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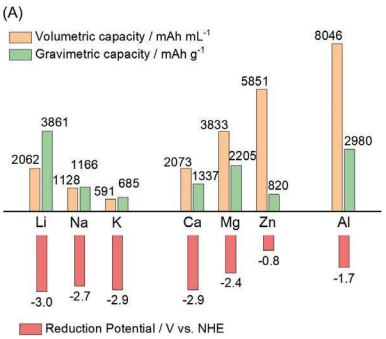
Enabling the battery chemistry beyond lithium ions with 2D materials

In the last decades, lithium-ion batteries (LIBs) have experienced rapid development and achieved great commercial success in various markets ranging from portable electronics and electrical vehicles to grid energy storage [1, 2]. However, current LIBs suffer from several intrinsic limitations in terms of cost, safety, and limited availability of raw materials, which has led to intense research interests in developing distinct battery chemistry (so-called 'post-LIBs') beyond lithium-ion chemistry [3, 4]. To this end, multivalent metal-ion (**MMI**, *e.g.* divalent ion: Ca^{2+}, [5] Mg^{2+}, [6] Zn^{2+}, [7] *etc.* trivalent ion: Al^{3+}, [8] *etc.*) chemistry offers feasible pathways to develop the next-generation energy storage technologies with higher energy density, better safety, and lower cost, as the corresponding metals can be directly used as ideal multielectron-redox anodes. **Figure 1** compares the electrochemical features of different metal anodes [3, 9]. In particular, Zn, Mg, and Al metal anodes stand out with outstanding volumetric capacity, low flammability, and good chemical stability when exposed to ambient atmosphere. Zn metal anodes possess approximately 2.8-fold volumetric capacity (5851 mAh mL^{-1}) in comparison with Li metal (2062 mAh mL^{-1}) [7]. Moreover, the relatively high stripping/plating potential of Zn metal (-0.76 V vs. standard hydrogen electrode) compared with other metal anodes allows the chemistry to occur in a cheap, safe, and high ion-conductive (up to 1 S cm^{-1}) water-based electrolytes, thus promoting the development of mild, green, and high-rate aqueous energy storage systems. Mg metal has a low stripping/plating potential (-2.37 V vs. standard hydrogen electrode), making the Mg-ion battery with potentially high voltage [6]. Meanwhile, the greater abundance of Mg resources than Li, both high volumetric (5851 mAh mL^{-1}) and gravimetric (2205 mAh g^{-1}) capacity, enable Mg-ion batteries to be a robust alternative for traditional LIBs. For the Al metal anode, the volumetric capacity reaches up to 8048 mAh mL^{-1}, four times higher than lithium [8]. Moreover, Al is the most abundant metal element in the earth crust, which leads Al-based batteries to a substantial advance in energy storage technologies. To date, the main challenge faced by **multivalent metal-ion batteries (MMIBs)** resides in the limited availability of cathode materials [3]. It is highly desirable to develop high-performance cathode materials for accommodating MMIs, that can be coupled with multivalent metal anodes to construct future upscalable and sustainable energy storage devices.



(B)

Species	Radii	Abundance of elements in earth's crust
Li^+	0.69 Å	17 ppm
Na^+	1.02 Å	2.3%
K^+	1.38 Å	1.5%
Ca^{2+}	0.99 Å	5.0%
Mg^{2+}	0.66 Å	2.9%
Zn^{2+}	0.74 Å	79 ppm
Al^{3+}	1.14 Å	8.2%

Fig. 1: (A) Capacity and standard reduction potential of various metal anodes. (B) Radii of various metal ions and abundance of corresponding elements.

Inspired by the experience learned from LIBs cathode study, considerable efforts have been devoted to exploring inorganic materials (such as MnO_2, [10] V_2O_5, [11] and TiO_2 [12]) as potential cathodes for MMIBs. Charge storage mechanism of these inorganic materials generally relies on the intercalation mechanism by hosting metal ions with their interlayer spacing or large channels. However, in comparison with Li^+, the higher charge density of MMIs impose a stronger electrostatic interaction between charge carriers and host materials, which results in poor solid-state diffusion kinetics of MMIs within inorganic cathodes [3]. Meanwhile, electrodes with an intercalation mechanism suffer from the inherent volume change during the charge/discharge process, so that they have unsatisfying cycling stability. **Therefore, it is highly demanding to develop new cathode materials with distinct redox chemistries for hosting MMIs.**

Two-dimensional (2D) materials can be used as both additive and active materials to tackle the aforementioned challenges related to MMI battery cathodes. Since the isolated graphene was achieved for the first time in 2004 [13], growing research efforts have been devoted to the search for atomically thin 2D crystals. To date, a variety of 2D materials are synthesized by either bottom-up or top-down routes [14], like black phosphorous (BP), transition metal dichalcogenides (TMDs), transition

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metal oxides (TMOs) /hydroxides (TMOH), transition metal carbides, nitrides or carbonitrides materials (MXene), organic 2D materials and *etc.* Layered 2D materials have attracted extensive research interests as battery electrodes [15]. The unique 2D structures with a thickness down to a few nanometers exhibit high surface-to-volume ratios, short diffusion pathways, efficient charge transfer, and excellent mechanical flexibility, i.e. these materials have a high potential to overcome the limitations of current energy storage technologies in terms of power density, energy density, and cycling stability.

Our group is developing general design principles and synthesis methods for **2D materials** that can be tailored on an atomic level to store, select and conduct the charges in the battery devices. In particular, we are developing **functionalized/hybrid inorganic 2D material** [16, 17, 18, 19, 20] and **2D carbon-rich framework materials** (including conjugated metal organic frameworks-MOFs and covalent organic frameworks-COFs) [21, 22, 23] with defined redox active sites as a novel class of multifunctional electrode materials for **MMI batteries.** For example, we have fabricated **dendrite-free full Zn-ion batteries** using COF anodes with MnO_2 cathodes, delivering excellent energy densities (23.9 ~ 66.5 Wh kg^{-1}) and supercapacitor-level power densities (133 ~ 4782 W kg^{-1}) [23].

We have also conceptualized the construction of artificial ion-regulating **electrode skins** based on precisely customized **2D polymer films** [24, 25] to promote battery chemistries that rely on complex charge carrier ions, such as multivalent metal ions. The developed artificial electrode skins enhance the performance of these types of batteries in terms of life cycle, coulombic efficiency, and capacity retention.

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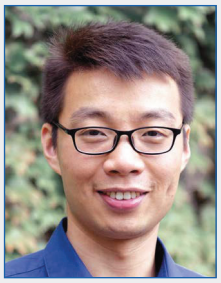

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Minghao Yu received his PhD degree in Material Physics and Chemistry from Sun Yat-sen University in June 2017. In March 2019, he became a research group leader of the Chair for Molecular Functional Materials at Technische Universität Dresden. His research interests focus on the development of advanced functional materials for applications of energy storage (supercapacitors and metal-ion batteries) and conversion (electrocatalysis and metal-air batteries).

ZITATBOX

Albert Einstein (1879 - 1955)

„Höchste Aufgabe des Physikers ist also das Aufsuchen jener allgemeinsten elementaren Gesetze, aus denen durch reine Deduktion das Weltbild zu gewinnen ist. Zu diesen elementaren Gesetzen führt kein logischer Weg, sondern nur die auf Einfühlung in die Erfahrung sich stützende Intuition."

„Wenn eine Idee nicht zuerst absurd erscheint, taugt sie nichts."

„Weisheit ist nicht das Ergebnis der Schulbildung, sondern des lebenslangen Versuchs, sie zu erwerben."

Quelle: https://gutezitate.com/autor/albert-einstein