (Ni/MH). The intercalation mechanism occurs via four primary steps (Fig. 3): (i) ion diffusion in the electrolyte to the electrode/electrolyte interface, (ii) surface diffusion of the ion to an intercalation site, (iii) charge transfer at the interface, and (iv) diffusion in the solid state. Each of these steps can be affected by the properties of the interlayer in layered transition metal oxides.

IV. BENEFITS OF INTERLAYER MODIFICATION FOR ELECTROCHEMICAL ENERGY STORAGE

Interlayer modification presents an additional level of control over the electrochemical behavior of oxides for electrochemical energy storage based on intercalation reactions. At the interface, interlayer modification of layered structures can affect the activation energy and
potential for charge transfer. In the bulk, it may affect the electronic conductivity of the structure if the interlayer modification involves the intercalation of cations to form a partially reduced compound. Interlayer modification will affect the transport of the intercalating ion, and may alter the ion storage sites. In this section, the effect of interlayer modification on interfacial charge transfer and diffusion is presented in detail.

A. Interfacial charge transfer

The charge-transfer stage is a critical step where an ion transfers from a (typically) liquid phase into a solid phase at the same time that an electron is transferred into the solid phase. When transferring from a liquid electrolyte, the ion typically needs to lose its solvation shell and, in the case of multivalent cations, other ions. In theoretical descriptions of charge transfer, an intermediate, transient step is assumed between the solvated stage and the intercalated stage. The difference in energy between the solvated stage and the transient stage is the activation energy for charge-transfer during intercalation. In the bulk, it may affect the transport of the intercalating ion, and may alter the ion storage sites. In this section, the effect of interlayer modification on interfacial charge transfer and diffusion is presented in detail.

B. Ion transport in the interlayer

Once the ion has been intercalated, it undergoes solid-state diffusion due to the concentration gradient developed between the surface and the bulk of the material. Typically, diffusion is the rate-limiting step for ion intercalation in electrochemical energy storage except in the case of intercalation pseudocapacitance, which is surface limited. In most layered compounds, the ions move via interstitial vacancies in a 2D plane. In a layered oxide with a modified interlayer, the ion may diffuse via different mechanisms. For example, in a hydrated, layered structure, the ion may move via the Grothuss mechanism responsible for rapid proton diffusion in water. The use of interlayer solvation in multivalent ion intercalation is beneficial for screening the diffusing ion from the inorganic framework.

The interlayer environment can lead to changes in the rate capability for ion intercalation due to its influence on the diffusion coefficient, $D$:

$$D = p\lambda^2 v^* \exp(-E_B/kT),$$  \hspace{1cm} (3)  

where $p$ is a geometrical factor related to the interstitial vacancy network (1D, 2D, or 3D), $\lambda$ is the hopping distance, $v^*$ is the vibrational frequency, and $E_B$ is the activation barrier for hopping, or the maximum energy point between the initial and final site of the diffusing ion. It is this activation barrier that will be affected by changes due to the interlayer environment, including the presence of interlayer molecules. As in the case of the activation energy barrier for charge transfer, the exponential dependence of the diffusion coefficient on $E_B$ indicates that even small changes in the diffusion environment will lead to significant changes in the diffusion coefficient.

V. INTERLAYER MODIFICATION OF LAYERED METAL OXIDES

Layered oxides form because of strong, directional bonding between oxygen and transition metal ions that results in the formation of weakly bonded atoms separated by large bonding distances. Therefore the general characteristic of layered structures is that there exists strong, covalent-ionic bonding within layers and weak, van der Waals bonding between layers. The interlayer binding energy for most layered compounds has been shown to be $\sim 20$ meV/Å$^2$ by computational methods. In comparison, the cleavage energy for a nonlayered compound such as NiO was calculated to be $333$ meV/Å$^2$ or approximately 16 times the energy of the interlayer bonding. In oxides, individual layers are negatively charged so the interlayer may be modified by charged or polar species. The interaction between the interlayer species and the layers can be weak, so the species themselves can be fairly mobile and thus removed via

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FIG. 3. The four primary steps of ion intercalation into a solid host, illustrated for Li$^+$ insertion from a non-aqueous electrolyte. Reprinted with permission from Ref. 47. Copyright 2011 American Chemical Society.
solvent exchange (the application of a concentration gradient) or, if they are charged, by application of an electric field. This section will highlight the means by which the interlayer spacing of layered oxides can be modified and the effect this has on the electrochemical energy storage properties.

A. Structural water

Interlayer water molecules can be present within a layered structure by three different means: (i) as structural water present in the as-synthesized oxide; (ii) as a result of water diffusion into the interlayer spacing; and (iii) via electrochemical cycling in aqueous electrolytes. This section will focus on layered oxides with structural water, which include WO$_3$$_2$H$_2$O, MoO$_3$$_2$H$_2$O, V$_2$O$_5$$_2$H$_2$O, and birnessite (δ) MnO$_2$. In particular, the molybdenum and tungsten oxides form a series of stable and metastable hydrous phases. The stable phases include monoclinic WO$_3$$_2$H$_2$O, WO$_3$$_2$H$_2$O, MoO$_3$$_2$H$_2$O, and MoO$_3$$_2$H$_2$O. The dihydrates and monohydrates of tungsten and molybdenum are isostructural; the structures of the tungsten oxide hydrates are shown in Fig. 4. These hydrates are built up of corner-sharing and tilted octahedra. In the case of the monohydrate, the water is located at the apex of the octahedra whereas in the dihydrate, the second water is hydrogen bonded within the interlayer.

The effect of structural water on electrochemical energy storage has been investigated with molybdenum oxide hydrates cycled in nonaqueous lithium ion electrolytes. Nazri et al. reported that molybdenum oxide hydrates (MoO$_3$$_2$H$_2$O and MoO$_3$$_2$H$_2$O) exhibited higher capacity and better cyclability than anhydrous MoO$_3$. Kumagai et al. reported that the Li$^+$ intercalated into the structure in between the hydrated layers, and, in the monohydrate, obtained capacities of up to 400 mA h/g at a current density of 0.2 mA/cm$^2$ between 3 and 1 V versus Li/Li$^+$. Due to the potential range for intercalation (3.5–1.5 V versus Li/Li$^+$) and lack of Li in the as-synthesized structure, the materials are best suited as cathodes for primary batteries or anodes for hybrid electrochemical capacitors.

In aqueous electrolytes, interlayer water molecules have been hypothesized to provide rapid diffusion channels for protons. The Grotthus mechanism of proton diffusion has been proposed in hydrated tunnel structures, such as those formed by hexagonal MoO$_3$, and is expected to occur in layered structures as well. This mechanism accounts for the rapid diffusion of protons in aqueous electrolytes via the formation and deformation of hydrogen bonds on water molecules. However, it is not clear whether the Grotthus mechanism occurs in all hydrated layered oxides. Recent density functional theory calculations indicated that protons do not intercalate via the water network in WO$_3$$_2$H$_2$O; instead, it was theorized that the mechanism of proton intercalation is binding to a bridging oxygen, the same as in WO$_3$. On the other hand, experimental results of electrochromic hydrated tungsten oxides show rapid coloration and bleaching in acidic electrolytes, which was ascribed to rapid proton diffusion via the Grotthus mechanism. The room temperature proton conductivity at ~50% relative humidity of WO$_3$$_2$H$_2$O was determined to be ~1 × 10$^{-5}$ S/cm for the dihydrate and monohydrate, and the proton conduction was hypothesized to occur via the interlayer hydrogen bonded network as in the Grotthus mechanism. These diverse results underscore the need for in-depth understanding of transport mechanisms during electrochemical intercalation in hydrated structures.

In addition to the potential for rapid proton diffusion via the Grotthus mechanism, the presence of interlayer water molecules has been correlated with improved
Intercalation kinetics of multivalent ions. Multivalent ions are those with a formal charge greater than 1; of particular interest to energy storage applications is the storage of the divalent cation Mg$^{2+}$. This is because Mg metal, with a theoretical capacity of 2205 mA h/g (for the reaction Mg$^{2+} + 2e^- \rightarrow $Mg$^0$), can be reversibly cycled in suitable nonaqueous Mg-ion electrolyte without the formation of dendrites, as in the case of lithium metal. Thus the use of Mg metal as an anode allows for achieving both high energy density and safety. One of the challenges of Mg batteries, however, is finding a high voltage and high capacity cathode material. Intercalation of Mg$^{2+}$ is not as facile as Li$^+$ due to the sluggish solid state diffusion of Mg$^{2+}$, which is due to (i) the Coulombic repulsion between the framework transition metals and the diffusing Mg$^{2+}$ ions, (ii) the need for a transition metal to accept 2e$^-$, which results in an increase in the ionic radius and thus unit cell volume, and (iii) the strong solvation and anion coordination of Mg$^{2+}$, which raises the activation energy for charge-transfer at the electrode/electrolyte interface.

The presence of interlayer water molecules can enable the reversible intercalation of Mg$^{2+}$ because these species can act as a solvation shell, and shield the diffusing divalent cation from the lattice anions and cations. For example, V$_2$O$_5$ aerogels are high-surface area oxide materials made via supercritical drying of a V$_2$O$_5$ gel. Their short-range structure is similar to that of V$_2$O$_5$ xerogels, which consists of V$_2$O$_5$ bilayers separated from each other by a large interlayer spacing (~11.5 Å) filled with water molecules. In the case of the aerogels, the nominal formula after supercritical drying is V$_2$O$_5$·2H$_2$O and ~1.5 H$_2$O molecules are removed by heat treatment at 120 °C. The maximum amount of intercalation in the aerogel is ~0.6 Mg$^{2+}$ per V$_2$O$_5$, which corresponds to a gravimetric capacity of 88 mA h/g. Figure 5(b) shows the cyclic voltammogram of a V$_2$O$_5$·0.5H$_2$O aerogel in Mg(ClO$_4$)$_2$ in propylene carbonate electrolyte. It should be noted that while Mg$^{2+}$ intercalation is reversible in V$_2$O$_5$ aerogels, the separation between the cathodic (Mg$^{2+}$ intercalation) and anodic (Mg$^{2+}$ deintercalation) peaks is larger than in the case of Li$^+$ intercalation [Fig. 5(a)], indicating that kinetics are still sluggish despite the benefit of interlayer water.

One potential drawback of structural water is that it may be removed during electrochemical cycling, leading to changes in the energy storage behavior, crystal structure, and potential contamination of a non-aqueous electrolyte with water. The significance of this issue on the stability of interlayer structural water during electrochemical cycling varies. In the case of V$_2$O$_5$ aerogels, Le et al. used chemical analysis to determine that structural water was retained after chemical and electrochemical intercalation of Li$^+$ and Mg$^{2+}$. On the other hand, Novák et al. reported that structural water was removed upon repeated electrochemical intercalation and deintercalation of Mg$^{2+}$ in hydrated layered vanadium oxide bronzes of the family MV$_2$O$_{3n}$H$_2$O, where M = Li, Na, K, Ca$^{0.5}$, and Mg$^{0.5}$, and this group reported the same water loss in V$_2$O$_5$ xerogel. The decrease in structural water content was correlated with decreased capacity for Mg$^{2+}$ in the materials. Recently, the decrease in capacity of V$_2$O$_5$·0.6H$_2$O with cycling in a Li$^+$ nonaqueous electrolyte was correlated with accumulation of LiOH. In the case of MoO$_3$·nH$_2$O cycled in a nonaqueous Li$^+$ electrolyte, the decrease in capacity with cycling of anhydrous MoO$_3$ was greater than that of the hydrous phases, MoO$_3$·H$_2$O and MoO$_3$·1/3H$_2$O. Kumagai et al. proposed that electrochemically intercalated Li$^+$ react with the interlayer water molecules of MoO$_3$·2H$_2$O because of the observed poor reversibility and decrease in interlayer spacing upon Li$^+$ intercalation from ex situ XRD; the monohydrate was more stable. Based on these reports, it is possible that the removal and reactivity of interlayer water is more likely in structures where the water molecules are bound via hydrogen bonds to the interlayer, and not covalently bound as in the case of MoO$_3$·H$_2$O.

![Cyclic voltammogram of V$_2$O$_5$·0.5H$_2$O aerogel](image)

**FIG. 5.** Cyclic voltammetry of V$_2$O$_5$·0.5H$_2$O aerogel in (a) LiClO$_4$ in propylene carbonate and (b) Mg(ClO$_4$)$_2$ in propylene carbonate electrolytes at 0.1 mV/s. The aerogel can be reversibly cycled in both electrolytes due to the nanostructured morphology and presence of structural water. Reprinted from Ref. 76, with permission from Elsevier.
B. Solvent cointercalation & exchange

The previous section discussed the behavior of layered crystal structures with interlayer water molecules present in the as-synthesized state. For other layered structures, water and other polar solvent molecules may be intercalated during electrochemical cycling (so-called co-intercalation) or by solvent exchange.\(^5\) Adapting the nomenclature established by Schöllhorn\(^8\) these reactions can be written as:

\[
\text{Cointercalation: } \text{MO} + xA^+ + xe^- + y(\text{solv}) \rightarrow A_x(y\text{solv})_y\text{MO},
\]

(4)

\[
\text{Solvent Exchange: } (y\text{solv})_y\text{MO} + y(\text{SOLV}) \rightarrow (y\text{SOLV})_y\text{MO} + y(\text{solv}),
\]

(5)

where MO is a layered oxide, A\(^+\) is metal cation, and SOLV and solv represent two different solvents. These reactions present an additional mechanism for the control of the interlayer of transition metal oxides for electrochemical energy storage.

Solvent cointercalation has been investigated for improving the kinetics of Mg\(^{2+}\) energy storage. Using first-principles calculation, Gautam et al.\(^81\) found that the cointercalation of water with Mg\(^{2+}\) into xerogel V\(_2\)O\(_5\) in nonaqueous electrolytes can increase the intercalation potential. Previously, Levi et al.\(^7\) proposed that the increase in potential occurs because the intercalation ion does not need to shed a solvation shell (or does so only partially) during the charge-transfer step. Solvent cointercalation can be used to synthesize electrochemically active materials, such as the transformation of spinel Mn\(_3\)O\(_4\) into \(\delta\)-MnO\(_2\) in aqueous electrolytes.\(^5\)\(^2\)\(^8\)\(^2\) Such hydrated \(\delta\)-MnO\(_2\) has been investigated as a potential cathode material for Mg ion batteries.\(^5\)\(^2\)\(^8\)\(^3\) The improved intercalation kinetics and reversibility of Mg\(^{2+}\) in \(\delta\)-MnO\(_2\) have been ascribed to efficient Coulombic screening of the intercalating Mg\(^{2+}\) from the host structure by interlayer water molecules [Fig. 6(a)]. First, spinel Mn\(_3\)O\(_4\) was cycled in an aqueous Mg\(^{2+}\) electrolyte to form hydrated, layered \(\delta\)-MnO\(_2\). Then, the material was cycled in a nonaqueous Mg\(^{2+}\) electrolyte with varying amounts of water. Compared with the completely anhydrous electrolyte, hydrated \(\delta\)-MnO\(_2\) cycled in a Mg\(^{2+}\) nonaqueous electrolyte with small amounts of water showed higher capacity and lifetime [Figs. 6(b) and 6(c)]. However, Sun, et al. found that the hydrated material undergoes a conversion reaction with Mg\(^{2+}\) in a nonaqueous electrolyte with the formation of MnOOH, MnO, and Mg(OH)\(_2\); reversible intercalation was only observed in an aqueous Mg\(^{2+}\) electrolyte.\(^8\)

The benefits of water co-intercalation for the reversibility of multivalent ion intercalation are not limited to Mg\(^{2+}\). González et al.\(^8\) reported on the reversible charge storage of Al\(^{3+}\) from an aqueous electrolyte into V\(_2\)O\(_5\) xerogel and proposed a co-intercalation reaction mechanism:

\[
V_2O_5 + x/3Al(\text{H}_2\text{O})_{n}^{3+} + xe^- \leftrightarrow Al_{1/3}V_2O_5 \cdot n\text{H}_2\text{O}.
\]

(6)

Since Al\(^{3+}\) is a small cation (ionic radius of 0.68 Å) with a large charge, it has a high standard hydration enthalpy, which means that it is very strongly hydrated. Therefore, it is reasonable to assume that solid state intercalation of Al\(^{3+}\) can only occur via solvent co-intercalation, otherwise, the activation energy for charge transfer at the interface is too high.

Solvent exchange of water for other polar molecules can be performed in structures that contain water in the as-synthesized state or in anhydrous layered oxides whose interlayer bonding is weak enough to be exchanged. Molybdenum oxides serve as model systems for investigating solvent exchange because both hydrated and anhydrous crystalline MoO\(_3\) form layered structures,\(^8\) which expands the number of precursors that can be used for solvent exchanged MoO\(_3\).

Schöllhorn et al.\(^5\) performed solvent exchange of Na\(_{0.5}\)(H\(_2\)O)\(_4\)MoO\(_3\) bronze with dimethylsulfoxide (DMSO); the interlayer spacing increased from 11.41 to 16.92 Å. In a related experiment, Na\(_{0.5}\)(H\(_2\)O)\(_4\)MoO\(_3\) bronze was used to intercalate various organic compounds; interlayer spacings as large as 37.9 Å were reported for MoO\(_3\) intercalated with tetradecylamine.\(^8\) Chen et al.\(^8\) utilized MoO\(_3\)-H\(_2\)O as the precursor for the solvent exchange of water with \(n\)-octylamines in ethanol. The reaction was described as an acid–base reaction between the water molecules and amines. The amines occupy the interlayer space in a bilayer arrangement with a 51° tilt angle and with an expanded interlayer spacing of 23.1 Å, as illustrated in Fig. 7; heat treatment of the materials at 550 °C yields anhydrous MoO\(_3\). The electrochemistry of these materials was not reported and bears further investigation as such large interlayer spacings may be beneficial for multivalent and high-rate intercalation.

C. Cation exchange

Layered metal oxides may also undergo cation exchange. In transition metal oxides, the layers are negatively charged and can thus accommodate cationic interstitial guest species. For cation exchange, the starting material may contain the exchangeable ion in the as-synthesized state (e.g., LiCoO\(_2\)) or as a result of electrochemical cycling (e.g., Li\(_x\)V\(_2\)O\(_3\)). Cation exchange may occur by the exchange of only the...
cation or with solvent co-intercalation, as described above. A recent review summarized the general features of cation exchange in nanoscale materials. A low-temperature route for the synthesis of LiCoO₂ and LiNiO₂ was proposed by Larcher et al. who performed the cation exchange of NiOOH and CoOOH in a hydrothermal reactor in the presence of LiOH; Fig. 8 shows the topotactic nature of the cation exchange. The oxyhydroxides are similar in structure to the LiMO₂ (M = Ni, Co). In the case of LiCoO₂, the electrochemical behavior of the cation-exchanged phase was inferior to the high temperature stacking sequence.
E. Exfoliation

An important property of bulk layered oxides is that they can be completely exfoliated into mono- or few-layer sheets (‘nanosheets’). There has been significant interest in discovering the electrochemical energy storage properties of such materials because, in theory, they exhibit short diffusion distances and a large number of surface redox sites which could lead to high power and high energy density storage. In this regard, the methods of modifying the interlayer described above have all been utilized as a means to expand the interlayer spacing of layered oxides, which decreases the force needed to pull apart the layers into nanosheets. The applied force can be mechanical acoustic thermal or a combination of these. Figure 10 shows the general mechanism of exfoliation of layered materials into few-layer sheets. A recent review described synthesis methods for controlling nanosheet size, composition, and structure.

Such exfoliated layered oxide nanosheets have primarily been investigated for use as electrochemical capacitor electrodes, and specifically as pseudocapacitors. This is because the nanosheet architecture would ideally expose all of the redox active sites directly to the electrolyte and enable rapid charge-transfer reactions with minimal solid state diffusion. As noted previously, MoO3 forms both hydrous and anhydrous layered polymorphs and it is a good precursor material for the synthesis of nanosheets. Bulk crystalline MoO3 can be exfoliated by sonicating a dispersion of the oxide in a solution of water and isopropanol; the mechanism of exfoliation is the intercalation of isopropanol between MoO3 layers and subsequent application of acoustic energy in the form of sonication. Hanlon et al. synthesized MoO3 nanosheets via liquid-phase exfoliation that consisted of sonicating MoO3 in isopropanol. Figure 11 shows the dispersion, absorbance, and TEM of the exfoliated nanosheets separated by size into small, very small, and large; the size selection was obtained by centrifuging the stock solution at different speeds and selecting the supernatant. The maximum capacitance (~200 F/g at 10 mV/s or 200 s) was obtained by combining the exfoliated MoO3 nanosheets with carbon nanotubes.

The benefits of synthesizing nanosheets from exfoliated bulk oxides is that this technique is readily scalable. However, there are several challenges for using exfoliated nanosheets as energy storage materials for large-scale devices. The high surface area of nanosheets can lead to increased side reactions with the electrolyte, which have to be avoided for long cycle life and safety. Second, the high surface area can also lead to low volumetric capacity/capacitance as compared with the bulk materials. Third, such materials contain many defects that can lead to limited cycle life and barriers.
for ion diffusion. On the other hand, nanosheets can be highly advantageous for small-scale energy storage devices.\textsuperscript{106} Also, restacked exfoliated nanosheets have recently been reported as precursors for the synthesis of Li-ion battery cathode materials, presenting an interesting strategy for the development of metastable layered oxides.\textsuperscript{107}

**F. Exfoliated metal oxide heterostructures**

Exfoliated layered oxide materials can be assembled into new heterostructured layered oxide materials.\textsuperscript{108} The motivation for synthesizing such materials is that they can exhibit improved properties over the individual components. In the case of oxide materials, this typically means improving their electronic conductivity to enable higher rate capability by forming heterostructures with graphene. One example of this method is the synthesis of graphene/MnO\textsubscript{2} hybrids via co-exfoliation for use as electrochemical capacitors.\textsuperscript{109} The highest capacitance was obtained with the co-exfoliated materials (as opposed to the individual components); a volumetric capacitance of 200 F/cm\textsuperscript{3} was obtained at a sweep rate of 100 mV/s (charge/discharge time of 10 s). The synthesis of these heterostructures opens up the possibility of entirely new metal oxide/hybrid materials assembled at the atomic layer. Most of these composites; however, are synthesized via self-assembly\textsuperscript{110,111} as opposed to bulk exfoliation.
VI. FUTURE OUTLOOK & CONCLUSIONS

Layered oxides have played a key role in the development of high energy density electrochemical storage, from the investigations of alkali ion intercalation in oxides in the 1970s by Whittingham\textsuperscript{112} to the identification of LiCoO\textsubscript{2} cathodes by Goodenough\textsuperscript{113} in the early 1980\textsuperscript{0} to subsequent commercialization of high energy density lithium-ion batteries for portable electronics. In the future, layered oxides will continue to be utilized as electrodes in next generation devices including advanced lithium-ion batteries, sodium-ion batteries, and electrochemical capacitors, that take advantage of their energy density, power density, environmental stability, high potential, and lifetime. Within this class of materials, the vacant site for energy storage can be modified, and this presents a unique ‘control knob’ to tune the atomic and nanoscale electrochemical environment of bulk oxides that is not readily available in other structures.

The interlayer can be modified by the presence of structural or co-intercalated water and solvent molecules, cation exchange, or polymeric and molecules species. These can enhance the charge transfer by increasing the interlayer spacing to allow solvent co-intercalation, or for partial solvation of the intercalating ion within the interlayer. Diffusion in the bulk can be enhanced by allowing either fast transport (e.g., proton hopping via hydrogen bonding) or, in the case of multivalent ion intercalation, partial charge screening. Further research is needed to understand the exact mechanisms and lifetime of interlayer modified materials and to extend these methods from model layered oxides such as V\textsubscript{2}O\textsubscript{5} and MoO\textsubscript{3} to cathode materials such as LiCoO\textsubscript{2}. There has been some recent promising work in this area for non-aqueous sodium-ion batteries. For example, interlayer modification of layered sodium metal oxide cathodes by doping of the interlayer with small amounts of Li\textsuperscript{114} or Mg\textsuperscript{115} improves the cycling stability by stabilizing the structure. The continuing need for better electrochemical energy storage, coupled with improvements in characterization capability and synthesis techniques, will push the properties of layered metal oxides forward. The methods of interlayer modification are an important design tool in the development of these advanced materials.

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