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Transition-Metal Oxide Pseudocapacitive Electrodes for Supercapacitors: Mechanisms, Design Rules, and Practical Constraints

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Abstract. Supercapacitors, combining high power density and long cycle lifetime, have attracted great attention in recent years. Particularly for applications that require both energy and fast power response, such as frequency regulation in power systems, rail transit, and high-power pulse application, supercapacitors are promising candidate energy storages. Transition metal oxides, with their high theoretical specific capacitance, are the most widely studied pseudocapacitive materials for SCs. Three most studied metal-oxide electrode materials including RuO_2, MnO_2, and $NiCo_2O_4$ are introduced. Despite RuO_2 is always treated as the benchmark material with metal-level conductivity, it is unfortunately expensive and rare. MnO_2, however, is environmentally friendly and relatively cheap, yet suffers from poor conductivity and Mn dissolution problem. $NiCo_2O_4$ with relatively excellent conductivity among transition metal oxides exhibits special pseudocapacitive behaviors under certain nanostructures and test conditions. The above three materials manifest the trade-off among cost, electrical conductivity, cycling stability, and high mass loading performance, and none of them shows overwhelming advantages in all items. Similar problems, poor conductivity, insufficient cycling stability, and poor high mass loading performance have been shared by metal-oxide electrode materials. Constructing conductive network has become a commonly used method to improve the performance of metal-oxide electrodes. Constructing porous structures is also a widely used approach to overcome the above challenges in metal oxides. A qualitative comparison of the three materials is also provided. Finally, future work should continue to improve conductivity, enhance cycling stability, and maintain fast charge transport at commercially relevant electrode loadings.

Keywords: transition-metal oxides, pseudocapacitance, supercapacitors, electrode architecture, mass loading

1. Introduction

With the profound transformation of the global energy structure and the introduction of the "dual carbon" goals [1], high-efficiency, clean, and sustainable energy storage technologies have become a key bottleneck constraining the development of the new energy industry [2].

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Supercapacitors, also known as electrochemical capacitors, are a new type of energy storage device that falls between traditional physical capacitors and secondary batteries [3]. With their ultra high-power density, ability to charge and discharge within seconds, excellent cycle stability, and wide working temperature range, they offer broad application prospects in fields such as new energy vehicles, smart grids, rail transit, portable electronic devices, and defense and military industries. The electrochemical signatures of rechargeable batteries, EDLCs, and pseudocapacitors are compared in Figure 1.

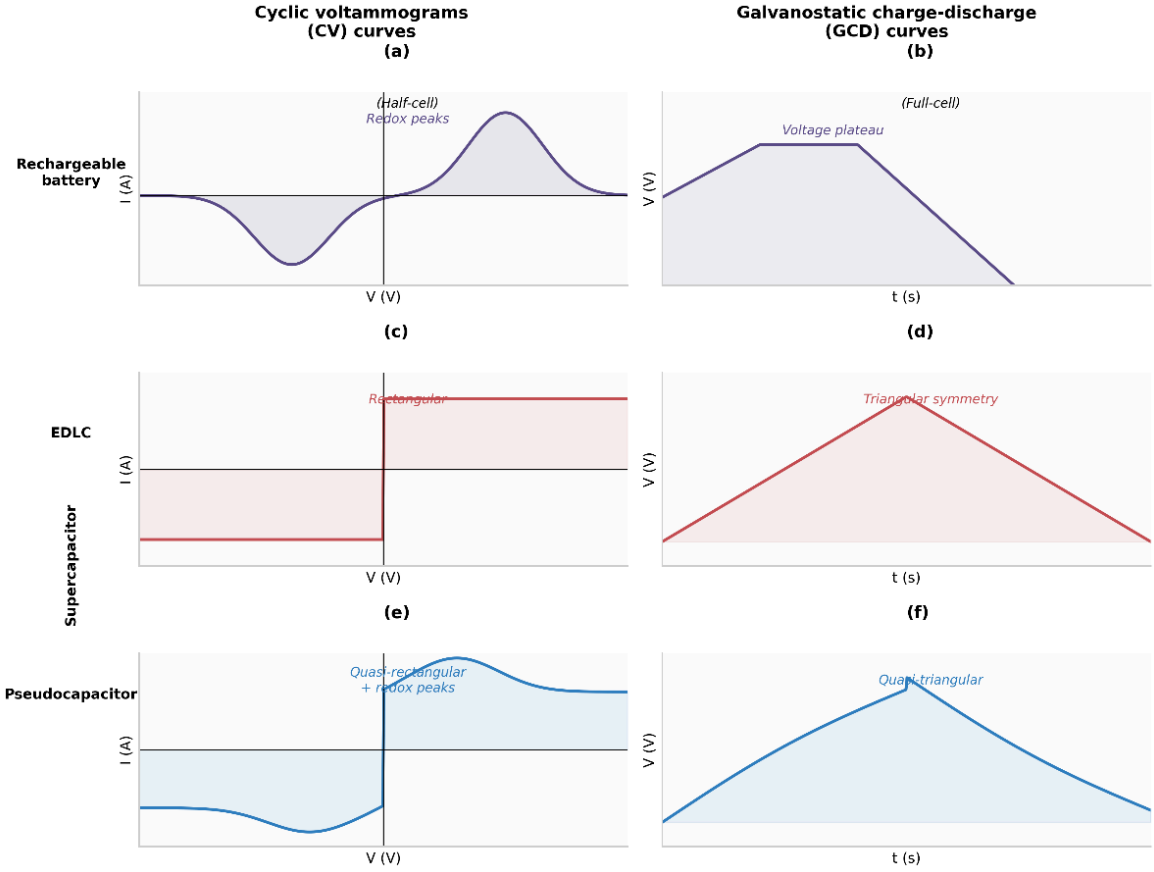

Figure 1. Schematic comparison of electrochemical signatures among rechargeable batteries, EDLCs, and pseudocapacitors. (a)–(c) Cyclic voltammetry (CV) curves; (d)–(f) Galvanostatic charge–discharge (GCD) curves. The pseudocapacitor exhibits intermediate characteristics: quasi-rectangular CV with redox peaks and quasi-triangular GCD, reflecting its position between batteries and EDLCs (adapted from [4])

Pseudo capacitors use transition metal oxides or conductive polymers as electrode materials and store charge through rapid, reversible Faradaic redox reactions occurring at the electrode surface or in the bulk material. They can achieve high specific capacitance, thereby significantly increasing energy density while maintaining high power density, becoming a current research focus in the field of supercapacitors [5]. Transition metal oxides have become a central focus of research into pseudocapacitive electrode materials due to their unique delocalized d-orbital electronic structure and highly variable valence characteristics. The pseudocapacitive energy storage mechanism of transition-metal oxides strongly depends on their structure because their unfilled d orbitals can be reversibly oxidized/reduced among multiple oxidation states. In order to maintain the local charge neutrality, a variation in oxidation state of cations requires the extraction/insertion of counter-ions

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from/to the electrolyte. However, the actually realized specific capacitance in these materials has been significantly inferior to the theoretical value owing to the lower electronic conductivity, poor ion diffusion kinetics, and structural instability under operating conditions during charge/discharge cycles [6]. Different types of crystal structures directly affect the diffusion pathways, diffusion rates, and structural stability of electrolyte ions in the bulk of the material during the insertion and extraction processes.

Here, three transition metal oxides, RuO_2, MnO_2, and $NiCo_2O_4$ as the representative pseudocapacitive electrode materials are considered and the properties, the challenges, and the modification strategies are comprehensively addressed. In addition, we comparatively discuss the materials as well as the common challenges including the low conductivity, inferior cycling performance, and capacitance fading under high loading amounts.

2. Common metal oxide electrode materials

This section introduces three types of transition metal oxides: RuO_2 (a noble metal oxide), MnO_2 (a low-cost binary metal oxide), and $NiCo_2O_4$ (a mixed-metal spinel oxide). The advantages and challenges, as well as a commonly used modification strategy, are summarized for each material.

2.1. RuO_2

RuO_2, an early pseudocapacitive electrode, is the benchmark material for the current studies [7]. RuO_2 can exhibit high specific capacitance with wide potential windows, excellent electrochemical reversibility, and metal-like intrinsic conductivity of ~200 S/cm. In terms of electrochemistry, the charge-storage capability of RuO_2 depends on the hydration and crystallinity. Hydrous RuO_2 ($RuO_2 \cdot xH_2O$) exhibits superior performance by fast and reversible redox reactions that involve different oxidation states of Ru coupled with protons. It has a theoretical specific capacitance value of ~2200 F/g. In the hydrous oxide, water aids proton diffusion while the crystalline lattice provides pathways for electron transport [8]. However, highly crystalline, anhydrous RuO_2 has much lower charge-storage ability. Thus, the annealing temperature needs to be optimized to balance the structural stability and capacitance of RuO_2.

Unfortunately, RuO_2 is difficult to commercialize for supercapacitors because Ru is a precious metal and it is rare and expensive in the earth's crust.

A common strategy to enhance the performance is to utilize hydrated RuO_2 in nanoscale and anchor onto graphene [9]. Graphene acts as a conductive carbon network to isolate nanoparticles and shorten the ion-diffusion length; thus resulting in a higher utilization of Ru element. This method not only maintains high specific capacitance but also reduces the amount of precious Ru metal. RuO_2 possesses a tetragonal (rutile-type) crystalline structure.

2.2. MnO_2

Moreover, MnO_2 has drawn great interest as a pseudocapacitive electrode material owing to its high theoretical specific capacitance (approximately 1,370 F/g), abundant reserve, low cost, and environmental friendliness, therefore showing high potential for commercial applicability. The charge storage behavior of MnO_2 in mild aqueous electrolytes can be described as surface cation adsorption with fast intercalation reactions near the surface accompanied by Mn (III)/-Mn (IV) reversible redox reactions. It should be noted that, owing to its unique structure of [MnO_6]

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octahedra, MnO_2 exists as various polymorphs, among which layered δ-MnO_2 with larger interlayer spacing shows excellent ion intercalation behavior in aqueous solution [10].

Nevertheless, MnO_2 suffers from poor intrinsic conductivity (about 10^{-5} to 10^{-6} S/cm), which is unfavorable for fast charge transfer processes and rate capability. More importantly, structural collapse and MnO_2 dissolution may happen during the charge-discharge processes, leading to the capacity fading.

To address these issues, many studies have been conducted to modify MnO_2 with conductive carbon materials including carbon nanotubes, graphene, and porous carbon, which not only build up fast electron transport pathways, but also provide mechanical support [11]. The resulting MnO_2/carbon nanocomposites combine advantages of fast electron conduction and structural stability of carbon with short ion diffusion paths of MnO_2 with nanometer-scale sizes, resulting in enhanced rate performance and better cycling stability.

2.3. $NiCo_2O_4$

Nickel-cobalt oxide is a mixed transition metal oxide with a spinel structure. Because multiple oxidation states of nickel and cobalt coexist on the octahedral sublattice, the electronic conductivity of $NiCo_2O_4$ is approximately two orders of magnitude higher than that of the single-metal oxides NiO and Co_3O_4 [12]. It can be prepared using various wet chemical methods, including sol-gel and hydrothermal methods, followed by heat treatment.

The electrochemical performances of $NiCo_2O_4$ depend critically on the morphologies and the experimental condition under which it is measured. $NiCo_2O_4$ can be synthesized by a simple wet chemical route (hydrothermal, sol–gel methods), followed by thermal treatment. It was demonstrated that when $NiCo_2O_4$ is synthesized in nanostructures (increased specific surface area), they undergo pseudocapacitive reaction and the redox reactions are primarily controlled by surface processes. However, $NiCo_2O_4$ with bulk/densely packed structures exhibited slow diffusion-controlled battery-like reactions [13].

However, challenges exist in improving its performance such as diffusion-limited reaction in thick electrodes and resulting poor rate capability, structural strain upon redox cycling causing loss in capacitance, and shortening of cycle life (particularly higher mass loading electrode). Moreover, the energy density is constrained due to the limited potential window offered in an alkaline electrolyte. These problems have been overcome in part by modifying the $NiCo_2O_4$ by making nanostructures (nanowires/nanosheets) directly on a conductive substrate or by incorporating with a carbon-based material. For example, $NiCo_2O_4$ nanostructures grown on Ni foam can eliminate the binder and current collector which shortens the transport pathways and increases electroactive surface sites, thus improving rate capability and long cycle stability [14].

3. Main challenges and improvement methods

As discussed above, metal oxide electrodes have three main challenges that must be tackled: low electrical conductivity, limited cycling stability, and poor performance in high-mass loading. In this section, we first determine the reasons for these challenges; then we explore solutions and present representative examples.

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3.1. Low electrical conductivity

Most transition metal oxides have low intrinsic conductivity, typically in the range of 10^{-6}-10^{-3} S/cm, which severely limits the rapid transport of electrons in the electrode bulk phase, resulting in poor rate performance and a practical specific capacitance far below the theoretical value. For example, the conductivity of MnO_2 is only 10^{-5}-10^{-6} S/cm, while NiO and Co_3O_4 also exhibit semiconductor-level conductivity. During low-rate charging and discharging, ions and electrons have ample time to reach internal sites within the active material, resulting in high capacity; however, at high rates, slow electron transport becomes the rate-limiting step, leading to a sharp decline in capacity.

To address this issue, adding a conductive network is the most common and effective strategy. Carbon materials (such as graphene, carbon nanotubes, and conductive carbon black) not only provide fast electron transport pathways but also serve as scaffolds that support the nanostructures of metal oxides and prevent their agglomeration during cycling. Taking MnO_2 as an example, loading nanoscale MnO_2 onto carbon nanotubes, graphene, or porous carbon allows electrons to reach the active material quickly through the continuous carbon network, while the nanoscale MnO_2 keeps the ion-diffusion distance short; as a result, both the rate capability and the utilization of MnO_2 are markedly improved [15].

3.2. Limited cycling stability

Poor cycling stability is one of the major challenges for metal oxide electrodes. During the long-term charging and discharging process, active materials undergo repeated insertion and extraction of ions, leading to expansion and contraction of lattice structure and generating a huge mechanical stress. As a result, the active materials would be crushed and/or peeled off from the current collector, resulting in fast capacity fading. In addition, some metal oxides, such as MnO_2, tend to dissolve during the electrochemical process, aggravating the capacity fading. Wu et al. systematically investigated the cycling stability of the supercapacitors, demonstrating the pseudocapacitive cycling stability is largely dependent on structural stability and interfacial property [16]. From the perspective of structure, porous or hollow nanostructures can effectively avoid such structural problems. Nanowires, nanosheets, nanotubes, or hollow spheres with hollow or porous features can accommodate the volume change upon the insertion/extraction of ions, effectively buffering the mechanical stress, thus keeping the structures stable.

3.3. Low performance at high mass loading

Practical applications of supercapacitors require loading a sufficient amount of active material onto the electrodes to achieve high areal capacitance and device-level energy density. However, as electrode thickness increases and mass loading rises, the transport path for electrolyte ions within thick electrodes lengthens significantly, leading to increased ionic diffusion resistance and deteriorated charge transport kinetics. This ultimately manifests as a decline in rate capability and a substantial reduction in effective specific capacitance. This phenomenon, known as "thick-electrode kinetic decay," is one of the factors limiting the transition of metal oxide-based supercapacitors from the laboratory to practical applications [17].

To resolve the trade-off between mass loading and kinetic performance, the same two types of strategies are commonly used. One is to construct three-dimensional porous electrodes with interconnected channels, which shortens the ion transport path inside thick electrodes; the other is to build a continuous conductive network throughout the electrode so that electrons can reach all of the

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active material [18]. Taking $NiCo_2O_4$ as an example, growing porous $NiCo_2O_4$ nanosheet arrays directly on nickel foam provides open channels for ion transport and a direct pathway for electron conduction at the same time, so that the capacitance is retained much better at high mass loading than in conventional powder electrodes.

4. Comparison of three materials

Although RuO_2, MnO_2, and $NiCo_2O_4$ all store charge through faradaic redox reactions, their reported behavior differs considerably. In terms of electrical conductivity, RuO_2 is generally highly conductive owing to its metal-like rutile framework; $NiCo_2O_4$ also shows relatively high conductivity among base-metal oxides because of the mixed valence states of nickel and cobalt in the spinel lattice; MnO_2 is much less conductive than the other two. In terms of cycling stability, hydrous RuO_2 is generally reported to be stable over long-term cycling, whereas MnO_2 may suffer from manganese dissolution and $NiCo_2O_4$ from structural stress caused by repeated faradaic redox reactions. At high mass loading, the performance of all three materials decays, because ion and electron transport through thick electrodes becomes increasingly difficult. Table 1 summarizes the above comparison in a qualitative manner, listing the main advantage, the main limitation, and one common improvement method for each material. Overall, RuO_2 offers high performance but at high cost, MnO_2 is the least expensive but the least conductive, and $NiCo_2O_4$ provides a compromise between activity and cost. For all three materials, the common improvement route is to combine nanostructuring with a conductive support.

Table 1. Comparison of RuO_2, MnO_2, and $NiCo_2O_4$ electrode materials

Material	Main advantage	Main limitation	Common improvement method
RuO_2	High conductivity and capacitance; wide potential window	Scarce and expensive; capacitance sensitive to crystallinity	Anchoring hydrous RuO_2 on graphene sheets
MnO_2	Low cost, abundant, environmentally benign	Very low conductivity; Mn dissolution during cycling	Compositing with conductive carbon materials
NiCo2O4	High conductivity among base-metal oxides; rich redox chemistry	Rate capability limited at high loading; cycling fading	Binder-free nanoarrays on Ni foam or carbon composites

5. Conclusion

In summary, RuO_2, MnO_2, and $NiCo_2O_4$ have been reviewed as typical transition-metal oxide pseudocapacitive electrode materials. RuO_2 is of relatively high conductivity and capacitance; however, its high cost and natural scarcity prevent it from large-scale application. Hence it serves as a benchmark for fundamental research. MnO_2 is of low cost and environmental friendliness, making it ideal for low-cost aqueous energy storage applications, but its electrical conductivity and manganese dissolution issues need to be overcome. $NiCo_2O_4$ possesses relatively high electrical conductivity among base-metal oxide systems and rich redox chemistry, making it a good compromise for applications where material cost and device performance must be well-balanced. In

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general, each material has its strengths and limitations with regard to cost, conductivity, cycling stability, and performance at high mass loading, so material selection should be made based on these four aspects. All the three materials suffer from challenges of low electrical conductivity, limited cycling stability, and poor performance at high mass loading. Therefore, future research should focus on incorporating conductive networks and/or components to improve electrical conductivity, developing porous and/or strain tolerant nanoarchitectures to enhance cycling stability, and ensuring fast ion/electron transport at high mass loading. Besides, in order to make these materials more relevant to practical application, future studies need to validate their performances in devices using the electrolyte at relatively high mass loading, and the test current density should be similar as well.

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