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Review: Transition metal oxides (RuO_2, Co_3O_4, MnO_2, and NiO) for pivotal electrode materials for high performance supercapacitors

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Abstract:- Because they offer quick energy storage, load-leveling, and grid stabilization, supercapacitors are essential to renewable energy applications. This paper highlights the substantial potential of supercapacitors in renewable energy applications and discusses their important advancements. Supercapacitors can benefit from high surface area, low cost, and high theoretical specific capacitance (3560 Fg^{-1}) of cobalt oxide (Co_3O_4) electrode materials. RuO2 can perform fast Faraday redox reactions and has a high theoretical capacitance of 2000 Fg^{-1}. Through quick surface - redox processes, cobalt (II,III) oxide (CoO_4) stores energy and frequently produces high specific capacitances more than 1100 Fg^{-1}. Transition metal oxide cobalt oxide has two direct optical band gaps (1.48 eV and 2.19 eV), making it an intrinsic p-type semiconductor. Because of its low cost, high theoretical capacitance (1387 Fg^{-1}), and environmental friendliness, manganese dioxide (MnO_2) is thought to be a perfect material for supercapacitors. A popular pseudocapacitive material for supercapacitors, nickel oxide (NiO) has a huge theoretical specific capacitance of about 2584 Fg^{-1}. With its strong redox activity, high theoretical capacitance, and affordability, nickel oxide (NiO) is a promising electrode material for energy storage. Pseudocapacitive electrode materials bridge the gap between high-power electric double-layer capacitors and high-energy batteries by storing energy through quick, reversible Faradaic surface redox processes.

Keywords: Metal oxides, supercapacitor, specific capacitance, current density

1. Introduction

Chemical batteries and conventional capacitors are separated by supercapacitors, sometimes known as ultracapacitors. Instead of using chemical reactions, they store energy electrostatically in an electric field. This enables them to produce enormous power bursts, manage millions of cycles, and charge and discharge very rapidly. Commercially accessible supercapacitors typically have energy and power densities of 4–5 Wh/kg and 10–20 kW/kg, respectively, although new research indicates that these numbers may be surpassed in the near future. Supercapacitors have many advantages over batteries, chief among them being an almost limitless lifespan, but having lower energy densities. In contrast to battery materials, they also have the capacity for quick charging, a greater temperature range, environmental friendliness, improved safety, increased dependability, and maintenance-free operation [1]. Pseudo-faradic reactions are the primary cause of capacitance in transition metal oxides and electronically conducting polymers, whereas double layer formation at the electrode–electrolyte interface is the cause in high-surface-area carbon materials. Lithium batteries and supercapacitors are examples of hybrid power sources that have demonstrated extremely high energy and power densities, making them feasible choices for EV applications [2]. Schematic representation of a Charged supercapacitor is shown in Fig.1.

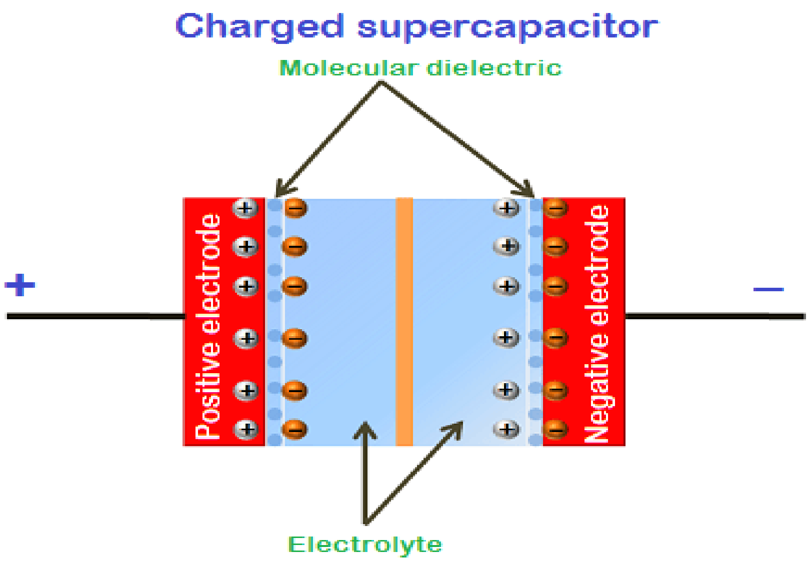

Fig. 1. Schematic representation of a charged supercapacitor

This Special Topic reports on recent developments in the knowledge of electrochemical mechanisms, the prediction of supercapacitors' remaining useful life (RUL), and new electrode materials and electrolytes with high-performance supercapacitor applications. Electric-doublelayer supercapacitors (EDLCs), free-standing supercapacitors, and novel hybrid supercapacitor designs are only a few examples of cutting-edge uses. Additionally, with an emphasis on electrode materials, electrolytes, interfaces, and logical designs aimed at achieving high-performance supercapacitors, this Special Topic addresses material development and problems. In particular, this Special Topic includes four original research articles and three perspectives on electrode materials and application-oriented aspects of supercapacitors [3]. Supercapacitors can endure hundreds of thousands of charge-discharge cycles without experiencing appreciable degradation, and they are also more efficient and have a longer cycle life than batteries [4]. Because of these qualities, supercapacitors are ideal for applications like electric cars, grid stability, and portable electronics that need for frequent cycling and great dependability [5]. Additionally, because supercapacitors are easier to recycle and do not contain hazardous chemicals or heavy metals, they are more environmentally benign than batteries [6]. Supercapacitors are a viable energy storage option for a variety of cutting-edge technologies and applications due to their special benefits, which include high power density, quick charging, long cycle life, and environmental friendliness. Batteries, supercapacitors (sometimes called electrochemical capacitors), and capacitors are the most conventional forms of energy storage [7]. Supercapacitors have a clear advantage in controlling power consumption when compared to batteries and capacitors [8]. Supercapacitors have much higher power densities than batteries, but having lower energy densities [9]. An energy storage system (ESS) that optimizes the use of both power and energy can be created by combining supercapacitors with batteries. Here, maximizing each person's skills and reducing their weaknesses is the main goal. Supercapacitors often have lower power densities than regular capacitors [10].

In addition to discussing the important developments in energy storage systems required for the widespread use of renewable energy, this review paper aims to highlight the enormous potential of supercapacitors within renewable energy applications.

2. Results And Discussion

2.1. Ruthenium Metal Oxide Supercapacitor

Ruthenium Oxide (RuO_2) is the gold standard for pseudocapacitor electrodes, storing energy via fast, reversible surface redox reactions. Particularly in its hydrous form ($RuO_2 \cdot xH_2O$), it delivers exceptional specific capacitance (often 700–1100 F/g), high energy/power density, metallic-level electrical conductivity, and a massive cycle life.

RuO_2 can perform fast faraday redox reactions and has a high theoretical capacitance of 2000 F g^{-1}. It has a large voltage window, excellent chemical and thermal stability, and outstanding electrical conductivity. RuO_2 is therefore referred to as the best material for pseudocapacitive electrodes [11, 12]. However, the cost of ruthenium makes it unsuitable for large-scale electrode material synthesis. In order to make ruthenium dioxide (RuO_2) supercapacitors, hydrous RuO_2 must be synthesized, mixed with conductive additives and binders to form an ink or slurry, and then coated onto current collectors. After that, the apparatus is put together using a separator and electrolyte using conventional methods for creating pseudocapacitors.

Carbon materials are added to many electrode materials. Theoretically, electrodes' surface area and conductivity can be increased by including carbon materials [13]. However, several publications noted that RuO_2 particles occluded the porous surface of carbon materials, resulting in lower double layer capacitance, limited electrochemical characteristics, and decreased surface area. RuO_2 serves as the core of hydrated RuO_2, a type of nanocrystalline material with a tiny quantity of water hydrogen bonds on the surface. Protons can enter the interior of RuO_2 through conduction channels provided by the porous structure [14]. The discontinuity of the electron route in particles is clearly improved by annealing activated carbon-$RuOx \bullet nH_2O$ composites for two hours in 200°C air. Additionally, a significant amount of active carbon (AC) powder is added, which lessens the barrier to electron hopping between particles. At 25 mVs^{-1}, the $RuOx \bullet nH_2O$ has a specific capacitance of 1340 F g^{-1}. Similarly, RuO2@SWCNTs/graphene (S/G) composites were created by Yang's group [15] using the sol–gel technique. RuO2@S/G-60 is a hybrid electrode material with an exceptional rate capability at 1 Ag^{-1} and a specific capacitance of up to 988 Fg^{-1}. The hydrothermal approach was used to prepare hydrous RuO_2 and hexagon WO_3 (h-WO_3) on three-dimensional conducting carbon cloth (CC). This resulted in a quick electronic pathway, a high conductivity substrate, a large surface area, and improved electrochemical performance.

2.2. Co_3O_4 Metal Oxide Supercapacitor

Cobalt (II, III) oxide (Co_3O_4) is a prominent transition metal oxide used in pseudocapacitor electrodes due to its high theoretical capacitance, cost-effectiveness, and excellent reversible redox behavior. It stores energy via fast surface-redox reactions, often yielding high specific capacitances exceeding 1100 F/g.

Cobalt oxide has been recommended as a good alternative to traditional electric double layer materials like activated carbons among several high-capacity materials. The earth's crust contains cobalt in a variety of integrated alloys, oxides, and complexes [16]. Transition metal oxide cobalt oxide has two direct optical bandgaps (1.48 eV and 2.19 eV), making it an intrinsic p-type semiconductor. Co_3O_4 has been identified as the most stable phase of cobalt oxide. It is chemically stable throughout a broad temperature range and has outstanding mechanical strength. Two sites for Co are present in the structure of Co3O4: octahedral 16(d) sites and tetrahedral 8(a) sites, which are occupied by Co(II) and Co(III) ions, respectively [17]. Co3O4's nanostructure enhances the material's qualities for the creation of various shapes, including nanorods, nanosheets, nanowires, and nanofibers.

A new hydrothermal technique was used to create cobalt oxide nanoparticles, and the electrode was made by growing the active material in-situ on nickel foam without additional calcination. The impact of the precursor solution's pH on the electrochemical characteristics of hydrothermally produced Co_3O_4 nanoparticles has not been reported. Direct cobalt oxide formation on the conductive nickel foam improves electron transport and active species diffusion. We created samples at three various pH levels (8, 9, and 10), and the capacitive nature of each sample differed noticeably. The capacitance performance of hydrothermally produced Co_3O_4

nanoparticles reported in previous studies is surpassed by the results of our investigation. Charge-discharge cycles, cyclic voltammetry, and impedance tests were used to assess the samples' electrochemical performance. Co_3O_4's potential in supercapacitors is being thoroughly examined. Finally, Co_3O_4 nanoparticles produced at a pH of 10 were used to create a binder-free symmetric supercapacitor that demonstrated exceptional specific capacitance and energy density values.

2.3. Manganese dioxide (MnO_2) Supercapacitor

Manganese dioxide (MnO_2) is a highly favoredpseudocapacitor material because of its low cost, environmental abundance, and high theoretical specific capacitance (1370 Fg^{-1}). However, it suffers from intrinsically poor electrical conductivity. This limitation is generally overcome by compositing MnO_2 with highly conductive substrates like graphene, carbon nanotubes.

Because of its low cost, eco-friendliness, and high theoretical capacitance (1387 F g^{-1}), manganese dioxide (MnO2) is considered an excellent material for supercapacitors [18]. In reality, Mathieu Toupin et al. recorded a record of 1380 F g^{-1}. Nevertheless, this high value can only be attained at a very low loading mass of MnO_2 (<10 μg cm^{-2}) [19]. Clearly, such a low mass is impractical for the supercapacitor's commercial applications, which require an increase in the loading mass of MnO_2 [20]. However, a large loss in electrical conductance tends to result in a significant decrease in the specific capacitance as the loading mass of MnO_2 increases [20]. In general, when the loading mass of MnO_2 reaches a high level (>0.6 mg cm−2), the actual specific capacitance will decrease to less than 300 F g^{-1} (current density of 1 A g^{-1}) [21]. During the charge-discharge process, the capacitance is influenced by the current density in addition to the loading mass, and it is well known that the specific capacitance will drop as the current density increases. The specific capacitance of MnO_2 can often reach up to 350 F g^{-1} at such a low current density as 0.2 A g^{-1}, but it would quickly drop to below 250 F g^{-1} at a current density of 1 A g^{-1}, and even below 200 F g^{-1} at a current density of 5 A g^{-1} [22]. Using the open porosity of dealloyed nanoporous gold, Jianli Kang et al. produced a MnO_2/nanoporous gold/MnO_2 sandwich electrode that loaded MnO_2 with a mass of 0.2 mg cm^{-2}, resulting in a specific capacitance of 550 F g^{-1} at a scan rate of 5 mV s^{-1} [23]. Furthermore, the capacitance of MnO2 (carbon-based MnO_2 electrodes) may be further enhanced by the inclusion of graphene and carbon. For instance, mesoporous MnO_2 nanosphere/graphene sheet electrodes can be synthesized to attain a high specific capacitance of 466.7 F g^{-1} at the current density of 1 A g^{-1} [24].

2.4. Nickel Oxide (NiO) Supercapacitor

Nickel Oxide (NiO) is a leading pseudocapacitive material for supercapacitors, offering a massive theoretical specific capacitance of ~2584 F g^{-1}. It stores energy via fast, reversible Faradaic redox reactions. However, pristine NiO suffers from poor intrinsic electrical conductivity. To overcome this, researchers synthesize nanostructures (nanosheets, aerogels) and composite it with conductive materials like carbon nanotubes (CNTs) or reduced graphene oxide (rGO).

With its strong redox activity, high theoretical capacitance, and affordability, nickel oxide (NiO) is a promising electrode material for energy storage [25]. Despite these benefits, poor electrochemical stability during prolonged cycling limits its practical implementation. In order to enhance the electrochemical behavior of NiO-based electrodes, researchers have looked into a number of strategies. For example, Siddiqui et al. considerably increased electrical conductivity, capacitance, and cycling stability by adding phosphorus (P) to NiO (P-NiO). Over 15,000 cycles, the P-NiO electrode maintained 100% of its capacitance, demonstrating remarkable durability [26]. In a similar vein, Kumbhar et al. created binder-free NiO cathodes on stainless steel substrates that demonstrated steady performance over 5000 cycles and a high specific capacity of 1147 Cg^{-1}. By adding copper (Cu), the same research team improved NiO electrodes even more and increased cycling stability [27]. Additionally, recent studies have shown that using a titanium dioxide (TiO_2) coating on NiO together with the addition of cobalt (Co) as a dopant greatly increased the specific capacity. In particular, at a current density of 0.5 Ag^{-1}, an impressive specific capacity of 1133.9 Cg^{-1} has been attained [28]. These results demonstrate the great potential of doped NiO-based materials in the creation of high-performance, next-generation supercapacitor technologies that offer significant gains in energy storage capacity and device efficiency.

Supercapacitors are vital for renewable energy, providing rapid energy storage, load-leveling, and grid stabilization. By bridging the gap between high-power capacitors and high-energy batteries via fast, reversible Faradaic surface redox reactions, pseudocapacitive electrode materials represent a massive leap forward in electrochemical energy storage.

3. Conclusions

Because of their numerous accessible oxidation states and remarkable theoretical specific capacitances, transition metal oxides are excellent electrode choices. With a high theoretical capacitance of 2000 Fg^{-1}, ruthenium oxide (RuO_2) is well-known for its capacity to conduct quick Faradaic redox processes. The inherent p-type semiconductor cobalt oxide (Co_3O_4) has direct optical bandgaps of 1.48 eV and 2.19 eV. With a specific capacitance of more than 1100 F/g, high surface area, and cost-effectiveness, it stores energy through quick surface-redox reactions. Because of its inexpensive cost, high theoretical capacitance, and natural abundance, manganese dioxide (MnO_2) is a very attractive pseudocapacitive material for supercapacitors. Because of its large theoretical capacitance (1387 Fg^{-1}), it is considered an ideal contender. One popular and reasonably priced pseudocapacitive material for supercapacitors is nickel oxide (NiO). It uses quick, reversible redox processes close to the electrode surface to store energy. It regularly produces high specific capacitances ranging from 600 to over 1000 Fg^{-1} when built into nanostructures (like nanosheets or aerogels) or paired with conductive materials like graphene. The best materials for high-performance supercapacitor electrodes are these transition metal oxides. Through quick, reversible Faradaic redox reactions at or close to the surface, they store energy.

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