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Ruthenium oxide–carbon-based nanofiller-reinforced conducting polymer nanocomposites and their supercapacitor applications

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Abstract

In this review article, we have presented for the first time the new applications of supercapacitor technologies and working principles of the family of RuO₂–carbon-based nanofiller-reinforced conducting polymer nanocomposites. Our review focuses on pseudocapacitors and symmetric and asymmetric supercapacitors. Over the last years, the supercapacitors as a new technology in energy storage systems have attracted more and more attention. They have some unique characteristics such as fast charge/discharge capability, high energy and power densities, and long stability. However, the need for economic, compatible, and easy synthesis materials for supercapacitors have led to the development of RuO₂–carbon-based nanofiller-reinforced conducting polymer nanocomposites with RuO₂. Therefore, the aim of this manuscript was to review RuO₂–carbon-based nanofiller-reinforced conducting polymer nanocomposites with RuO₂ over the last 17 years.

Keywords RuO₂ nanosheet · Faradaic redox reactions · Pseudocapacitance · Asymmetric supercapacitors · Energy storage · Nanocomposite · Carbon materials · Conducting polymer

Abbreviations

AC	Active carbon
ACNF	Active carbon nanofibers
AQ	Antraquinone
CeO ₂	Cerium oxide

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CF	Carbon fiber
CNTs	Carbon nanotubes
Co ₃ O ₄	Cobalt oxide
C _{sp}	Specific capacitance
CV	Cyclic voltammogram
CVD	Chemical vapor deposition
DAAQ	1-4-Diaminoantraquinone
EDLC	Electrochemical double-layer capacitance
EPD	Electrophoretic deposition
EQCN	Electrochemical quartz crystal nanobalance
GO	Graphene oxide
GN	Graphene
RuO ₂	Ruthenium oxide
h-RuO ₂	Hydrous ruthenium oxide
h-RuO ₂ /MWCNT	Hydrous ruthenium oxide/multi-walled carbon nanotube
HRGO	Holey reduced graphene oxide
MnO ₂	Mangane(IV) oxide
NiO	Nickel(II) oxide
PAN	Polyacrylonitrile
PANI	Polyaniline
PEDOT	Poly(3,4-ethylenedioxythiophene)
PEG	Polyethylene glycol
PEO	Polyethylene oxide
PCL	Poly(epsilon-caprolactone)
PCM	Phase change materials
PVA	Polyvinyl alcohol
PMA	Poly(methylmethacrylate)
PPy	Polypyrrole
PSS	Poly(styrene-4-sulfonate)
PTh	Polythiophene
R _{ct}	Charge transfer resistance
RuO ₂	Ruthenium oxide
RuO _x ·nH ₂ O	Hydrous ruthenium oxide
rGO	Reduced graphene oxide
SWCNT	Single-walled carbon nanotubes
TM	Thermal management
XRD	X-ray diffraction
QGN	Quasi-graphene
VACNT	Vertically aligned carbon nanotubes

Introduction

Supercapacitors can be divided into two sections: pseudocapacitors and electrochemical double-layer capacitors (EDLC) by means of their energy storage mechanisms [1, 2]. Metal oxides are used to prepare electroactive materials for supercapacitors

due to enhancing of their higher energy and power density capabilities [3, 4]. These materials have both deposit energy and supply Faradaic reactions [5]. We mostly reviewed ruthenium oxide (RuO_2), which were used in many studies due to its high capacitance, large voltage range, reversibility, good conductivity, and high charge/discharge capability [6, 7]. RuO_2 and its composites have Faradaic redox reactions via cyclic voltammetry (CV) method, which is a broad quasi-reversible rectangular box shape [8]. The specific capacitance (C_{sp}) of RuO_2 was obtained as $C_{\text{sp}} = 700 \text{ F/g}$ in the literature [9–11]. The nanocomposites of metal oxides such as RuO_2 , Co_3O_4 , V_2O_5 , and NiO and carbon-based materials were given as electrode materials for supercapacitors [12–14]. The inner d orbitals are responsible for the metallic conduction between ruthenium and oxygen elements [15].

Nanocomposites with RuO_2

Nanofillers and nanographene platelets have important effect to stabilize the nanocomposites [16]. In the literature, we have found that the addition of IrO_2 to RuO_2 improved the capacitive performance and cycle life of the thermally prepared Ir-Ru oxide coatings [17]. RuO_2 has been mostly employed in supercapacitor applications due to its high conductivity and reversibility processes [18–21]. However, there are some drawbacks associated with RuO_2 such as oxide delamination which are attributed to the breaking of the surface in acidic media [22–25]. Therefore, new composite materials were synthesized to develop the electrochemical performance and stability of RuO_2 . Active carbon [26], carbon aerogel [27], carbon black [28], carbon nanotubes (CNTs) [29], graphene [30], conducting polymers [31], and metal oxides [32] have been extensively studied as supercapacitors in the literature [33, 34]. RuO_2 is used as a pseudocapacitor in supercapacitor [35, 36]. There is an important strategy to obtain higher capacitance by using a large surface area of materials [37]. rGO/RuO_2 nanocomposites has a capacitance value of $C_{\text{sp}} = 879.1 \text{ F/g}$ at 0.5 A/g . Moreover, the specific capacitance was maintained over 98% for carbon nanotubes or reduced graphene oxide at 1 A/g . Shu et al. [38] indicated that MoN and Mo_2N showed capacitive behavior very similar to RuO_2 . IrO_2 has also similar capacitance value compared to RuO_2 [39].

Zhang et al. [40, 41] reported composite structures containing RuO_2 and carbon materials, which are used as next-generation supercapacitor. Ambare et al. [42] stated metal oxides of Co_3O_4 and RuO_2 . Results show that the highest C_{sp} was obtained as 628.33 F/g at 1 mV/s in 1 M KOH . Both materials Co_3O_4 [43] and RuO_2 [44, 45] show p-type semiconducting nature. Lee et al. [46] showed RuOx/polypyrrole nanocomposite which had C_{sp} values to be $C_{\text{sp}} = 681 \text{ F/g}$ at 10 mV/s in $0.1 \text{ M H}_2\text{SO}_4$. The $\text{Ru}\%$ incorporation into the composite material affects the voltage range [47]. In the literature, the percent amount of RuO_2 in the total weight percent, C_{sp} was found to be 633 F/g for $\text{RuO}_2/\text{ordered mesoporous carbon}$ structure [48].

Terasawa et al. [49] presented the incorporation of metal oxide particles such as RuO_2 , NiO_2 , MnO_2 , or IrO_2 [50] with carbon materials. $1 \text{ wt}\%$ of RuO_2 into multi-walled carbon nanotubes (MWCNTs) electrode can increase the C_{sp} from 30 to 80 F/g . In addition, the relationship between charge/discharge ratio

performance is higher than polymer/CNT composites [51]. Wang et al. [52] fabricated a supercapacitor device by plasma etching method. The results showed that a specific capacitance was found to be $C_{sp} = 272 \text{ mF/cm}^2$ at 5 mV/s in neutral Na_2SO_4 solution. Figure 1 presents the CV of all electrocoated samples including modified electrodes given at 20 mV/s [53].

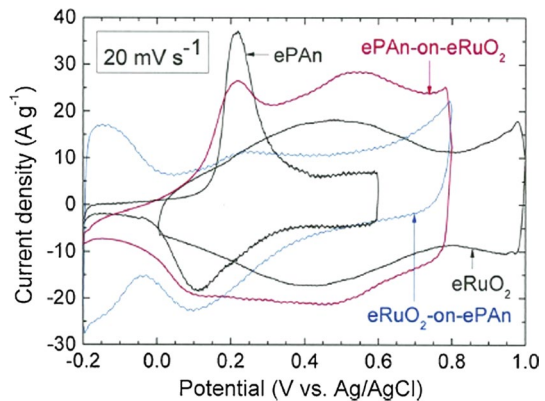
Commercial value of RuO_2

Thermal management (TM) has an important effect on electronic devices due to its performance and reliability of the devices [54]. The main aim is to obtain photoelectrochemical devices which have an efficiency of 8.5% [55]. Vita et al. [56] reported the activity of Pt/CeO_2 as a catalysts, which were studied toward the stream reforming (SR) of n-dodecane, used as surrogate fuel for marine diesel.

Transition metal oxides are important candidates for pseudocapacitance; however, RuO_2 and its composites are very expensive [57]. To circumvent this problem, more economic materials have been employed such as MnO_2 [58]. Xiong et al. [59] developed ternary cobalt ferrite/graphene/polyaniline composite for energy storage applications in industry. Aqueous electrolytes have some disadvantages such as small voltage range ($\sim 1 \text{ V}$) [60]. This problem may be solved via using metal oxides such as RuO_2 [61].

RuO_2 is the most widely used metal oxide due to its high conductivity, capacitance, and chemical stability [62]. RuO_2 has been widely studied as an electrode material for electrochemical capacitance applications [63]. However, there are major limitations to its commercial applications due to its elevated cost [64]. Therefore, the commercialization is not promising due to its high cost as well as toxic effects [65–67].

Fig. 1 CV of the electrocoated electrodes at 20 mV/s in 1.0 M H_2SO_4 electrolyte. Reprinted with permission from Ref. [53]. Copyright@Elsevier



RuO₂ and carbon fibers

The composites including micro-sized continuous fibers together with nano-sized fillers such as carbon nanotubes have limited studies which include these materials effects in the prediction of fracture energy [68]. Carbon fibers (CFs) have been employed for biosensor applications such as synthesis of poly(epsilon-caprolactone) (PCL)-based nanocomposite films [69]. Graphene fibers have been used for coating in textile industry for supercapacitor applications [70]. The hybrid fiber with a polyvinyl alcohol (PVA)/graphene oxide (GO) composites in the weight ratio of 10/90 has a capacitance of $C_{sp} = 241 \text{ F/cm}^3$ in 1 M H₂SO₄.

Yang et al. [71] have prepared RuO₂/AC nanofibers by electrospinning method and thermal process. It shows good morphology and high C_{sp} value as 180 F/g. In addition, high energy density between $E = 14 \text{ Wh/kg}$ and $E = 20 \text{ Wh/kg}$ and high power density range were obtained as $P = 400\text{--}10,000 \text{ W/kg}$ in aqueous KOH electrolyte. A number of RuO₂ nanocomposites have been reported in the literature [72–74]. Chervin et al. [75] synthesized a self-limiting conformal RuO₂ film that coated around the nanofibers via silica paper in aqueous electrolyte [76]. RuO₂-containing mesoporous active carbon nanofiber (ACNF) composites were obtained by electrospinning, and then it was used as a supercapacitor application [77].

Fam et al. [78] stated a single-walled carbon nanotube (SWCNT)/RuO₂ or MnO₂ composites on glass fiber for supercapacitor. The specific capacitances were obtained as $C_{sp} = 72 \text{ F/g}$ for the SWCNT/MnO₂ and $C_{sp} = 98 \text{ F/g}$ for SWCNT/RuO₂. Liu et al. [79] identified that RuO₂ and MnO₂ had high capacities of $C_{sp} = 824 \text{ F/g}$ in 1 M H₂SO₄ and 1080 F/g in 2 M LiOH. Kim et al. [80] synthesized active carbon nanofiber with RuO₂ by electrospinning via poly(methyl methacrylate) (PMMA) for supercapacitors. The TEM images showed hollow spheres which were made up of carbon fiber (Fig. 2a). The EDS spectra are shown in Fig. 2b, where carbon, oxygen, and ruthenium elements exist in the polymer matrix. Only carbon and oxygen elements were observed in blue line of Fig. 2c. However, ruthenium element was not observed in amorphous phase of RuO₂ [81] (Fig. 2d). Moreover, two composite materials were shown in a broad and clear peak between 20° and 30° in X-ray diffraction (XRD) spectroscopy (Fig. 2e).

RuO₂ and carbon nanotubes

Nowdays, the interest of the carbon nanotube usage increased to aerospace technology [82]. Therefore, new substances were obtained in the form of film formation with nanomaterials inside the composite matrices [83]. CNTs are used toward the solubilization of chemical and physical modifications [84] and synthesis of materials [85]. CNTs have a unique chemical structure, which have high electrical and thermal conductivity, high chemical stability, and a high surface-to-volume ratio [86, 87]. CNTs have good mechanical properties, such as a high

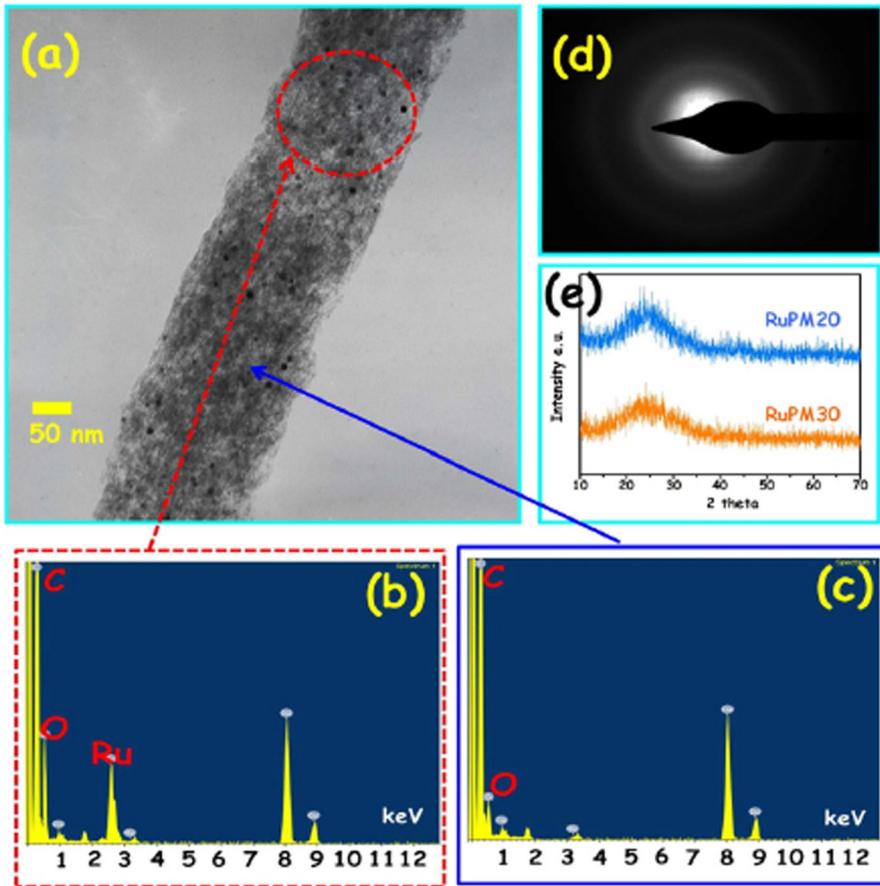


Fig. 2 TEM images **b**, **c** EDX data, **d** SEAD pattern of RuPM30, and **e** XRD peaks of RuPM30 and RuPM20. Reprinted with permission from Ref. [80]. Copyright@Elsevier

Young's modulus, high tensile strength, and high elongation at break [88]. The combination of RuO_2 and CNT mesoporous carbon provides an enhancement of the $C_{\text{sp}} = 1102 \text{ F/g}$, $E = 0.15 \text{ Wh/kg}$ and $P = 0.237 \text{ W/g}$ values. These values are greater than mesoporous carbon. Lo et al. [89] studied the particle size of RuO_2 (10 wt%) to be $\sim 2\text{--}5 \text{ nm}$ which affects the increase of capacitance from 281 to 890 F/g at 2 mV/s. The carbon-based nanocomposites also support the capacitance results [90, 91]. Wu et al. [92] investigated three-dimensional hydrous RuO_2 nanotubes on Ti electrode at $90 \text{ }^\circ\text{C}$ [93]. Moreover, there is any binder usage in this study. The specific capacitance of RuO_2 nanotubes had a value of 745 F/g at 32 A/g. The electrode's retention was obtained to be 88.7% compared to the value of 840 F/g at 2 A/g. Chaitra et al. [94] synthesized RuO_2 and $\text{RuO}_2/\text{MWCNT}$ nanocomposites by a simple hydrothermal method. The C_{sp} values of RuO_2 and $\text{RuO}_2/\text{MWCNT}$ were presented to be 604 and 1585 F/g, respectively, at

2 mV/s in the voltage range from 0 to 1.2 V. Liu et al. [95] reported the functionalization of MWCNTs using 1-4-diaminoanthraquinone (DAAQ) and the synthesis of Pt-RuO₂ nanoparticles with different morphologies on DAAQ-MWCNTs by a microwave-assisted polyol method. Jung et al. [96] presented a vertically aligned carbon nanotubes (VACNT)/RuO₂ core-shell cathode for non-aqueous Li-O₂ batteries (Fig. 3). The VACNT is synthesized via chemical vapor deposition (CVD) method and used as the core material to obtain a binder-free and hierarchical porous structure.

RuO₂ and graphene nanosheets

Graphene (GN) has a carbon-based material which constitutes of a few layers of graphite nanocrystals. It supplies a synergetic effect in composite materials to enhance mechanical and capacitive properties [97]. Hu et al. synthesized rGO/RuO₂ hydrogel nanocomposites by hydrothermal technique in which RuO₂ had a particle size of 2–3 nm [98]. Hwang et al. [99] reported a simple laser-scribed rGO/RuO₂ nanocomposites for supercapacitors. Its C_{sp} and E values were

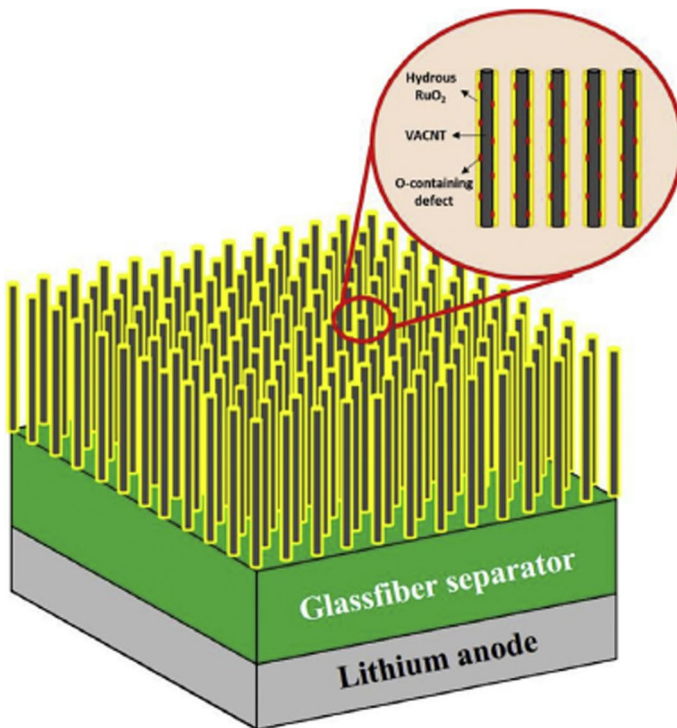


Fig. 3 Schematic illustration of the VACNT and RuO₂ cathode employed in a non-aqueous Li-O₂ battery. Reprinted with permission from Ref. [96]. Copyright@Elsevier

obtained to be $C_{sp} = 1139 \text{ F/g}$ and $E = 55.3 \text{ Wh/kg}$. Leng et al. [100] made a nanocomposite of rGO/RuO₂/TiO₂, which had a facile in situ co-assembly without any surfactants. Ensafi et al. [101] synthesized Ni–Al/layered double hydroxide on GO and RuO₂ coated on GO. The RuO₂/graphene nanocomposite showed a good C_{sp} as 528.5 F/g at 0.1 A/g with a minimum charge transfer resistance (R_{ct}) of 0.4 Ω , an excellent rate capability as well as cycling stability [102]. Amir et al. [103] reported the synthesis of RuO₂/rGO nanocomposites via sol–gel method, followed by the electrophoretic deposition (EPD) of the material into thin films. The SEM and TEM images of rGO/RuO₂ films are shown in Fig. 4. Each nanosheet was fully coated with ultra-small RuO₂ nanoparticles. Moreover, the mean size of RuO₂ nanoparticles was found to be between 1.0 and 2.0 nm, homogeneously coated on the rGO.

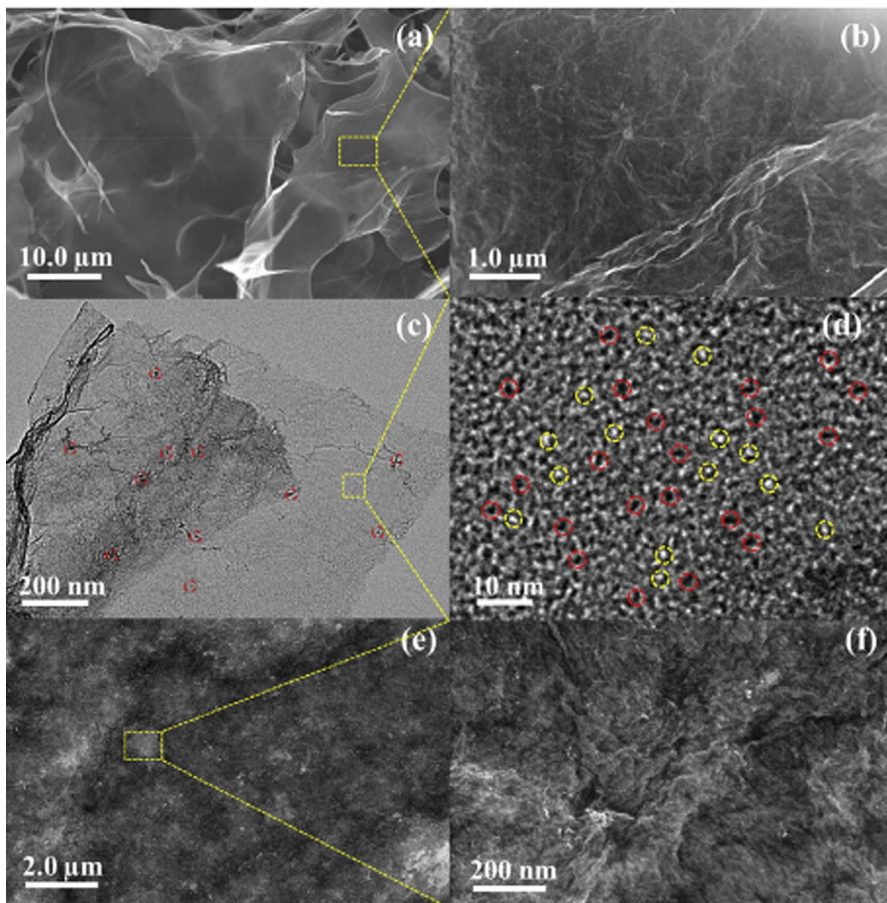


Fig. 4 a, b SEM images of freeze-dried HRGO-RuO₂, c, d TEM images of HRGO-RuO₂ (yellow and red circles were used to highlight the representative RuO₂ nanoparticles and the in-plane nanopores, respectively, and e, f SEM images of the surface of HRGO/RuO₂ film electrochemically deposited on gold coated PET (color figure online). Reprinted with permission from Ref. [103]. Copyright@Elsevier

RuO₂ and nanofiller-reinforced conducting polymers

The combination of nanofillers with polymer matrix showed the improvements of dielectric constant and lower loss tangent values [104]. Moreover, it supplies mechanical, dielectric, and thermal properties of polymer, which was followed by X-ray transmission electron microscopy for the morphology of nanofillers. In the literature, a nanocomposite of cerium oxide (CeO₂) dispersed in polyethylene oxide (PEO) polyethylene glycol (PEG) polymer electrolyte was prepared by standard solution casting method [105]. Graphite nanofibers [106], carbon nanotubes [107], carbon nanofibers [108], and graphene nanoplatelets [109] were used as nanofillers for preparing high-conductivity composite phase-change materials (PCM).

Conducting polymers already has been used as an active electrode material in supercapacitors [110]. However, there are some disadvantages associated to it, such as low stability and limited capacitance, causing limited commercial applications. To solve these problems, conducting nanofillers were added to nanocomposite materials so that the conductivity and capacitance of the active electrode material would be increased. Lean et al. [111] studied the energy storage systems of nanofillers. In the literature, a mesoporous silica MCM-48 was added to poly(methyl acrylate) (PMA) to improve mechanical and thermophysical properties [112]. This material in polymer shows a good dielectric constant and lower loss tangent values [113]. In general, nanofiller materials enhance the performance of nanocomposites in various applications [114]. Ann et al. [115] reported PPy hollow nanoparticles as the specific capacitance of $C_{sp} = 326 \text{ Fg}^{-1}$, which had two times higher than PPy. Its charge/discharge capacitance retention was obtained to be 86% even following 10,000 cycles.

Pseudocapacitors based on RuO₂

Pseudocapacitors based on Faradaic redox reactions have been reviewed in the literature [116, 117]. These redox reactions occur such as polyaniline, polypyrrole, MnO₂, and RuO₂ [118–120]. Anodic pseudocapacitors have been developed for many types of metal oxides [121]. The C_{sp} values show up to 700 F/g [122, 123]. RuO₂ is one of the most used metal oxides due to easy synthesis, high theoretical capacitance ($C_{sp} = 1358 \text{ F/g}$) [124], rapid charge/discharge processes, long life cycle [125, 126], and high gravimetric capacity [127]. RuO₂·xH₂O has been synthesized by vapor-phase deposition from RuO₄ [128–130].

RuO₂ has high C_{sp} values from 1300 to 2200 F/g for pseudocapacitor applications, [131, 132] and high electrical conductivity (10^5 S/cm) [133–135]. As it is an expensive metal oxide the more economic metal oxides such as MnO₂, NiO, and Co₃O₄ have been used with C_{sp} values of 698 F/g [136–140]. Arnold et al. [141] presented a laser scribing to obtain hydrous ruthenium oxide for supercapacitors. Sopcic et al. [142] studied the capacitance performance of RuO₂ which

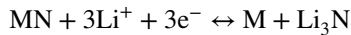
was measured by CV and electrochemical quartz crystal nanobalance (EQCN) in H_2SO_4 , Na_2SO_4 and K_2SO_4 solution. Nguyen et al. [143] investigated RuO_2 electrodes by CV method and investigation of protic ionic liquids in supercapacitor device (Fig. 5).

RuO_2 -based symmetric and asymmetric supercapacitors

Supercapacitors have higher capacitance, energy, and power densities than batteries [144, 145]. There are some advantages for using hydrous ruthenium oxide ($\text{RuO}_x \cdot n\text{H}_2\text{O}$) such as ultra-high pseudocapacitance [146], wide potential range of stability, charge/discharge performance, and good cycle life [147]. Crystalline RuO_2 has poor capacitance despite of d-band metallic conductor [148]. However, amorphous RuO_2 has high capacitance as $C_{\text{sp}} = 720 \text{ F/g}$.

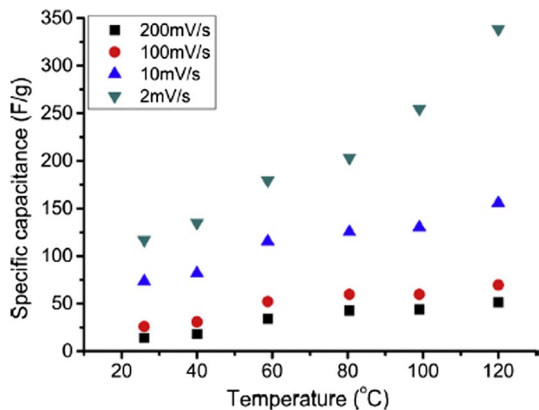
Nanostructured RuO_2 materials have been synthesized using a great variety of methods, such as chemical precipitation, potentiostatic, potentiodynamic coating, hydrothermal and chemical vapor deposition, electrolytic methods and electrostatic spray deposition [149, 150]. These materials are used in a symmetric/asymmetric supercapacitor device fabrication. For instance, carbon fiber (CF) modified with anthraquinone (AQ)/ RuO_2 nanocomposite was obtained as $E = 12.7 \text{ Wh/kg}$ [151]. RuO_2 and Co_3O_4 metal oxides on CF showed good electrochemical performance with $E = 1.44 \text{ Wh/cm}^3$ and $P = 0.89 \text{ W/cm}^3$.

The reversible reaction shown during charge/discharge process is presented below:



Such phase transformation in case of metal nitrides MN ($\text{M} = \text{Cr}, \text{Co}$) are not observed when cycled against carbon electrode materials, like RuO_2 [152], which is used as electrode materials for supercapacitors [153]. Zhang et al. [154] studied transparent, electroactive materials with $\text{RuO}_2/\text{PEDOT:PSS}$ (Fig. 6).

Fig. 5 Specific capacitance is increased by increasing the temperature. The values were calculated using the anodic current from the cyclic voltammograms. Reprinted with permission from Ref. [143]. Copyright@Elsevier



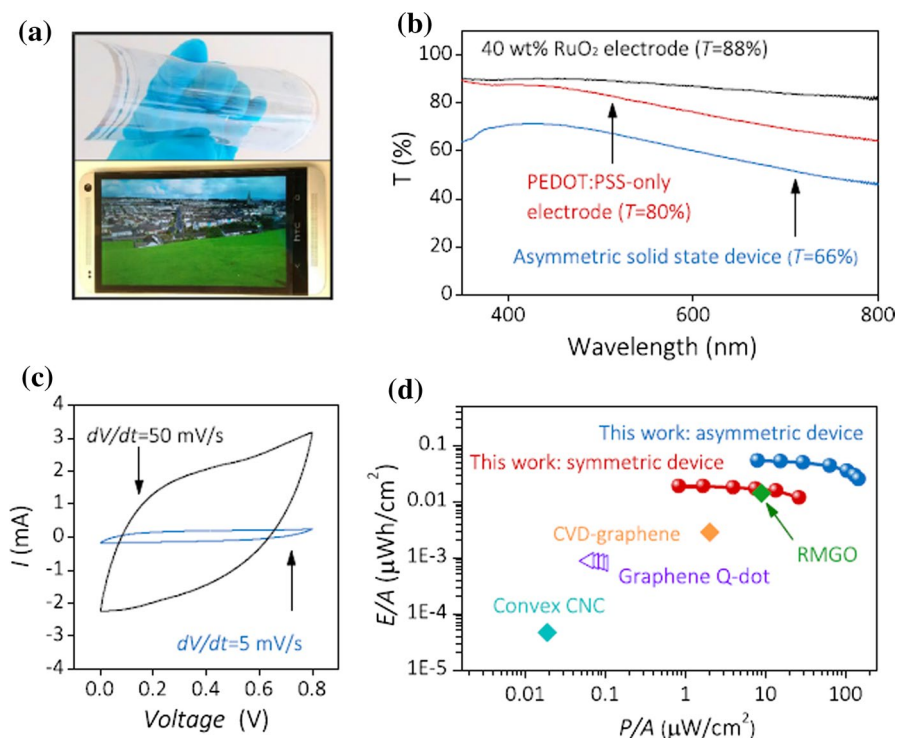


Fig. 6 **a** Photograph of flexible asymmetric solid-state supercapacitor and the same device overlaid on a mobile phone display. **b** Transmittance spectra of the constituent electrodes and the complete device (with the same solid electrolyte). **c** CVs of the device at 5 mV/s. **d** Ragone plot for the 40 wt% RuO₂-based solid-state symmetric and asymmetric devices featured in this work, along with values for other devices described in the literature. Reprinted with permission from Ref. [154]. Copyright@Elsevier

A table was obtained from the literature reports of this review article reports on RuO₂-carbon-based conducting polymer nanocomposites for supercapacitors during the years 2000–2017 as shown in Table 1.

Concluding remarks

This review article summarizes the nanocomposites with RuO₂ such as carbon fibers, carbon nanotubes, and graphene nanosheets. Economical value of RuO₂ was presented in this study. Moreover, pseudocapacitance behaviors of RuO₂-based symmetric and asymmetric supercapacitors were given in this study. As a result, RuO₂ is an expensive metal oxide but has higher capacitive behaviors in various nanomaterials compared to other metal oxides, such as NiO₂, TiO₂.

Table 1 Literature reports on ruthenium oxide–carbon-based conducting polymer nanocomposites for supercapacitors during the years 2000–2017

System	Electrolyte	Capacitance/(F/g)	References
RuCo ₂ O ₄	KOH	1469 F/g at 6 A/g	[9]
Hydrous RuO ₂	1 M H ₂ SO ₄	977 F/g at 1 mA	[20]
Ru/carboxylated graphene	0.5 M H ₂ SO ₄	756 F/g by CV	[34]
RuO ₂ × H ₂ O/CF	2 M H ₂ SO ₄	440 F/g at 23 mA/cm ²	[36]
RuO ₂ /Co ₃ O ₄	1 M KOH	628.33 F/g at 1 mV/s	[42]
RuO ₂ in amorphous phase	0.5 M H ₂ SO ₄	551 F/g at 5 mV/s	[44]
RuO _x /PPy	0.1 M H ₂ SO ₄	478 F/g at 10 mV/s	[46]
RuO ₂ /Fe ₂ O ₃	1 M H ₂ SO ₄	1668 F/g	[48]
RuO ₂ /ACNFs	1 M KOH	180 F/g	[71]
RuO ₂ /graphene	1 M H ₂ SO ₄	528.5 F/g at 0.1 A/g	[102]
HRGO/RuO ₂	PVA-H ₂ SO ₄	418 F/g at 1 A/g	[103]
QGN/RuO ₂	1 M KOH	453.7 F/g	[116]
RuO ₂ /AC 20 wt% RuO ₂	1 M H ₂ SO ₄	260 F/g	[137]

Compliance with ethical standards

Conflict of interest There is no conflict of interest in this review article.

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