Emerging nanostructured electrode materials for water electrolysis and rechargeable beyond Li-ion batteries

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\textbf{ABSTRACT}

This review describes recent advances in electrochemical water electrolysis and rechargeable beyond Li-ion battery research, two emergent and widely employed technologies playing important roles in clean energy production and storage. The principle components of these electrochemical processes are electrode materials, which are currently facing challenges in performance improvement, thus motivating the development of novel electrode materials. This development requires synergistic interactions between experimentalists and theorists with backgrounds in solid state chemistry, condensed matter physics, and materials science and engineering. In light of a large amount of literature covering the topic, we will focus this review on the seminal electrode materials that have been discovered in the last five years, such as transition metal chalcogenides, carbides, and phosphides, as well as 2D layered materials. Intensive cross-disciplinary research is also dedicated to nanostructuring and hybridization of the emerging electrode materials in order to maximize the efficiency and simultaneously to lower the cost of the processes. As the understanding of the nanoscale-related effects deepens, it opens important pathways to the discovery of further materials and their improvement.
1. Introduction

Modern electrochemistry is an increasingly cross-disciplinary field of research, bringing together chemists, physicists, materials scientists, and engineers. Among many electrochemical processes, water electrolysis (WE) and energy storage play an important role in future clean energy technologies, especially in applications that require uninterrupted autonomous power and readily scalable and portable solutions. The inherently intermittent nature of the renewable energy production places a strong emphasis on the development of efficient methods for energy conversion, storage, and transport. Promising solutions for these challenges are offered by the emerging hydrogen economy and a new generation of rechargeable batteries. Notably, advanced and high-performance electrodes are the principle components of the underlying technologies for hydrogen generation and electrochemical energy storage.

Material challenges are currently the bottleneck for the improvement in the performance of the electrodes used in electrochemical energy generation and storage. For example, the best-performing electrocatalysts for water splitting are expensive and critical platinum-group metal (PGM) systems which have to be replaced with cheap and abundant catalysts for practical industrial applications. Similarly, in the rechargeable batteries field, critical Li element will be eventually replaced with other abundant ions, such as Na and Mg, and those batteries have multiple challenges associated with the stored energy density, charge-discharge rates, cycling stability, and cost to fabricate. Given the mature state of the traditional electrode technologies, the new physical and chemical characteristics of materials enabled by nanoscience and nanotechnology offer a sustainable pathway to design novel electrodes for future applications. Herein, we will highlight some specific examples of the emerging electrode materials with electrochemical performance significantly enhanced by exploiting nanoscale effects and nanosstructuring of materials.

2. Electrochemical water splitting

2.1. Hydrogen economy

Hydrogen, H₂, plays an important role in clean energy technology, complementing intermittent solar/wind power [1]. Lightweight H₂ has the highest specific energy of any known non-nuclear fuel, and it can be used for both energy generation and storage purposes. Remarkably, H₂ is an environmentally friendly fuel, since only energy and water are the end products of the reaction between hydrogen and oxygen, O₂, giving rise to emerging fuel cell devices. Notably, there are no natural sources of H₂ gas on Earth, and therefore, large-scale production of H₂ is always driven by energy input. Currently, more than 95% of H₂ is produced through steam reforming reaction of water with natural gas or fossil fuels, typically over a nickel catalyst at \( T \geq 700 \, ^\circ\text{C} \) [2]. The main drawbacks of steam reforming are the
high energy and cost demands of the process, low purity of the resultant H₂, and emission of greenhouse gases.

Electrochemical WE is the industrial process currently used to produce pure H₂ through a non-spontaneous electrochemical reaction:

\[
2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2(g) + \text{O}_2(g)
\]  

At present, WE accounts for about 5% of the total H₂ production, but it is foreseen to increase in the future as, when coupled with renewable external energy sources, it represents an attractive clean and sustainable option to produce H₂ without use of fossil fuels.

### 2.2. Electrochemical cells for WE

From a historical point of view, WE was discovered in 1789 by van Troostwijk and Deiman, and it was further investigated and better defined by Volta and later on by the experiment of Nicholson and Carlisle [3–5]. An example of WE is given in Figure 1(a), where a simple scheme of an electrolytic cell for water splitting is shown. The electrolytic cell consists of two electrodes immersed in aqueous electrolyte solution and connected to an external power source. When an electric current at a certain voltage is passed through the circuit, two half-reactions take place on the electrodes, resulting in the formation of H₂ gas at the cathode and O₂ gas at the anode. Specifically, the cathode and anode have negative and positive charges, respectively, and accordingly the positive protons, H⁺, move towards the cathode, while the negative hydroxyl anions, OH⁻, move towards the anode. Gases are then produced when the potential applied to the electrodes is sufficient to reduce H⁺ to H₂(g) and to oxidize OH⁻ to O₂(g).

![Figure 1. Schematic representations of the cell for WE (a) and proton exchange membrane (PEM) WE cell (b).](image)
Typically, the electrodes for WE are conductive and highly chemically stable materials, such as titanium, graphite, transition metals alloys, etc. The electrocatalyst is deposited on the electrode surface, ensuring a good electrical contact between the electrode and the electrocatalyst, as well as a good mechanical stability of the electrode-catalyst system. The role of the electrocatalyst in WE is to reduce the overpotential arising from slow charge transfer and insufficient chemical reaction rates. To date, the best performing and long-lasting electrocatalysts for the cathode and anode are Pt and IrO$_2$, respectively [6,7]. Also, other PGMs and PGM-containing compounds exhibit high electrocatalytic performance in WE.

Alkaline WE is a mature and commercially available technology to produce H$_2$. The main limits associated with this technology are the relatively low current density, low operating pressure, cross-over of gases, and low partial-load range [8–12]. On the other hand, the proton exchange membrane (PEM) electrolyzer is an emerging H$_2$ production technology. In a PEM electrolysis cell (Figure 1(b)), the two electrodes are assembled with the membrane in a membrane electrode assembly (MEA). The thickness of the membrane is usually in the range of 20–300 μm. The main role of the PEM is to ensure proton transfer from the anodic side of the cell to the cathodic side, where they are reduced, generating H$_2$. Importantly, the PEM assembly has a low permeability to H$_2$, thereby minimizing the intrinsically dangerous crossover of H$_2$ and O$_2$ gases. It should be emphasized that PEM electrolysis is carried out only in acidic electrolyte, since alkaline anion exchange membranes are still not commercially available.

Several positive features, such as high current density, good transport of the electric charges and low Ohmic losses, good partial-load range, the possibility of operation at elevated temperatures (≤150 °C) and pressures (>50 bar), as well as compact system design can be achieved using the PEM electrolyzer [8,13].

2.3. Thermodynamic considerations

From a thermodynamic point of view, WE is a non-spontaneous reaction. The change in the Gibb’s free energy, $\Delta G$, is positive in the range of common operating temperatures. Under standard temperature and pressure (STP), $\Delta G$ can be expressed as a function of the reversible cell potential $V_{\text{rev}}^\circ$:

$$\Delta G^\circ = -nFV_{\text{rev}}^\circ$$  \hspace{1cm} (2)

where $n$ is a number of electrons transferred, $F$ is the Faraday constant (96485 C mol$^{-1}$), and $V_{\text{rev}}^\circ$ is equal to 1.23 V under STP. During normal operating conditions, the real cell potential applied to the electrodes ($V_{\text{cell}}$) is determined by different contributions, including the activation overpotential, $\eta_{\text{act}}$, which represents the overpotential related to the activation energy at the two electrodes. Another contribution is the Ohmic overpotential, $\eta_{\text{ohm}}$, which accounts for all the different cell resistances that affect the charge flow, such as external circuit, electrodes, and electrolyte. Hence, the actual operating cell potential to drive the reaction is:
Currently, many research efforts are concentrated on improving the electrolytic cell efficiency, namely, the current density, by minimizing the electrical losses.

### 2.4. Mechanistic considerations

There are two half-reactions, namely anodic oxygen evolution reaction (OER, 4a) and cathodic hydrogen evolution reaction (HER, 4b), which take place during electrochemical WE:

\[
2\text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4\text{H}^+ + 4e^- \quad (4a)
\]

\[
2\text{H}^+ + 2e^- \rightarrow \text{H}_2(g) \quad (4b)
\]

The complex mechanism of the OER has been carefully studied during the past years using a combination of kinetic measurements and analytical methods [14–17]. A structure-reactivity relationship in the reaction by Shao-Horn and co-authors [17] showed that OER is a multi-electron reaction exhibiting four distinct single-electron charge-transfer steps in an acidic electrolyte, which are represented in Figure 2(a) together with the Equations (5)–(8), where * denotes a generic radical species adsorbed on an active site.

\[
\text{H}_2\text{O}(l) \rightarrow \text{OH}^* + (\text{H}^+ + e^-) \quad (5)
\]

\[
\text{OH}^* \rightarrow \text{O}^* + (\text{H}^+ + e^-) \quad (6)
\]

\[
\text{O}^* + \text{H}_2\text{O}(l) \rightarrow \text{OOH}^* + (\text{H}^+ + e^-) \quad (7)
\]

\[
\text{OOH}^* \rightarrow \text{O}_2(g) + (\text{H}^+ + e^-) \quad (8)
\]

In the more studied HER, the accepted mechanism is illustrated in Figure 2(b) following the Equations (9)–(12) [18–21]. The initial step, called the Volmer reaction, constitutes the interaction of one proton with an electron on an active site, resulting in the adsorption of one H⁺ ion on the surface,

\[
\text{H}^+ + e^- \rightarrow \text{H}^* \quad (9)
\]

At this point, molecular hydrogen H₂ evolves either by electrochemical recombination, known as the Heyrovsky step or ion + atom reaction, wherein a second electron is transferred to the adsorbed hydrogen followed by the reaction with a second proton, thus resulting in the desorption of a H₂ molecule from the surface,

\[
\text{H}^* + e^- + \text{H}^+ \rightarrow \text{H}_2 \quad (10)
\]
Figure 2. Simplified mechanisms for electrochemical WE: OER (a) and HER (b).
or by chemical recombination, known as the Tafel step, where a second ion of hydrogen is adsorbed onto the surface, followed by the recombination of the two adsorbed atoms into a $H_2$ molecule,

$$H^+ + e^- \rightarrow H^* \quad (11)$$

$$H^* + H^* \rightarrow H_2 \quad (12)$$

Herein, polarization curves (cell potential vs. log of current density) provide important information about reaction mechanism and kinetics of the HER. The overpotential $\eta$ can be described with the following Equation [22]:

$$\eta = b \times \log \left( \frac{j}{j_0} \right) \quad (13)$$

Therefore, $\eta$ is dependent on the exchange current density, $j_0$, which is correlated with the rate of exchange of electrons at the interface under reversible conditions (i.e. at zero overpotential), and on the Tafel slope $b$ (in mV dec$^{-1}$), which is simply the voltage increase needed to rise the current by an order of magnitude (e.g. from 0.1 to 1 mA cm$^{-2}$); $j$ is the current density.

Typically, the performance of the electrocatalysts relies directly on the following parameters: $\eta_{\text{onset}}$, onset potential for driving 1 mA cm$^{-2}$; $\eta_X$, the onset potentials to drive a certain current density $X$ mA cm$^{-2}$ (e.g. $X = 10, 20, 100, 200$ mV); $j_0$, the exchange current density; and $T_S$, the Tafel slope. Herein, the $j_0$ and $T_S$ are the most important descriptors of the electrode efficiency. The $j_0$ is basically the inherent activity of the catalyst, whereas $T_S$ gives important insights into the rate-determining step, and accordingly the mechanism of the reaction taking place at the electrode surface [19,22–25]. For instance, in the case of HER, supported Pt exhibits a $T_S$ of about 30 mV dec$^{-1}$ in acidic electrolyte and around 60 mV dec$^{-1}$ in alkaline electrolyte, which indicates that the HER reaction follows a Heyrovsky mechanism, i.e. the electrochemical recombination is the rate-determining step. Generally, high values of $j_0$ and low values of $T_S$ are the target when designing efficient electrodes for WE.

### 2.5. The challenge

Whereas the best electrocatalysts for WE are PGMs, their main drawback is obvious: they are scarce on the Earth’s crust and therefore expensive. These ecological and cost aspects strongly limit the viability of PGMs for widespread applications. Accordingly, the current research trend is aiming at searching for alternatives to PGMs or at least to reduce their use in electrodes. Importantly, the electrocatalysts for PGM replacement have to satisfy several requirements such as high efficiency, low cost, high stability, and durability. In search for effective PGM replacement in WE, significant recent work has focused on both theoretical and experimental approaches combined with nanoscience and nanotechnology, as will be discussed in the following sections.
2.5.1. Predictive modeling

In the design of new competitive electrocatalytic materials, it has to be considered that the surface reactivity of a metal-based electrocatalyst is strictly dependent on its intrinsic electronic structure and on the electronic structure resulting from the interaction of the surface of the electrocatalyst with the adsorbates (reactants, intermediates, and products). The identification of the descriptors correlating electrocatalytic activity with electronic structure modifications is crucial. From this point of view, the significant development of computational chemistry techniques in recent years, in particular, in the field of electrochemistry, gives an important support to the design and development of new electrocatalytic materials.

An example of this can be found in the plot presented in Figure 3, showing the experimental values of $j_0$ as a function of the DFT-calculated Gibbs free energy change of adsorbed atomic hydrogen ($\Delta G_{H^*}$) on different catalytic materials. PGMs are almost at the top of the volcano, showing the highest current density and a small negative $\Delta G_{H^*}$. The metals on the left side of the volcano have a larger negative $\Delta G_{H^*}$, which means that H adsorption is stronger than on PGM atoms resulting in a more difficult hydrogen evolution. In contrast, the materials on the right side of the volcano bind hydrogen more weakly, thus preventing the formation of stable intermediates on the electrode surface and consequently suppressing the HER \[15,19,26–28\].

The design of novel electrocatalysts for HER can be guided by means of a DFT-based computational approach known as the $d$-band model. This model considers the electronic structure modifications of the valence band (VB) of the surface metal atoms resulting from the interaction with the adsorbates. The change in the position of the $d$-band center relative to the Fermi level gives an indication of the strength of the adsorption of the adsorbate on the transition-metal atom, the higher the $d$-band centre the stronger the adsorption \[26,28–33\]. Furthermore, formation of alloys results in a perturbation of the electronic structure, as shown

![Figure 3. Activity of the electrocatalysts towards HER has a volcano plot relationship with free energy change of adsorbed atomic hydrogen. Reproduced from Ref. [19] with permission from The Royal Society of Chemistry.](image-url)
in Figure 4, where the modification of the density of states and the $d$-band center in the Pd–Ag alloy is compared to Pd [32]. The $d$-band model can predict the reactivity of bimetallic surfaces and the effect of strain caused by the difference in the atomic radii. Specifically, compressive strain results in a lowering of the $d$-band center, thereby weakening the adsorbate–surface interaction. On the other hand, expansive strain produces the opposite effect [34]. Hence, a theoretical design of the optimal supported surface is possible, and in principle, the strength of the adsorption can be tuned by engineering ad hoc the surface structure [19,28,30,32,35–38].

2.5.2. Strategies with nanocatalysts

Generally, nanostructuring of electrocatalysts is a powerful concept to prepare advanced electrode materials for WE that benefit from such nanoscale effects as high specific surface area, quantum confinement, large number of low-coordinated sites, and enhanced charge transfer kinetics. Usually a reduced size of the catalyst gives rise to catalytic activity, as a decrease in particle size means an increase in the specific surface area available to accomplish catalytic reactions, i.e. more active sites are exposed and available. Going from bulk catalyst to its nanoscale counterpart strongly affects the local physicochemical properties of the catalyst surface, as illustrated in Figure 5(a). In addition, morphology and electronic structure are connected at the nanoscale, as shown in Figure 5(b) [39]. The chemical activity in terms of bond breaking, stabilization of intermediates on the surface, and formation of new bonds is more pronounced at discontinuities or defects such as edges, corners, steps, or kink sites. In turn, when the active sites are low-coordinated and the motion of the electrons is restricted, the electronic structure of the catalyst is affected.

Specifically, $d$-band valence electrons, which move in a continuum in a bulk system, are subjected to a confinement when the surface is restricted to the
The confinement of the electrons results in a rise in the surface free energy, which favors chemical interactions. Accordingly, the catalytic activity of the nanostructured catalysts with a large number of low-coordinated active sites can be ascribed to the so-called ‘confinement,’ ‘quantum size,’ or ‘site isolation’ effects [19,36,40–46]. For example, gold, which is known to be chemically very inert in the bulk form, shows an excellent catalytic activity for a number of reactions when the size of the particles is below 5 nm, thus exhibiting low coordinated structures and forms [47]. Another positive effect is enhanced charge-transfer kinetics in electrochemical reactions. This is a result of shorter electron-transfer distances and faster diffusion rates of the charged species towards the active sites in the case of nanostructured catalysts in comparison with bulk systems (Figure 5(d)).

In the case of HER, the structure sensitivity and particle size effects are still under debate, and a few studies have been published. Ultra-high vacuum studies on Pt revealed a sensitivity of HER to the surface structure [48]. Under usual electrochemical operating conditions, Marković and Conway found better activity for HER on Pt(110) than on other Pt surfaces [49,50]. In the case of particle size effects, the lack of studies is mainly due to the complexity in controlling the particle size and its distribution on the nanometer scale during the synthesis process [51,52].
2.6. Towards PGM-free electrocatalysts

During the last decade, research efforts addressing PGM replacement in electrochemical WE have increased largely, aiming at (i) reducing the usage of PGM in the electrocatalytic system or (ii) a complete replacement of PGMs by earth-abundant electrocatalysts. Current theoretical screening of Pt-free materials mostly address economical compounds based on transition metals (TMs). In particular, Fe, Co, and Ni exhibited good Gibb's energy change values for hydrogen activation and they are quite abundant on the Earth's crust (Fe and Ni more than Co). Notably, the electrocatalytic activity, stability, and durability of the metallic TMs are quite low, but fortunately, significant improvements can be made through the introduction of other non-metal elements, such as S, C, and P. On the other hand, excellent experimental results towards PGM-free electrocatalysts have been obtained by alloying Pt with TMs and by complete substitution of PGMs by TM chalcogenides, carbides, and phosphides. These emerging electrocatalytic systems will be highlighted in sequence based on electrode materials. Notably, the field of WE is broad, and therefore in the following sections we will mostly concentrate on the emerging electrode materials for HER, since this reaction is one of the most attractive and environmentally benign ways to produce H₂.

2.6.1. Pt alloys

Alloying Pt is considered an important pathway to minimize its concentration in the working electrodes. Optimization of the d-band centre of Pt alloys resulted in less expensive materials than Pt with electrochemical properties and efficiency comparable or even higher than Pt, as in the case of Pt–Ni alloys (Pt₃Ni, PtNi, and PtNi₃) [53]. Another example of successful Pt alloying is BiPt, which was predicted to be high performing in WE by a computational approach, and further experimentally found to be more active than pure Pt, showing 50% higher $j_0$ than that of pure Pt film ($j_0 = 0.56 \text{ mA cm}^{-2}$) [28]. Moreover, PtAu core-shell nanoparticles exhibited promising electrochemical properties, making them appealing for WE [42]. The next important group derived from alloys consists of the less expensive PtNi core-shell nanocrystals, which are of very high utility since they show a WE performance even better than supported Pt electrocatalysts [54,55]. Although the use of Pt electrocatalysts currently ensures a broad applicability of WE, the development of novel Pt-TM alloys (e.g. Pt–M (M = Fe, Co, Ni, Cu)) is a more environmentally sustainable and cost-effective approach, wherein the discovery of PtNi₃, with its, low content of Pt, has led to the most impressive results [56].

2.6.2. Chalcogenides

Transition metal dichalcogenides (TMDCs), especially MoS₂, are an emerging class of compounds, attracting considerable interest as potential Pt-free electrocatalysts for HER. Studies performed in the 1970s demonstrated that bulk MoS₂ is inactive towards HER. However, in 2005, Nørskov et al. have reconsidered this
compound from a theoretical point of view [57]. The authors found many similarities of MoS$_2$ with metalloenzymes, such as hydrogenase and nitrogenase, which are known as natural HER catalysts [57]. Inspired by theoretical insights, Jarmillo and co-authors showed experimentally that nanostructured MoS$_2$ is an active electrocatalyst for HER [58]. Interestingly, MoS$_2$ is a particularly structure-sensitive material [59–61]. There are two main polymorphic modifications of MoS$_2$, H modification, where all Mo atoms surrounded by trigonal prisms of sulphur atoms, and T, modification, where all Mo atoms are octahedrally coordinated. Numbers in front of the H and T letters indicate different stacking sequences of the MoS$_2$ layers [62]. The exfoliated 1T–MoS$_2$ nanosheets show remarkable catalytic activity towards HER, about 600 times higher than the few-layer 2H–MoS$_2$ [61].

Significant research has been conducted aiming at providing a solution for 1T–MoS$_2$ structure stabilization and to synthesize MoS$_2$ structures with a maximized exposure of the active sites, thus improving the overall activity. Accordingly, MoS$_2$ has been produced in different nanostructured forms such as nanoparticles, defective nanosheets, porous films, nanowires, and amorphous films [37,61,63]. Furthermore, covalent functionalization of the 1T–MoS$_2$ monolayer modifies its electronic structure, thus allowing an ad hoc tuning of the $d$-band centre [61]. Also, the incorporation of other transition metals as Fe, Co, Ni, and Cu, as dopants resulted in an enhancement of the electrocatalytic activity [37]. Although MoS$_2$ performed well in HER and represents a suitable alternative to Pt-based electrodes, several challenges remain, mainly dealing with the stabilization of the structure, dopant, and substrate effects, that need to be resolved for their scalable application as electrocatalyst for WE. The structural peculiarity and physicochemical characteristics of the 2D TMDCs are described in detail in Section 3.2 within the context of rechargeable batteries.

In the recent years, the variation in TM elements allowed further expansion of emerging HER electrode materials towards other TMDC compounds. In particular, the cubic pyrite-phase TMDCs with the general formula MX$_2$ (M = Fe, Co, Ni; X = S, Se, Te) have been found to be efficient electrocatalysts, CoS$_2$ and NiS$_2$ phases in particular [27,64]. Although the HER performance of the TM pyrite phases is reasonably higher than that of MoS$_2$, these highly active electrocatalysts suffer from stability and durability drawbacks. High reactivity of the MX$_2$ pyrites often results in undesired corrosion of the electrocatalysts, for example, simple dissolution in acidic electrolyte. The degradation of this type of the materials can be suppressed, however, to some extent by nanostructuring, compositional modifications, and supporting the electrocatalyst on an inert substrate. For example, the good HER activity and reasonable stability in acidic electrolyte of thin-film CoS$_2$ electrodes have been improved by developing CoS$_2$ microwire and nanowire arrays on a graphite support (Figure 6) [64]. The resultant CoS$_2$ microwires have $T_s$ and $j_0$ as high as 58.0 mV dec$^{-1}$ and $5.27 \times 10^{-3}$ mA cm$^{-2}$, respectively [64].

Future studies in the field of TMDCs should address the robust and scalable syntheses of metastable but electrocatalytically active 1T-MoS$_2$, although the low
activity of this 2D material may limit its feasibility for WE. Over the past few years, it has also become clear that highly active pyrite-type TMDCs possess issues associated with their low chemical stability. Here, interconnection between the crystal structure, chemical composition, activity, and stability will be of special relevance to benefit from the emerging pyrite-type TMDCs.

2.6.3. Phosphides
Another earth-abundant class of compounds of considerable interest as potential electrocatalysts for WE are TM phosphides (TMPs), the performances and stability of which are comparable to those of Pt-based systems [65,66]. TMPs are known to be active catalysts for the hydrodesulphurization reaction, while their activity as hydrogenation catalysts has been known for more than 50 years [67,68]. Hydrogenation catalysts are known to show good performance in HER because both processes are determined by the adsorption of intermediate H atoms. In particular, a theoretical DFT-based approach revealed the potential activity of the (0 0 1) plane of Ni$_2$P towards HER [69]. In Ni$_2$P, the negatively charged non-metal atoms and isolated metal atoms work as proton and hydride acceptor sites, respectively. The co-existence of the proton-acceptor and the hydride-acceptor sites on the surface of Ni$_2$P (0 0 1) is the so-called ‘ensemble effect,’ which facilitates the HER. Furthermore, the presence of P eases the removal of the H strongly adsorbed onto the Ni sites of the Ni$_2$P (0 0 1) surface [38,69].

In 2013, the activity of Ni$_2$P towards HER was confirmed experimentally by the Lewis and Schaak groups [70]. They synthesized Ni$_2$P nanoparticles with an
average size of 17 nm by colloidal synthesis. Interestingly, the obtained nanoparticles were hollow with highly exposed (0 0 1) Ni$_2$P planes. The resultant Ni$_2$P nanoparticles exhibited excellent HER activity but their stability was still not satisfactory. After this initial study, research groups of Sun, Hu, and Lewis did some of the pioneering work on the TMP electrode materials. For instance, the Hu group achieved a highly active and stable HER electrode containing Ni$_2$P nanoparticles (10–50 nm) by a simple and scalable solid-state reaction route [71]. In addition, the Sun group successfully prepared nanosheet arrays supported on carbon cloth driving a large cathodic current at low overpotentials with strong durability in acidic electrolytes. The resultant electrode shows $T_S = 51$ mV dec$^{-1}$, $j_0 = 0.26$ mA cm$^{-2}$, and $\eta_{10} = 75$ mV, while maintaining its electrocatalytic activity for at least 57 h [72].

Kolen’ko, Kovnir, and Liu groups have also together investigated the synthesis of TMPs for WE, mainly focusing on the fabrication of monolithic self-supported HER electrodes [36,73,74]. Intensive research has been dedicated to Ni–P systems (Ni$_2$P, Ni$_5$P$_4$, NiP$_2$), addressing nanostructuring, electrocatalytic activity, stability, and robust fabrication process of the electrodes for HER and OER, the most sensitive steps towards the introduction of PGM-free electrodes to the market. Figure 7 shows the microstructures of the obtained nickel phosphate nanorods [73] and nanosheets [74], which exhibit excellent performance towards HER. More specifically, the cathode shows $T_S = 79$ mV dec$^{-1}$, $j_0 = 0.116$ mA cm$^{-2}$, and $\eta_{10} = 120$ mV. Furthermore, the cathode exhibits good long-term durability toward HER during 72 h while driving a cathodic current density of 10 mA cm$^{-2}$. Based on predictive DFT modeling, the performance of the Ni–P system was improved through chemical doping of Ni–P by Al, while the stability and durability were found to be comparable with pure Ni–P. Furthermore, a novel, easy, one-step synthesis process of Ni–P was developed, rendering the electrode fabrication process scalable and thus opening a gateway towards industrial production [36,73,74].

Apart from Ni–P, a few other TMPs, such as Cu, Fe, and Co derivatives, have been reported to be highly active towards HER. Of special interest is the Co–P system due to its increased stability and durability in WE. For instance, cobalt phosphides with different morphologies such as nanoparticles, nanoporous nanowire arrays, nanosheets, and nanoparticles supported on carbon nanotubes (CNTs) exhibited excellent activity in HER, and more importantly, long-term stability in acidic conditions with better performance than Ni$_2$P [27]. In particular, the CoP supported on carbon cloth has low $\eta_{\text{onset}} = 38$ mV and $\eta_{10} = 67$ mV, as well as a small $T_S = 51$ mV dec$^{-1}$, while preserving its activity for at least 22 h in acidic electrolyte [75].

Iron phosphides have been also investigated, since Fe is the most abundant transition metal. Several supported nanostructured systems, such as FeP nanowire arrays on both Ti plate and carbon cloth, FeP–graphene hybrid nanosheets, and FeP–carbon nanotube materials have been prepared. In particular, the FeP nanoparticle-modified carbon cloth exhibits high activity towards HER, which is
Figure 7. Nickel phosphide nanorods array cathode: SEM image (a), EDX spectrum (b), and dark-field (c) and bright-field (d) TEM images. [75] – Reproduced by permission of The Royal Society of Chemistry. Nickel phosphide nanosheet array cathode: low (e) and high (f, g) magnification SEM images and EDX spectrum (h). Reproduced from Ref. [76] with permission from John Wiley and Sons.
comparable to that of commercial Pt/C, while simultaneously exhibiting a good stability in acidic and neutral media [75].

All in all, these studies reveal the central role played by phosphorus in the TMPs, and especially, the versatility by which phosphorus regulates the electronic structure, active metal site isolation, hydrogen adsorption behavior, and stability in acid or alkaline electrolytes of the resultant TMPs. It should be emphasized that despite a range of important findings and comprehensive electrocatalytic studies of TMPs, the long-term stability of Pt-based electrocatalysts has not been outperformed, and examples of highly durable TMP electrocatalysts are still scarce. To achieve this, other important aspects need to be thoroughly investigated and optimized, including the chemical composition of the TMP and the corresponding additional VB states.

### 2.6.4. Mixed anion/cation

An interesting newcomer in the field of TM-based electrocatalysts is the class of TM compounds with mixed cation or anion sublattices, for instance, Fe–Ni and Co–Fe phosphides or cobalt phosphosulphide P–S, respectively. In the case of mixed cation electrocatalysts, one of the most noteworthy emerging compounds is Co–Fe–P nanoparticles, which show notable electrochemical performance in OER [76]. Also, Kolen’ko and Kovnir groups have prepared Fe–Ni diphosphide (Fe_{0.2}Ni_{0.8}P_{2}) by sputtering Permalloy onto carbon paper gas diffusion layer followed by gas transport phosphorization reaction. The as-prepared nanostructured Fe–Ni pyrite-type diphosphide shows excellent electrocatalytic performance towards HER. The observed high activity of the electrode correlates well with its electronic structure predicted by DFT calculations [35].

Concerning mixed anion TM compounds, from theoretical structure investigations and the strong similarities between the active metal centers of Fe-only hydrogenase, it has been suggested that the active sites are the square-pyramidal surface metal centers bridged by dichalcogenide dumbbells. Stability and reactivity (hydricity) can be influenced by the electron-donating character of the chalcogen ligands X, and therefore, the HER catalytic activity of metal chalcogenides could be improved through tuning the hydrogen adsorption free energy by changing the atomic components of the X₂− dumbbells, while still preserving the pyrite structure. Given the weaker electronegativity of phosphorus in comparison to sulphur, Jin et al. and Wang et al. have investigated pyrite-type mixed anion systems based on cobalt phosphosulphide (CoPS) as a novel ternary catalyst for the HER. The results show that this mixed anion CoPS with different morphologies exhibits excellent performance in terms of electrocatalytic activity and stability (Figure 8) [77]. More specifically, having mass load of electrocatalyst of only 1.6 mg cm⁻², the electrode has a negligible $\eta_{\text{onset}}$, low $\eta_{10} = 48$ mV, as well as favorable $j_0 = 1.14$ mA·cm⁻² and $T_\text{s} = 55$ mV dec⁻¹. The stability and durability of the electrode for 100 h was also confirmed. [77,78].
Overall, mixed cation and/or anion sublattices is an effective way for the preparation of complex, high-performing, stable, and durable electrodes for WE. When combined with nanostructuring, this methodology can in the future allow one to design and create chemical complexity and structural diversity, desirable in active and stable PGM-free electrode materials for WE. The continuous development of DFT methods as well as the broad availability of Fe, Co, Ni, S, and P should further expand the use of mixed TM cation/anion materials in WE.

3. Emerging 2D electrode materials

3.1. Rechargeable beyond Li-ion batteries

Energy storage is essential for a large variety of applications ranging from small-scale portable and wearable electronics and implantable biomedical devices to
middle-scale electrification of transport to large-scale sustainable grid systems and space exploration missions. To fulfill the continuously growing demand for high performance batteries, new electrochemical systems are explored and new materials are sought for. Up to date, lithium-ion battery (LIB) remains the most used energy storage device to power portable electronics and electric cars. The operation mechanism of LIBs is based on intercalation reactions [79,80]. Intercalation is usually a reversible process that involves the introduction of a guest species into empty crystallographic sites without major modification of the overall original host structure. In the case of lithium-ion batteries (Figure 9(a), $M^{x+} = \text{Li}^+$), on discharge, $\text{Li}^+$ ions are intercalated into the cathode material, and the reverse process on charge is associated with the intercalation of ions into the anode material. To preserve charge balance, ion intercalation is accompanied by addition of electrons. Materials with layered crystal structures have proven themselves among the most reliable hosts that provide the highest performance. Graphite and lithium cobalt oxide (LiCoO$_2$), both with layered crystal structures, are employed for use as the anode and cathode materials, respectively, in many commercial lithium-ion batteries [79,80]. However, concerns about limited abundance and uneven distribution of lithium on the planet trigger development of other intercalation-based electrochemical energy storage systems [81]. So-called ‘beyond lithium ion’ (BLI) batteries operate due the similar mechanism as LIBs, but with other ions, such as $\text{Na}^+$, $\text{K}^+$, $\text{Mg}^{2+}$, $\text{Al}^{3+}$, $\text{Zn}^{2+}$, in electrolytes (Figure 9(b)). Although heavier than lithium, BLIs are more abundant, hence having lower costs, and therefore they are promising for future affordable energy storage devices, especially for the large-scale applications [82]. In addition to larger mass, BLIs are also either bigger ($\text{Na}^+$, $\text{K}^+$) or possess higher charge ($\text{Mg}^{2+}$, $\text{Al}^{3+}$, $\text{Zn}^{2+}$), which significantly impacts the ion transport and reaction kinetics within the

![Figure 9](image-url)

**Figure 9.** Schematic illustration of a battery operating due to the reversible intercalation of charge carrying ions, such as $\text{Li}^+$, $\text{Na}^+$, $\text{K}^+$, $\text{Mg}^{2+}$, and $\text{Al}^{3+}$, in 2D materials-based electrodes (a). The characteristics of the ions and their natural abundance (b) [84]. The schematics of the crystal structures of selected 2D materials (c).
electrode. In many cases, electrode materials analogous to ones used in LIBs do not function well in BLI batteries. Therefore, finding suitable electrode materials enabling rapid insertion and extraction of BLIs remains a challenge.

The report of graphene by Geim and Novoselov [83] opened a new era of innovative 2D materials and their application in functional devices. High electronic conductivity, high surface area, and mechanical strength of graphene make it especially attractive for energy storage applications, and the first graphene-based supercapacitor was realized in 2008 [84]. Since then, due to its high conductivity, flexibility, and surface area, graphene has been widely used both individually and as one of the components in composite electrodes [85–89]. Discovery of graphene was followed by identification of a wide variety of 2D materials (Figure 9(c)) including 2D TMDCs, layered transition metal oxides (TMOs), transition metal carbides and carbonitrides (MXenes), and layered group 14 pnictides. The large interlayer spacing of 2D materials offers large open diffusion channels for the electrochemically cycled ions, which can alleviate host–guest interactions, thus enabling facilitated diffusion of BLIs. By rationally designing 2D materials with specific chemical composition and interlayer spacing, it is possible to create BLI battery electrodes with high charge storage capabilities and rapid kinetics of charge/mass transfer.

In this part of the review, we summarize recent progress on electrochemical performance of beyond graphene 2D materials (TMDCs, TMOs, MXenes, and group 14 phosphides) in intercalation-based beyond lithium-ion batteries. Most reports up to date are focused on sodium-ion and magnesium-ion batteries (SIBs and MIBs, respectively). Here, we define 2D materials as materials with layered crystal structure and relatively large interlayer distance, without requiring these materials to have flake or sheet morphology. Graphene-based 2D materials and layered transition metal oxides synthesized using high-temperature annealing are beyond the scope of this article. To gain knowledge in this area of research, the readers are encouraged to review the following publications: [90–92]. However, graphene containing hybrids of TMDCs, TMOs, and MXenes are thoroughly discussed here. Computational studies predict that beyond graphene 2D materials can demonstrate advanced electrode characteristics [93–103], but in this review, we focus on experimental research and strategies that proved to be successful to improve performance of 2D materials in BLI batteries.

3.2. Transition metal dichalcogenides

TMDCs are a family of layered materials with the general formula of MX₂, where M is a transition metal from group 4–10 and X is a chalcogen, S, Se, or Te [104]. Each layer of a TMDC crystal structure is built by three stacked atom layers (X–M–X), with the different layers held together by van der Waals forces. Each transition metal is coordinated by six chalcogen atoms, and the d-electrons of the transition metal strongly affect the MX₂ electronic structures, giving rise to
a variety of physical properties. The relative arrangements of the MX₂ layers may vary resulting in multiple polymorphic modifications. More details regarding the relationship of the crystal structure, chemical bonding, and electronic structures of MX₂ can be found in the works of Budett [105,106]. Electron transport behavior in TMDCs depends on their composition and ranges from semiconducting to metallic to superconducting [106]. Bulk TMDC particles can be exfoliated to create 2D nanoflakes or nanosheets with reduced ion diffusion pathways. In addition, the anisotropic structure of 2D nanosheets can offer large surface area opening access to 2D permeable diffusion channels facilitating insertion/extraction of electrochemically cycled ions [103,107].

The most studied TMDC phases in energy storage application include MoS₂ [108–125], MoSe₂ [126–131], WS₂ [132–135], and WSe₂ [136–138]. MoS₂, with the interlayer distance of 6.2 Å, is explored as an anode material for SIBs. The initial discharge curves of bulk and nanostructured MoS₂ electrodes are shown in Figure 10(a) and (b), respectively. The mechanism of MoS₂ charge storage in SIBs has been revealed through detailed in situ and ex situ XRD and TEM experiments. It was established that when MoS₂ is cycled between 0.4 and 3.0 V, it functions due to the intercalation reaction with Na⁺ ions occupying sites between S–Mo–S

**Figure 10.** Initial discharge potential profile of Na intercalation in (a) bulk and (b) nanoscaled MoS₂. Insets show SEM images of the respective materials. (c) The high-angle annular dark-field (HAADF) image of electrochemically cycled bulk MoS₂. The purple, yellow, and blue circles are overlaid in the image for Mo, S, and Na atoms, respectively. (d) The annular bright field (ABF) image of nanoscaled MoS₂ obtained by discharging with cutoff voltage of 1.0 V along the [100] zone. The Na⁺ ion intercalation leads to phase transition from 2H to 1T phase, schematically shown in (e). Reprinted with permission from ACS Nano 8 (2014) p. 11394. Copyright 2014 American Chemical Society.
layers (Equation (14)). The material undergoes a series of two-phase transitions upon sodiation: $2\text{H–MoS}_2 \rightarrow 2\text{H–Na}_{0.5}\text{MoS}_2$; $2\text{H–Na}_{0.5}\text{MoS}_2 \rightarrow 1\text{T–Na}_{0.5}\text{MoS}_2$; $1\text{T–Na}_{0.5}\text{MoS}_2 \rightarrow 1\text{T–NaMoS}_2$, where the $2\text{H–MoS}_2$ is a semiconductor, while the $1\text{T–MoS}_2$ phase is metallic [139]. The transition from $2\text{H–MoS}_2$ to $1\text{T–MoS}_2$ is accompanied by a glide of interatomic planes [140]. It was found that the upper plateau at $\approx 0.85$ V corresponds to the intercalation of Na$^+$ ions in every other interlayer of MoS$_2$, resulting in a formation of Na$_{0.5}$MoS$_2$. Before the interlayer space is fully filled, the Na$^+$ ions begin to occupy the other spaces between S–Mo–S layers, generating strain and inducing glide of the sulphur plane along an interlayer atomic plane and phase transition from $2\text{H– to 1T–MoS}_2$ (Figure 10(c)–(e)) [109,113].

$$\text{MoS}_2 + x\text{Na}^+ + xe^- \rightarrow \text{Na}_x\text{MoS}_2 \quad (1\text{st step above 0.4V})$$  \hspace{1cm} (14)$$

$$\text{Na}_x\text{MoS}_2 + (4 - x)\text{Na}^+ + (4 - x)e^- \rightarrow 2\text{Na}_2\text{S} + \text{Mo} \quad (2\text{nd step below 0.4V})$$  \hspace{1cm} (15)$$

$$\text{MoS}_2 + 4\text{Na}^+ + 4e^- \rightarrow 2\text{Na}_2\text{S} + \text{Mo} \quad \text{(overall reaction)}$$  \hspace{1cm} (16)$$

When the lower voltage limit is further decreased down to $\approx 0.001–0.01$ V, MoS$_2$ follows the intercalation/conversion mechanism. The products of the conversion reaction (Equation (15)) are Na$_x$S and nanostructured, often amorphous, metallic Mo. It was found that if less than 1.5 Na$^+$ ions per formula of MoS$_2$ are inserted, the structure of MoS$_2$ can be partially recovered on charge (to 1T–MoS$_2$). However, MoS$_2$ structure cannot be restored once it decomposes to Na$_x$S and metallic Mo [109]. The same mechanism on deep discharge was reported for MoSe$_2$ [128]. It was proposed that MoSe$_2$ is converted to Mo and Na$_2$Se in the first discharge process. It was also established that the product of the first charge process is Se, not MoSe$_2$, and the reaction mechanism follows the route similar to Se/C composite [128].

The overall reaction (Equation (16)) describing the first discharge process of MoS$_2$ involves transfer of 4 electrons and corresponds to the theoretical capacity of 670 mAh g$^{-1}$ (due to the larger molar mass, theoretical capacity of MoSe$_2$ is 422 mAh g$^{-1}$).

Because of this change in mechanism, TMDC electrodes suffer from low initial Coulombic efficiency caused by large volume change accompanying electrode transformations during electrochemical cycling. Additional factors that contribute to low Coulombic efficiency include the formation of solid electrolyte interphase (SEI) [141] originating from electrolyte decomposition and considerable side reactions. Because of this large first cycle irreversibility, the capacity retention in TMDC electrodes is usually reported with respect to the discharge capacity exhibited by the electrode in the second cycle.
The van der Waals gap between two adjacent S–Mo–S slabs in MoS\(_2\) significantly suppresses the electronic conductivity across the layers, resulting in fast capacity fading for bare MoS\(_2\) electrodes upon cycling and poor rate capability. To overcome these limitations, several strategies were shown to be successful. First, using nanotechnology methods the size and morphology of TMDC particles can be controlled. Exfoliation results in the formation of thin flakes, which are usually also smaller in diameter compared to the original particles, enabling shorter diffusion distances for the electrochemically cycled ions and thus facilitating ion transport. In addition, chemical exfoliation can introduce functional groups on the surface of materials which can further facilitate diffusion of ions improving both rate capability and cycling stability of the electrodes. To improve electronic conductivity, integration of TMDCs with conductive carbon materials (carbon fibers, graphene, carbon nanotubes, etc.), often resulting in sophisticated electrode architectures, proved to be an efficient approach to achieve high performance of TMDCs in BLI batteries by enabling fast electron/ion transport. The latest reports demonstrate hybrid TMDC@carbon electrode architectures that enable increased surface area through the exfoliation of MoS\(_2\) and introduction of hierarchical porosity. The larger pores are believed to be beneficial for the electrolyte penetrations, while the smaller nanovoids favor electrode/electrolyte interaction. In addition, porous hierarchical architectures provide space for accommodating volume changes during cycling and prevent aggregation of nanoscale particles resulting in enhanced structural stability and cycling performance.

Many examples of the hybrid TMDC@carbon structures demonstrating enhanced electrochemical properties have been reported [115–120], however in this review we would like to highlight several successful strategies applied to integrate MoS\(_2\) with carbon, which could be used to improve performance of other 2D materials in BLI energy storage systems.

Hierarchically structured free-standing anode for SIBs was fabricated by depositing vertically aligned MoS\(_2\) nanosheets on carbon fibers derived from a paper towel, MoS\(_2@C\) [109]. Such smart integration not only ensures good electronic connection between MoS\(_2\) and carbon, but also enables preferred orientation of MoS\(_2\) diffusion channels allowing easy access of ions from electrolyte into electrode material. This provides shortened diffusion distances and helps to reduce the mass-transfer limitations. The randomly woven carbon fibers offer a 3D conducting network that facilitates electron transport. As the result of both improved ionic and electronic conductivities in such integrated electrode architecture, a high reversible capacity of 446 mAh g\(^{-1}\) at 20 mA g\(^{-1}\) and promising high power performance were achieved. In addition, with such binder-free architecture, carbon is protected from direct contact with electrolyte, diminishing interactions between inactive electrode components and electrolyte, thus reducing side reactions responsible for irreversible capacity. As a result, these electrodes were able to solve the problem of low initial Coulombic efficiency typical for TMDC materials. The MoS\(_2@C\) electrode demonstrated high initial Coulombic efficiency, of 79.5%.
The improvement in the cycling performance was achieved by the dip-coating of the MoS$_2$@C electrodes with carboxy methyl cellulose sodium salt. After 100 cycles at a current density of 80 mA g$^{-1}$, a high reversible capacity of 286 mAh g$^{-1}$ was achieved. Even at a high current density of 1000 mA g$^{-1}$, a reversible capacity of 205 mAh g$^{-1}$ was maintained. This promising electrochemical performance can be ascribed to the tailored hierarchical architecture of MoS$_2$@C hybrid electrode.

Another strategy for improving storage properties of TMDCs is based on atomic interface engineering of the exfoliated nanosheets with the goal to increase the intrinsic electronic conductivity of materials and expand adjacent layers for easier ion movement. Previously described composites had limited interface contact between TMDC and carbon. Rationally constructing TMDC/carbon hybrid architecture was proven to be a successful approach to maximize the heterointerface between TMDC and carbon and gain high rate capability and long cycle life [116]. Novel hierarchically structured nanotubes were synthesized by a one-pot solvothermal synthesis coupled with in situ carbonization of organic solvent (Figure 11). The walls of the nanotubes were assembled by many 2D superstructured nanosheets consisting of alternative monolayers of MoS$_2$ and carbon (Figure 11(d)). This 2D superstructure exhibits an ideal interface contact between MoS$_2$ and carbon. In addition, intercalation of octylamine molecules between MoS$_2$ layers enabled enlarged interlayer distance of 9.8 Å allowing faster diffusion of Na$^+$ ions (Figure 11(e)). The MoS$_2$:C superstructure nanotubes delivered an initial discharge capacity of 620 mAh g$^{-1}$ with a Coulombic efficiency of 84% at the current density of 200 mA g$^{-1}$ and maintained a reversible discharge capacity of 477 mAh g$^{-1}$ after 200 cycles (Figure 11(f)–(i)). Importantly, the discharge capacity of 415 mAh g$^{-1}$ after 200 cycles was observed even at high current density of 1000 mA g$^{-1}$ [116].

Many advantages of magnesium-ion batteries (MIBs) originate from the divalent nature and small ionic size of Mg$^{2+}$ ion (Figure 9(b)). However the search for electrode materials that allow fast Mg$^{2+}$ ion diffusion has proved problematic due to a high energy barrier for ion diffusion resulting from strong interaction between highly polarizing Mg$^{2+}$ guest ion and electrode material host lattice [142]. Two strategies were shown to improve reversible intercalation of Mg$^{2+}$ ion. First, nanostructuring of material particles down to 10-nm scale significantly reduces diffusion distances and leads to substantial magnesium diffusivity [143]. Second, introducing H$_2$O molecules in the electrolyte or host lattice transforms Mg$^{2+}$ into less polarized solvated ion thus reducing host–guest interaction, which favors fast ion diffusion [144].

A recent report demonstrated that expanding the interlayer distance in MoS$_2$ by incorporating polyethylene oxide (PEO) molecules, serving as pillars that hold S–Mo–S layers apart, was an effective approach to increase intrinsic magnesium diffusivity (Figure 12(a)) [124]. The interlayer distance of pristine MoS$_2$ (com–MoS$_2$) is 6.15 Å. After delamination–reassembly, the resulted res–MoS$_2$ had a less ordered structure and a slightly increased spacing of 6.33 Å. Upon intercalation
Figure 11. Structural models of the pristine 2H–MoS$_2$ and the MoS$_2$:C interoverlapped superstructure with expanded interlayer spacing (a). Schematic illustrations of the rational design of MoS$_2$:C interoverlapped superstructure with discontinuous carbon monolayers benefiting for Na$^+$ ion insertion/extraction (b), and the process of growing MoS$_2$:C superstructure nanosheets (c). TEM (d) and HRTEM (e) images of the MoS$_2$:C superstructure nanotubes after post thermal treatment. The expanded interlayer spacing is indicated in (e). Electrochemical characterization of the annealed MoS$_2$:C nanotube electrode: CV curves at a scan rate of 0.1 mV s$^{-1}$ (f); discharge-charge curves at the current density of 200 mA g$^{-1}$ (g); cycling performance (h); and rate performance (i). Reproduced from Ref. [121] with permission from Elsevier.
of PEO, the spacing further increases to 11.9 Å (peo1−MoS₂) and 14.5 Å (peo2−MoS₂), corresponding to 93 and 136% increase, respectively (Figure 12(b)–(e)). The materials delivered the following initial discharge capacities in Mg-ion cells:
com–MoS$_2$ = 22 mAh g$^{-1}$; res–MoS$_2$ = 37 mAh g$^{-1}$; peo1–MoS$_2$ = 51 mAh g$^{-1}$; peo2–MoS$_2$ = 75 mAh g$^{-1}$, which is over 3.4 times higher than that of com–MoS$_2$ (Figure 12(f)). Peo2–MoS$_2$ has also shown the best rate performance (Figure 12(g)). These results confirm that the interlayer expansion approach can boost performance of the 2D electrode materials in BLI batteries.

### 3.3. Transition metal oxides with layered crystal structures

Due to their high redox activity, leading to high capacity, layered transition metal oxides (TMOs) have been extensively explored as electrode materials. Some TMOs demonstrate relatively high working voltage, which makes them attractive candidates for cathode applications [90,143]. Many TMOs exhibit poor electronic conductivity and therefore they are combined with a conductive additive, such as carbon, to achieve their full capacity when used in battery electrodes. BLI batteries exhibit lower operation voltages compared to LIBs; therefore to meet the requirement of high energy density, they should utilize electrode materials with high capacities. This need for high capacity is especially important for the cathode materials, but finding TMOs with large interlayer spacing that would enable high capacity and fast ion transport of BLIs remains a challenge.

In bilayered V$_2$O$_5$, the 2D bilayered stacks are separated by large interlayer spacing of $\sim$10–13 Å (Figure 13(a)). The adjustable interlayer spacing can accommodate volume changes associated with reversible intercalation of BLIs. Bilayered V$_2$O$_5$ with nanobelt morphology (≈50 nm in thickness) and interlayer spacing of 11.5 Å was synthesized using solvothermal treatment and cycled in Na-ion cells [145]. The interlayer channels were oriented perpendicular to the exposed (1 0 0) facets providing easy access to Na$^+$ ions from electrolyte. Bilayered V$_2$O$_5$ nanobelts demonstrated an initial capacity of 231 mAh g$^{-1}$. Due to the intercalation of sodium, the interlayer distance has expanded from 11.5 to 15.4 Å. The electrode still delivered a discharge capacity of 170 mAh g$^{-1}$ after 100 cycles and showed good rate capability [145]. Na-containing bilayered vanadium oxide nanowires were synthesized using chemical pre-intercalation approach combining soft chemistry and hydrothermal treatment steps [146]. Na$_x$V$_2$O$_5$ nanowires demonstrated record high initial discharge capacity of 365 mAh g$^{-1}$ in Na-ion cells. However, the capacity decayed rapidly with cycling and at high current rates [146]. Pre-intercalation of electrochemically inactive iron ions into interlayer space [147] was shown to be an effective approach to stabilize the structure of the electrode during cycling through strong interactions between pre-intercalated ion and V$_2$O$_5$ bilayers. While the absolute capacity value of Fe$_x$V$_2$O$_5$ was significantly lower than that of Na$_x$V$_2$O$_5$ nanowires (the first discharge capacity of Fe$_x$V$_2$O$_5$ was 184 mAh g$^{-1}$), Fe$_x$V$_2$O$_5$ displayed a more stable cycling performance with 80% of capacity maintained after 50 cycles [147].

Similar to TMDC electrodes, tailoring of the nanoscale electrode architecture offers unprecedented opportunities for the improvement in functional properties
of TMOs in BLI batteries. For example, electrochemically deposited nanostructured bilayered V$_2$O$_5$ exhibited excellent performance in both Na-ion [148] and Mg-ion batteries [149]. In SIBs, bilayered V$_2$O$_5$ was grown on Ni substrate, and it formed interconnected ribbons with highly porous structure (Figure 13). Keeping the thickness of the material in such architecture down to nanoscale allowed making electrodes without conductive carbon additives and a binder. At the same time, the electrode exhibited high electronic conductivity and short diffusion distances for ion transport [148]. The bilayered V$_2$O$_5$ electrode demonstrated higher electrochemical activity and stable reversible capacity on extended cycling than the

Figure 13. Synchrotron X-ray diffraction patterns of (a) bilayered V$_2$O$_5$ annealed in vacuum at 120 °C (blue) in conjunction with diffraction simulation (dotted blue) based on the model of monoclinic base-faced bipyramidal layered structure depicted in the inset and (b) orthorhombic V$_2$O$_5$ annealed in oxygen at 500 °C (green). (c) HRTEM image of electrochemically grown V$_2$O$_5$ annealed at 120 °C and (d) the image section shown in the rectangle area in conjunction with the lattice model of monoclinic bilayered base-facing square-pyramid V$_2$O$_5$. (e) Electron nanodiffraction of the selected area shown in (c) in conjunction with corresponding XRD diffraction represented in reciprocal space (blue line). (f) First four charge-discharge cycles of bilayered V$_2$O$_5$ and orthorhombic V$_2$O$_5$ electrodes cycled at 20 mA g$^{-1}$. (g) Cycle life of bilayered V$_2$O$_5$ electrodes. (h) SAXS and WAXS spectra for bilayered V$_2$O$_5$: electrochemically deposited vacuum annealed sample (blue); after discharging with the current of 630 μA (black), 120 μA (gray), 20 μA (light gray); and after cycling at 120 μA in charge state (red). Model structures and critical interlayer spacing depicting transformations occurring upon Na$^+$ ion intercalation and deintercalation are also shown. Reprinted with permission from ACS Nano 6 (2012) p. 530. Copyright 2012 American Chemical Society.
orthorhombic V$_2$O$_5$ (Figure 13). The large interlayer spacing of 13.5 Å is believed to be crucial for high capacity (250 mAh g$^{-1}$) of the bilayered structure. Contrary to the orthorhombic V$_2$O$_5$, the discharge/charge curves of the bilayered V$_2$O$_5$ do not exhibit plateaus indicating phase transition. Instead, intercalation of Na$^+$ ions into bilayered phase shows smooth curves typical for solid state solution behavior (Figure 13(f)). This difference in mechanism of Na$^+$ ion storage can attribute to better electrochemical stability of the bilayered structure (Figure 13(g)). Sodium intercalation induces organization of overall structure with both long- and short-range order, however deintercalation is accompanied by the loss of long-range order, whereas the short-range order is preserved (Figure 13(h)).

In case of MIBs, nanostructured bilayered V$_2$O$_5$ was electrochemically deposited on a carbon nanofoam. The synthesized material contained structural water and hydroxyl groups in the interlayer space, which were shown to foster electron transfer and reversible intercalation of highly charged Mg$^{2+}$ ions. In addition, interlayer species are believed to stabilize the structure of the material. The open 2D diffusion channels of the nanoscale bilayered V$_2$O$_5$ film and strong interface with highly porous conductive carbon substrate enabled an electrode with the specific capacity of 240 mAh g$^{-1}$ [149]. Chemically pre-intercalated Mg$_{0.1}$V$_2$O$_5$·1.8H$_2$O with the similar crystal structure and the interlayer spacing of 12.3 Å was prepared using sol–gel method and investigated as the cathode in MIBs [144]. This material showed a first discharge capacity of 300 mAh g$^{-1}$ and good initial capacity retention.

3.4. Transition metal carbides and carbonitrides

Transition metal carbides and/or carbonitrides, labeled MXenes, are synthesized by etching out the A layers from MAX phases with the general formula of M$_{n+1}$AX$_n$, where M is an early transition metal, A is mainly a group 13 or 14 element, X is C and/or N, and $n = 1, 2, 3$ [150]. MXenes demonstrate several unique characteristics that make them especially attractive for energy storage applications. One of the greatest advantages of MXenes is that they are good conductors. An ability to enable rapid electron transport underlies excellent performance of MXenes in supercapacitors [151]. MXenes are hydrophilic, enabling good wettability with battery electrolytes. In addition, they are exceptionally rigid with bending stiffness values that theoretically are orders of magnitude higher than those of graphene. The MXenes produced up to date include Ti$_3$C$_2$, Mo$_2$C, TiNbC$_2$, Ti$_3$CN, Ta$_4$C$_3$, Ta$_2$C, V$_2$C, Nb$_2$C, etc. making them one of the most chemically diverse families of 2D materials.

Extraction of the A layers of MAX phases leads to not only chemical but also substantial morphological modification of the materials. In this process (Figure 14), the MAX phase powder reacts with aqueous HF solution followed by centrifugation, filtration, and excessive washing of the product until neutral pH is reached. This treatments results in exfoliation of dense MAX particles into
**Figure 14.** (a) Schematic describing the synthesis process of MXenes from MAX phases. (b) Schematic illustration of the structural changes during Ti$_3$C$_2$X synthesis. Reprinted with permission from ACS Nano 6 (2012) p. 1322. Copyright 2012 American Chemical Society. (c, d) SEM and (e) HAADF images of Ti$_3$C$_2$X. (f) HAADF image of Ti$_3$C$_2$X electrodes upon Na intercalation with cutoff potential of 0.0 V. Na$^+$ ions that are intercalated into Ti$_3$C$_2$X from the surface fully occupy interlayer space and stay on top of the C atoms rather than on top of Ti atoms in the Ti$_3$C$_2$X layer. Moreover, double Na-atomic layers are observed in one interlayer of the fully intercalated sample (labeled with double yellow arrows). Reprinted with permission from J. Am. Chem. Soc. 137 (2015) p. 2715. Copyright 2015 American Chemical Society.
loosely packed puckered structures [150]. In addition, aqueous HF etching leads to surface modification with various surface-terminating functional groups, such as –OH, –F, =O. Therefore, the general formula of $M_n^{n+1}X_nT_x$, where $T$ stands for surface terminations, is often used to properly designate chemical composition of MXene phases.

Most research aimed at understanding performance of MXene phases in BLI batteries is carried out by computational scientists [96–102], and experimental characterization, focused on Na-ion batteries, has emerged only in recent years. Ti$_3$C$_2$ and Ti$_2$C are two of the most studied MXene phases because of their well-established synthesis process and high electrochemical performance. In the first report on sodium intercalation into MXene phase from nonaqueous electrolyte [152], Ti$_2$CT$_x$, prepared by HF etching of the parent Ti$_2$AlC compound, was chosen as the electrode material. The relatively low voltage of $\approx$1.3 V vs. Na/Na$^+$ observed in discharge suggested that this material can be used as an anode in Na-ion batteries. In the first discharge process, Na$^+$ ions intercalated/adsorbed into/onto the Ti$_2$CT$_x$ sheet, delivering a relatively large capacity of 360 mAh g$^{-1}$. However, the Coulombic efficiency of only 65% was observed in the first cycle. After the initial few cycles required for activation, Ti$_2$CT$_x$ exhibited stable performance with the capacity of $\approx$175 mAh g$^{-1}$.

The mechanism of sodium intercalation into Ti$_3$C$_2$T$_x$ electrode was investigated using aberration-corrected scanning transmission electron microscopy [153] and solid-state $^{23}$Na magic angle spinning NMR spectroscopy [154]. The atomic scale study by STEM showed that double layer of Na$^+$ ions can accommodate within the Ti$_3$C$_2$T$_x$ interlayer space upon deep discharge down to 0.0 V vs. Na/Na$^+$ (Figure 14(e) and (f)). The extensive sodium intercalation occurs via two-phase transition and solid-solution reaction in sequence. Ti$_3$C$_2$T$_x$ electrode exhibited a reversible capacity of $\approx$200 mAh g$^{-1}$ in Na-ion cells for 200 cycles. This high performance was attributed to the increased number of intercalation sites and large interlayer spacing of 9.8 Å which allow for the double-layer intercalation mechanism [153]. Solid-state NMR and XRD analyses demonstrated that the interlayer distance expands in the first sodiation process by 2.8 Å [154]. It was found that such significant interlayer expansion is caused by both Na$^+$ ion intercalation and electrolyte solvent penetration. A fraction of the electrochemically intercalated Na$^+$ ions is trapped in Ti$_3$C$_2$T$_x$ electrode and serves as pillars, while the penetrated solvent molecules swell the interlayer space. As a result of the presence of these two species, the interlayer distance of $\approx$12.5 Å is constant during further sodiation/desodiation, leading to high cycle stability and fast Na$^+$ ion diffusion in the expanded interlayer space [154]. The initial capacity of 270 mAh g$^{-1}$ was attributed to Na$^+$ ion intercalation, adsorption of Na$^+$ ions on material surface, and electrolyte decomposition leading to the formation of SEI layer, suppressing electrolyte decomposition in the subsequent cycles. After several initial cycles, Ti$_3$C$_2$T$_x$ shows good cycling stability with the specific capacity of $\approx$100 mAh g$^{-1}$ over 100 cycles.
Electrodes with high volumetric performance can be fabricated by exfoliating MXenes into thin few-layer flakes and assembling these flakes into freestanding films without using polymer binders or metal current collectors, leading to minimized dead volume. It was shown that aggregation and restacking of MXene flakes can be prevented by preparing Ti$_3$C$_2$T$_x$/CNT films, where CNTs were utilized as spacers [155]. Hybridization of Ti$_3$C$_2$T$_x$ nanosheets and CNTs into a hierarchical porous structure improved the accessibility of MXene nanosheets to electrolyte and created multidimensional ion diffusion pathways (Figure 15) [155]. The Ti$_3$C$_2$T$_x$/CNT film electrode showed an initial discharge capacity of 501 mAh g$^{-1}$ and a charge capacity of 179 mAh g$^{-1}$ at a current density of 20 mA g$^{-1}$ in Na-ion cells. The irreversibility was attributed to the formation of a SEI and the irreversible reaction of Na with the surface functional groups (–OH, –F, –O) and/or water molecules confined between Ti$_3$C$_2$T$_x$ layers [155]. This hybrid electrode exhibited high volumetric capacity of 421 mAh cm$^{-3}$ at 20 mA g$^{-1}$, good rate performances, and excellent cycling stability. The superior electrochemical performance of Ti$_3$C$_2$T$_x$/CNT

![Figure 15. Schematic showing preparation of the porous MXene/CNT electrode by the self-assembly method (a). The MXene nanosheets are negatively charged due to their functional groups, and the CTAB-grafted CNTs are positively charged. Top view (b–d) and cross-sectional (e–g) SEM images of pure Ti$_3$C$_2$T$_x$ (b, e), Ti$_3$C$_2$T$_x$/CNT-SDS (c, f), and porous Ti$_3$C$_2$T$_x$/CNT-SA (d, g). Scale bar is 1 mm. Electrochemical performance of electrodes in a two-electrode cell with Na foil as the counter and reference electrode (h–l). Charge-discharge curves of Ti$_3$C$_2$T$_x$/CNT-SA at 20 mA g$^{-1}$ (h). Cycling performance of pure Ti$_3$C$_2$T$_x$, Ti$_3$C$_2$T$_x$/CNT-SA, and Ti$_3$C$_2$T$_x$/CNT-SDS papers at a current density of 20 mA g$^{-1}$ (i). The coulombic efficiency of Ti$_3$C$_2$T$_x$/CNT-SA electrode is also shown. Linear fit of the Warburg impedance of Ti$_3$C$_2$T$_x$, Ti$_3$C$_2$T$_x$/CNT-SA, and Ti$_3$C$_2$T$_x$/CNT-SDS electrodes (j). Volumetric capacities of Ti$_3$C$_2$T$_x$/CNT-SA, carbon, MoS$_2$/graphene paper, multilayered Ti$_3$C$_2$T$_x$ powder, porous carbon nanofiber film, and N-doped carbon nanofiber film (k). Reversible capacities and Coulombic efficiencies of Ti$_3$C$_2$T$_x$/CNT-SA electrodes at 100 mA g$^{-1}$ (e). Reproduced from Ref. [161] with permission from Elsevier.](image-url)
electrodes was attributed to the rationally designed structure that is beneficial for both electronic conductivity and ionic transport [155].

### 3.5. Tetrel (Si, Ge, Sn) phosphides

Tin and silicon phosphides are attractive electrode materials for BLI batteries since Si, Sn, and P are abundant, cheap, and nontoxic components. This family of electrode materials has not been studied as intensively as other aforementioned 2D materials [156]. However, high energy density, substantial capacity, and high capacity retention make group 14 phosphides attractive materials of choice.

Tin forms three different phosphides in the range of 43–57 at. % of tin: $\text{Sn}_3\text{P}_4$, SnP, and $\text{Sn}_4\text{P}_3$ [157–161]. All three compounds have layered crystal structures with some similarities (Figure 16). In their crystal structures, the alternating layers of tin and phosphorus atoms are combined into Sn-terminated blocks that stack along the $c$-axis. Sn atoms confining the block have $[3 + 3]$ coordination of three phosphorus and three remote tin atoms, which confine a neighboring block (Figure 16). The interlayer distance (if defined as the distance between the two tin planes terminating adjusting blocks) varies among the tin phosphides. The shortest distances are found in the $\text{Sn}_4\text{P}_3$ (2.1 Å) and $\text{Sn}_3\text{P}_4$ (2.2 Å), while the distance in the SnP is significantly longer (2.4 Å). Upon sodiation the interlayer distances...

*Figure 16. Crystal structures of tin phosphides. A: $\text{Sn}_3\text{P}_4$; B: SnP; C: $\text{Sn}_4\text{P}_3$. In the structures of $\text{Sn}_3\text{P}_4$ and SnP all possible positions of P atoms are shown. The ordered models of one layer are shown below. Sn: black; P: orange.*
increase drastically, up to 4.5 Å in NaSnP (Figure 17(A)) [162]. Sn₄P₃ exhibited metallic-type electrical conductivity, while SnP and Sn₃P₄ are electron-balanced semiconductors.

The replacement of P with As leads to the increase in the distances within the layer, but preserves the interlayer distance. In the Sn₄As₃ which is isostructural to Sn₄P₃ the interlayer distance is 2.2 Å [163].

Tin phosphides Sn₄P₃ and SnP have been studied as anodes for Li-ion batteries [164–166]. Based on the analysis of the crystal structure, the maximum possible content of the M⁺ cation intercalation should not exceed γ = 2 for the reaction γNa + SnP → NaγSnP. Indeed, there are alkali and alkaline-earth compounds with stoichiometries MSn₂P₂ and MSnP (γ = 0.5 and 1), where M (Na⁺, Sr²⁺) cations are situated in between the Sn–P layers (Figure 17) [162,167,168]. Thorough structural characterization of the alkali ion intercalation in tin phosphides and arsenides revealed that alkali metal atoms can share the crystallographic site with the Sn atoms in the crystal structure, as in the example of [Li₁₋ₓSnₓ]Sn₂As₂, which is isostructural to NaSn₂As₂ (Figure 17(C)) [169].

All tin phosphides can be synthesized by traditional solid-state synthetic methods [158–161], chemical vapor deposition [170], mechanochemical [164,165], and solvothermal methods [171,172], including a facile solvothermal procedure which involves the reaction of metallic tin and red phosphorus in the ethylenediamine solvent [173]. Unsupported [166,174] and carbon-supported [175,176] nanoparticles of tin phosphides have been also synthesized.

Layered tin phosphides exhibit an excellent cycling stability in Na-ion cells. Tin phosphides are capable of operating at relatively low potentials of 0.5 V vs. Na/Na⁺, which allows Na-ion batteries with high energy density (Figure 18(a)).
High volumetric and gravimetric energy density and reasonably high capacity makes tin phosphides promising anode materials [156]. A stable capacity of up to 600–720 mAh g⁻¹ can be sustained during 100 cycles at 100 mA g⁻¹ current density for ball-milled samples of Sn₄P₃ (Figure 18(b)) [177,178]. To improve cycling stability, several approaches have been applied, such as modifying electrolyte [179] and synthesizing nanocomposites with various forms of carbon or reduced graphene oxide [175,176,180]. Tin phosphides produced by the solvothermal synthesis exhibited lower performance which might be attributed to the surface modification during hydrothermal synthesis (Figure 18(b)) [181,182].

Investigations of the mechanism of the sodiation of Sn₄P₃ reveal that this is a conversion reaction which did not preserve the structure of Sn–P layers: Sn₄P₃ + 24Na⁺ + 24e⁻ → Na₁₅Sn₄ + 3Na₃P. Theoretical capacity of this reaction, 1130 mAh g⁻¹ (6633 mAh cm⁻³), has been never achieved (Figure 18(b)). Sodium stannide is a conductive metallic material while sodium phosphide is a semiconductor. A nanocomposite of Na₁₅Sn₄ and Na₃P exhibits high conductivity and no particles aggregation and phase separation, which provides high stability upon electrochemical cycling [177–180,182].

Layered tin phosphides are promising anodes for the Na-ion batteries, but Sn-P layers are not stable under electrochemical conditions and the conversion reaction with sodium occurs. The improved stability of the layer can be achieved upon replacement of Sn with lighter group 14 elements, which form stronger covalent bonds with P, Si, and Ge. Binary Si and Ge phosphides are also layered, but their crystal structures are different from the structures of Sn phosphides (Figure 19).
SiP, SiAs, GeP, and GeAs are isostructural and crystallize in the GaTe structure type [183–186]. Within each layer, Si–Si (Ge–Ge) pairs are surrounded by six P atoms forming a distorted trigonal antiprism. In the crystal structure of SiP₂, which is isostructural to SiAs₂ and GeAs₂, each Si atom is coordinated by four phosphorus atoms [187,188]. SiP or SiP₂ layers stack through lone-pair interactions between the P atoms that confine the layer. Thus, in Si and Ge compounds P atoms terminating blocks have taken the role of Sn atoms confining blocks in the structures of tin phosphides, compare Figures 16 and 19.

The interlayer distances in monopnictides ranges from 2.1 Å (SiP) to 1.8 Å (GeAs), while in dipnictides the interlayer distance is shorter, 1.1 Å for both SiP₂ and GeAs₂. Upon full conversion reaction such materials will form metallic Na₄₋δ Si(Ge) and Na₃P, similar to tin phosphides. In turn, the intercalation of sodium atoms will result in a semiconductor (SiP) to metal (NaₓSiP) transition due to the partial filling of the conduction band. This assumption has been confirmed experimentally on the example of GeAs. This compound is a semiconductor which turns into metallic phase upon formation of Na₀.₁₇GeAs [189]. The interlayer separation increases from 1.8 Å (GeAs) to 2.3 Å (Na₀.₁₇GeAs), and, which is

Figure 19. Crystal structures of Si and Ge pnictides with 1:1 and 1:2 compositions. Si/Ge: black; P/As: orange. Unit cells are shown in magenta.
even more important, due to sliding of the GeAs layers, the large channels able to accommodate sodium ions are formed.

Si and Ge pnictides exhibit properties typical for the van der Waals solids, such as strong anisotropy of the thermal and electrical transport properties and exfoliation upon applying mechanical or chemical forces [185,186]. They were proposed as promising anodes for Li intercalation electrodes [190]. No experimental electrochemical properties have been yet published for such compounds. However, a recently reported crystal structure of the Na-intercalated in between the GeAs layers [189] together with theoretical predictions [190] indicate Ge and Si phosphides as promising candidates for the non-conversion intercalation of Na ions.

4. Conclusions and outlook

Due to the scalable and portable energy solutions provided by WE and rechargeable beyond Li-ion (BLI) batteries, these two technologies have found an increased number of current and future applications. Although platinum, graphite, and lithium cobalt oxide are still the most commonly used electrode materials for these electrochemical processes, interesting alternatives, such as alloys and 2D transition-metal-based materials have emerged over the past several years. We have discussed some selected examples here, focusing largely on cost-effective and high-performing materials benefiting from nanoscale size effects. Advances in our understanding of these nanomaterials promise to yield commercially viable next-generation electrodes in the future.

Nevertheless, we have identified several crucial directions, which have to be explored in order to further expand the application of WE. One of the next frontiers in understanding the new HER electrocatalysts for WE will be detailed studies of chemical composition in combination with predictive modeling that could yield active, stable, and durable electrodes outperforming Pt. Significant advancement will be achieved through investigation of the structural and chemical stability of the emerging HER electrodes by in situ state-of-the-art and beyond analytical methods, crucially, under operation conditions [191]. This is particularly important for PEM electrolysis, which is typically conducted under high temperatures (80–150 °C) and pressures (>50 bars). Many catalysts are known to exhibit a special state of the active sites only at the reaction conditions which are unstable and undetectable by ex situ techniques [191]. Such studies would also help to elucidate the exact mechanistic details at the nanoscale and atomic level regarding the interaction of the reactant/intermediate/product species with the active surface sites during H₂ production [192]. When combined with creative thinking, this data will offer unprecedented control over the design and development of advanced electrode materials. Next, given the wide applicability of theoretical modeling in the current research topic, it will be important to improve the accuracy of the DFT models and their predictive power, perhaps with the help of machine
learning techniques and algorithms. Finally, the development of innovative synthesis methods feasible for large-scale preparation of new electrocatalysts and electrode materials with precise phase composition, nanostructure, and uniform size distribution would represent a remarkable step forward.

Battery electrode materials represent an even more challenging task for the theoretical and computational screening due the higher degree of heterogeneity. Similar to the WE case, the electrode research is in high demand of joint efforts of both experimentalists and theorists. Undoubtedly, 2D materials offer characteristics that are advantageous for intercalation-based beyond lithium-ion batteries, especially when materials are integrated into smart-tailored electrode architectures. Although here we focused on the application of these materials in Na-ion and Mg-ion batteries only, 2D structures are promising for the intercalation of other ions, such as Al^{3+} and K^{+}, and maybe even larger ions if the interlayer spacing is right. At the same time, issues related to the use of 2D materials in energy storage have been identified and need to be addressed to move towards their application in commercial energy storage devices. First, high surface area of 2D materials causes significant contribution to the first cycle discharge by initiating secondary reactions related to the consumption of the electrolyte with the formation of SEI layer and decomposition of the electrolyte. These secondary reactions lead to high initial irreversible capacity and low Coulombic efficiency. They can also cause poor cycling stability due to the deterioration of electrolyte after decomposition. Second, serious aggregation and/or restacking of 2D particles during discharge/charge processes lead to the loss of the surface area, which in turn results in decrease of capacity and slower kinetics of the battery operation. Third, the mechanism of charge storage in 2D materials needs to be elucidated further, and the roles of three well-known processes – (i) bulk ion intercalation, (ii) intercalation pseudocapacitance, and (iii) surface storage – need to be understood. In addition, methods of large-scale low cost 2D materials synthesis, including exfoliation, with controlled structure, composition, morphology, and surface are required. Integration of 2D materials into hybrid architectures with controlled orientation of the nanoflakes need to be further explored as well. Therefore, future research on 2D materials for energy storage has a potential for grand discoveries and breakthroughs that can enable next-generation affordable BLI batteries with high performance.

The complex nature of the envisioned objectives related to the emerging nanostructured electrode materials for WE and rechargeable BLI batteries calls for interdisciplinary research efforts, which are the foundation to ensure progress in the field.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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