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Review

Manganese monoxide-based materials for advanced batteries

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ABSTRACT

Manganese monoxide (MnO) with high theoretical capacity, low operation potential, natural abundance, and low environmental impact has recently been researched. However, MnO as a transition metal oxides (TMOs), Mn^{2+} ions with tetrahedral and octahedral coordination own six coordination number, with medium conductivity shows a poor rate capability and cycle life. Furthermore, MnO composites combined pure MnO with carbon and metal-based materials have demonstrated improved electrochemical performances for applications in electrochemical energy storage due to the short transport length of Li ions and the enhancement of the conductivity. This review focuses upon the applications of MnO and its composites in advanced batteries such as lithium-ion batteries, Li–S batteries and sodium-ion batteries. Finally, challenges and perspectives for the development of the advanced batteries are also given.

Contents

Abbreviations: MnO, Manganese monoxide; TMOs, Transition metal oxides; LIBs, Lithium-ion batteries; LSBs, Li-S batteries; NA, Nitrilotriacetic acid; PTCDA, 3,4,9,10-tetracarboxylic dianhydride; 1D, One-dimensional; 2D, Two-dimensional; 3D, Three-dimensional; CNTs, Carbon nanotubes; SCs, Supercapacitors; PLD, Pulsed laser deposition; RF, Radio-frequency; $Mn(OAc)_2$, $Mn(CH_3COO)_2$; GO, Graphene oxide; PVP, Polyvinylpyrrolidone; OP-10, Polyoxyethylene octylphenol ether; PAN, Polyacrylonitrile; Mn(PTA), Mn(terephthalic acid); MOF, Metal-organic framework; PANI, Polyaniline; CVD, Chemical vapor deposition; Mn-BTC, Mn-based metal-organic frameworks; PU-PAA, Polyurethane-polyacrylic acid; MZO, MnO/ZnO; ZIF-8, Zn-MIM (MIM: methylimidazole); NC, Nitrogen-doped carbon; ESD, Electrostatic spray deposition; NPs, Nanoparticles; PCNTs, Porous carbon nanotubes; MWNTs, Multi-walled CNTs; GNs, Graphene nanosheets; GSC, Graphene scrolls; GRs, Graphene ribbons; rGO, Reduced graphene oxide; MGC1, MnO/rGO with the precursors $KMnO_4$/GO=1; MGC2, MnO/rGO with the precursors $KMnO_4$/GO=2; nMCs, Spherical carbon dispersed-MnO composite; P-MnO@C, Peanut-like MnO@C core-shell composites; PHC, Porous hard carbon; CCN, Continuous carbon nanosheets; CF, Carbon framework; CNFs, Carbon nanofibers; GM-3:1, The mass ratio of MnO_2 to GO being 3:1; CCVD, Catalytic chemical vapor deposition; KB, Ketjen black; NDCT, Nitrogen-doped carbon nanotubes; MnO-m-N-C, MnO NPs pasted on mesoporous N-doped carbon.

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1. Introduction

In the 21st century, the demand for sustainable and clean energy is continuously increasing [1,2]. Furthermore, many electronic accessories with the requirement of smaller and more powerful rechargeable batteries such as lithium-ion batteries (LIBs), Li–S batteries (LSBs), sodium-ion batteries (SIBs) have attracted much attention [3,4]. Over the past few years, LIBs with high energy densities and environmental friendliness have been explored separately for smart electronic devices [5]. LSBs are a promising next-generation energy storage systems with a two-electron reaction, possessing a higher theoretical capacity (1675 mA h g^{-1}) and energy density (2600 Wh kg^{-1}) than LIBs [6]. In addition, SIBs have also been widely studied because of the high abundance and low cost of Na and its similar intercalation chemistry to Li [7].

Manganese oxides with a natural abundance, environmental friendliness and low cost have been studied as anode materials and have demonstrated a theoretical capacity of 755 mA h g^{-1} for MnO, 1232 mA h g^{-1} for MnO_2, 1018 mA h g^{-1} for Mn_2O_3, 937 m A h g^{-1} for Mn_3O_4 [8]. Mn^{2+} ions with six coordination number possess tetrahedral and octahedral coordination and certain magnetic anisotropy, exhibit strong crystal field strength in octahedral position. Moreover, Mn^{2+} ions with smaller size and lower coordination number than Mn^{3+} ions can exhibit better cycle stability. However, MnO exists drawbacks such as poor electronic conductivity and drastic volume change, which is similar to other transition metal oxides. Thus, the design and fabrication of pure MnO with carbon and metal materials are developed to effectively improve the cyclability and rate performance of MnO [9]. For example, MnO nanowire/graphene displays good electrochemical performances because graphene can contain the collapsed MnO particles and inhibit separation of the active materials and the collector [10]. In terms of coordinating environment, porous MnO/C composite can be fabricated via pyrolysis process of manganese-based coordination polymer precursor, such as Mn-NA (nitrilotriacetic acid) nanotubes, [11] Mn-NA nanowires [12], and Mn-PTCDA (3,4,9,10-tetracarboxylic dianhydride) [13]. Such approaches can not only improve the electronic conductivity among MnO nanocrystals, but also efficiently relieve the volume expansion during the lithiation/delithiation process. Although challenging, it is of great interest to develop high-performance MnO-based batteries [14].

Many reviews focusing on metal oxides have been reported [15–18]. However, there are few review articles focusing on MnO-based batteries. For instance, Deng et al. discussed the preparations of manganese oxides nanomaterials with nanostructures and compositions and their applications as anodes for LIBs [19]. Liu et al. provided an in-depth discussion of recent developments of the synthesis of manganese oxides nanomaterials and their applications for LIBs [20]. Zhai et al. described recent progress in the application of MnO_2 materials for the development of flexible supercapacitors (SCs) and summarized the intrinsic modification of MnO_2 *via* crystallinity, crystal structure, and oxygen vacancy introduction and the extrinsic modification of MnO_2 *via* two-dimensional (2D) and three-dimensional (3D) flexible conductive scaffolds for high performance flexible SCs [21]. Thus, due to the increase number of publications on MnO-based batteries, it is necessary to systematically summarize the advances in this field and introduce further trends (Fig. 1).

In this review, we summarize the latest studies of MnO-based materials for advanced batteries. First, we introduce LIBs based on MnO and its composites such as pure MnO, MnO/carbon, MnO/metal-based composites, and MnO/carbon/metal-based composites. MnO/carbon, including MnO/carbon nanotubes (MnO/CNTs), MnO/graphene, MnO/pure carbon, and so on, are mentioned in this review. Additionally, other MnO-based batteries with high performance are introduced, followed by the challenges and perspectives for the development of MnO-based batteries.

2. Lithium-ion batteries

Similar to other pure metal oxide anodes, drawbacks such as low electronic conductivity, poor cycling performance owing to large volume expansion/shrinkage and agglomeration during the lithiation and delithiation processes, and low rate performance arising from the kinetic limitations continue to be barriers towards manganese oxides serving as LIB anode materials. To improve the electrochemical performance, various strategies have been reported, including particle downsizing, carbon coating, constructing hybrid nanocomposites, and so on [22]. Among them, the combination of nanostructured MnO with conductive materials, mainly carbon materials, have attracted a wide-spread attention. Fig. 2 describes the cycle stability of MnO-based composites for LIBs, which demonstrates that MnO/carbon materials tend to possess better cycle stability, and MnO-based materials have a certain potential for electrochemical applications. The fabrication methods, Mn source, precursors, morphologies and electrochemical performances of MnO-based materials for LIBs are shown in Table 1. Furthermore, the connections between fabrication methods and MnO-based materials are concluded (Fig. 3).

2.1. Pure MnO

Currently, although MnO composites show great potential in LIBs, pure MnO as an electrode is also essential [24]. Early on, MnO particles [69], cubes [70] and microspheres [27,71,72] were developed. Recently, utilization of conductive substrates has been adopted to synthesize MnO with different thin film [23–26,73,74], nanoflake [75] and nanowire morphologies [76]. Different from MnO_2, MnO film nanostructures are often synthesized by PLD and sputtering methods along with metal substrates.

Thermal reduction of $Na_{0.55}Mn_2O_4$ [27], Mn_3O_4 [69] or $MnCO_3$ [70,72] is a common method for synthesizing pure MnO without growth on conductive substrates. Such precursors can be obtained through dealloying of Mn_5Al_{95} [27], heat treatment of MnO powder [69], wet chemical approach of $KMnO_4$ [72], and low temperature hydrothermal treatment of $Mn(NO_3)_2{\cdot}4H_2O$ [70]. Butala et al. prepared nonporous MnO with a higher capacity and lower over potential during the first discharge [69]. The electrochemical performances of micrometer-sized grains of MnO and MnO prepared by the reduction of Mn_3O_4 were compared (Fig. 4b,c). With a lower potential limit of 0.01 V at the first discharge, the theoretical capacity was exceeded for both porous and nonporous MnO. The 0.6 V plateau in the first discharge contributed 25 and 50 mA h g^{-1} for nonporous and porous MnO. However, a micrograph of cycled porous MnO showed that the pores were destroyed, and the dominant feature sizes resembled those of non-