Research Progress of Supercapacitors based on Transition Metal Oxide Electrode Materials

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Abstract

Supercapacitors (SCs) have great potential in portable electronic devices, renewable energy systems and hybrid vehicles. The introduction of low-cost and efficient SC has become a hot topic in the industrial and scientific fields. Transition metal oxides (TMOs) are considered to be the most suitable electrode materials for SC due to their inherent characteristics, economic attractiveness, environmental friendliness and rich availability. In this review, the different preparation methods, electrochemical properties and research progress of several transition metal oxide-based electrode materials commonly used in supercapacitors are summarized. Secondly, the problems existing in the practical application of TMOs are put forward, and the corresponding feasible solutions are expounded in detail. Finally, the future development trend of transition metal oxide electrode materials is prospected.

Keywords

Supercapacitor; Transition Metal Oxides; Composite Material; Electrochemical Performance.

1. Introduction

Energy storage devices have always been the focus of research due to the strong growth in demand for portable electronic devices and their ability to serve as energy storage media for renewable energy. Among them, batteries and supercapacitors have good application prospects in many fields and are considered to be two major types of energy storage devices. Compared with batteries, supercapacitors (SCs) have large specific capacity, higher specific power, higher specific energy/capacity density, relatively low cost and fast charge and discharge performance, ultra-long life cycle and environmental friendliness. Therefore, it is recognized as an excellent alternative to other energy devices such as batteries in the field of energy storage, which has attracted extensive research from scholars. However, low energy density is still the bottleneck of SC[1, 2]. According to the energy density formula $E = 1/2\times C\times V^2$ (Cis the specific capacitance, V is the voltage window), the energy storage density of the device can be improved by increasing the potential window and using high-capacity electrode materials. In other words, the design and synthesis of electrode materials are important factors affecting their electrochemical performance.

There are many factors that affect the performance of SC, among which the electrode material plays a leading role. Some characteristics of the electrode materials, such as energy density, redox properties, surface area, porosity, surface functional groups and charge transfer ability, have a great influence on the performance of SC. Therefore, researchers are currently exploring electrode materials with high surface area and layered pore size distribution to improve the interaction between the electrode and the electrolyte interface.[3-5]. In this regard, transition metal oxides (TMOs) have attracted great interest in the category of active pseudocapacitive materials due to their high energy density and excellent redox properties[6, 7]. The charge storage and release of transition metal oxide electrode materials are mainly achieved by a highly reversible redox reaction of metal ions at or near the electrode-electrolyte interface. In addition, compared with carbon-based electrode materials, its excellent electrochemical performance is relatively excellent.

In the early studies, different TMO pseudocapacitive materials were mainly used, such as NiO[8] MnO_2[9], V_2O_5[10], Co_3O_4[11] and so on, because they have higher specific capacitance and power density. Nowadays, binary and ternary TMOs are taken into account due to their remarkable electrical conductivity and electrochemical performance compared to monometallic oxides. Based on the current research on transition metal oxide electrode materials, this paper reviews the latest progress of TMO materials and the specific research of related multi-component composites. Finally, the future development trends of various important factors affecting the electrochemical performance of TMOs-based composite electrodes in SC applications are also discussed.

2. The Working Principle of Supercapacitors

Supercapacitors can be divided into two types according to different charge storage mechanisms : electric double layer capacitors (EDLC) and pseudocapacitors (PC). EDLC stores electrical energy through the electrostatic accumulation of the electric double layer interface charge between the electrode and the electrolyte. The breaking / formation of chemical bonds, the adsorption / desorption of ions / molecules / substances, and the phase transition process are involved. Because it does not undergo chemical reaction during charging and discharging, the structure of the electrode remains unchanged. Therefore, EDLC is characterized by long service life, and the specific capacitance depends largely on the effective specific surface area of the electrode material and the surface characteristics of the carbon material.

The pseudocapacitor is located between the EDLC and the battery. Their energy storage mechanism is the Faraday charge transfer process of metal ions on the electrode surface or several adjacent surface layers, which can be achieved by ion insertion or adsorption. Compared with electric double layer capacitors, pseudocapacitors can obtain higher energy density and 10-100 times specific capacity due to their excellent electrical conductivity and faster cation diffusion rate. However, because it involves reversible reduction and oxidation reactions on the electrode, the long-term chemical reaction in the fast charge and discharge cycle will lead to the structural change of the electrode[12].Therefore, the service life of the pseudocapacitor is low and the recyclability needs to be improved.

3. Research Progress of Transition Metal Oxides

The main feature of metal compounds, especially transition metal oxides (TMOs), is the effective storage and release of their charges. It is a highly reversible oxidation-reduction reaction at or around the electrode-electrolyte interface, and the structure of the electrode material will not be damaged during charge and discharge, because the reaction is limited to the electrode / electrolyte interface inside the bulk material. It has higher specific capacitance (100-2000 $F\ g^{-1}$), higher energy density and better chemical stability. At present, TMOs with different structures and various characteristics have become one of the promising and outstanding active material choices for manufacturing energy storage devices. However, its low conductivity, unchangeable volume and slow bulk ion transport speed seriously hinder its application in reality and industry. Metal oxides as electrodes alone cannot meet the requirements of high-performance energy devices, mainly due to their relatively low conductivity. Compared with the single-component electrode, the TMO-based composite electrode material exhibits better electrochemical performance.

In the exploration of pseudocapacitor electrodes, transition metals play a very important role in the preparation of excellent compositions of electrode active materials. The research community continues to study many effective components, such as metal oxides, sulfides, nitrides, carbides, and phosphides. Transition metals form more than one oxidation state due to partially filled d orbitals. Therefore, when used in pseudocapacitor devices, the change of oxidation state allows charge transfer under a fast and reversible working principle. TMO has been proved to be the best catalyst for pseudocapacitors or positive electrodes due to its remarkable reversibility during reduction and oxidation. The increased charge storage due to Faraday contribution is observed near the oxide layer[13]. In addition, the size, morphology and crystal orientation of TMOs are easy to adjust, which helps to fully understand the relationship between electrode materials and electrochemical properties. Numerous attempts have been made to study the physicochemical and electrochemical properties of TMOs for the development of efficient SCs.

3.1 Ruthenium Oxide

Ruthenium oxide (RuO_2) is one of the first widely studied TMOs, due to its high specific capacitance (theoretical capacitance, 1300-2200 F g^{-1}), high ionic conductivity, reversible redox reaction, high thermal stability and long cycle life. However, its toxicity, low abundance and high cost make it necessary to find alternative materials. At present, it is attempted to effectively improve the utilization efficiency of ruthenium by material compounding. Different forms of RuO_2-based composite electrodes have been successfully prepared, including metal sulfide-ruthenium oxide, metal oxide-ruthenium oxide, carbon material-ruthenium oxide and multi-component RuO_2. Asim et al.[14] modified carbon cloth (CNTs-CC) grown from carbon nanotubes (CNTs) with RuO_2 nanorods (RuO_2-NRs) by chemical vapor deposition and annealing process. The prepared electrode has the characteristics of both supercapacitor and lithium battery. The results show that the composite electrode has a high specific capacitance (176 F g^{-1}) and excellent cycle stability (97 % after 10,000 cycles at 40 mA cm^{-2}). In addition, as a lithium ion battery electrode, it exhibits a current density of about 3.85 mAh cm^{-2} at a current density of 100 mA cm^{-2}. The excellent electrochemical performance lies in the synergistic effect of metal oxide NRs and the unique structure of CNTS-CC. The increased surface area and exposed active sites allow the ion / electrolyte to approach the electrode.

3.2 Manganese Oxide

As one of the most widely studied electrode materials, manganese dioxide (MnO_2) has the advantages of low price, diverse crystal structure, good environmental compatibility, and high theoretical pseudocapacity (1370 F g^{-1}). So far, various wet chemical and electrochemical methods have been developed to prepare nanostructured MnO_2 electrode materials. However, due to the low conductivity of MnO_2 (10^{-5}-10^{-6} S m^{-1}), its power and specific capacity are greatly reduced. Improving the conductivity of MnO_2 is the key to achieve high specific capacity and high rate charge and discharge. Assembling asymmetric capacitors is considered to be the best way to solve this problem. Because of its combination of different positive and negative electrode materials, it has a good separation potential window. Wang et al. [15]developed low-cost MnO_2 NW and Fe_2O_3 NT through a simple and scalable method. The all-solid-state flexible asymmetric supercapacitor constructed with α-MnO_2 nanowires as the positive electrode and amorphous Fe_2O_3 nanotubes as the negative electrode has high energy density (0.55 mWh cm^{-3}) and excellent rate performance.

3.3 Vanadium Pentoxide

Vanadium pentoxide (V_2O_5) is an intercalation compound for electrochemical energy storage, with high capacitance, excellent cycle stability and variable oxidation state. However, its poor conductivity, easy aggregation and high solubility in liquid electrolytes will affect the rate and cycle performance. The conversion of vanadium pentoxide into nanostructures is considered to be an effective method to overcome the limitation of poor conductivity[16]. In order to solve the agglomeration problem of V-based materials, it is very important to construct a three-dimensional network structure with high energy density and excellent cycle stability. Zhang et al.[17]prepared ultrathin hybrid reduced graphene oxide (rGO) and vanadium pentoxide (V_2O_5) nanostructures. The high conductivity and large surface area of rGO nanosheets promote the efficient transport of charge. The well-crystallized V_2O_5 nanobelts can provide more active sites and diffusion paths to enhance the pseudocapacitive kinetics. In addition, the layered structure of V_2O_5 nanobelts further inhibits the agglomeration of rGO nanosheets. Thanks to this unique structure, the rGO/V_2O_5 hybrid structure exhibits excellent electrochemical performance with high specific capacitances of 310.1 F g^{-1} (1A g^{-1}) and 195.2 F g^{-1} (10A g^{-1}). Due to the synergistic effect between different materials, heterostructures and hybrid structures are effective ways to improve the electrochemical performance of electrode materials.

3.4 Molybdate

Multi-metal oxides are considered to be more promising electrode materials. In theory, it has more active sites and faster redox reaction than single metal oxide, so its electrochemical performance is also relatively good. As a hot spot of mixed transition metal oxides, transition metal molybdate $AMoO_4$ (A=Co, Mn, Ni, Zn) has attracted much attention due to its abundant resources, high theoretical specific capacitance and low price. The overall performance of the device depends largely on the morphology and structure of the electrode material. Therefore, it is particularly important to design electrode materials with unique spatial structure characteristics. At present, the promising structures in the field of energy storage are usually hierarchical nanostructures constructed by low-dimensional modules such as two-dimensional nanosheets and one-dimensional nanorods. Yu [18] and his colleagues proposed a cost-effective, simple and compatible strategy for the growth of strongly coupled honeycomb (NHC) $CoMoO_4$ on 3D graphene foams. The $CoMoO_4$-3D graphene hybrid (NSCGH) shows an excellent specific capacitance of 2741 F g^{-1} at a current density of 1.43 a g^{-1}, and maintains 96.36 % of the initial capacitance after 100,000 cycles. The device can still provide a high energy density of 21.1 Wh kg^{-1} at a power density of 300 W kg^{-1}.

4. Exploration on Improving the Performance of Transition Metal Oxides

Although TMOs-based composites have shown good performance in SC applications, there are still challenges in further improving the performance of these materials in SC. The biggest problem for TMO is its conductivity. It is well known that the band gap determines the intrinsic conductivity of the metal oxide-based electrode material, which is usually lower than the carbon-based electrode of SC. Some methods used to improve the conductivity of materials are doping elements, generating oxygen vacancies, compounding, etc. The development of high-performance TMOs-based electrode materials for practical applications of SCs requires more research, especially to optimize the performance of TMOs and their composites. The details of further research may include the following aspects:

(1) In further research, we should focus on the development of pore size distribution, aspect ratio, morphology and specific surface area of TMOs. The overall design and the presence of nanostructured mesopores help to improve the electrochemical activity and enhance the specific capacitance of nanomaterials. Similarly, the specific surface area, the diffusion of electrolyte ions and the quality of water absorbed by the electrolyte greatly affect the microstructure of the electrode. The morphology and structure of the material have an important influence on the active sites and surface of the electrode material. Nanoparticles provide a shorter diffusion path, allowing ions and electrons to transport faster, thereby reducing the internal resistance and improving the electrochemical conductivity of the electrode.

(2) Defect engineering should be considered as an important strategy to improve the performance of TMO in SC. It is worth noting that the growth of these TMOs under oxygen-enriched or anoxic conditions will have a significant impact on their photoelectrochemical properties, such as redox activity, charge and electron distribution, and active sites. The intentional generation of oxygen vacancies in metal oxides will generate more anionic active sites, larger surface area, and larger interlayer gaps to promote electrochemical kinetics and embedded pseudocapacitive mechanisms. Composite materials with special structure were synthesized. The porous structure, core-shell structure and hollow structure can expand the surface area by abundant electrochemical active sites, reduce the resistance of ion and electron transfer, and improve the conductivity and redox reaction rate. In addition, the doping in the material forms an additional redox reaction mechanism, which reduces the charge transfer resistance of the structure in the SC and ensures a higher specific capacitance without affecting the charge and discharge time.

(3) Studies have shown that composites of transition metal oxides with conductive materials (such as carbon-based materials or conductive polymers) exhibit significantly improved performance in SC. The combination of TMO with carbon nanotubes, graphene, carbon fibers, graphite, and amorphous carbon can effectively improve its conductivity, thereby improving its specific capacity and rate performance. Carbon-based SCs have no chemical changes during charging/discharging, and they show significant cycle stability. Most transition metal oxides are classified as semiconductors with a wide band gap energy, which leads to poor electron and hole concentration, resulting in poor conductivity. On the contrary, the conductive polymer not only solves the disadvantage of poor conductivity of the electrode material, but also retains the advantage of storing charge by rapid faraday charge transfer.

(4) In principle, a material with a lower molar mass but a higher number of electrons involved in electron transfer has a larger specific capacitance. Therefore, the important parameters with higher electrochemical performance are the different composition, the oxidation state of metal ions and the composition of metal oxides in composite materials or hybrids. The synergistic characteristics between multiple TMO species are more inclined to improve the overall performance by assisting ion adsorption, diffusion and migration comparable to the activity of a single species. Such as synthetic composite materials, binary metal oxides, ternary metal oxides. This is because the increase in the number of MOs creates more electronic pathways for faster conduction of ions and electrons, and creates more electroactive sites for charge storage. The introduction of surface functional groups is another way to change the chemical composition of TMOs, which is used to enhance the charge storage active sites and shorten the electron/ion mobility.

5. Conclusion

Supercapacitors are the most promising energy devices to replace batteries in the field of energy storage. Low energy density has always been an important defect that hinders its large-scale practical application. One of the key factors affecting the performance of supercapacitors is the design of electrode materials. Among them, transition metal oxides are most favored because of their higher specific capacity and energy density than carbon materials, and better chemical stability than conductive polymers. Although TMOs-based composites have shown good performance in the application of capacitors, it is still a challenge to further improve the performance of these materials in SC. On the other hand, it is still a serious challenge to construct the best structural integrity and stability between transition metal oxides and other conductive materials such as carbon nanotubes, graphene, activated carbon and conductive polymers, so that they have excellent charge transfer and synergistic effects. Therefore, it is necessary to carry out theoretical and practical research to develop more affordable and effective TMOs-based supercapacitor electrodes on an industrial and domestic scale.

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