Manganese Oxide Carbon-Based Nanocomposite

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The application of Manganese oxide (denoted as MnOx hereafter) in SCs was first reported in 1999. Since then, MnOx has been widely studied as an active, low-cost, and biofriendly ECs material. Why are manganese or its oxides are so appealing for SCs applications? First, manganese is a transition metal with five unpaired electrons, which possesses the most oxidation states, including the highest oxidation state (VII) in the entire periodic table. Due to its unique electronic structure, manganese is extremely redox-active, thus, it exists in several oxide forms. Second, Manganese is the most abundant transition metal among oxides which are pseudocapacitive. Third, MnOx exhibits high theoretical capacitance (1370 F/g for MnO2 for instance) with a wide positive potential window compared to other transition metal oxides.

Keywords: manganese oxide ; carbon-based composites ; electrochemical capacitors ; supercapacitors energy storage ; nanostructures

1. Introduction

The global energy demand is rising with population growth and improved standards of living [1]. The advance in technology, the fast growth of portable electronic devices, and hybrid electric vehicles added to the urgent and increasing need for sustainable and renewable high-power energy sources. To address this problem, the development of alternative energy storage/conversion devices with high power and high energy densities is crucial. Thus, renewable and sustainable energy sources are being extensively pursued [1][2][3].

Batteries, the most common electrical energy storage device, provide a suitable level of power for numerous applications and needs of everyday life. On the other hand, owing to their higher power density, excellent durability, and fast charge-discharge processes, electrochemical capacitors (ECs), or supercapacitors (SCs) have drawn tremendous attention as an alternative or supplement to batteries in energy storage systems [1][2][4][5][6]. To tackle these challenges, numerous efforts have been made to combine high power density SCs with high energy density batteries to form hybrid SCs (Figure 1) [1][3]. However, increasing the energy density of SCs to approach that of batteries, or enhancing the power density of batteries to reach that of SCs, comes at the cost of losses in the power of SCs and deteriorations in the energy of batteries [3][7][8].

Depending on their energy storage mechanisms, ECs are categorized into the electrical double layer (EDL), the redox capacitors, aka faradaic pseudo-capacitors, and hybrid capacitors [1][9][10] (Figure 2A). The EDL capacitors store energy by charge separation formed at the interface between the electrode and the electrolyte. During the charging process, the positive surface of EDL capacitors attracts the anions of electrolytes, while the cations accumulate on the negative electrode surfaces (Figure 2B). Since only ions which are accessible to the electrode surface contribute to the capacitance, optimization of surface properties and conductivities of the electrode materials are necessary for the development of improved ECs.

The development of improved SCs depends on the discovery of new electrode materials as well as a clear understanding of active ions in the electrolyte. For most EDL capacitors, carbon-based materials with a high surface area were frequently employed as electrode materials. These materials include activated carbon, carbon nanotubes, graphene, mesoporous carbon, and carbon-fiber-based materials, etc. Among these carbon-based materials, owing to their high specific surface area and long-term conductivity, single-layered graphene, and multiwalled carbon nanotubes attracted much research attention [1][11][12][13].

However, they suffer from low power density, poor electrical conductivity, and lack of stability due to framework inflating during cycling. Significant efforts were made to find alternative, new, and cheaper materials. Certain transition metal oxides and/or conducting polymers with high capacitance were identified and applied as the electrode materials in faradaic pseudo-capacitors [1][3][4][10][14]. To enhance ECs, the various research trends either prepare composite electrodes by coating thin films of metal oxides or by coating conducting polymers on substrates with high surface area, such as carbon nanotubes, which additionally presents a high double-layer capacitance [3][15][14].

Amorphous hydrated ruthenium oxide (RuO_2) has been known to exhibit an ideal pseudocapacitive property, noticeably high specific capacitance, excellent reversibility in a wide potential range, and much longer cycle life. [16] prepared a hybrid nanostructure of hydrous RuO_2 nanoparticles deposited on the surface of SWCNT/graphene composite via a sol-gel process and low-temperature annealing and obtained a specific capacitance of 988 F/g. [17] have obtained ultrahigh-specific capacitance (1500 F/g) by constructing 3D-RuO_2-nanoporous gold hybrid composites. In this review, progress in manganese oxide (Section 2) and its carbon-based nanocomposite materials (Section 3) application towards the development of improved ECs is briefly discussed.

2. Manganese Oxide

Due to its unique electronic structure, manganese is extremely redox-active, thus, it exists in several oxide forms (including MnO, MnO_2, Mn_2O_3, Mn_3O_4 ($MnO.Mn_2O_3$), and Mn_2O_7). Second, Manganese is the most abundant transition metal among oxides which are pseudocapacitive. Third, MnO_x exhibits high theoretical capacitance (1370 F/g for MnO_2 for instance) with a wide positive potential window compared to other transition metal oxides [18][19]. MnO_x offers outstanding electrochemical behavior, environmental compatibility, and excellent structural multiformity, combined with novel chemical and physical properties [1][2][20][4][5][6][9][10][21][22][18][19][23].

The pseudocapacitance of MnO_x electrodes arises from the redox reactions of the oxide with ions in the electrolyte solution. Since manganese has several oxidation states, there are plenty of opportunities for redox reactions involving the ion exchange between MnO_x and electrolytes, and between oxidation state transitions (such as Mn (III)/Mn (II), Mn (IV)/Mn (III), and Mn (VI)/Mn (IV)) According to recent studies, charge storages by MnO_x electrodes are influenced by several factors, such as the bandgap, point of zero charges, tunnel sizes of the electrode material, work function, pH, and stability window of the electrolyte. The detailed charge storage mechanism is still being studied using various techniques [14].

Various nanostructures of MnO_x with improved electrical conductivity, novel morphology, high surface area, and controlled pore sizes were developed, and their specific capacitances were studied [14][24][25][26][27][28][29][30][31]. [22] anodically electro-deposited MnO_2 nanocrystals with three types of crystal structures, i.e., ε-MnO_2 (Figure 3A), rock salt-MnO_2 (Figure 3B), and antifluorite-MnO_2 (Figure 3C), by introducing complexing agents such as EDTA disodium salt and sodium citrate salt. Anti fluorite-MnO_2, which has a morphology with few surface areas and similar chemistry compared to rock salt-MnO_2 and ε-MnO_2, showed superior capacitive behavior. Defective antifluorite-MnO_2 possesses more octahedral vacancies than rock salt-MnO_2.

Based on a 1-electron redox reaction per manganese atom, the theoretical specific capacitance of MnO_2 was estimated to be 1370 F/g [6][32][28][33]. Such a maximum value can only be achieved using ultrathin films of MnO_2. Moreover, due to the high ion/charge transfer resistance and poor conductivity of pure MnO_2, the release and utilization of its high theoretical capacitance are difficult [32][14][34]. In Section 3 of this review, applications of hybrid electrodes, comprising MnO_x, electrically conductive components, and carbon-based materials as the supportive backbone for the development of improved supercapacitors are briefly explained.

3. Carbon-Based Material/MnO

Carbon-based materials, in various forms and textures, have a high specific surface area and outstanding electrical conductivity [35][36]. MnO_x, although suffering from poor electrical conductivity and less tunable specific surface area, displays higher ECs compared to carbon-based materials [4][37]. In the hybrid electrode, carbon-based materials are used as a supporting backbone and exposed large specific surface area for MnO_x deposition, enhanced electrical conductivity, increased mechanical strength, and provide channels for fast charge transport, while MnO_x is responsible for the charge storage [32][14][38][39]. In this section, we briefly discussed the applications of various carbon-based materials/MnO_x composites for the development of better specific capacitive SCs.

The specific capacitance was enhanced by the synergistic effect of the two components, i.e., the bamboo-based AC displayed an extraordinary 3D microstructure and high absorptive capacity, while the nano-sized MnO_2 with a large surface area offered many sites for the redox reaction. The as-prepared hybrid electrode yielded a specific capacitance of 290 F/g. MnO_2 nanostructures were electro-deposited on graphene/AC working electrodes at various reaction times. This high capacitance is due to the synergistic effects among the graphene, porous AC, and high theoretical capacitive MnO_2.

[37] synthesized a MnO_2/AC composite with high electrochemical performance via a grafting oxidation method, which resulted in a specific capacitance of up to 332.6 F/g at a scanning rate of 2 mV/s. The as-prepared composite showed an excellent capacitive performance (specific capacitance of 485.5 F/g, calculated from discharge curve with a current

density of 2.0 A/g). [40] prepared a MnO2/ACP composite by activating commercial carbon paper (ACP) using potassium dichromate lotion and then anchored MnO2 nanoribbons onto ACP via an electro-deposition route. This high specific capacitance was probably due to the enlarged specific area and improved electronic conductivity of the as-prepared composite.

CNT comes in various forms, the most dominant being single-walled (SWNT) and multi-walled nanotubes (MWNT). Due to their excellent mechanical property, good electrical conductivity, unique pore structure, and chemical stability, carbon nanotubes have been applied in ECs as electrode materials [41][42][43][44][45][46][47][48][49][50][51][52][53][54][55][56]. [6] reported LbL-MWNT/MnO2 ultrathin film electrodes through a layer-by-layer (LbL) assembly of functionalized MWNTs and continuous redox deposition of MnO2 onto MWNTs. As noted above, the MWNT network created fast electronic and ionic conducting channels in the presence of an electrolyte, and the coatings of MnO2 on the network provided high volumetric capacitance (246 F/cm3).

This high capacitance was due to the presence of massive nanopores on the walls of PCNTs (6 nm), which led to the loadings of a large amount of MnO2 nanoparticles (2.42 nm), both in the nanocavity and on the surface of PCNTs as electroactive sites. The results imply a new designing strategy for supercapacitor materials with outstanding performance. [57] synthesized aqueous inorganic ink comprised of hexagonal MnO2 nanosheets using a simple chemical reduction method. A flexible electrode for capacitive energy storage was obtained by printing the MnO2 ink onto commercially available A4 paper, which was pretreated with MWCNT.

The use of carbon spheres (CS) in ECs and capacitive flowable suspension electrodes was investigated [58][59][60]. To date, only a few papers reported the preparation of low-sized CS and tested for capacitive flowable electrodes. Zhang's group prepared highly porous monodispersed CS with a very high specific surface area (2900 m2/g) and narrow pore size distribution (<3 nm) and reported a specific capacitance of 168 F/g. The bare CS with smooth surfaces was not aggregated (Figure 6B).

The carbon nanoparticles in the composite effectively prevented graphene from restacking and agglomeration while MnO2 nanospheres were dispersed on the graphene surface (Figure 7). The images of the MnO2/C/G composite (Figure 7c,d) revealed that the honeycomb MnO2 nanospheres were covered by wrinkled and transparent graphene (G) (indicated by red arrows) with few exposed surfaces. TEM images (Figure 7f) of the composites clearly showed the presence of graphene (wrinkled and folded), honeycomb MnO2 (green rounds), and carbon nanoparticles (blue rounds). MnO2 and carbon nanoparticles were well dispersed on graphene surfaces without forming aggregation.

Ranjusha et al. [61] presented the synthesis of carbonized MnO2 nanowires, using carbon nanobeads to fabricate a rechargeable electrode with a large surface area, high power, and energy density for supercapacitor or battery applications. The electrodes showed a specific capacitance as high as 1200 F/g. The practical application of the thin films, tested in a working model of a button cell, exhibited a capacitance of about 1.2 F/g, an energy density of 96 Wh/kg, and a peak power density of 32 kW/kg, suggesting the future potential application of such electrodes.

Fiber-based SCs have drawn tremendous attention due to their very low volume, high flexibility, and weave-ability of the fibers, which are desired for the development of high-performance electrodes. CNFs with a smaller diameter is desired for higher loading of MnOx. [62] demonstrated the construction of a novel high-performance asymmetric supercapacitor based on freestanding MnO2/CNF hierarchical composites and activated carbon nanofibers (ACNF) as the (+) and (−) electrodes, respectively, in an aqueous electrolyte solution of Na2SO4 (Figure 8). The results suggest an effective and convenient route for the construction of asymmetric SCs based on freestanding electrode materials for high-energy and high-power density systems.

[63] demonstrated the design and fabrication of a novel flexible nanoarchitecture by a facile coating of ultrathin MnO2 films onto highly electrically conductive Zn2SnO4 nanowires grown radially on carbon microfibers (CMFs) to achieve high specific capacitance, high-energy density, and long-term life for supercapacitor electrode applications. [64] designed and fabricated a flexible asymmetric supercapacitor (ASC) with high energy density using flower-like Bi2O3 and MnO2 grown on carbon nanofiber (CNF) paper. [65] reported self-grown MnO2 on carbon fiber paper via a facile redox reaction, which was constructed by an interconnected ultrathin nanosheets array. A composite textile electrode with high specific capacitance (1516 mF/cm2) was fabricated by introducing graphene/MnO2 into activated carbon fiber felt (ACFF)

Owing to their high specific surface area (SSA), graphene and CNT are frequently employed in hybrid electrodes. However, their practical application was hindered due to the presence of high contact resistance between graphene–graphene, CNT–CNT, or graphene–CNT. Recently many efforts have been made to combine MnOx with CNTs and/or graphene to form ternary composites. Hybrid electrodes made of these composites showed higher specific capacitance and better cycle life compared to the individual components [66].

The graphene nanosheet in the composite provided conductive support and a large surface area for the deposition of nanostructured MnO2. The graphene–MnO2 composite showed almost three times higher specific capacitance (310 F/g) than that of pure graphene (104 F/g) and birnessite-type MnO2 (103 F/g). The increase in specific capacity of the graphene/MO2 composite might be due to the excellent interfacial contact area between graphene and MnO2, and the high electrical conductivity of graphene. They confirmed the bonding between amorphous MnO2 and graphene-based materials and explained its potential for a significant reduction of polymer binding content.

[67] have reported high specific capacity by synthesizing ultrathin MnO2 nanowire-intercalated 2D-MXenes. It was noted that the multiple redox sites provided by MnO2 nanowire and the high conductivity of MXene played synergistic roles to enhance the overall performance of the SCs. [68] applied oxidized carbon fibers as a support substrate for MnO2 flowers-like sponge layer growth, followed by deposition of high-density grape-like Mn3O4 nanospheres, which expanded in the MnO2 layer. The composite (MnO2/Mn3O4) resulted in very high specific capacitance (1709 F/g at 1 A/g).

4. Summary and Future Perspective

Over the past two decades, the electrochemical performance of MnOx-based supercapacitor electrodes has improved compared to earlier studies where MnOx showed a specific capacitance of less than 200 F/g, with low retention at high current densities or scan rates [24][69][70]. Significant advances were achieved by investigating and incorporating carbon-based materials, which improved the accessible large surface area and active sites for redox reactions. Most MnOx/carbon-based composites yielded a specific capacitance higher than 500 F/g [26][40][56][57][61][71][63][72][65]. However, only a few articles reported a specific capacitance higher than 1000 F/g [57][61].

Of all the assessed nanostructures, ultrathin films of MnOx with few nanometers thickness deposited on conductive substrates showed high specific capacitance (close to the theoretical values), due to the exposed electrochemically active sites of the substrates and the shortening of charge/electron transportation routes [31][34][57][61]. To attain these high capacitances, very low loading masses of MnO2 are required, which are not practical yet. Extensive efforts are still needed to improve the electrochemical utilization of MnOx, especially in cases where high mass loading is desired. Besides, the selection of counter electrodes, current collectors, electrolytes, membrane separators, and handling/packaging of ECs cells need to be thoroughly examined.

We are still far from achieving the theoretical capacitive values. However, as briefly outlined in the present review, a solid foundation for future technological advancements has been corroborated. It is anticipated that the above research findings might provide some technical insights to enhance the electrochemical performances of MnOx/carbon-based materials [68]. Based on the wide applications of MnOx and the scalability of carbon-based materials, it is believed that MnOx/carbon-based hybrid electrodes offer promise for the development of high energy density with high power SCs.

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