



An Overview on Ruthenium Oxide Composites – Challenging Material for Energy Storage Applications

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Abstract

Ruthenium oxides owing to their high specific capacitance have been widely identified as promising materials for electrochemical charge storage devices. However, high priced ruthenium precursors restrict their commercial usage. Accordingly, numerous explorations investigated the influences on capacitive behavior of ruthenium oxide on blending with varied materials like other metal oxides, activated carbons, conducting polymers, CNTs and functionalized graphene systems as composites. The aim had been to optimize the material cost without compromising with but improving the composite electrochemical performances. The scientific explorations reveal that the overall specific capacitance of composites is a strongly related to the ruthenium oxide (RuO_2) present in the system since it is the main electro-active material providing the Faradaic pseudo capacitances besides the electrical double layer contributions from the base carbon component of the composite. Major progress in the theoretical and practical research and development in this particular field has evinced a large number of research articles and technical reports in the recent past. The current investigations focus on utilizing minimum amount of metal in the composite; upholding the synergistic effect from the metal oxide and the support (carbon materials generally) to obtain better electrochemical signatures. Optimization of important factors leading to reduced nanostructure agglomeration, minimum electrostatic resistance and ultrafast proton/ electrons diffusion through the hollow porous structures may ultimately result to the theoretically expected specific capacitance. Nonetheless, to the best of knowledge of the author, there is no systematic review available pertaining to recent advancement of the composites of RuO_2 . Thus, this overview categorically narrates recent progresses on the fabrication, performances and achievements of ruthenium oxide composite as electrode material in energy storage applications which will be beneficial especially to the newcomers in this field of research.



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Introduction

Electrostatic field storage has become one of the key issues of research today to cope up with high energy demands of the modern society. Recent advances in this technological field have lead to emergence of supercapacitors/ ultracapacitors or electrochemical capacitors. Supercapacitors (SCs) use electrodes with large specific surface area and thinner dielectrics to attain higher capacitances so as to have higher energy densities as well as power densities¹⁻². Ultracapacitor is best suited for devices that demand high current at faster rate. Current researches focus on how to improve the energy density so as to be employed comprehensively in commercial domains. The performance of supercapacitor depends on several factors such as electrochemical characteristics of materials used as electrode; electrolyte added and voltage window³⁻⁴. Nonetheless, most explorations are thrust on the development and fabrication of new electrode materials that would capitate better and till date improved performances⁵⁻⁸.

As previously stated, electrode materials play key roles in supercapacitor cell performances. Use of metal oxides or conducting polymers as electroactive materials has been found to provide significant increase in the specific capacitance and /or of the energy density. However, conducting polymers such as polypyrrole polyaniline, and polythiophene derivatives have limited practical-based applications, in spite of low production cost and ease of preparation, due to the fact that these organic based materials swell up and contract during charging or discharging respectively, degrade easily on long exposure to chemical environment and also the cycle life is considerably poor⁹⁻¹². Metal oxides owing to their thermal and mechanical stability are superior in that respect especially oxides, hydroxides of the transition metals such as RuO_2 , MnO_2 , VO_x , WO_3 , Ni(OH)_2 , Co_2O_3 , Co(OH)_2 , Fe_3O_4 , etc., that have been widely tried as the electrode materials of pseudocapacitors¹³⁻¹⁶.

Among the wide range of metal oxides employed, hydrous ruthenium dioxide (denoted as $\text{RuO}_2 \cdot x\text{H}_2\text{O}$) has been considered to be the most important for practical implementations due to its superior reversibility, high-valued specific capacitance together with the very long cycle

life¹⁷⁻¹⁸. It is reported that Ruthenium oxide, RuO_2 , has outstanding electrocatalytic features for several electrochemical processes¹⁹⁻²⁰. Its' important technological application lies in chlor-alkali industry, as the active component of dimensionally stable titanium anodes²¹. The high specific capacitance is attributed to pseudocapacitance behavior (storage of Faradic charges) from the redox transitions of RuO_2 involving the reversible mixed electron/proton exchange between the oxide active sites and the solution as shown below²²,



The above electron-proton transfer reaction has been recently confirmed by means of electrochemical quartz crystal microbalance studies^{22,23,24}. Here, the diffusion of proton subdues hydrogen evolution in acid solution due to both proton intercalation as well as under-potential deposition on the $\text{RuO}_{2-\gamma}(\text{OH})_\gamma$ surface during redox switching thereby widening the range of operating voltage. This reaction has been theoretically estimated to provide an ultrahigh specific capacitance ($\sim 1400\text{--}2000\text{Fg}^{-1}$) of RuO_2 ²⁵.

Amorphous structure is generally annealed at elevated temperatures under air to obtain the above properties²⁶. Unlike the anhydrous, crystalline Rutile (RuO_2) phase which is a metallic conductor, the hydrous ruthenium oxide phase exhibits mixed proton/electron conductivity, that promotes it as a promising candidate for not only in supercapacitor devices (shown in Figure-1) but also for proficient electrocatalyst in direct methanol fuel cells (DMFCs)^{22,26}. Based on the mechanism of simultaneous double injection and ejection of protons and electrons, pseudocapacitances of $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ have been optimized through balanced electronic and protonic transports in these systems^{22,26}. Therefore, effective control of electron and proton conducting pathways are the key issues for optimizing the pseudocapacitive performance of $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ ²⁶⁻²⁷.

This mini-review is a representation of the recent development and advances achieved by this material regarding energy storage applications. It is noteworthy that few results are reported for these materials for practical implementations in spite of their superior features. Most results reported

simply for a three electrode system and their performances differ significantly when employed in practical supercapacitor devices. Accordingly, it is very important to evaluate and analyze the obtained results for the better designing and development of

active materials to meet the above requirements - an interesting and motivating subject for many scientists, especially to the new minds coming to this area of research.

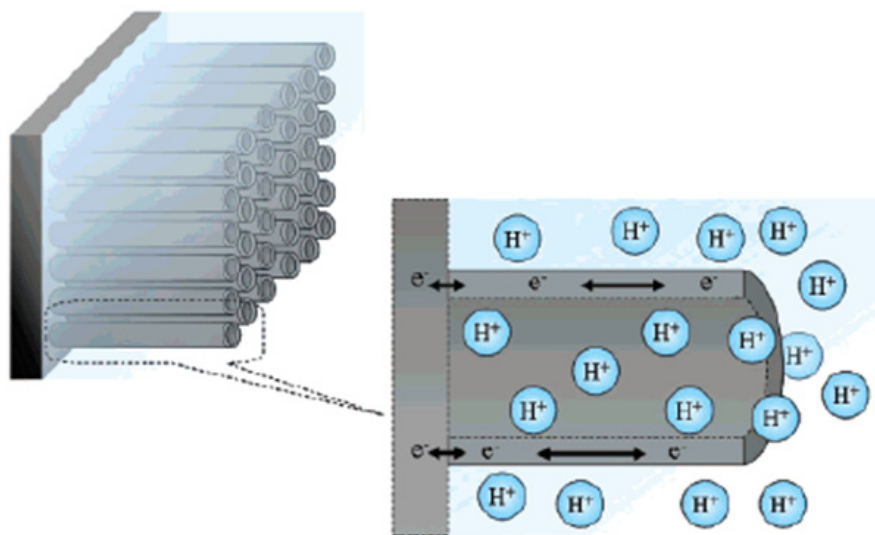


Fig. 1: Model showing mesoporous architecture of hydrous $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ nanotubular arrayed electrode for ultrafast proton and electron exchange processes. Reproduced on permission Copyright (2006) American Chemical Society, Ref: Hu *et al.*, *Nano Lett.*, 2006, 6 (12), 2690–2695

Methods of Preparation

A variety of methods are available for the preparation of $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ material^[27-30,31]. Most commonly used wet chemical sol-gel method that employs $\text{RuCl}_2/\text{RuCl}_3$ in presence/absence of surfactants and alkali followed by annealing at optimum temperatures to yield desired nanostructures²⁷. The material has primary particles sizes in the nano-range with a domination of orderly arranged nanopores of lower and higher size. Even electrochemical preparation involving direct cyclic voltammetric (CV) deposition on metal substrates such as titanium, steel, Si, Pt, Ni, etc. from an aqueous chloride solution are available in the literature³⁰⁻³². RuO_2 can also be obtained by oxidation on Ru metal surface by cyclic voltammetry in H_2SO_4 electrolytes³¹. Electrochemical deposition is a facile, one-step and cost-effective widely employed technique; where the texture,

surface morphology and homogeneity of electrode can be tuned and controlled. During the cathodic deposition of RuO_2 , co-deposition of metal lowers the specific capacitance of the system. However, it can be overcome successfully by the anodic deposition of RuO_2 . Besides, atomic layer deposition (ALD) is also often employed to produce RuO_2 films as well³³. Method of nanostructure preparation significantly changes the porosity of the material and hence the electrochemical performance also alters to appreciable extent. Figure-2 shows the outline for the formation of such RuO_2 films as well as its composites using various methods such as sol-gel, hydrothermal, lithography, anodic electrodeposition, microwave plasma chemical vapor deposition, atomic layer deposition and various other methodologies to tune the electrochemical behavior in the resultant systems.

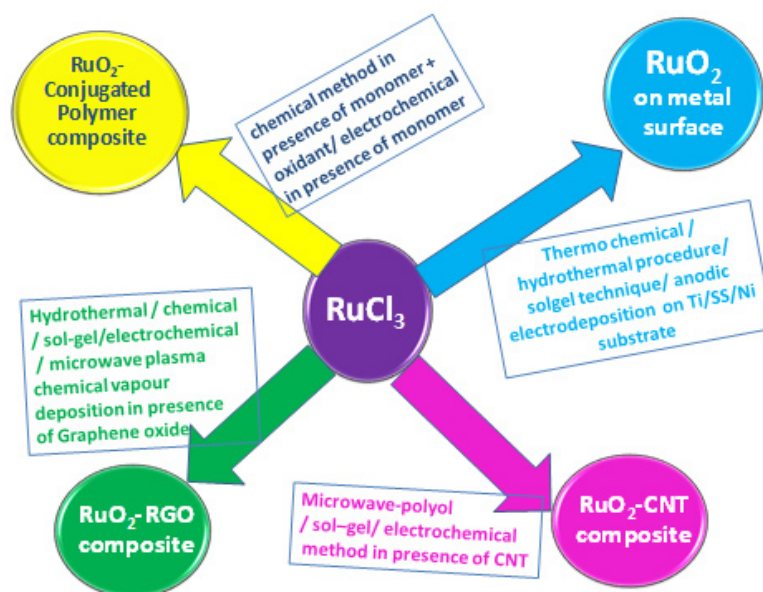


Fig. 2: Representation of the common techniques used to synthesize RuO_2 nanocomposites

Results and Discussion

Various synthetic methodologies have been employed for preparing nanostructured hydrous RuO_2 such as RuO_2 nanoparticles, nanotubes, nanorod arrays, and hollow fusiform nanostructures to obtain better electrochemical performances^{25,34-35}. It has been observed that hollow RuO_2 nanotubes structures show enormous advantages owing to their ability to provide ultrafast electrons and protons transfer, reduced ion-diffusion pathways, and high effective surface areas³⁶⁻³⁷. However, the tedious fabrication process and the essential need for a binder to construct these electrodes highly influences the electrical conductivity and more often lead to significant lowering of charge storing performances³⁸. Thus to combat the existing problem, other alternative facile and effective binder-free route may be of great implication for enhancing the charge storage performances of hollow hydrous nano- RuO_2 -based supercapacitors. For instance, cathodic electrodeposition of RuO_2 thin films onto Ti substrate showed specific capacitance of 788 Fg^{-1} for low RuO_2 loading level ($\sim 1.4 \text{ mgcm}^{-2}$)³¹. Even binder-free three-dimensional criss-crossed hollow hydrous ruthenium dioxide nanotubes fabricated on a Ti substrate electrode exhibited remarkable high-rate performance with a specific capacitance of 745 Fg^{-1} at a high current density of 32 Ag^{-1} .³⁹

However, to cope up with the high cost and environmental toxicity, reduced mass consumption of the Ru-precursor material has been opted without compromising with the electrochemical output by employing several mixed oxides, conducting polymer blends and obtained superior cyclic performances as shown in Table 1.

Table 1: Comparison of specific capacitance of RuO_2 and its composites with metal oxide/ conducting polymers

Materials	Specific Capacitance Fg^{-1} [Ref]
RuO_2	745 ³⁹
NiO/RuO_2	210 ⁴⁰
$\text{RuO}_2/\text{Polyaniline}$	830 ⁴¹
$\text{SnO}_2/\text{RuO}_2$	150 ⁴²
$\text{RuO}_2/\text{TiO}_2$	1263 ⁴³
$\text{RuO}_2/\text{Ag}_2\text{O}$	175 ⁴⁴
Cone-Shaped, well-aligned Polypyrrole / RuO_2	302 ⁴⁵
Nano-composite	

Even nanoporous gold have been used to improve the performance of ruthenium dioxide that exhibited the specific capacitance a value around 1500 F/g⁴⁶. Nonetheless, rapid agglomeration and easy detachment from the electrode surface promptly lowers the cyclic performances. Moreover, the effective production cost of the electrode using pristine RuO₂ is large that limits its commercial usage considerably. Consequently, electrodes of ruthenium dioxide in various composite forms have been investigated for supercapacitor applications.

fibers(CFs)] and carbon aerogels (CAGs) are some of the materials that have been introduced in metal oxide composites for their improved conductivity and charge-storage capacities⁴⁷⁻⁵⁰. Especially, the CNTs exhibit high mechanical strength and superior electrical conductivity that promote massive ion and electron transportation which is very much advantageous in high power electrochemical capacitors⁵¹⁻⁵². Ruthenium oxide nanocomposites with carbon nanotubes, and carbon composites have been widely studied some of which have been summarized in Table-2.

Various carbon forms for instances- Activated carbons (AC), carbon nanotubes (CNTs), carbon

Table 2: Electrochemical performances of Ruthenium oxide –carbon based composites

Composite	Method of preparation	Performance	References
ruthenium oxide nanoparticles / multi-wall carbon nanotubes	microwave-polyol process	Specific capacitance of 450 Fg ⁻¹ at scan rate of 10mVs ⁻¹ for potential window 0-1V, in 1 M H ₂ SO ₄ electrolyte	53
ruthenium oxide/carbon nanocomposite	Sol-gel colloidal synthesis	Specific capacitance of 407 Fg ⁻¹ at scan rate of 1mVs ⁻¹ for potential window 0-0.9V, 1 M H ₂ SO ₄ electrolyte.	54
Ruthenium oxide anchored multi-walled carbon nanotubes	Wet Chemical method	Specific capacitances of 213±16Fg ⁻¹ and 184±11Fg ⁻¹ obtained for Ru oxide/pure-MWCNT and Ru oxide/acid functionalized-MWCNT composites, 1(M) H ₂ SO ₄ scan rate of 20 mVs ⁻¹ for potential window 0-0.8V	55
RuO ₂ thin film deposited on carbon paper	dip-coating method	Specific capacitance of 620 Fg ⁻¹ 1 (M) H ₂ SO ₄ electrolyte, 0-0.8V potential scan rate of 5 mVs ⁻¹	56
ruthenium oxide particles anchored on activated carbon	sol-gel method	Specific capacitance of 208 mFcm ⁻² in electrolyte: 1-ethyl-3-methyl imidazolium tetrafluoroborate dissolved in acetonitrile at scan rate of 2 mVs ⁻¹ for -1-0.5V potential range	57
hydrous RuO ₂ /multi-walled carbon nanotubes composite	hydrothermal	Specific capacitance of 1585 Fg ⁻¹ at scan rate of 2mV/s in the potential range 0–1.2 V.	49
ruthenium oxide/carbon nanotubes composite	deep-ultraviolet lithography	Specific capacitance of 208.5 mFcm ⁻² at scan rate 10 mVs ⁻¹ in a neutral Na ₂ SO ₄ solution -0.3-0.7V potential window	58

Hu *et al.*, carried out a study on RuO_2/CNT where they found a capacitance of 1340 F/g ⁵⁹. Hydrous ruthenium oxide nano-composite with multi-walled carbon nanotubes ($\text{h-RuO}_2/\text{MWCNT}$) were synthesized by facile hydrothermal method provided specific capacitance of 1585 F/g at a scan rate of 2 mV/s in the potential range of $0 - 1.2 \text{ V}$ ⁴⁹. $\text{RuO}_2/\text{H}_2\text{O}$ /carbon black nanocomposite material prepared by impregnation method displayed impressive specific capacitance of about 700 F/g ⁶⁰. $\text{RuO}_2/\text{MWCNT}$ Electrode on Ti current collector prepared in two steps, firstly by growing MWCNT on Ti followed by electrodeposition of hydrous RuO_2 showed superior specific capacitance of 1652 F/g at scan rate of 10 mV/s ⁶¹. These composites are characterized by superior electrochemical reversibility, high-energy density, excellent stability, and improved frequency response but limited by high production cost and tedious-fabrication methods. Moreover, typical CNTs varying in micrometers length simply gets

aggregated into macroscopically entangled rope-bundles that drastically diminish their specific surface area and hence the overall charge storage capacity. Therefore, further innovative fabrication methods are essential to surmount the agglomeration problem as well as reduce the overall cost of the electrode material.

It is lately reported that CNTs, can be split into curved graphene nanosheets that on further oxidation by modified Hummers method⁶². The so-obtained graphene oxide nanosheets possess unique hybrid characteristics of 1D nanotubes and 2D flat nanosheets which can be effectively employed in composite systems. The specific capacitances of the composite obtained by splitting MWCNTs with $40.0 \text{ wt\%}$ RuO_2 loading by one-step hydrothermal synthesis without adding any reducing agent in 1 (M) KOH , 1 (M) H_2SO_4 , and 1 (M) Na_2SO_4 are 453.7 , 415.7 , 287.5 F/g respectively⁶².

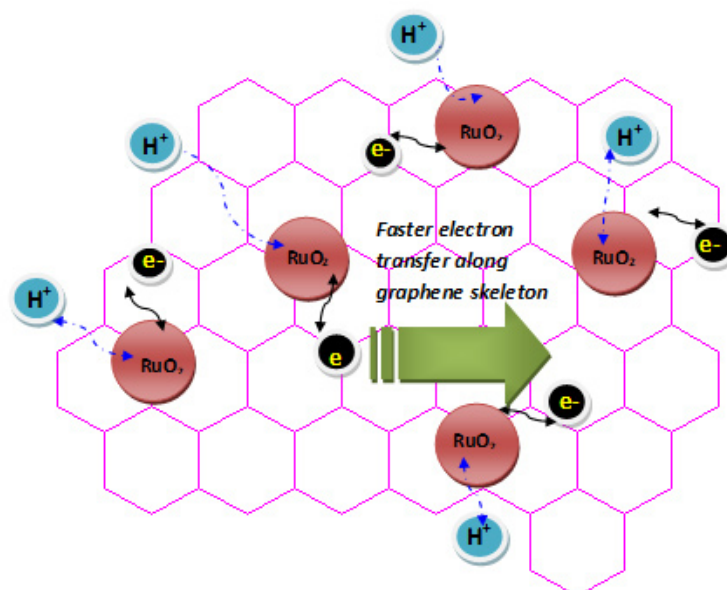


Fig. 3: Schematic representation showing mechanism of charge storage via electro-proton switching in the RuO_2 /functionalized-graphene composite

Among the various carbon substrates, graphene and its functionalized derivatives are suitable for electrochemical applications due to its tunable electrical conductivity, high surface area, and faster electron transfer rates besides low fabrication cost⁶³⁻⁶⁴. Very recently, ruthenium dioxide/graphene

sheet composite prepared by hydrothermal followed by low temperature annealing process showed specific capacitance of 551 F/g at current density of 1.0 Ag^{-1} in 1 (M) H_2SO_4 electrolyte solution with very low ruthenium content. The fine RuO_2 particles with a size of $5-20 \text{ nm}$ anchored on the graphene

sheets experienced super electrochemical behavior (as shown in Figure-3,) leading to appreciable cyclic performances of 97.9 % capacitance retention after 1000 cycles⁶⁵. RuO₂/reduced graphene oxide nanoribbon composites containing 72.5 wt% RuO₂ has been synthesized in wet chemical method in aqueous phase achieves specific capacitance up to 677 Fg⁻¹ at the current density of 1 Ag⁻¹ in three-electrode system using 1 (M) H₂SO₄ as electrolyte with excellent rate capability (91.8% retention at even 20 Ag⁻¹) at high current density⁶⁶. Recent reports show that RuO₂/graphene oxide composites when treated with polymeric dispersant Polyvinylpyrrolidone (PVP) faced less aggregation and exhibited significant cycling durability properties⁶⁷. Even ALD technique has been employed to abate RuO₂ nanoparticles agglomeration, showing improved performances of ~92% capacitive retention after 4000 CV cycles at a scanning rate of 100mV/s⁶⁸. Vertically aligned nanocrystalline-RuO₂ synthesized on Few Layered Graphene (FLG) nanoflakes, by microwave plasma chemical vapour deposition. The so-produced very small RuO₂ nanoparticle (diameter <2 nm) containing composite exhibited high specific capacitance of ~ 650 Fg⁻¹ with good cyclic performances⁶⁹. RuO₂/graphene sheet nanocomposites, with different amount of ruthenium loadings, prepared by combination of sol-gel and low-temperature annealing techniques furnished specific capacitance of 570 Fg⁻¹ for 38.3 wt% Ru loading, with notable rate capability and enhanced electrochemical stability (~ 97.9% capacitive retention after 1000 cycles)⁷⁰. In recent past, facile, scalable method of preparation of 3D – architecture with <5nm hydrous -RuO₂ anchored onto graphene and CNT hybrid foam (RGM) have been reported showing impressive electrochemical stability with excellent capacitive performances⁷¹.

Conclusion

The above studies reveal the following inferences about the RuO₂ composites:

- High content or loading of RuO₂ increases the specific capacitance due to its pseudocapacitive property.
- High conductivity compared of RuO₂ to other metal oxides is an additional advantage for reversible electron transfer.

- RuO₂ exhibits high cyclic electrochemical performances.
- High production cost of RuO₂ limits its commercialization
- RuO₂ /carbon composites (PPY, PANI, ACs, etc.) show high degree of agglomeration and poor electrochemical reversibility.
- RuO₂ /CNTs although exhibit high specific capacitance but high rate of agglomeration, high production cost limits practical application.
- RuO₂ /functionalized graphene systems till date exhibit moderate specific capacitance compared to RuO₂ /CNTs but advantageous with respect to lower rate of agglomeration, lower production cost with improved cyclic performances.

Till date, appreciable capacitance values, good stability, lower production cost, along with reversible electrochemical behavior of the RuO₂/functionalized graphene composites electrodes has high-ranked the system as very promising electrode material for future micro-supercapacitor devices. The composite has envisioned such superiority attributed to the synergistic contribution of individual constituents along with three dimensional structures that promote efficient and faster ion and electron transportation. Still it appears that to obtain better electrochemical behavior, optimization of all the components in the composites are very essential. Address to the problems related to high rate of electrode material agglomeration; minimization of production cost with controlled cyclic performances to achieve the desirable specific capacitance close to theoretical value for RuO₂ based supercapacitors remains to be the main goal in the near future. Facile, green synthetic methods suitable for large-scale production with appropriate morphology ought to be a nonstop concern for the purpose of designing real supercapacitor devices.

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Conflict of Interest

The author(s) declare(s) that there is no conflict of interests regarding the publication of this article.

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