



Recent advances in pseudocapacitor electrode materials: Transition metal oxides and nitrides

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Received 29 June 2017; accepted 14 December 2017

Abstract: Faraday pseudocapacitors take both advantages of secondary battery with high energy density and supercapacitors with high power density, and electrode material is the key to determine the performance of Faraday pseudocapacitors. Transition metal oxides and nitrides, as the two main kinds of pseudocapacitor electrode materials, can enhance energy density while maintaining high power capability. Recent advances in designing nanostructured architectures and preparing composites with high specific surface areas based on transition metal oxides and nitrides, including ruthenium oxides, nickel oxides, manganese oxides, vanadium oxides, cobalt oxides, iridium oxides, titanium nitrides, vanadium nitrides, molybdenum nitrides and niobium nitrides, are addressed, which would provide important significances for deep researches on pseudocapacitor electrode materials.

Key words: pseudocapacitor; transition metal oxides; transition metal nitrides; energy density; power density

1 Introduction

With the expansion of the information society and the appearance of the energy crisis, energy storage and conversion are becoming more and more important. Among the various energy conversion systems, electrochemical power sources have been widely used since they exhibit the highest energy conversion efficiency. Batteries [1] and supercapacitors are two kinds of typical electrochemical power sources. Supercapacitors are also known as electrochemical capacitors, which include electric double-layer capacitors (EDLCs) and Faraday pseudocapacitors. In the 1980s, NEC Corporation started to prepare supercapacitor products, heralding the era of commercial supercapacitor applications. Supercapacitors exhibit high power density, long cycle life, quick charging rate, relatively high safety, eco-friendliness and more suitable for charging and discharging under high power conditions than batteries [2], and can be applied as back-up power, start-up power, electrical network balance power, pulse power and so on [3]. The power characteristics of supercapacitors change little during long-term storage compared with those of batteries, hence supercapacitors

can also work as hybrid power supply systems combined with nickel-metal hydride batteries, lithium-ion batteries or fuel cells to improve efficiency and lifetime.

The major shortcoming of supercapacitors is that their energy density is much lower than that of secondary batteries represented by lithium-ion batteries. Therefore, improving the energy density is one of the major objectives of the supercapacitor research field.

Improving the energy density of a supercapacitor generally starts from the following two approaches. First is to promote the manufacturing technique of supercapacitors by reducing the amount of attachment, including electrolyte membrane, current collector and the capacitor cases, and increasing the amount of electrode materials. Second is to improve the energy density of the electrode materials. The latter is the key issue since the manufacturing technology of supercapacitors is basically fixed and attachment reduction is difficult to achieve.

According to the supercapacitor energy calculation formula, $E=1/2CU^2$, improving the working voltage (U) and capacitance (C) is an effective way to improve the supercapacitor energy density. However, due to the limits of breakdown voltage of the electrolyte, the working voltage of a single supercapacitor is very low. More specifically, the working voltages of a single

supercapacitor in an aqueous or organic electrolyte are no more than 2 and 3 V, respectively. Undoubtedly, the working voltage can be improved by placing the capacitor units in series. Using an electric vehicle as an example, high working voltage requirements need hundreds of units in series. Thereby, the overall capacitance will decrease and the equivalent series resistance will increase by series. However, such a large series can easily breakdown locally due to the differences in the performances and parameters among different units, finally breaking down drastically overall. Thus, increasing the energy density of supercapacitors mainly depends on improving the specific capacitance.

EDLCs, whose energy storage has been achieved by double-layer capacitance at the interface between electrodes and electrolytes [4], mainly use carbon-based materials with high specific surfaces. In general, the specific capacitance of EDLCs is not high since their density is low.

Compared with EDLCs, Faraday pseudocapacitors exhibit much larger specific capacitance since the capacitance takes place both at the interfaces and in the bulk of the electrode materials. Thus, pseudocapacitors can improve the energy density greatly. The energy storage mechanism is based on the highly reversible redox reaction in the electrodes [5]. Differing from the completely reversible process of physical charge-absorption and charge-desorption in EDLCs, pseudocapacitors are irreversible partially due to the involvement of chemical reaction processes in the electrodes, which leads to their relatively poor cycling performance and rate capability. Nowadays, the mainstream direction of capacitor research is to improve the energy and power densities simultaneously, so pseudocapacitor is an excellent choice. Supercapacitors have attracted considerable attention from researchers and the number of publications on pseudocapacitors has increased rapidly in recent years (Fig. 1).

Pseudocapacitor electrode materials mainly belong to three categories: transition metal oxides, transition metal nitrides and conductive polymers. Conductive polymers include polyaniline (PANI), polythiophene (PT) and polypyrrole (PPY), which possess long-chain conjugated double bonds. The obvious shortcoming of conductive polymers is that their conductivity is relatively low, which makes their rate performance and capacitance capability poorer. The practical capacitances of PANI, PT and PPY are only 150–190 F/g [6,7], 78–117 F/g [8,9] and 80–100 F/g [10,11], respectively, which are much lower than the expected values and can hardly meet practical needs. Transition metal oxides and nitrides show great potential in capacity performance. Thus, a timely and comprehensive review of transition metal oxides and nitrides is addressed in this work.

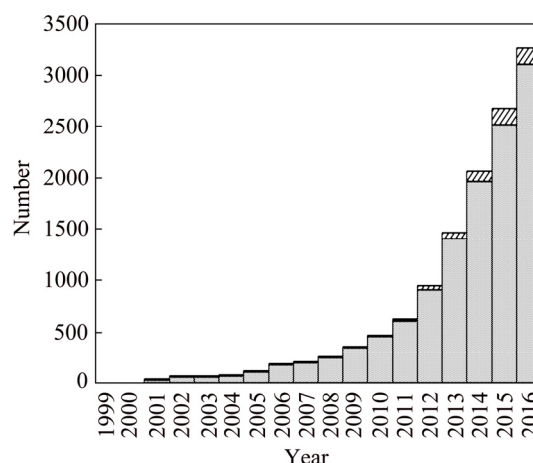


Fig. 1 Trends in number of publications on supercapacitors (■) and pseudocapacitors (▨) (data obtained from Web of Science on January 19th, 2017)

A significant amount of researches have been completed on pseudocapacitor material target strategies to improve the electrochemical performance of these devices, which is often achieved through the formation of composite materials [12]. Composites of carbon with redox active materials, prepared by the insertion of electroactive particles of transition metal oxides or nitrides into the carbon materials [13], have been evaluated as electrode materials for electric capacitors and show improved performance. Various approaches have been proposed to synthesize well-defined electrode networks to minimize the resistivity, as shown as in Fig. 2. The same strategy can be applied for most pseudocapacitor electrode materials.

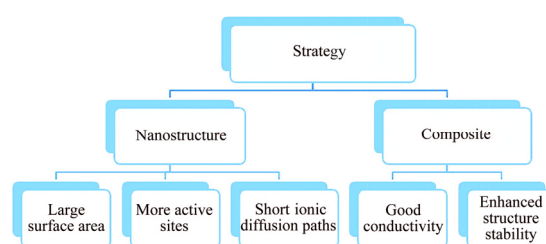


Fig. 2 Strategy for enhancing performance of pseudocapacitors [14]

2 Transition metal oxides

Transition metal oxides, including RuO_2 , MnO_2 , NiO , V_2O_5 , Co_3O_4 and IrO_2 , undergo fast reversible redox reactions on their surface (Fig. 3) and displaying strong pseudocapacitive behavior. The reversibility of these electrodes can be indicated by cyclic voltammetry (CV) curves, which shows that the symmetric redox peaks are dramatically different from the rectangular CV curves seen in EDLCs (Fig. 4). These oxides have been extensively studied as their capacitance usually greatly

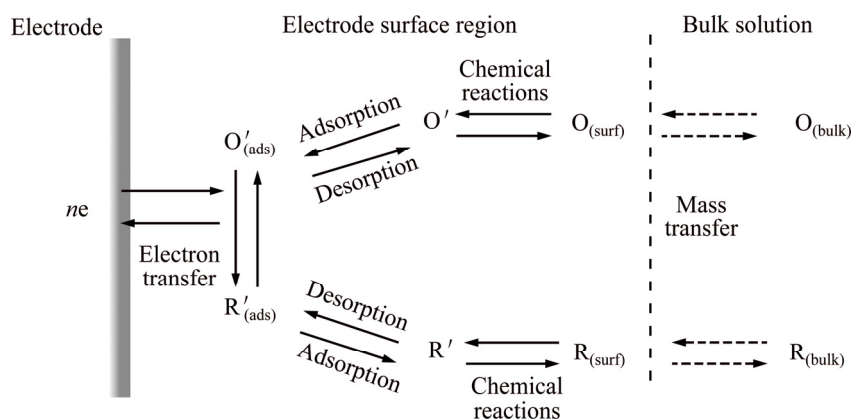


Fig. 3 Schematic diagram of reversible redox reaction at electrode/electrolyte interface leading to pseudocapacitance [15]

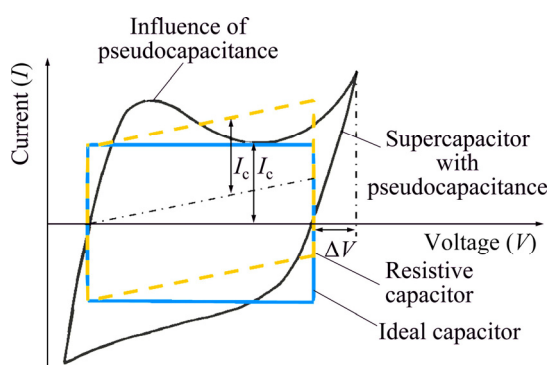


Fig. 4 Fundamental difference between current curves of EDLCs and pseudocapacitors [16]

exceeds the double-layer capacitance achievable with carbon materials. The theoretical capacitances of RuO_2 , MnO_2 , NiO , V_2O_5 and Co_3O_4 are 2200, 1370, 2584, 2120 and 3560 F/g (Fig. 5), respectively, which makes the energy density of transition metal oxides very attractive.

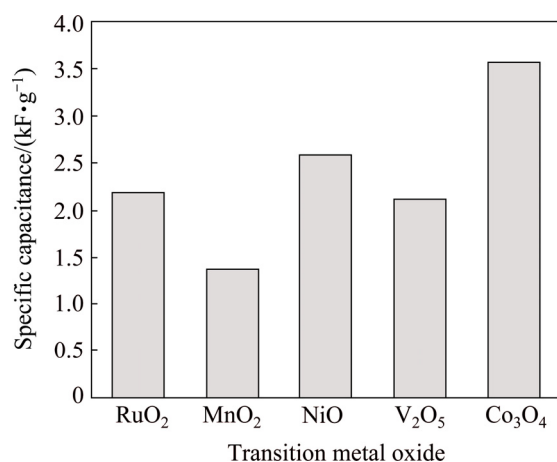


Fig. 5 Theoretical capacitances of different transition metal oxides

2.1 Ruthenium oxides

Nanocrystalline hydrous ruthenium dioxide ($\text{RuO}_2 \cdot x\text{H}_2\text{O}$), as an excellent pseudocapacitor electrode

material, is widely known for its extremely high theoretical specific capacitance, good electronic conductivity, excellent thermostability and chemical stability. RuO_2 prepared by thermal decomposition (350–550 °C) of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ showed an enhanced total cathodic and anodic charging ability and featureless voltammetric curves, quite different from the redox process of RuO_2 single crystals, which was first discovered by TRASATTI and BUZZANCA [17]. The electrically conductive $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ [18] prepared via a sol-gel method exhibited a reasonably large specific capacitance of 720 F/g through a proton migration process, at least twice as high as crystalline RuO_2 , and opened a new insight in fabricating high-energy density electrochemical capacitors. Tremendous efforts have been continuously geared to understand the influence of precursors of the heating process, which determine the crystallinity, exposed crystal phase, structural water content, particle size and specific surface area of as-prepared products, on the electrochemical capacitance and underlying mechanism.

Various methods, such as chemical vapor deposition, pulsed laser deposition, electrostatic spray deposition, anodic deposition and hydrothermal processing [19–21], have been developed to prepare RuO_2 films or powders featuring a highly reversible redox reaction, a wide potential window (1.2 V) and good thermal and chemical stability. For example, DESHMUKH et al [22] deposited $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ thin film through a simple chemical bath process, and it revealed 41.6 W·h/kg and 1.5 kW/kg at 300 $\mu\text{A}/\text{cm}^2$ with 95% Coulombic efficiency. ADAMS et al [23] summarized the conductivity and capacitive properties of RuO_2 , derived from the single crystal to a highly disordered structure (Fig. 6).



As for the preparation of RuO_2 , the increase of accessible surface, the formation of highly ordered or

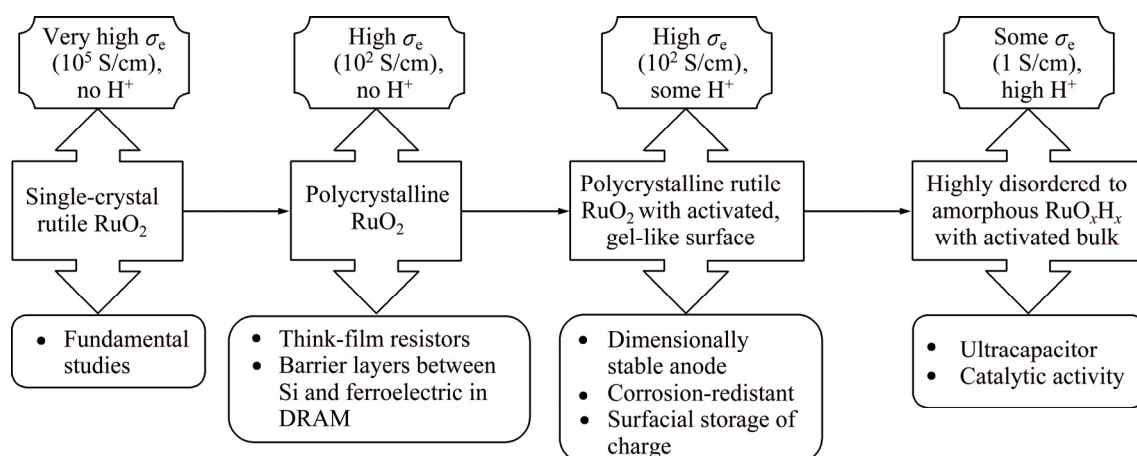


Fig. 6 Ruthenium dioxides—An example of spectrum of properties with different crystal structures [23]

hollow structures and the exploration of optimum annealing conditions are major factors for achieving high practical specific capacitance [24] and superior rate capability. Therefore, versatile hard templates (a mesoporous silica template [25], α - Fe_2O_3 [26] and $MnOOH$ [27]) and/or surfactants acting as soft templates or pore-directing agents [28], were adopted to construct three-dimensional (3D) nanoporous or mesoporous networks for fast electron and ion transportation. WU et al [26] prepared hollow $RuO_2 \cdot xH_2O$ with α - Fe_2O_3 sacrificial template and it exhibited 772, 671, 502 and 360 F/g at 0.5, 4, 20 and 40 A/g, respectively, which also experienced an activation period and achieved 823 F/g after 1000 cycles at 1 A/g. ZHANG et al [27] proposed the mechanism of forming nanotubular RuO_2 from a sacrificial template of manganite nanorods, which showed 861, 787, 722 and 654 F/g at 0.5, 1, 2 and 4 A/g, respectively, benefiting from the reduced resistance of electrolyte penetration and diffusion. JEONG et al [29] electrochemically deposited hydrous ruthenium oxide with open pores and numerous dendritic morphologies with a dynamic hydrogen template, with capacitance of 809 F/g at 1.5 A/g. LIN et al [28] fabricated a 3D mesoporous crystalline RuO_2 film with enhanced electrochemical active centers via an evaporation-induced self-assembled method, which exhibited an ultrahigh power density with an acceptable energy density.

Layered ruthenic acid, $H_{0.2}Ru_{2.1} \cdot nH_2O$ (HRO), featuring a crystalline ruthenium oxide layer interleaved with water, shows comparable inner electronic conductivity with rutile RuO_2 and similar capacitive performance to hydrous RuO_2 , benefiting from the utilization of the interlayer surface and surface active sites [30]. SUGIMOTO et al [31] revealed that pristine HRO reached 392 and 329 F/g at 2 and 500 mV/s, respectively, while exfoliated HRO exhibited 658 and 601 F/g at 2 and 500 mV/s, respectively. Other

elaborately designed electrode constructions have also been developed. HYUN et al [32] electrochemically deposited $RuO_2 \cdot nH_2O$ overlayers on conductive crystalline RuO_2 (~10 nm) fibers, which showed 886.9 F/g at 10 mV/s based on the mass of $RuO_2 \cdot nH_2O$, corresponding to 104.3 F/g based on the total mass of RuO_2 fiber mats and $RuO_2 \cdot nH_2O$ coating layer. SUSANTI et al [33] encased anhydrous RuO_2 nanorods with hydrous RuO_2 via an electrochemical deposition. The annealed structure revealed 526 F/g (878 mF/cm²) at 5 mV/s, which decreased to 78.6 F/g (131 mF/cm²) at 500 mV/s. When metallic Pt was used as the core, significantly improved capacity retention at high discharge rates seemed to be achieved. PONROUCH et al [34] fabricated Pt@ RuO_2 core-shell nanotube arrays for micro-supercapacitor electrodes, which demonstrated 320 and 256 mF/cm² at 2 and 500 mV/s, respectively, with ~80% capacity retention. RYU et al [35] constructed transparent supercapacitors by electrodepositing hydrous RuO_2 on 1D indium tin oxide (ITO) nanopillars, and a maximum specific capacitance of 1235 F/g at 50 mV/s was achieved, which also showed excellent capacitance retention of ~94.3% from 10 to 200 mV/s. A schematic representation of the construction of the coaxial ITO core- RuO_2 shell nanopillar electrode is shown in Fig. 7.

The commercial of RuO_2 -based electrodes used in supercapacitors is seriously hindered by the high cost of RuO_2 . Therefore, a number of studies have focused on composing RuO_2 with other materials that store charge through double layers and reversible redox processes. Combining RuO_2 with carbon materials has several advantages [36]: 1) Carbon materials can work as a matrix possessing a high surface area to disperse and lower the size of RuO_2 particles, which creates higher utilization; 2) A porous carbon support can accelerate the transporting rate of ions into the bulk of the electrode, or act as an “electrolyte reservoir” that prevents depletion

or oversaturation of protons at high voltage scans, which would improve the power performance; 3) Well-crystallized carbon might also reduce the contact resistance between RuO_2 particles and enhance the conductivity of RuO_2 /carbon composites. Various forms of carbon materials have been investigated to achieve these benefits, such as carbon aerogel, activated carbon, carbon black, carbon nanofibers, carbon nanotubes and carbon spheres [37–39]. AN et al [40] prepared surface-modified RuO_2 /carbon nanofiber composites, which exhibited outstanding energy densities of 26.9–21.5 $\text{W}\cdot\text{h/kg}$ at 349.0–17545.5 W/kg , and a cycle stability of 90% after 3000 cycles, owing to the well-connected structure and the synergistic effect from the two components. HSIEH et al [41] electrochemically deposited (50 mV/s) hydrous RuO_2 on multi-walled carbon nanotubes, and the composite revealed excellent specific capacitances of 1652 and 863 F/g at 10 and 500 mV/s, respectively. WANG et al [42] adopted a core-shell template approach to fabricate carbon or carbon nanotube-supported hollow RuO_2 nanoparticles (referred to as hRuO_2/C and hRuO_2/CNT , respectively) for supercapacitor electrodes. The hRuO_2/C and hRuO_2/CNT reached 817.1 and 819.9 F/g at 0.2 A/g, and retained 750.4 and 655.0 F/g at 5 A/g, respectively. The power and energy densities achieved by the hRuO_2/C and hRuO_2/CNT were 427.6 W/kg and 133.8 $\text{W}\cdot\text{h/kg}$, and 557.3 W/kg and 127.9 $\text{W}\cdot\text{h/kg}$, respectively, which showed the advantages of the hollow nanostructure. A schematic illustration of hRuO_2/C and hRuO_2/CNT and the corresponding TEM images are presented in Fig. 8. The core-shell hybrid of the RuO_2 -coated carbon

nanotubes composite [38] also exhibited a competing performance of 11.9 $\text{W}\cdot\text{h/kg}$ at 3000 W/kg . When switching the role of RuO_2 and the carbon support, a RuO_2 matrix decorated with carbon quantum dots reported by ZHU et al [43] reached 594 F/g at 1 A/g, and ultrahigh rate capabilities of 88.6%, 84.2%, and 77.4% capacity retention at 10, 20 and 50 A/g, respectively.

Introducing RuO_2 to graphene, which features a 2D nanostructure, could prevent the agglomeration of RuO_2 or the stacking of graphene sheets, thus providing more electrolyte accessible surface. Some RuO_2 -graphene composites have been prepared through sol-gel or hydrothermal methods. WU et al [44] pioneered the synthesis of RuO_2 /graphene, the sample with 38.3% Ru loading showed 570 F/g at 1 mV/s, and a high energy density of 20.1 $\text{W}\cdot\text{h/kg}$ at 50 W/kg and a superior power density of 10 kW/kg at 4.3 $\text{W}\cdot\text{h/kg}$. DINH et al [45] fabricated on-chip micro-supercapacitors based on RuO_2 /carbon nanowalls (consisting of graphene domains), which delivered 1094 mF/cm^2 at 2 mV/s and a high energy density of 49 ($\mu\text{W}\cdot\text{h/cm}^2$). The electrochemical performance of these micro-supercapacitors is comparable to state-of-the-art lithium-ion micro-batteries. A new trend is to combine transition metal oxides with different types of carbon materials to form a ternary composite to enhance the energy and power densities simultaneously. The backbone of graphene/CNT for depositing RuO_2 can be formed through chemical vapor deposition (CVD) or wet chemistry. WANG et al [46] deposited a graphene/MWCNT foam via CVD and subsequently dip-coated it with RuO_2 suspension to form a RuO_2 /graphene/CNT hybrid (RGM). The schematic

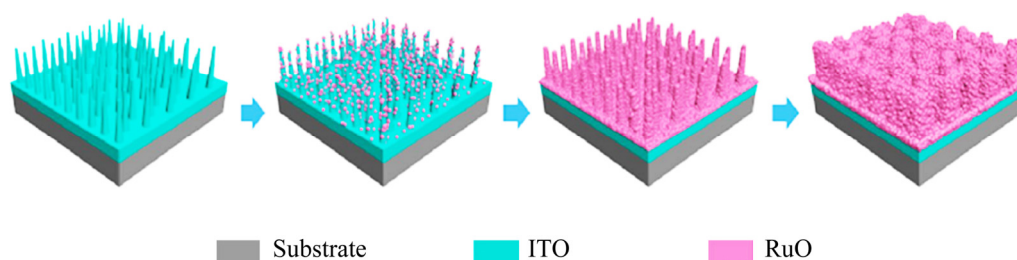


Fig. 7 Schematic diagram of construction of coaxial ITO core- RuO_2 shell nanopillar electrode [35]

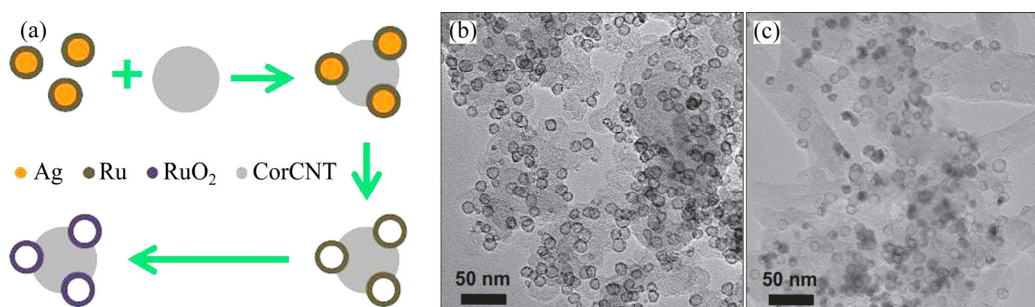


Fig. 8 Schematic illustration of C- or CNT-supported RuO_2 (a) and TEM images of hRuO_2/C (b) and hRuO_2/CNT (c) [42]

illustration of the preparation process is shown in Fig. 9. The RGM showed the highest gravimetric and per-area capacitive performance of 502.8 F/g and 1.1 F/cm², and it exhibited an exceptionally high energy density of 39.3 W·h/kg and a power density of 128.0 kW/kg. HU et al [47] also explored the applicability of graphene/CNT/RuO₂ composites for fabricating supercapacitor electrodes. The composite annealed at 150 °C exhibited 135 W·h/kg and 12 kW/kg, and the corresponding symmetric supercapacitor delivered 33.8 W·h/kg and 3 kW/kg.

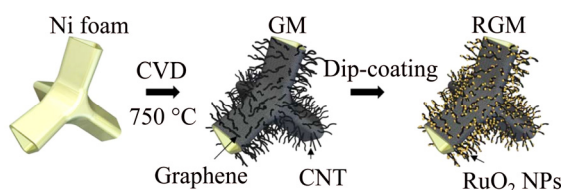


Fig. 9 Schematic illustration of fabrication of RGM nano-structure foam [46]

In order to enhance the utilization of RuO₂ in pseudocapacitance storage at a more reasonable cost, inorganic oxides with promising pseudocapacitance or metallic conductivity, such as MnO₂, NiO, Co₃O₄, SnO₂, TiO₂, Ta₂O₅, SrRuO₃ and ZrO₂, have been incorporated with RuO₂ to form hybrid electrodes. CHOU et al [48] chemically deposited a MnO₂ coating on 1D RuO₂ nanorods through a radio-frequency magnetron sputtering system. The RuO₂/MnO₂ core-shell nanorods with a good rate capability reached 793 F/g at 2 mV/s and 556 F/g at 1 A/g. RAKHI et al [49] electrodeposited nanocrystalline, hydrous RuO₂ to mesoporous Co₃O₄ to form a RuO₂/Co₃O₄ composite with enhanced rate

performance. The RuO₂/Co₃O₄ with the optimal RuO₂ electrodeposition time resulted in 905 F/g at 1 A/g and a high retention of 78% at 40 A/g. BRUMBACH et al [50] fabricated ruthenium oxide-niobium hydroxide composites with varying precursor ratio. As the niobium hydroxide worked as an effective proton conductor and induced a decrease in RuO₂ particle size, the energy storage of Nb:Ru composites with only half to a third of Ru exceeded that of the pure RuO₂ electrode.

Many conductive polymers with high pseudocapacitance, have also been incorporated with RuO₂ to alleviate the aggregation of RuO₂ and improve its mechanical stability. DESHMUKH et al [51] prepared a PANI–RuO₂ composite thin film via a chemical bath deposition. The growth mechanism is shown in Fig. 10. The PANI–RuO₂ composite thin film exhibited 830 F/g at 5 mV/s, and a specific energy and power of 216 W·h/kg and 4.2 kW/kg, respectively. The same group [52] also synthesized a polyaniline–ruthenium oxide composite via a successive ionic layer adsorption and reaction method, and it yielded 664 F/g at 5 mV/s. CHO et al [53] designed a ternary flexible system based on a RuO₂ nanoparticle-decorated PEDOT:PSS/graphene nanocomposite, which exhibited 820 F/g at 0.5 A/g and 73 W·h/kg at 67 W/kg.

2.2 Nickel oxides

Nickel oxide (NiO) has been suggested to be the optimal alternative material for pseudocapacitors because of its lower cost and more environmental friendliness when compared to RuO₂ [16]. It has an unusually high theoretical specific capacitance [54] and higher electrical conductivity compared to other metal oxides/hydroxides or polymers [55], as well as a high surface area, making it very attractive as an electrode material for

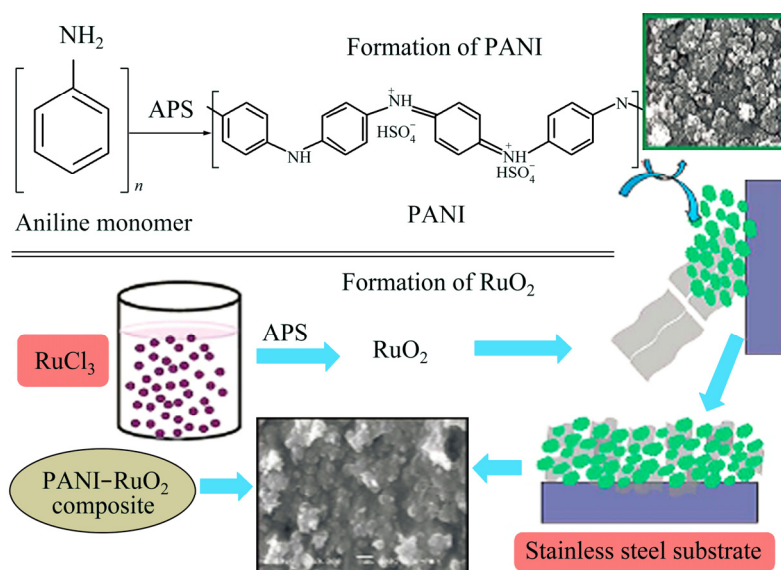


Fig. 10 Growth mechanism of PANI–RuO₂ composite thin film [51]

pseudocapacitors. As a result, many effective efforts have been devoted to synthesizing different morphologies of NiO nanomaterials by various wet chemical methods, such as nanoparticles, nanoplates, hollow octahedrons and complicated hierarchical nanostructures [56,57].

The capacitance of NiO mainly results from a fast redox reaction according to the following equation:



However, the real specific capacitance obtained from NiO materials is far below its theoretical value because of its high resistance (less than 10^{-1} S/cm at room temperature [58]). ZHANG et al [59] synthesized porous NiO nanostructures with a specific capacitance of 390 F/g at a discharge current of 5 A/g. VIJAYA-KUMAR et al [60] adopted a microwave route to prepare NiO nanoflakes, which exhibit a specific capacitance of 401 F/g at a current density of 0.5 mA/cm². Therefore, it is desirable to produce electrode materials with high specific surface areas as well as suitable pore size distributions (2–5 nm) to improve the specific capacitance of pseudocapacitors.

By decorating NiO nanostructures on graphene foam [61], the composite exhibited an increased electrochemical performance of about 1225 F/g at 2 A/g. LU et al [62] reported a simple, cost-effective and potentially scalable technique for fabricating monolithic NiO/Ni nanocomposite electrodes with a remarkably high specific capacitance of 900 F/g. Moreover, WANG et al [16], reported a novel approach to synthesize hierarchical composite electrodes of nickel oxide nanoflakes with 3D graphene for high-performance pseudocapacitors, with a remarkable specific capacitance of 1829 F/g at a current density of 3 A/g. In their study, NiO nanoflakes were created with a simple hydrothermal method on 3D graphene scaffolds grown on Ni foams by microwave plasma enhanced chemical vapor deposition. Such as-grown NiO-3D graphene composites (NGC) were then applied as monolithic electrodes for a pseudocapacitor application without the requirement for binders or metal-based current collectors. Another nickel-based material, Ni(OH)₂, is also the most promising candidate for supercapacitors with its high theoretical specific capacitance of 2082 F/g [63].

Encouraged by its remarkable potential application, effective efforts have been devoted to the synthesis of Ni(OH)₂ nanostructures with different morphologies and structures, such as platelet-like, flower-like, nanoparticles, microspheres, nanotubes and nanorods [64–66]. Among these different morphologies, flower-like nanostructured Ni(OH)₂ has attracted considerable attention because of its short diffusion path lengths for both electrolyte ions and electrons, favoring

the diffusion and migration of electrolyte ions during the rapid charge/discharge process, consequently improving its effective electrochemical utilization [67]. Furthermore, the composite coupled with graphene exhibits high specific capacitance. WANG et al [63] synthesized Ni(OH)₂ nanocrystals grown on graphene sheets (NGS) with various degrees of oxidation (Fig. 11), which exhibited a high specific capacitance of 1335 F/g at a charge and discharge current density of 2.8 A/g.

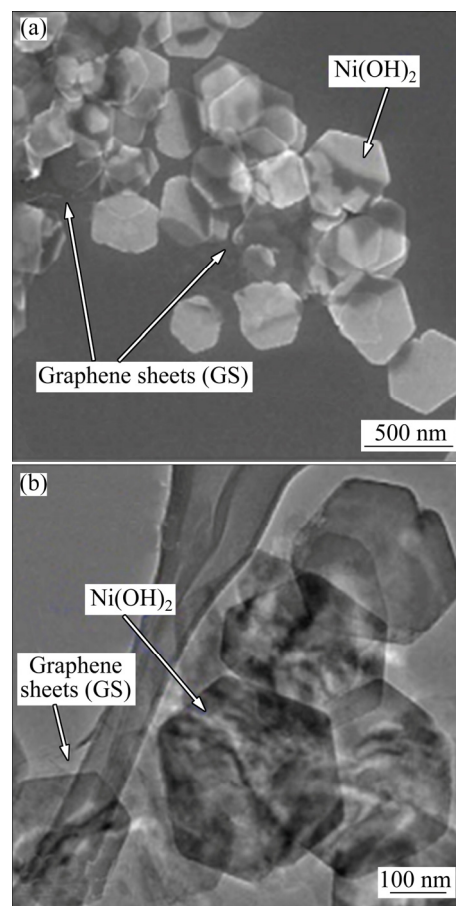


Fig. 11 SEM (a) and TEM (b) images of NGS composite [63]

YAN et al [68] reported a novel strategy to prepare hierarchical flower-like Ni(OH)₂ decorated on graphene sheets using a fast, facile and cost-effective microwave heating method without any templates or additional agents. The Ni(OH)₂/graphene hybrid exhibited a high specific capacitance of 1735 F/g and high rate capability compared to a pure Ni(OH)₂ electrode (Fig. 12).

A comparison of some experimental results for the NiO redox couple is shown in Table 1. With different morphologies of NiO or Ni(OH)₂ materials, a broad range of capacitance from 124 to 1335 F/g can be obtained. The crystal phase, structural morphology and surface area are of critical importance for the development of high performance electrochemical energy storage devices with simultaneous high energy and power densities.

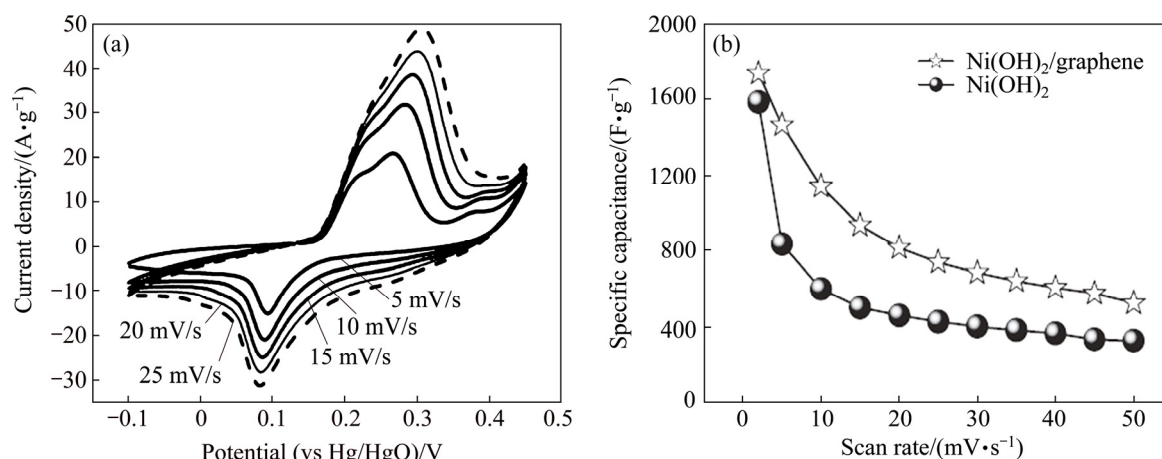


Fig. 12 CV curves of Ni(OH)₂/graphene composite at various scan rates in 6 mol/L KOH (a) and specific capacitance of pure Ni(OH)₂ and Ni(OH)₂/graphene composite as function of scan rate based on CV curves (b) [68]

Table 1 Comparison of experimental results for NiO redox couple [69]

Material	Phase	Morphology	Capacitance/(F·g ⁻¹)	Surface area/(m ² ·g ⁻¹)	Electrolyte
NiO	Cubic	Porous ball	124	477	3% KOH
NiO	Cubic	Nanoflake	140	108	2 mol/L KOH
NiO	Cubic	Thin film	590		3% KOH
NiO	Cubic	Thin film	1110		1 mol/L KOH
NiO	Monoclinic	Petal	710	216	6 mol/L KOH
		Nanocolumn	390	103	
NiO	Monoclinic	Nanoslice	285	20	1 mol/L KOH
		Nanoplate	176	11	
NiO	Cubic	Nanoflake	411	227	2 mol/L KOH
NiO–MWNT	Cubic	Nanoflake	206	228	2 mol/L KOH
Ni(OH) ₂ on activated carbon	β-Ni(OH) ₂	Irregular	194	134	6 mol/L KOH
Ni(OH) ₂ on activated carbon	β-Ni(OH) ₂	Nanoparticle	315		6 mol/L KOH
Ni(OH) ₂ on graphene	β-Ni(OH) ₂	Nanoparticle	1335		1 mol/L KOH

2.3 Manganese oxides

Manganese dioxide (MnO₂) has a high theoretical specific capacitance of 1370 F/g [70] and is considered to be one of the alternatives for pseudocapacitors. The pseudocapacitive behavior of MnO₂ was first studied by LEE and GOODENOUGH in 1999 [71]. Porous hydrous MnO₂, which has been facilely and widely prepared by the organic-aqueous interfacial method [72], exhibits a capacitance of 261 F/g and good cyclic performance, but only at low charge/discharge rates, showing that pure manganese oxide cannot be applied for capacitor applications.

Recently, many research efforts have been focused on its compounds in order to provide high charge/discharge rates. The mechanism of MnO₂ charge storage behavior can be explained according to Eq. (3) [73].



However, the performance of MnO₂ supercapacitors is very disappointing, only less than 30% of the theoretical capacitance of MnO₂ (<100–300 F/g) can be retained [74] since its electrochemical properties strongly depend on its dimensionality, powder morphology, crystalline structure and bulk density [75]. In addition, the poor conductivity of MnO₂ (1×10^{-5} – 1×10^{-6} S/cm) also limits the charge/discharge rate for high-power applications [76].

Thus, many studies have been carried out to synthesize reasonable structures and compositions of MnO₂ for the purpose of improving electrolyte access and electron transportation. LANG et al [77] synthesized hybrid structures (NPG/MnO₂) made of nanoporous gold (NPG) and nanocrystalline MnO₂, exhibiting a specific capacitance of 1145 F/g, acting as a double-layer

capacitor. This high specific capacitance is attributed to the nanoporous gold, which not only allows electron transport through the MnO_2 , but also facilitates fast ion diffusion between MnO_2 and the electrolytes.

By using hydrothermally synthesized $\alpha\text{-MnO}_2$ nanowires, OZKAN et al [78] uniformly coated on graphene/multi-walled carbon nanotube (GM) foam. The GM foam was grown on nickel foam (NF) via ambient pressure chemical vapor deposition. Symmetrical ECs based on graphene/multi-walled carbon nanotube/ MnO_2 nanowire (GMM) foam electrodes show an extended operational voltage window of 1.6 V in aqueous electrolyte, which also exhibit an excellent specific capacitance of 1109 F/g.

2.4 Vanadium oxides

Vanadium pentoxide (V_2O_5) is a favorable candidate as a supercapacitor electrode because of its accessible layered structure, high potential (about 3 V), high specific capacity, mixed valence states (V^{2+} , V^{3+} , V^{4+} and V^{5+}), low cost, easy procedure for synthesis and nontoxic chemical properties [79].

There are many methods used to obtain different nanostructures of V_2O_5 or VO_2 , such as hydrothermal, electrospinning, sol-gel and template-assisted growth [80–82]. The various synthesized nanostructures of V_2O_5 or VO_2 also have been applied in a variety of fields, including sensors, optical switching devices, optical data storage media and electrode materials for Li-ion batteries [83]. The V_2O_5 bulk lattice are shown in Fig. 13. Equation (4) implies the intercalation of protons (H^+) in the bulk of the material upon reduction:



The electrochemical properties of vanadium oxide were evaluated by CV measurements at various scan rates in electrolytes. WEI et al [85] synthesized vanadium oxide nanoribbons by a facile and effective hydrothermal treatment whilst controlling the condensation speeds of precursors in the solution along the $\langle 010 \rangle$, $\langle 100 \rangle$ and $\langle 001 \rangle$ directions. The prepared nanoribbon structure exhibited a high capacitance of 453 F/g. Figure 14 shows CV curves with a nearly rectangular shape, which indicates good conductivity and good charge propagation within the electrodes. Two pairs of obvious oxidation/reduction peaks (P1/P1' and P2/P2') and a pair of small oxidation/reduction peaks (P3/P3') were observed in the CV curves at five different scan rates. These CV curves displaying a nearly rectangular shape with three pairs of redox peaks, even at very high scan rates, indicate the supercapacitor features of fast charging and discharging.

Recently, 3D hybrid architectures composed of metal oxides and graphene have been shown to

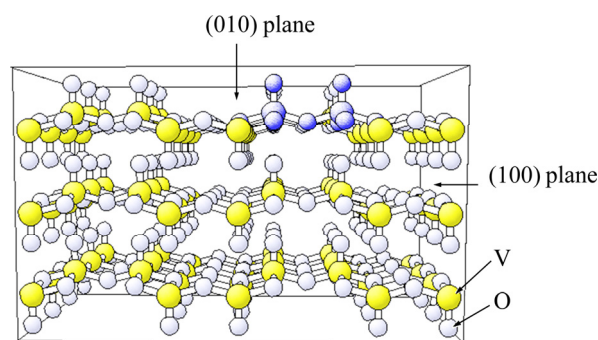


Fig. 13 Bulk lattice of V_2O_5 [84]

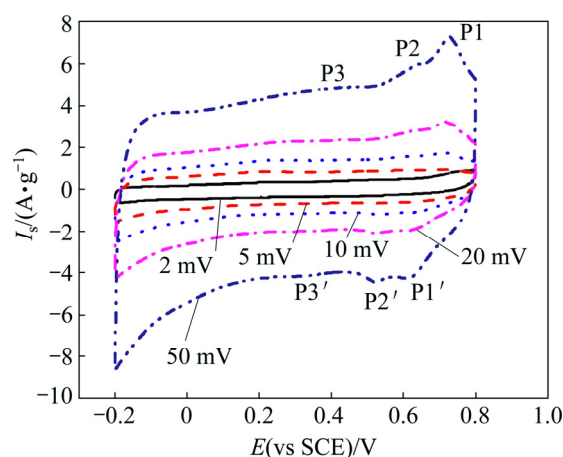


Fig. 14 CV curves of V_2O_5 at different scan rates [86]

potentially have better performance if a composite electrode possesses both the good rate performance of the carbon-based materials and the high specific capacitance of the metal oxides [87]. YE et al [88] synthesized a unique 3D architecture constructed by ultrathin single-crystalline V_2O_5 nanoribbons (V_2O_5 NRs) with reduced graphene oxide (rGO) layers via a simple hydrothermal synthesis and subsequent oxidation treatment (see Fig. 15).

The unique 3D V_2O_5 NR/rGO architecture exhibits a high capacitance of 437 F/g at a current density of 1 A/g, good stability and superior rate performances when applied as an electrode material for energy storage.

CHEN et al [89] developed a class of pseudo-capacitive anode materials for asymmetric supercapacitors composed of interpenetrating networks of CNTs and V_2O_5 nanowires. The CNTs and nanowires were intimately intertwined into a hierarchically porous structure, enabling effective electrolyte access to the electrochemically active materials without limiting charge transport. The structure exhibited a high specific capacitance (>300 F/g) at a high current density (1 A/g) in aqueous electrolyte.

QU et al [90] uniformly grew PPy on the surface of V_2O_5 NRs using anionic dodecylbenzenesulfonate (DBS^-) as a surfactant to overcome poor electronic conductivity and high dissolution in the liquid electrolyte (Fig. 16).

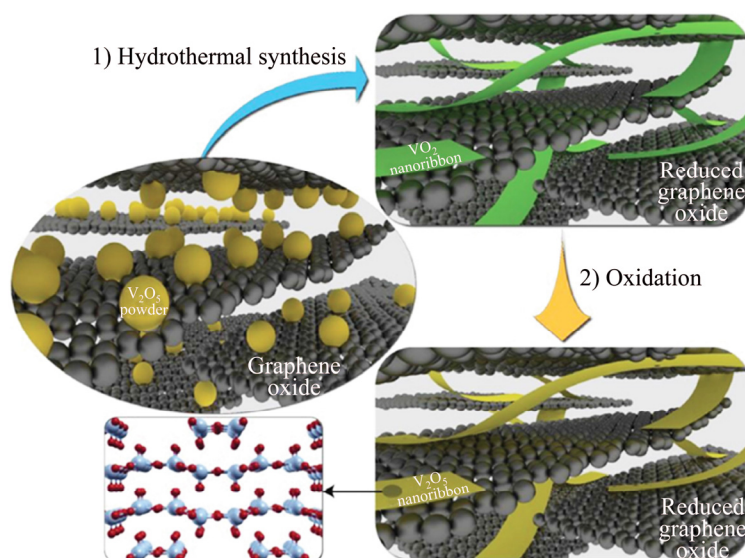


Fig. 15 Fabrication procedure of 3D V_2O_5 NR/rGO architecture [88]

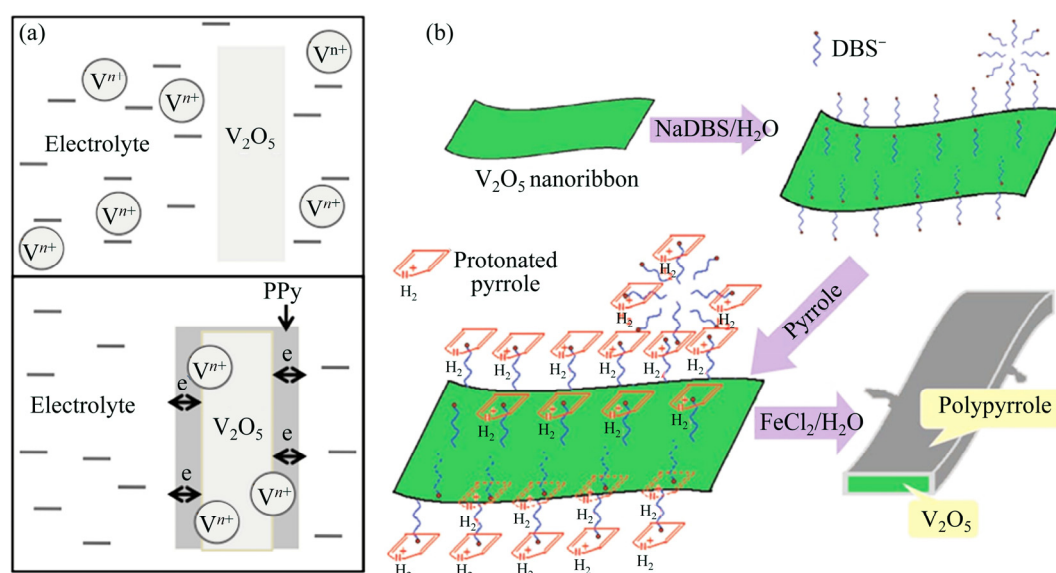


Fig. 16 PPy coating for facilitating electronic transport and preventing dissolution of vanadium in electrolyte (a) and schematic illustration of PPy growth on V_2O_5 NR surface (b) [90]

2.5 Cobalt oxides

Cobalt oxide has been paid significant attention for its importance in various scientific fields, such as solar selective absorbers, catalysts in the hydrocracking process of crude fuels, pigments for glasses and ceramics, catalysts for oxygen evolution and oxygen reduction reactions [91]. It has also newly used as an electrochemical material in supercapacitors. The theoretical specific capacitance of Co_3O_4 is 3560 F/g [92], much higher than for RuO_2 , proving itself as a promising alternate to expensive RuO_2 .

As a supercapacitor material, nanocrystalline Co_3O_4 can offer a large surface area, high conductivity, electrochemical stability and pseudocapacitive behavior,

which are beneficial for developing high energy and power density electrochemical capacitors. Although this oxide is customarily identified with its chemical formula Co_3O_4 , it is in fact, non-stoichiometric. Cobalt has less affinity for oxygen than iron has but more than nickel [93]. It has three well-known polymorphs: monoxide or cobaltous oxide (CoO), cobaltic oxide (Co_2O_3) and cobaltous oxide or cobalt cobaltite (Co_3O_4).

Figure 17 shows the CV curves of the Co_3O_4 product within a potential range of -0.4 to 0.55 V (vs Hg/HgO) at different scan rates of 5, 15 and 20 mV/s. It can be clearly seen that there are two strong distinct pairs of redox peaks during the anodic and cathodic sweeps. These redox peaks correspond to the conversion between

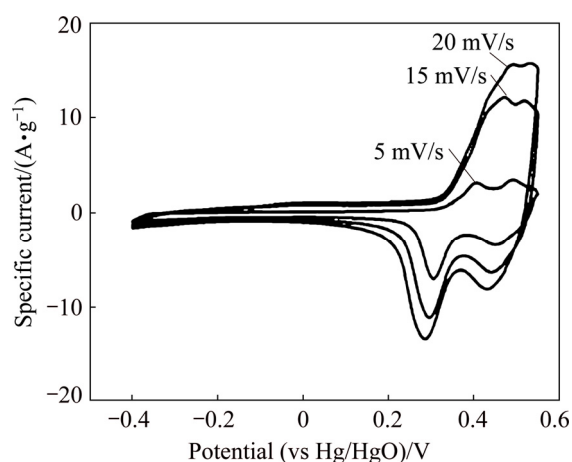
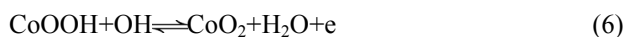


Fig. 17 CVs of Co_3O_4 product at different scan rates [94]

different cobalt oxidation states. In the case of oxidation, the two sequential reactions are described as follows [95]:



Recently, an emphasis has been given to the preparation of cobalt oxides using various physical and chemical techniques. Cobalt oxide thin films have been prepared by various methods, such as spray pyrolysis, sputtering, CVD, pulse laser deposition, sol-gel processes and electrodeposition on a variety of substrates [96,97]. Reports have proved that Co_3O_4 with a special microstructure and morphology possessed excellent electrochemical capacitive behavior. GAO et al [95] successfully prepared Co_3O_4 nanowire arrays on NF, which showed a maximum specific capacitance of 746 F/g measured at a current density of 5 mA/cm². Single crystal Co_3O_4 nanorods [98] were used as electroactive materials for supercapacitors and exhibited a high capacitance of 456 F/g. HU and LU [99] prepared aerogel-like mesoporous Co_3O_4 with an epoxide addition procedure, which exhibited a high specific capacitance of 600 F/g.

Although some improved properties have been achieved, the energy and power densities per unit area were relatively low. A 3D hybrid nanostructure, with short ion diffusion paths and an enlarged surface area, provides more efficient contact area between electrolyte ions and active materials for faradaic energy storage [100]. Carbon materials are considered as attractive electrode materials due to their superior electrical conductivity, high theoretical surface area and good electrochemical stability [86,101]. Carbon-based composites with metal oxides have been successfully synthesized for supercapacitors [102]. This could be a promising method to build better electrochemical materials.

DONG et al [103] reported a simple hydrothermal procedure which synthesized cobalt oxide (Co_3O_4) nanowires grown in-situ on 3D graphene foam using CVD (Fig. 18). The 3D graphene/ Co_3O_4 composite was used as the monolithic free-standing electrode for supercapacitor applications, it exhibited a high specific capacitance of ~1100 F/g at a current density of 10 A/g.

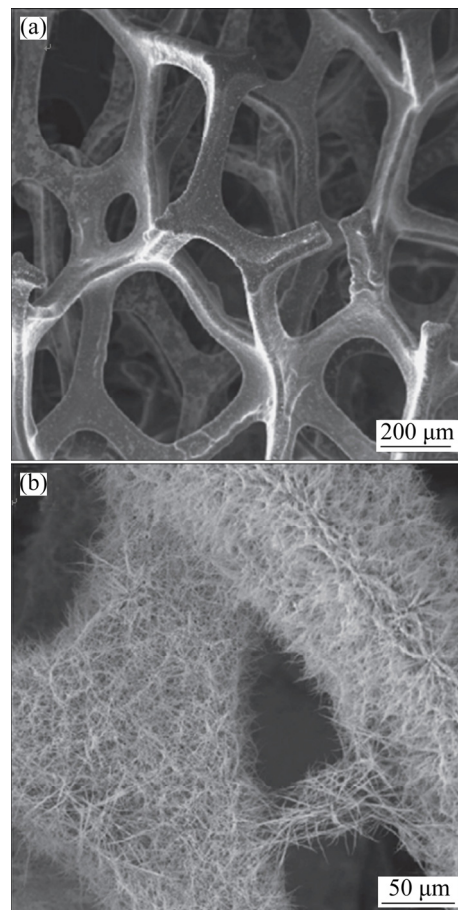


Fig. 18 SEM images of 3D graphene foam (a) and 3D graphene/ Co_3O_4 nanowire composite (b) [103]

WANG et al [104] presented the formation of porous NiCo oxide nanowires from single crystal nickel cobalt bimetallic carbonate hydroxide nanowires for supercapacitor applications. The porous nickel cobalt oxide ($\text{Ni}_x\text{Co}_{3-x}\text{O}_4$) nanowire array is formed by the heat treatment of nickel cobalt bimetallic carbonate hydroxide nanowires on NF for the assembly of supercapacitors, showing a high specific capacitance of 1479 F/g at 1 A/g.

Cobalt hydroxide ($\text{Co}(\text{OH})_2$) with layered structure, which can result in high utilization of the electrode material, exhibits higher capacitance than cobalt oxides [105].

Figure 19 shows the CV curves of the $\text{Co}(\text{OH})_2$ product. For the $\text{Co}(\text{OH})_2$ electrode material, two plausible reactions could occur as quasi-reversible redox processes during the potential sweep of the film electrode. The mechanisms of electric energy storage for

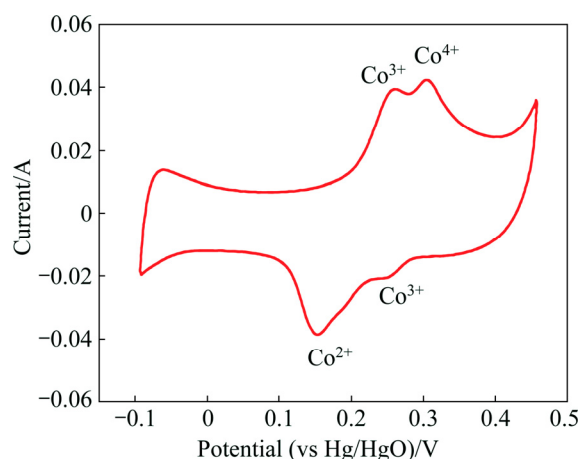
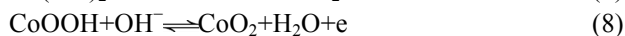
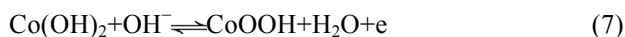


Fig. 19 CV curves of α -Co(OH)₂ at 10 mV/s [106]

the pseudocapacitor are proposed as follows:



ZHOU [107] successfully synthesized ordered mesoporous cobalt hydroxide films on substrates. Various electrochemical test results show that the ordered mesoporous cobalt hydroxide film on foamed Ni mesh has a much high specific capacitance.

2.6 Iridium oxides

In 1977, HORKANS et al [108] reported that an IrO₂ multicrystalline electrode showed distinct CV current peaks in 1 mol/L H₂SO₄, and it achieved approximately equal anodic and cathodic charges. Rutile IrO₂ has metal-like conductivity, excellent chemical stability and versatile oxidation states, and shows promising application in pseudocapacitive energy storage and electrochemical catalysis (i.e. chlorine and oxygen evolution) [109]. For example, LIU et al [110] investigated the supercapacitive properties of IrO₂ thin films prepared by radio frequency magnetron sputtering from room temperature to 300 °C. The amorphous film sputtered at room temperature exhibited the highest value of 293 F/g at 5 mV/s and retained 271 F/g after 1000 cycles.

The prohibitive price of IrO₂ has provoked much interest in compositing it with other oxides or carbon materials for practical use. GRUPIONI et al [111] reported that, compared with IrO₂ annealed at 450 °C exhibiting 21 F/g, IrO₂ in Ir_{0.3}Mn_{0.7}O₂ showed a significant increase to 410 F/g, and 550 F/g annealed at 400 °C, due to the promoted Ir active surface sites. SHAO et al [112] investigated the electrochemical performance of a binary oxide of 70% IrO₂–30%ZrO₂ coating annealed at 340–400 °C. It was demonstrated that 360 °C is the optimal annealing temperature, which produced IrO₂ nanocrystals (1–2 nm in diameter) embedded in an amorphous matrix with the highest

specific capacitance of 182.7 F/g. CHEN et al [113] grew IrO₂ nanocrystals on vertically aligned CNTs, revealing 3590 $\mu\text{F}/\text{cm}^2$, which was apparently better than 580 $\mu\text{F}/\text{cm}^2$ for just CNTs. SHIH et al [114] first grew CNTs with a honeycomb arrangement based on graphene via a CVD procedure, then decorated them with sheet-like shape IrO₂ by RFMS. The composite exhibited 139.1 F/g at 10 mV/s and 129.4 F/g after 1000 cycles at 1 mA, which showed higher specific capacitance and a more stable structure compared with IrO₂/CNT/graphene with the bundle arrangement.

3 Transition metal nitrides

Transition metal nitrides, such as TiN, VN, WN, MoN_x, Nb₄N₅, TaN and CrN, can be used as pseudocapacitor electrode materials. In 1985, VOLPE et al [115] found that a temperature-programmed reaction between MoO₃ or WO₃ with NH₃ could produce Mo₂N and W₂N powders with specific surface areas as high as 220 and 91 m²/g, respectively, thereby providing a new direction for transition metal nitride research in the field of catalysis. As a result of such research, a broad range of application prospects for transition metal nitrides have been discovered. They have excellent electrochemical performance, good electrochemical stability and are stable in aqueous electrolyte. Moreover, the raw materials are low cost, meaning that transition metal nitrides have become a hot topic in the field of supercapacitor electrode materials.

The synthesis of transition metal nitrides is usually divided into physical synthesis and chemical synthesis [116]. Physical synthesis mainly includes ball milling, physical vapor deposition and laser vaporization, which can only composite several transition metal nitrides, such as TiN and CrN. Metal oxides or other metal precursors can be used as raw materials, and ammonia gas or nitrogen can be used as the nitrogen source at high temperatures (800–2000 °C) [117], which can be widely used in the preparation of nitrides.

These nitrides exhibit similar electrochemical behavior to that of RuO₂ and show capacitive behavior at high scan rates due to their high electronic conductivity and fast reversible redox process. Among all the transition metal nitrides, only VN, TiN and MoN_x have shown relatively good capacitance [118]. Currently, VN, TiN and its complex have a wide range of applications in supercapacitors. The theoretical specific capacitance is calculated by Eq. (9) (n is the change of valence states, F is the faraday constant, V is voltage window and M is relative molecular mass), and the calculated results are shown in Table 2.

$$c = \frac{nF}{VM} \quad (9)$$

Table 2 Relevant data for transition metal nitrides

Transition metal nitride	Relative molecular mass	Change of valence state	Voltage window/V
TiN	62	1	0.6 (−0.3 to 0.3)
VN	65	1	1.2 (−1.2 to 0)
MoN	110	1	0.7 (0–0.7)
Nb ₄ N ₅	442	2	0.6 (0–0.6)
RuN	115	2	1 (−0.5 to 0.5)
CrN	66	1	3 (0–3)
CoN	73	1	3 (0–3)

3.1 Titanium nitrides

As one of the most common nitrides, TiN and its complex are widely used as pseudocapacitor electrode materials. Though TiN has a minor capacity, its electronic conductivity is proved to be excellent, and is usually used as a current collector. LI et al [119] prepared mesoporous TiN through a solvothermal reaction and a short-time nitridation process (Fig. 20(a)). The surface area of TiN reached 50.6 m²/g and the pore sizes are in the range of 2–4 nm.

DONG et al [120] fabricated mesoporous TiN spheres through a facile template-free strategy. Under an ammonia atmosphere, mesoporous TiO₂ spheres are directly converted into mesoporous TiN spheres with the addition of cyanamide to retain the original morphology. The energy density of TiN can reach 45 W·h/kg at a power density of 150 W/kg, and still remains 12.3 W·h/kg at a power density of 3 kW/kg, which shows that mesoporous TiN and its complex have great potential. By modifying and loading, its performance can be further improved.

The TiN nanotube arrays can provide a large surface area, fast electron transport and can enhance structural stability. XIE et al [121] prepared TiN nanotube arrays with a short nanotube and long nanopore structure by anodizing ultra-thin titanium foil in an

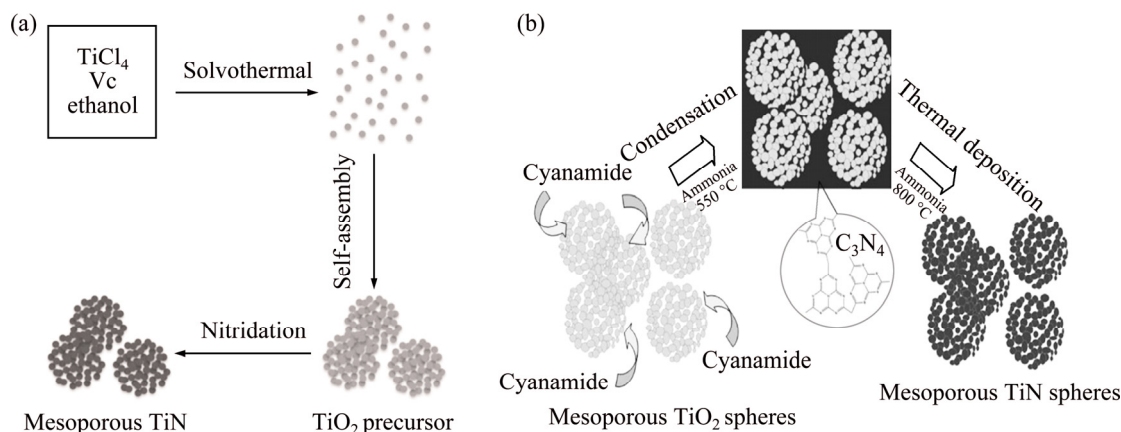
ethylene glycol solution containing ammonium fluoride, calcining in air and nitriding in ammonia. The specific capacitance of the TiN nanopore array reached an extraordinarily high level of up to 99.7 mF/cm² at a current density of 0.2 mA/cm², which is a significant improvement on the TiN nanotube array. At a high current density of 5 mA/cm², the TiN nanoarray supercapacitor maintained a specific power of 8.15 mW/cm² (204 mW/cm³) and a specific energy of 35.98 (mW·s)/cm² (900 (mW·s)/cm³). The power and energy densities of the flexible TiN nanoarray supercapacitor are higher than those of the traditional activated carbon supercapacitor.

By compounding with other electrochemical materials, the performance of TiN has been improved. PENG et al [122,123] successfully fabricated PANI or MoO_x on the outer and inner surfaces of TiN nanotubes to form an interpenetrating 3D network, forming PANI/TiN or MoO_x/TiN NTA hybrid nanostructures (Fig. 21(a)).

Coaxial PANI/TiN/PANI nanotube arrays were fabricated by electrochemical polymerization of PANI on nanoporous TiN nanotube arrays. They exhibit a high specific capacitance of 242 mF/cm², excellent rate capability with the capacitance remaining at 69% when the current density increases from 0.2 to 10 mA/cm², and a long cycling life with less than 0.005% decay per cycle.

Porous dual-layered MoO_x NTAs with highly conductive TiN cores were fabricated by depositing MoO_x on porous TiN. The coaxial MoO_x/TiN/MoO_x NTA electrode shows a high specific capacitance of 97 mF/cm² (323 F/g) at a current density of 1 mA/cm², and still retains 60% capacitance when the current density is increased 20 times.

MnO₂–TiN nanotube hybrids were prepared by loading electroactive MnO₂ into well-aligned TiN nanotubes through a cyclic voltammetry electrodeposition process, which was directly supported on ultra-thin

**Fig. 20** Schematic illustration for preparation of mesoporous TiN [119]

and supply titanium foil. Due to the coaxial heterogeneous structure, the specific capacitance of $\text{MnO}_2\text{-TiN}$ was determined to be 853.3 F/g (213.2 mF/cm^2) at a current density of 1 A/g (0.25 mA/cm^2) [124].

SHANG et al [125] prepared $\text{Ni}_x\text{Co}_{2x}(\text{OH})_{6x}/\text{TiN}$ by directly depositing $\text{Ni}_x\text{Co}_{2x}(\text{OH})_{6x}/\text{TiN}$ into a self-standing TiN NTA grid monolithic (Fig. 21(b)). It exhibits superior pseudocapacitive performance due to the coaxial nanostructure. The specific capacitance reaches 2543 F/g at 5 mV/s , the rate performance reaches 660 F/g at 500 mV/s , and a loss of only about 6.25% capacitance after 5000 cycles is observed, which are much better than for the $\text{NiCo}_2\text{O}_4/\text{TiN}$ electrode.

LU et al [126] produced TiC@C by coating a uniform and ultrathin carbon shell to the TiN nanowire surface through hydrothermal methods, followed by annealing at 800°C in a N_2 gas atmosphere (Fig. 22).

3.2 Vanadium nitrides

Among the various options, nanocrystalline VN, which has been reported to deliver a specific capacitance of up to 1340 F/g at a scan rate of 2 mV/s , and still maintain 554 F/g at a higher scan rate of 100 mV/s [127], is clearly one of the most promising candidates for pseudocapacitors. Nanocrystalline VN has been synthesized by a two-step ammonolysis reaction of VCl_4

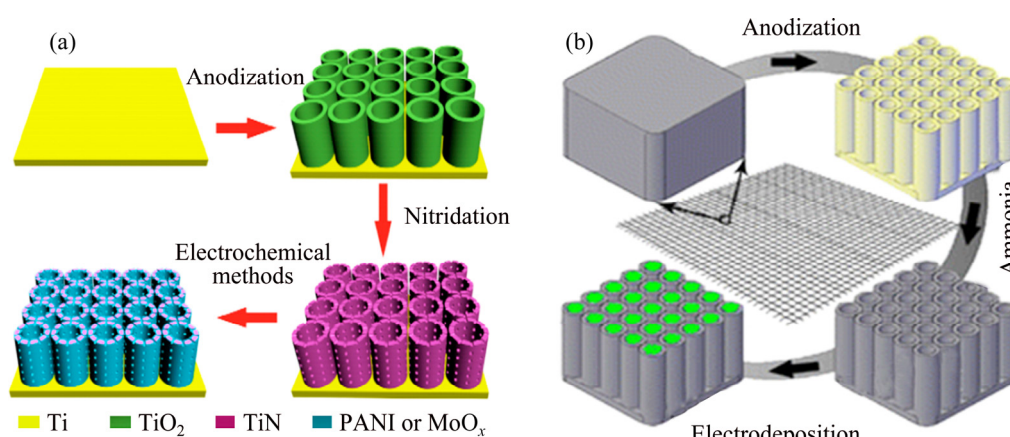


Fig. 21 Fabrication process of TiN-based composite nanostructures (a) and $\text{Ni}_x\text{Co}_{2x}(\text{OH})_{6x}/\text{TiN}$ (b) [120]

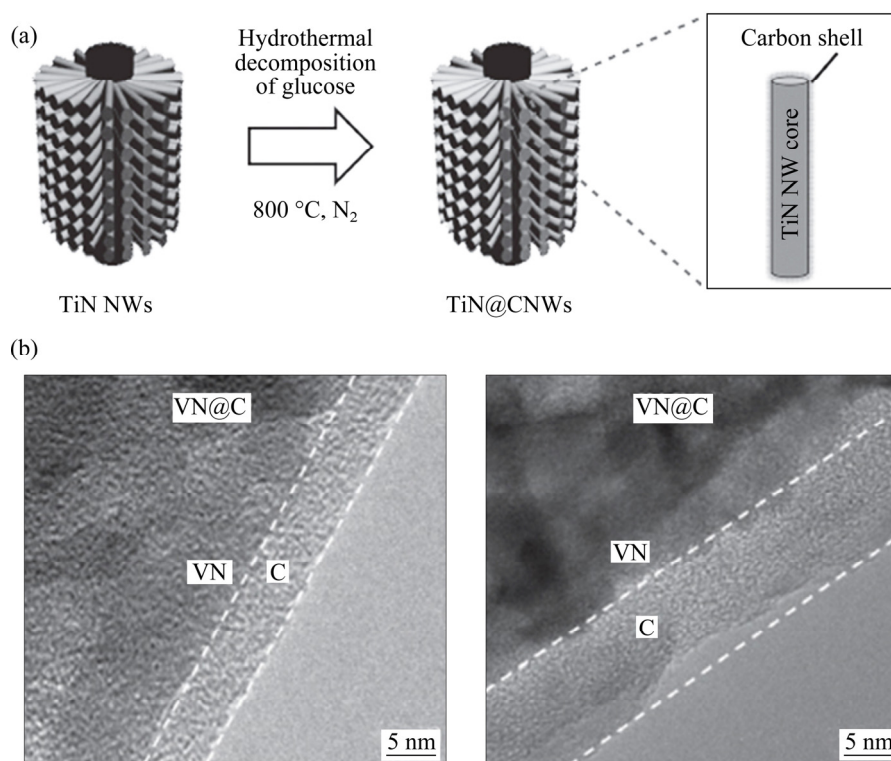


Fig. 22 Schematic illustration (a) of process of applying carbon shell to TiN NWs and HRTEM images of VN@C (b) and VN@2C NWs (c) [126]

in anhydrous chloroform. Such a high capacitance is obtained due to the pseudocapacitance contribution from the low specific surface area of nitride ($38 \text{ m}^2/\text{g}$) [128].

ZHOU et al [129] found another way to produce VN powder by calcining V_2O_5 xerogel in a furnace under an anhydrous NH_3 atmosphere at 400°C . The specific capacitance of VN reached 161 F/g at 30 mV/s . Furthermore, 70% specific capacitance remained when the scan rate was increased from 30 to 300 mV/s . GLUSHENKOV et al [130] used the same method to produce VN and capacitance of 186 F/g was obtained at 1 A/g . The large volume of pores in VN is represented by the range of $15\text{--}110 \text{ nm}$.

VN was reported to exhibit an excellent electrochemical performance, especially with regards to specific capacity. However, it also exhibits poor electronic conductivity, resulting in its limited rate capability. To improve the performance of VN, the fabrication of hybrid devices based on VN has become a new and promising strategy. SU et al [131] prepared VN-MWCNT by annealing V_2O_5 mixed with pre-treated CNTs at 800°C in a N_2 gas atmosphere for 3 h. The

results indicate that VN-MWCNT electrodes exhibit good capacitance retention, good cycling stability and a high specific capacitance of 160 F/g at a scan rate of 2 mV/s .

DONG et al [132] combined VN and TiN to seek both faster electronic transportation and excellent storage performance, since both VN and TiN feature the same diffraction patterns and similar cell parameters. TiN/VN core-shell composites were prepared by a two-step strategy involving coating the commercial TiN nanoparticles with V_2O_5 sols followed by ammonia reduction (Fig. 23). The highest specific capacitance of 170 F/g was obtained at a scan rate of 2 mV/s and a promising rate capacity performance is maintained at higher voltage sweep rates.

ZHANG et al [133] synthesized 3D electrochemically supercapacitive arrays, the multiwalled carbon nanotubes covered by nanocrystalline VN were firmly anchored to glassy carbon or Inconel electrodes (Fig. 24). These nanostructures demonstrate a respectable specific capacitance of 289 F/g at a scan rate of 20 mV/s , and at least 80% capacitance still remains at

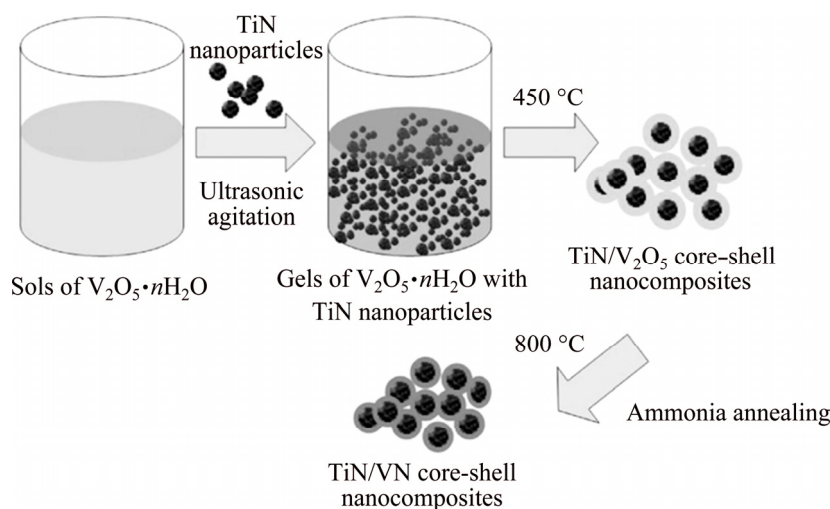


Fig. 23 Schematic illustration of preparation of TiN/VN nanocomposites [132]

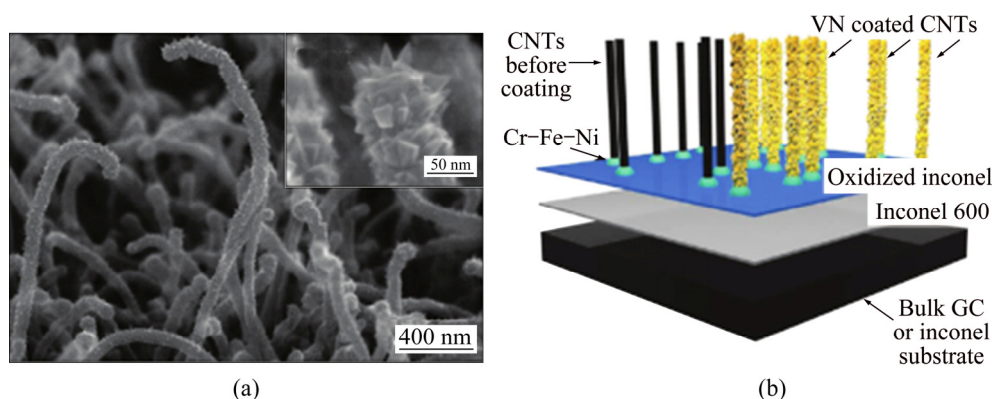


Fig. 24 SEM images of VN/CNT/Inconel/GC (VN mass = 0.037 mg/cm^2) (a) and schematic illustration of preparation of ultimate morphology of VN/CNT 3D array (b) [133]

20 mV/s, which is the highest rate capability reported for VN materials. Analysis of the post-electrochemically cycled samples indicates negligible changes occurring in the VN nanocrystallite morphology, but a modification in the structure of the oxidized surface.

3.3 Molybdenum nitrides

In 1995, FINELLO et al [134] applied Mo₂N/MoN films, produced by ammonolysis of MoO₃, to supercapacitor electrode materials for the first time. These compounds are stable in aqueous H₂SO₄. Their redox behavior is similar to that of RuO₂ [135], but their capability was limited due to their smaller electrochemical window of ~0.7 V compared with the ~1.4 V for RuO₂. The most studied nitrides of molybdenum are the rocksalt-type γ -MoN_x ($x=0.39$ – 0.54), also known as γ -Mo₂N [136]. There are another three types of molybdenum nitrides, including δ_1 -Mo₂N, δ_2 -Mo₂N and δ_3 -Mo₂N [137].

IMRAN et al [138] produced cubic γ -Mo₂N and hexagonal δ_1 -MoN through the reactions of MoCl₅ or Mo(NMe₂)₄ with ammonia at different temperatures and reaction times (Table 3). Most molybdenum nitrides show relatively smaller surface areas and capacitances, while their redox capacitance are high enough to be used in charge storage devices. The highest capacitances can reach 275 F/g at 2 mV/s, indicating that it can be used as a pseudocapacitor electrode. A MoN/nitrogen-doped graphene sheets composite delivers specific capacitance of 422 F/g at the current density of 0.05 A/g, and can maintain more than 80% after 900 cycles [139]. The energy density remains as high as 32.5 W·h/kg when the power density is 3000 W/kg. However, due to its lower working voltage window in water electrolysis systems and low density, its performance cannot be fully utilized.

3.4 Niobium nitride and other transition metal nitrides

Some niobium nitrides, including Nb₂N, Nb₄N₃ and NbN, are famous for their excellent superconducting properties [140]. Recently, CUI et al [141] found

Table 3 Refined parameters and analytical data for molybdenum nitride samples produced by pyrolysis of imide precursor [138]

Temperature/ °C	Heating time/h	Crystallite size/nm	Composition	Surface area/ (m ² ·g ⁻¹)
1000	2	14 or 28	MoN _{0.58}	2
900	2	4.4 or 14	MoN _{0.80}	2.8
800	2	8.8	MoN _{0.84} C _{0.03}	3.1
700	2	6	MoN _{0.81} C _{0.03}	4.9
600	2	4	MoN _{0.83} C _{0.05}	9.8
500	2	4	MoN _{0.74} C _{0.08} H _{0.5}	9
500	48	4	MoN _{1.02}	8

nitrogen-rich Nb₄N₅ phases that comprise high valence Nb⁵⁺ ions and could be a new high-performance electrode material for supercapacitors. Nb₄N₅ is proved to have a capacitance of 225.8 mF/cm² for the first time, and Nb₄N₅ nanochannels electrode remains 70.9% capacitance after 2000 cycles, moreover, it shows nearly 100% capacitance retention after 2000 CV cycles when coating an ultrathin carbon to the surface (Fig. 25). This new advanced material can also be used as a support to deposit other electrochemical active materials and is expected to be useful for industry applications.

There are many other transition metal nitrides that can be regarded as excellent pseudocapacitor materials, such as chromium nitride, cobalt nitride, ruthenium nitride and so on. DAS et al [142] prepared CrN and CoN nanoparticles of particle size 20–30 nm from Cr₂O₃ and Co₃O₄ at relatively low temperature under a NH₃+N₂ atmosphere. The specific capacitances of CrN/AC and CoN/AC are, respectively, 75 and 37 F/g at a current density of 30 mA/g. CrN/AC showed almost stable performance, while the capacitance of CoN/AC fade quickly. The energy densities of CrN/AC and CoN/AC calculated from galvanostatic cycling were 30 and 44 W·h/kg, respectively. BOUHTIYYA et al [143] use sputtered ruthenium nitride thin films as electrode material, and the capacitance shows 37 F/g at a scan rate

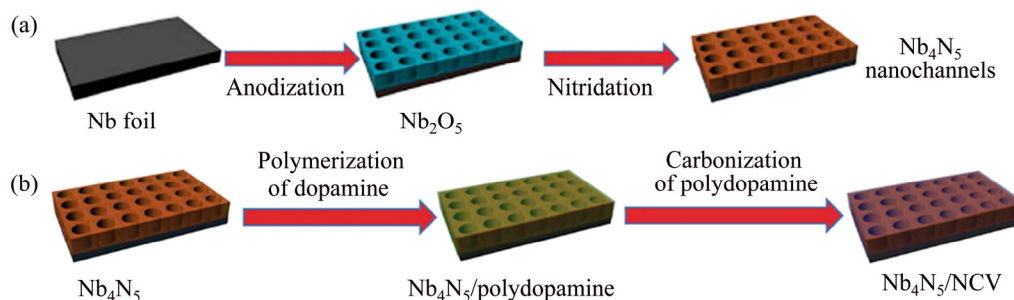


Fig. 25 Schematic illustration of fabrication of Nb₄N₅ nanochannels (a) and N-doped carbon coating on surface of Nb₄N₅ nanochannels (b) [141]

of 200 mV/s. Those preparation methods can be tried to open up other new nitrides or hydroxide systems, such as Ti, W, Zr and Ta.

4 Summary and outlook

Several pseudocapacitor electrode materials, including transition metal oxides and nitrides, have been discussed along with the fabrication challenges involved with increasing energy density.

Different from EDLCs, whose performance is limited by low-capacitance carbon materials, pseudocapacitors have much higher energy density and wide application prospects. Since protons, electrons and ions transmission are required for an efficient exploitation of pseudocapacitance, appropriate microstructure and morphology control for transmission channels is necessary. Nowadays, nanofabrication technology has enabled the development of nanoarchitected electrodes, where the oxide or nitride component was deposited in various forms, such as nanorods, nanoflowers, nanoflakes, nanosheets, nanoparticles, etc. The specific capacitance of various pseudocapacitor materials or its composites and carbon materials are shown in Fig. 26. Metal oxides and nitrides have much higher practical specific capacitance than those of carbon and conducting polymers. Research into transition metal oxides is relatively mature, while for transition metal nitrides, their potential application has yet to be exploited.

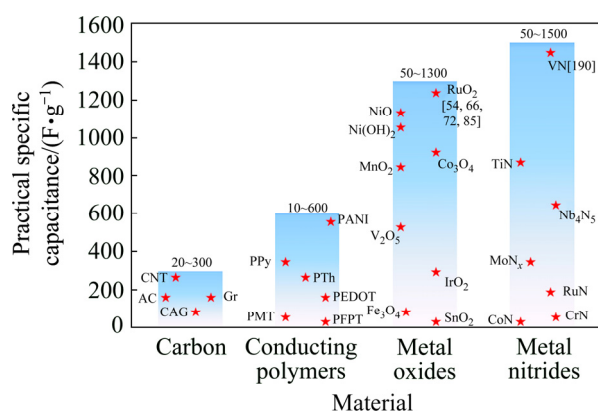


Fig. 26 Specific capacitance of various pseudocapacitor materials (or their composites) and carbon materials

To improve the relatively low conductivity and cycling stability, several electrochemical active materials are composited with transition metal oxides and nitrides. Taking into account the mechanism involving the surface, as well as the bulk of metal oxides or nitrides, the diffusion of protons accompanying the charge transfer must be ensured by the presence of mesoporous structure. Building a hierarchical structure of the

composite could develop the specific surface area of oxides or nitrides maximally. Carbon materials are excellent accessible candidates with relatively high specific surface areas to act as perfect supports for such pseudocapacitive materials. Also, well-distributed carbon in the composite can greatly enhance the low conductivity of transition metal oxides and nitrides. However, compounding carbon with metal oxides or nitrides still requires considerable effort to avoid adversely affecting the overall performance of the composite. Multitudinous carbon materials provide plenty of possibilities. It is still difficult to monitor the characteristics, such as surface area, pore size/distribution, density and conductivity, to optimize composite properties, as many of these properties can be mutually exclusive.

The application of such a redox-active reaction presents a new attractive trend in capacitor development to increase both the energy density and the power density. Pseudocapacitor electrode materials have shown excellent performance and great potential. As research goes further, lighter, smaller, higher energy and more stable electrochemical pseudocapacitors will be realized in the near future, which will play an important role in the field of energy storage and conversion.

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过渡金属氧/氮化物赅电容器电极材料的研究进展

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摘 要: 法拉第赅电容器兼具二次电池高能量密度和超级电容器高功率密度的优点, 而电极材料是决定法拉第赅电容器性能的关键。过渡金属氧化物/氮化物作为两种主要的赅电容器电极材料, 能在提高能量密度的同时保持高功率密度。本文综述钽氧化物、镍氧化物、锰氧化物、钒氧化物、钴氧化物、铌氧化物等过渡金属氧化物和钛氮化物、钒氮化物、钼氮化物、铌氮化物等过渡金属氮化物的纳米结构设计和高比表面积复合材料制备的最新进展, 为法拉第赅电容器电极材料的深入研究提供重要的借鉴意义。

关键词: 赅电容器; 过渡金属氧化物; 过渡金属氮化物; 功率密度; 能量密度

(Edited by Xiang-qun LI)