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The Influence of Carbon Nanotube Composites of Precious Metals and Non-precious Metal Oxides on the Electrode Performance of Supercapacitors

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Abstract: As the problems of energy shortage and environmental pollution are increasingly escalating, the development of efficient and sustainable energy storage technologies has become extremely important. Among these technologies, supercapacitors are receiving significant attention due to their relatively high energy density and power density, making them a promising solution for future energy needs. The unique combination of fast charge-discharge capability, long cycle life, and reliability makes supercapacitors attractive in fields such as portable electronic devices, electric vehicles, and renewable energy integration. In particular, composite materials containing carbon nanotubes and metal oxides are of great research interest in improving the performance of supercapacitors. For example, incorporating non-precious metal oxides (such as manganese oxide and nickel oxide) or precious metal oxides (such as ruthenium oxide) into carbon-based materials can significantly enhance electrochemical performance. An appropriate loading quantity of active materials plays a crucial role in achieving high specific capacitance. Furthermore, different composite preparation techniques have a significant impact on the microstructure of the materials, thereby markedly changing the electrochemical characteristics of the electrode and affecting its overall performance in energy storage systems.

Keywords: Supercapacitors, Carbon Nanotubes, Metal oxides.

1. Introduction

As human society advances at an accelerated pace, the issues of energy scarcity and environmental pollution have become increasingly pronounced. Simultaneously, renewable energy sources such as wind, hydropower and solar power are constrained by their uneven geographical and temporal distribution. Consequently, to address the issue of energy scarcity, it is essential to actively promote the advancement of technologies for energy conversion and storage.

Supercapacitors represent a green and sustainable advanced energy storage apparatus that is extensively applied in various energy conversion domains. Compared with fuel cells and conventional batteries, they can offer more stable and efficient energy output, and their power density far exceeds that of traditional batteries[1]. These characteristics have allowed supercapacitors to be extensively commercialized in domains such as electricity, industry, transportation, including the omnipresent mobile electronic devices nowadays, components of power systems, and advanced energy storage solutions for electric vehicles of the future.

Supercapacitors mainly consist of positive and negative electrode materials, separators, electrolytes, and other components. According to the energy storage mechanisms utilized by their electrode materials, supercapacitors are classified into two categories: one being electrochemical double-layer capacitors and the other Faraday pseudocapacitors. In the aforementioned first type of supercapacitor, the operational mechanism primarily relies on surface physical processes occurring at the interface double layer, while pseudocapacitors attain higher energy density by fully leveraging the highly reversible chemical reactions. Nevertheless, due to the generally relatively slow reaction process, the power density of pseudocapacitors is often lower.

Currently, widely employed electrode materials in supercapacitors comprise carbon nanotubes(CNTs), metal oxides, and a range of other compounds. Carbon nanotubes possess a distinctive lattice structure and exceptional electrical properties, with their microporous size being tunable through synthetic methods, thereby establishing them as promising candidates for electrode materials[2]. Nevertheless, the energy density of electrodes fabricated with pure carbon nanotubes is relatively low, which is not conducive to practical applications. Transition metal oxides are another research direction in this field. In the course of operation, metal oxides undergo chemical reactions with the electrolyte to generate pseudocapacitance, thereby achieving an enhanced capacitance. However, metal oxide electrode materials encounter several challenges, such as inadequate electrical conductivity, substantial volume fluctuations, and slow ion diffusion in the bulk phase. As a result, their overall performance often does not meet the standards required for practical applications.

To address the aforementioned issues, the prevailing approach at present is to combine metal oxides with carbon nanotubes, integrating the superiority of metal oxides in terms of specific capacitance and that of carbon nanomaterials in power density and rate performance, thereby overcoming their respective drawbacks, in the hope of obtaining electrode materials with more excellent comprehensive properties. Specifically, in the carbon nanomaterial/metal oxide composite electrode, carbon nanomaterials can serve as physical carriers, enabling metal oxides to possess a more stable structure while providing a circuit channel for charge transmission. Simultaneously, their relatively high electrical conductivity also compensates for the deficiencies in power density and rate performance during high-current charging and discharging. Meanwhile, metal oxides, as the primary components for charge and energy storage, offer higher energy density to the composite electrode.

Therefore, this article emphasizes the investigation of the influences of the composite methods involving precious metals, non-precious metals, carbon nanotubes, and metal oxides on the energy storage performance of supercapacitors.

2. Precious metal oxides

Among various metal oxides, ruthenium oxide can produces high capacitance by reacting with the electrolyte during operation. Moreover, due to its outstanding electronic transport and ion diffusion properties, it is unanimously regarded as the most ideal pseudocapacitive material. Nevertheless, because of its exorbitant price, it is currently only utilized in domains such as military and aerospace. Since the composite of ruthenium oxide and carbon nanotubes can significantly enhance the utilization ratio of ruthenium oxide and lower the application cost of the material, it has emerged as one of the principal research directions.

In order to create RuO_2/CNT composite electrodes, Kim[3] used an electrochemical process to deposit RuO_2 onto the CNTs film substrate and an effect of the annealing temperature on the composite electrode's capacity was noted. The electrode showed a specific capacitance of 1170.00 F/g at a temperature of 200.00 °C during the annealing process (assessed at a cyclic voltammetry scan rate of 10.00 mV/s). The result is 180.00 % higher than that found for the pure RuO_2 electrode. At a scan rate of 400.00 mV/s, the composite exhibited a specific capacitance consistently measured at 965.00 F/g. This phenomenon can be ascribed to the intricate interweaving and connectivity of carbon nanotubes, which resulted in the creation of a uniform film distinguished by three-dimensional nanopores, in conjunction with a uniformly deposited 3 nm thick layer of RuO_2 on the surfaces of the CNTs. This particular microstructural arrangement significantly enhanced the contact area with the electrolyte, which optimizing the electrochemical performance.

Ji-Young Kim[4] successfully prepared highly dispersed ruthenium oxide nanoparticles within a short period through microwave heating and hydrolysis approaches, without the need for additional thermal oxidation or electrochemical oxidation, and loaded them onto carbon nanotubes. The synthesized crystalline partially hydrated ruthenium oxide ($RuO_2 \cdot 0.64H_2O$) nanoparticles, approximately 2 nanometers in diameter, were heterogeneously nucleated and uniformly deposited onto carbon nanotubes, resulting in a three-dimensional nanoporous architecture. The RuO_2/CNTs sample demonstrates a remarkable specific capacitance of 450.00 F/g at a scan rate of 10.00 mV/s; however, upon increasing the scan rate to 500.00 mV/s, the result experiences only an 18.00% reduction, yielding a value of 362.00 F/g.

Wang[5] utilized ruthenium chloride and sodium bicarbonate as precursors and fabricated ultrafine ruthenium oxide electrode materials with a particle size of less than 70.00 nm via the sol-gel method. The voltammetric characterization test revealed that the composite electrode, which incorporated 20.00% carbon nanotubes, attained a capacitor rated at 860.00 F/g during discharge at a current density of 5.00 mA/cm², exhibiting minimal capacity degradation under high current discharge conditions. The specific capacity could still reach 742.00 F/g during discharge with a current density of 25.00 mA/cm², suggesting that the RuO_2/CNTs composite electrode possesses outstanding high-current discharge characteristics in supercapacitors.

In conclusion, the combination of ruthenium oxide and carbon nanotubes not only enhances the utilization rate and energy storage performance of the material but also significantly reduces the cost, thereby demonstrating broad application prospects in the field of electrode materials.

3. Non-precious metal oxides

Although precious metal oxides such as RuO_2 exhibit excellent pseudocapacitance performance in supercapacitor electrode materials, they are difficult to be applied on a large scale due to the scarcity of resources and high cost. Consequently, exploring transition metal oxides as substitutes for RuO_2 may facilitate the advancement of supercapacitor electrode materials that are not only more cost-effective but also provide enhanced specific capacitances. Nickel oxide has rich resources, low price and the conditions for generating pseudocapacitance. As a result, it possesses considerable promise for prospective applications within the domain of energy storage and conversion.

Roy[6] synthesized NiO/CNTs composite materials characterized by interconnected porous structures and enhanced specific surface areas through wet chemical methodologies. When the scan rate was 2.00 mV/s, the specific capacitance of this composite was found to be 878.19 F/g, indicating exceptional energy storage performance, while also demonstrating remarkable cycling stability over numerous charge-discharge cycles. This suggests that NiO-CNT composite materials exhibit considerable potential for utilization in the domains of supercapacitors and electrocatalysis. Nam[7] fabricated NiOx/CNTs composite materials by depositing $Ni(OH)_2$ on the surface of carbon nanotubes through the constant current pulse deposition method. In the structural characterization, it was confirmed that nickel oxide formed a uniform and favorable thin-layer distribution on the CNTs substrate. In the electrochemical test, it was found that when the mass fraction of NiOx was 8.90%, the specific capacitance of the composite electrode reached the maximum value of 1701.00 F/g. However, as the mass fraction of NiOx further increased, the specific capacitance decreased instead. This suggests that the quantity of nickel oxide significantly affects the specific capacitance performance of the composite electrode. Either an excessive or insufficient loading amount will lead to a decrease in specific capacitance.

Furthermore, manganese oxide (MnO_2) is a resource-rich, low-cost, multi-valent oxide with environmental friendliness, which has extensive application potential in commercial battery and electrode material fields, thus becoming a hot spot in research on supercapacitor composite electrode materials. Jia[8] synthesized carbon nanotubes (CNTs) in situ on the MnO_2 nanoflake structure to obtain a MnO_2/CNTs composite material with a vertically aligned and layered porous structure. The in situ synthesized CNTs significantly enhanced the electrical conductivity and structural integrity of the composite material. When the current density was 1.00 A/g, the capacitance reached an impressive 1131.00 F/g, while the capacitance retention rate was maintained at 94.40% after 10,000 cycles. Similarly, Xia[9] synthesized a MnO_2/CNTs composite material containing 72.00 wt% MnO_2 through a hydrothermal reaction. Owing to the porous morphology of the MnO_2 layer and the 3D electronic path network formed by the CNTs core and MnO_2 nanoflakes, the material promoted rapid electron and ion transport, resulting in excellent electrochemical performance. Madhuri[10] utilized a sol-gel technique at low temperatures to synthesize Mn_3O_4, Mn_3O_4/AC, and Mn_3O_4/CNTs composite materials. The results demonstrated that the specific capacitances of Mn_3O_4/CNTs and Mn_3O_4/AC were 59.00 F/g and 49.00 F/g, respectively, when the current density was 1.00 A/g, accompanied by energy densities of 18.20 Wh/kg and 14.50 Wh/kg. In comparison, pure Mn_3O_4 demonstrated a specific capacitance of 45.00 F/g and an energy density of merely 6.00 Wh/kg. These findings underscore that the incorporation of oxides with carbon nanomaterials can substantially enhance electrochemical performance.

4. Preparation Methods

In addition to the selection of different transition metal oxides for combination with carbon nanotube, different preparation and combination methods also influence the structural characteristics of carbon nanotube/metal oxide composites, ultimately resulting in significant differences in electrochemical performance. In the experimental study of utilizing wet spinning to fabricate MnO_2/SWCNTs fibers for wearable supercapacitors, the content of MnO_2 in the dispersion (33.00%, 50.00%, 67.00%, and 75.00%) was adjusted, and it was observed that the specific capacitance of the composite electrode was significantly greater than that of individual SWCNTs. Moreover, in the constant current galvanostatic charge-discharge curve, this material also exhibited excellent electrical performance[11]. Gueon[12] prepared tightly wound CNTs assemblies by drying the CNTs-dispersed aerosol and formed a composite material with MnO_2 nanoplatelet shells on the surface through oxidation with $KMnO_4$ under acidic conditions.The specific capacitance of this composite material achieved 370.00 F/g when the current density was 0.50 A/g, which was 14 times that of pure CNTs particles and 3 times that of pure MnO_2 particles, and still maintained 76.00% of capacitance stability after 4000 cycles. Yan[13] synthesized MnO_2/CNTs composites via a microwave reduction method. When the mass fraction of MnO_2 reached 75.00%, the composite exhibited an optimal specific capacitance of 944.00 F/g and the power density was 45.40 kW/kg. An[14] fabricated Mn_3O_4/CNTs composites via a thermal decomposition method, resulting in a specific capacitance of 293.00 F/g. Additionally, He[15] employed H_2TDA as the organic ligand to synthesize Ni-MOFs on the surface of CNTs using Ni^{2+} through a solvothermal approach, resulting in the formation of the CNT@Ni-MOFs composite material. Structural analysis revealed that this composite displayed a network-like architecture, with flexible CNTs effectively interlinking the rod-shaped Ni-MOFs. This configuration significantly reduced the tendency for agglomeration among Ni-MOFs. Furthermore, electrochemical performance evaluations indicated that the CNT@Ni-MOFs composite exhibited excellent electrochemical characteristics. In particular, CNT@Ni-MOFs12 demonstrated that the specific capacitance was 719.80 F/g when the current density was 1.00 A/g, and maintained a specific capacitance retention rate of 95.70% after undergoing 1000 CV cycles.

In conclusion, the implementation of various fabrication techniques and the optimization of conditions can markedly enhance the electrochemical performance of composite materials, which is essential for progress in supercapacitors and energy storage systems.

5. Conclusion

This article summarizes the application research of composites of precious and non-precious metal oxides and carbon nanotubes in supercapacitor electrodes. Through combination with carbon nanotubes, the utilization rate of RuO_2 is significantly enhanced, the cost is reduced, and good energy storage performance is displayed. Non-precious metal oxides such as NiO and MnO_2, due to their abundant resources and low cost, have become alternative materials, and the composite materials exhibit excellent electrochemical performance and cycling stability. Different preparation methodologies significantly affect the structure and performance of composite materials. Reasonable process optimization can further enhance their electrochemical performance. In the forthcoming years, as the demand for novel energy materials increases, composites of carbon nanotubes and metal oxides are anticipated to play a pivotal role in research on energy storage. Concurrently, the optimization of the preparation process and the development of cost-effective, high-performance materials are essential for facilitating their large-scale application.

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