Journal of Energy Chemistry xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Journal of Energy Chemistry

journal homepage: www.elsevier.com/locate/jechem

http://www.journals.elsevier.com/journal-of-energy-chemistry/

Review

Two-dimensional metal oxide nanosheets for rechargeable batteries

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ARTICLE INFO

Article history:
Received 24 September 2017
Revised 7 October 2017
Accepted 12 October 2017
Available online xxx

Keywords:
2D nanomaterials
Metal oxide
Lithium-ion battery
Rechargeable batteries
Sodium-ion battery

ABSTRACT

Two-dimensional (2D) metal oxide nanosheets have attracted much attention as potential electrode materials for rechargeable batteries in recent years. This is primarily due to their natural abundance, environmental compatibility, and low cost as well as good electrochemical properties. Despite the fact that most metal oxides possess low conductivity, the introduction of some conductive heterogeneous components, such as nano-carbon, carbon nanotubes (CNTs), and graphene, to form metal oxide-based hybrids, can effectively overcome this drawback. In this mini review, we will summarize the recent advances of three typical 2D metal oxide nanomaterials, namely, binary metal oxides, ternary metal oxides, and hybrid metal oxides, which are used for the electrochemical applications of next-generation rechargeable batteries, mainly for lithium-ion batteries (LIBs) and sodium-ion batteries (NIBs). Hence, this review intends to functionalize as a good reference for the further research on 2D nanomaterials and the further development of energy-storage devices.

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https://doi.org/10.1016/j.jechem.2017.10.012
2095-4956/

1. Introduction

With the purpose to address the tough challenge originating from the global climate change and the limited fossil fuels on earth, sustainable energy-related technologies are being persistently pursued [1–7]. Among them, energy storage systems are essential as the uninterrupted power supply sources. As one of primary energy-based storage systems, rechargeable batteries have been extensively applied for electric vehicles (EVs) and portable electronic devices [8–12], which is primarily due to their remarkable capacity, attractive specific energy density, outstanding cycling stability, and low self-discharge as well as low memory effect [13,14]. These rechargeable batteries, however, still need further improvement in order to meet the increasing demands for long-life service, lighter weight, and higher safety [15,16]. Practically, most of these concerns are in connection with the electrode materials, which significantly influence the overall battery performances. To date, a wide range of electrode materials have been studied, their electrochemical performances, however, are still far from satisfaction for practical applications [17–21].

Recently, the development of graphene nanosheets has ushered two-dimensional (2D) nanomaterials into the limelight for energy conversion and storage devices [22–28]. These graphene-like nanostructures, including metal oxide nanosheets, transition metal dichalcogenides (TMDs), layered double hydroxides (LDHs), graphitic carbon nitride (g-C_3N_4), MXene, etc., feature atomic-level thickness, large surface area, tunable electronic properties, remarkable mechanical strength, and unique confined effect [29–35]. Among them, the low-cost 2D metal oxide nanosheets possess many distinctive characteristics for electrochemical reactions, such as ample active sites resulting from the high surface area and superior reaction kinetics contributing by the short-distance transport pathway. Particularly, as the thickness of 2D nanosheets reduced into a few unit-cell layers, some physical and chemical properties (e.g. bandgap, wettability, in-plane transport, etc.) will become distinct from their bulks or rigid and thick nanosheets, and these changes may affect their electrochemical properties for ion transport and storage [2,26,36–38]. Up to now, a variety of metal oxide nanosheets (e.g. V_2O_5, MnO_2, SnO_2, Co_3O_4, Fe_2O_3, etc.) have been successfully fabricated and explored as cathode/anode materials for different types of batteries, including lithium-ion batteries (LIBs), sodium-ion batteries (NIBs), metal–sulfur batteries, metal–air/oxygen batteries, and so on [26,36,39,40]. Most studies on using metal oxide nanosheets as electrode materials focus on LIBs and SIBs. Furthermore, metal oxide nanosheets are good candidates for metal–air/oxygen batteries owing to their highly catalytic activity toward oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) [41–44]. In addition, these metal oxide nanosheets can be employed as efficient sulfur hosts for metal–sulfur batteries to effectively promote the redox activities and reduce the dissolution of polysulfides into electrolytes [45–47]. Meanwhile, in the emerging magnesium-ion batteries (MIBs), some layered metal oxides, such as MnO_2 [48,49] and V_2O_5 [50], have been reported as promising candidate as cathode materials.

In this review, three typical types of 2D metal oxide nanomaterials, e.g., binary metal oxides, ternary metal oxides, and hybrid metal oxides, for rechargeable batteries are summarized, as the schematic illustration shown in Fig. 1. The 2D binary metal oxides refer to the oxides consisting of only one metal element in the formula, such as Co_3O_4, V_2O_5, MnO_2, Fe_2O_3, SnO_2, NiO, etc., while the 2D ternary metal oxides represent the three-element oxides with two metal elements in the composition, such as $LiCoO_2$, $NiCo_2O_4$, $NaMnO_2$, etc. Generally, the simple binary metal oxides are one class of the most widely studied electrode materials, but they often possess relatively low conductivity. As a result, they often suffer obvious volume expansion/contraction during the repeated ion insertion/deinsertion processes, which further leads to the serious agglomeration and even crack or pulverization of the active materials. Compared with the simple binary metal oxides, the ternary metal oxides with one more metal cation can alloy more active ions such as Li^+ and Na^+ and often manifest a higher conductivity originating from the lower activation energy for electron transfer. The hybrid metal oxides are composed of one 2D metal oxide and a proper-complementary material (e.g. nanocarbon, carbon nanotubes (CNTs), graphene, etc.). These hybrid multifunctional composites have various configurations, such as particles-on-sheet (0D–2D), wire-on-sheet (1D–2D), sheet-on-sheet (2D–2D), and 3D multiscale structures assembled from low-dimensional constituents, which usually exhibit unique synergistic effects owing to a combination of the merits of each individual component [51–54]. The introduction of conductive heterogeneous materials can effectively overcome the intrinsic issues of the low conductivity and the large volume change of individual metal oxides, making these 2D metal oxides more attractive for electrochemical applications [55–57].

2. Fabrication of 2D metal oxide nanomaterials

The fabrication of well-controlled 2D nanomaterials is always a grand challenge. To date, many excellent review articles have been published on the fabrication of 2D nanostructures [60–66]. In summary, the fabrication methods for 2D metal oxide nanosheets are classified as two main categories, namely, “top-down” and “bottom-up” routes (Fig. 2a). The former is often achieved by the exfoliation of their corresponding layered host crystals into metal oxide nanosheets under thermal treatment or in some organic solutions. This is a simple method and can produce high-crystallinity products in a large scale. Zhao et al. reported the massive production of large quantities of ultrathin binary metal oxide nanosheets (e.g. Cr_2O_3, ZrO_2, Al_2O_3, Y_2O_3, etc.) by directly heating the corresponding metal chloride precursors (e.g. $CrCl_3{\cdot}6H_2O$, $ZrOCl_2{\cdot}8H_2O$, $AlCl_3{\cdot}6H_2O$, $YCl_3{\cdot}6H_2O$, etc.) [67]. The effective exfoliation of this method relies on a rapid evaporation of the water vapor and/or other gas molecules generated from the decomposition of precursor salts during thermal treatment process [46]. In this study, the as-obtained Cr_2O_3 nanosheets exhibited stronger adhesion to copper foils than the referenced particles without the use of binder and presented enhanced electrochemical performances [67]. Some drawbacks, however, are still remaining in this method, such as that products are not uniform and this strategy is unsuitable for non-layered metal oxide precursors. Further study on the synthesis parameters to improve the quality of 2D nanomaterials is still requested.

The “bottom-up” route, including physical/chemical vapor deposition (PVD/CVD) and wet-chemical synthesis, is another common fabrication strategy for various metal oxide nanosheets [60]. Wet-chemical synthesis, for example, is a dominant technology to produce 2D metal oxide nanomaterials as electrode materials for batteries. As summarized in Table 1, most of these reactions are conducted through a hydrothermal/solvothermal process. The bottom-up synthesized metal oxide nanosheets usually possess a thickness in a few nanometers and a large specific surface area. This approach is advantageous for the massive production of uniform products in high-yield. Sun et al. proposed a generalized molecular self-assembly approach for the first time to achieve the controllable synthesis of ultrathin 2D nanosheets of transition metal oxides (TMOs), including TiO_2, ZnO, Co_3O_4, WO_3, Fe_3O_4, MnO_2, etc. [30]. In this synthetic procedure, the inverse lamellar reverse micelles, formed by a co-surfactants system composed of the amphiphilic block copolymers (P123) and short-chain alcohol (ethylene glycol), play a crucial role for the confined growth of

Please cite this article as: J. Mei et al., Two-dimensional metal oxide nanosheets for rechargeable batteries, Journal of Energy Chemistry (2017), https://doi.org/10.1016/j.jechem.2017.10.012