Review Article

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Recent progress in supercapacitors based on the advanced carbon electrodes

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Abstract: This paper demonstrates a brief review of the research progress of the advanced carbon-based materials for the supercapacitor electrodes. Diverse types of carbon-based electrodes exploited and reported to the literature are summarized and classified into pure carbon electrodes, carbon/metal oxides composite electrodes, carbon/metal oxides/conducting polymers composite electrodes as well as carbon electrodes based on other materials. Pure carbon electrodes are firstly introduced, confirming their merits and shortcomings. To cover the shortage of pure carbon electrodes and further enhances their electrochemical performance, a composite electrode, combined with metal oxides and conducting polymers, is respectively presented. It is worth noticing in this article that combining various materials to form composites has been one main direction to own a positive synergistic effect on the carbon-based electrodes.

Keywords: supercapacitor; carbon electrode; composite electrode

1 Introduction

The past decades have witnessed the increased demands for energy. Petroleum-based fuels are primarily used for the power needs of the society. With limited petroleum resources, there is an urgent need for alternate energy sources. As a result, in recent years, there has been a growing interest in high power and efficient energy density storage devices and systems. An example of such a device is the supercapacitor, known as an electrochemical supercapacitor or an ultracapacitor.

Supercapacitor has attracted considerable interest in both academia and industry due to some distinct advantages such as high power density induced by a prompt charging/discharging rate and a long cycle life in contrast to batteries and fuel cells. As supercapacitors supply hundred to thousand times higher power in the same volume, they are unable to store the same amount of charge as batteries do, usually 3-30 times lower. This necessitates coupling with cells for applications call for energy supply for more extended periods [1]. Thus, supercapacitors are appropriate for those applications in which power bursts are needed but high energy storage capacity is not required [2], or can be included within a battery-based ESS to decouple the power and energy features on the ESS, ameliorating the sizing while fulfilling the power and energy demands and perhaps enlarging its lifetime.

Depending on the charge storage mechanism, the supercapacitor can be briefly classified as electrochemical double-layer capacitors (EDLCs), pseudocapacitors and hybrid capacitors. Compared to both pseudocapacitors and hybrid-capacitors, chiefly due to their technical maturity, EDLCs constitute the majority of currently available commercial energy storage systems. In EDLCs, the energy storage and release mechanism are based on nanoscale charge separation from the electrochemical interface formed between an electrode and electrolyte [3]. The charge storage mechanism is nonfaradaic, and no chemical oxidation-reduction reactions are involved. EDLCs have correlatively long cycle lives since only physical charge transfer occurs. In contrast, pseudocapacitors are based on faradaic redox reactions including high energy electrode materials grounded in metal oxides, metal-doped carbons, or conductive polymers, which contribute supercapacitors to higher energy density [4]. Consequently, pseudocapacitors usually offer higher energy density at the price of shorter cycle lives and lower rates than EDLCs. As the name indicates, the hybrid supercapacitor incorporates mechanisms from both EDLCs and pseudocapacitors. The power output of supercapacitors is lower than that of electrolytic condensers but is capable of ex-

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tending to 10 W h kg^{-1} for EDLCs and even 50 W h kg^{-1} for both pseudocapacitors and hybrid- capacitors [5].

Supercapacitors can be fabricated from diverse materials depending on the type of energy storage required by the application at hand and demanded capacitance scopes. The electrode materials for supercapacitors can be classified into three subsections comprising carbon-based materials, metal oxides, and conducting polymers, according to their usage for EDLCs, pseudocapacitors and hybrid supercapacitors. As a significant commercial material, carbon is extensively used and can be converted into numerous forms [6]. Other materials include metal oxides such as nickel, cobalt, manganese, and ruthenium [7–11]. In recent years, carbon nanotubes (CNTs) are increasingly employed in supercapacitors. The use of CNTs and other nanomaterials allows for a remarkable increase in surface area, among other pros [12]. The other types of frequently-used supercapacitor materials are composites attained by two or more constituent materials, which can include a nanomaterial. For instance, a composite is constituted by incorporating CNTs with conducting polymers or metal oxides.

To expand the application scope of these materials, substantial work has been devoted to improving the energy density of supercapacitors practically, increasing either or both of the capacitance and cell voltage. They can be achieved through the progress of electrode materials with high capacitance, electrolytes with huge potential windows, and integrated systems with a new and optimized structure. Up to now, these advancements can be briefly summarized as follows. The specific capacitance of carbon-based electrodes gets increasing as a novel carbon structure develops, with an extremely active specific surface area and a high packing density [13]. Pseudocapacitors based on pseudocapacitive materials is developing with high specific capacitance contributed from the pseudo-capacitance, such as some electroactive transition-metal oxides [14] and conducting polymers [15]. The cell voltage is enlarging via the advancement of a novel electrolyte. Supercapacitors with novel structures or new concepts are being explored, such as the hybrid capacitors, especially the lithium-ion capacitors [16].

This article aims to overview the recent progress in advanced carbon-based electrodes that simultaneously possess high power density, high energy and excellent rate capability and cyclic stability. In the past decade, carbon materials were engineered to combine with various materials, such as metal oxides and conducting polymers, to form composites for supercapacitor electrodes. Hence, this review article will be arranged based on the following four parts in the carbon-based electrodes, including pure carbon electrodes, carbon/metal-oxides composite electrodes and carbon/metal-oxides composite electrodes as well as combinations with other materials.

2 Pure carbon electrodes

Pure carbon materials are currently regarded as prospective electrode materials for industrialization. The preponderances of pure carbon materials comprise the higher specific surface area, excellent electronic conductivity, high chemical stability, wide operating temperature range, etc [17–19]. Typically, carbon materials store charges primarily in an electrochemical double-layer formed at the interface between the electrode and the electrolyte, instead of storing them in the bulk of the capacitive material. Thus, the capacitance principally depends on the surface area accessible to the electrolyte ions [20]. The two significant factors affecting their electrochemical property include specific surface area and pore size distribution. Pure carbon materials with larger specific surface areas show a higher capability for charge accumulation at the interface between the electrode and electrolyte [21]. Numerous approaches have been researched to increase the specific area, which is commonly characterized by effectively making micropores and defects on the carbon surface. As for pore size distribution, there is still no universal agreement about the effect of optimal pore size on the performance of carbon electrode materials. However, either the pore size of 0.4 or 0.7 nm may be appropriate for aqueous electrolytes, while that of 0.8 nm is better for organic electrolytes [22, 23].

Ru-Juan Mo *et al.* [24] presented the production of activated graphene-like carbon beginning from sheet cellulose attained by a simple approach of ball milling. The unique pore structure contributed to the specific surface area value of up to 2045 m^2/g, offering adequate storage sites and channels for electrolyte species. The large specific surface area and hierarchical pore size distribution of the carbon electrode supercapacitor indicated highest gravimetric and volumetric capacitances of 353 F/g and 309.7 F/cm^3 at 1 A/g in a three-electrode system utilizing aqueous electrolyte. As Figure 1a illustrates, the quasi-rectangular shape is retained with little distortion at the scan rate up to 200 mV/s, indicating the excellent rate capability due to the low inner resistance and fast electrolyte ions diffusion owing to the hierarchical pore structure of graphene-like porous carbon. Figure 1b illustrates highly symmetrical and linear patterns, confirming excellent electrochemical reversibility and columbic efficiency. These unique properties make the chemically activated carbon

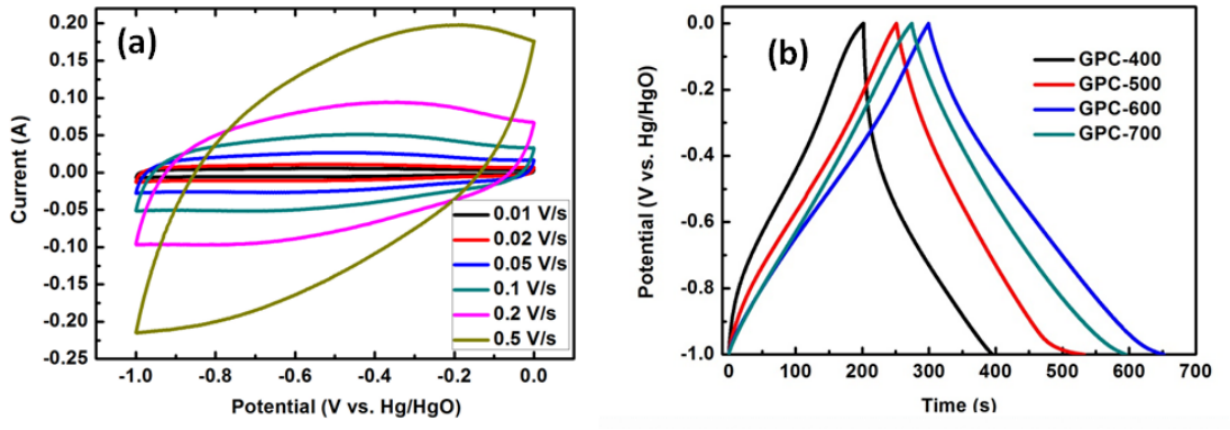

Figure 1: Electrochemical characteristics of GPC in a three-electrode system in 6M KOH. (a) CV of GPC-600 at various scan rate. (b) Galvanostatic charge-discharge curves at 1 A/g.

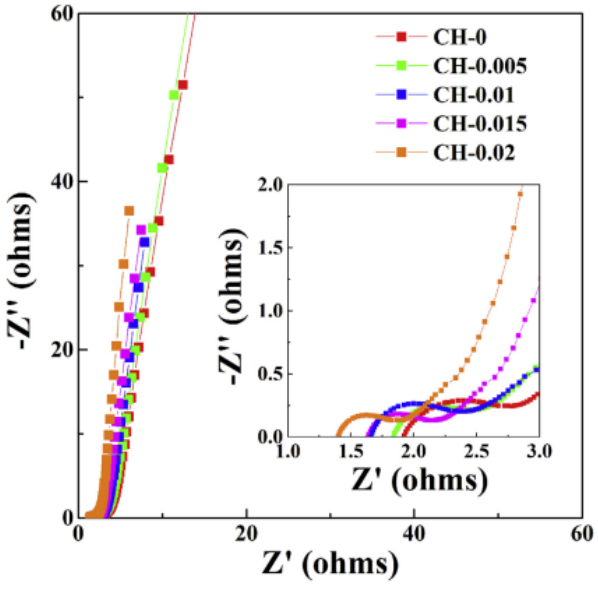

Figure 2: The Nyquist plots of CH-Xs samples that measured at an AC of 5 mV.

from sheet-like cellulose a potential and useful candidate for supercapacitors.

Chunfeng Xue *et al.* [25] produced graphitic porous carbon by directly carbonizing Ni cation-exchanged resin at a moderate temperature of 800°C. The similarly dispersed Ni nanoparticle not only well acted as the catalyst for the commercial resin graphitization, but also took part in manufacturing matched micropore and mesopore structure. The graphitic carbon exhibiting stable microporosity and mesoporosity at the ratio of 1:2, supplied a superior specific capacitance 66 μF/cm^2 and high volumetric capacitance of 552.6 F/cm^3 at the current density of 0.5 A/g in the electrolyte of 1 M H_2SO_4. In the double-electrode system, the graphitic carbon presented high energy density of 7.43 Wh/kg at a power density of 125 W/kg. The electrode basing on the graphitic carbon finally revealed 95% specific capacitance retention after 400 h utilizing the grid floating technique but also 10000 cycles of GCD measurement at the current density of 5.0 A/g, further indicating excellent cyclic stability. Taking into account the broadly acceptable standards to measure end-of-life for the supercapacitor, the graphitic carbon is extremely promising and potential for supercapacitors.

Cheng Lu *et al.* [26] demonstrated the viable preparation of carbon materials originated in pollen with the help of hydrothermal processing and pursuant carbonization. The evaluation of the electrochemical performance of the adopted samples was illustrated in Figure 2. The Nyquist plots of CH-Xs attained in a frequency varying from 0.01 Hz to 100k Hz at an AC of 5 mA with the open circuit possibility. The resistance of the CH-Xs was decreased by treating with more NH_4BF_4. The adjacent lines in the low-frequency range revealed a characteristic capacitive behavior of the samples. Finally served by 0.015 g/ml NH_4BF_4 during the process of hydrothermal, the sample presented the highest specific area of 526 m^2/g together with the largest specific capacitance of 205 F/g at a current density of 0.5 A/g in 2M KOH solution. After 10000 cycles 96% of the initial capacitance of CH-0.015 still existed, mirroring its superior cycling property.

Though high capacitance is generally achieved at a low current density, a considerable loss in capacitance is attained at high current density, giving rise to reduced rate performance. The poor rate performance is chiefly sluggish ion diffusion within micropores, which is not capable of catching up with the fast rate of charging and discharging [27, 28]. In order to address this issue, Yan Zhong

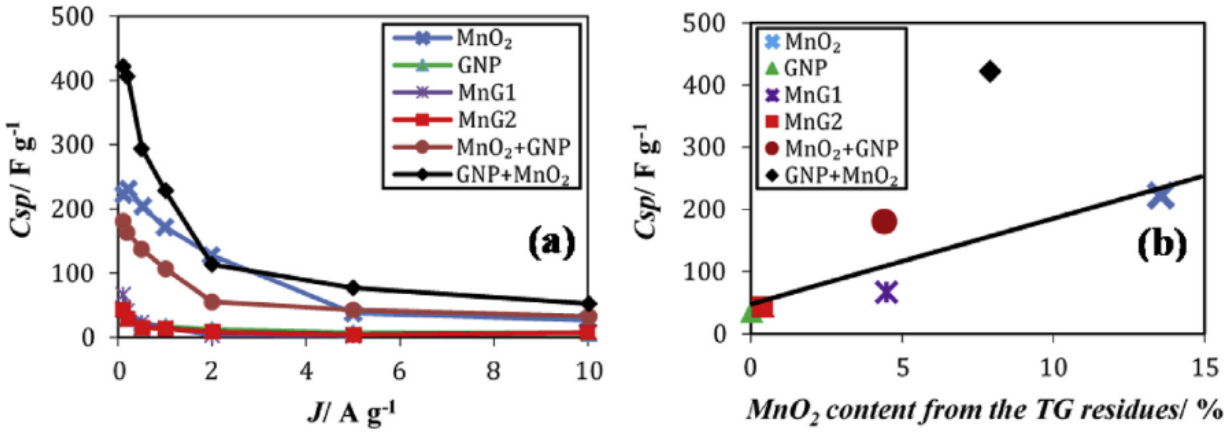

Figure 3: (a) Dependence of the specific capacitance as a function of the current density and (b) dependence of specific capacitance measured at 0.1 A/g as a function of the MnO_2 content deduced from the residue of the thermogravimetric analyses.

et al. [29] prepared a novel low-cost and straightforward binder-free activated carbon electrode that derived from starch on the carbon cloth through a plain sol-gel and carbonization approach and still conducted excellent conductivity at high current density. The binder-free electrode was attained by the following procedure, including making full use of the viscosity of the gel, soaking the precursor in the carbon cloth, and final carbonization. In that work, the different mass of KOH was utilized to tune the porosity of carbon electrode, thus attaining a high surface area where electrolyte was accessible, which could assure a high capacitance at lower current densities. With the current densities increasing, the binder-free electrode offered an excellent conductivity, enabling a broader voltage window for energy storage. Meanwhile, the multiple synergistic influences of its porous carbon structure and the production approach free of binder brought about a high rate performance. For instance, the gravimetric capacitance of the optimized binder-free electrode was up to 272 F/g at a current density of 1 A /g, and 75.9% gravimetric capacitance retention remained at a superhigh current density of 50 A/g. The porous carbon structure, as well as the low-cost and straightforward design, lays the foundation for manufacturing supercapacitors with enhanced rate capability.

These carbon supercapacitors mentioned above are typically made in two steps. While they demonstrate superior properties, the high-cost two-step technique is far inferior to one step in advantages of the competition of supercapacitors with lithium-ion batteries in numerous applications [30]. Lixing Zhang *et al.* [31] fabricated activated carbon via simple one-step calcination of deoxygenated agar in a hot KOH aqueous solution. KOH, simultaneously mixed with agar in the hot solution by a soft chemical approach, played both deoxidant and activation agent, which left out high-temperature carbonization in the traditional techniques and gave rise to molecular level activation of agar in subsequent one-step calcination. The one-step activated carbon had a superior specific surface area of 1672 m^2/g and total pore volume of 0.81 cm^3/g, naturally higher than those of the activated carbon by the traditional two-step approach. Consequently, the maximum specific capacitance in the KOH electrolyte for one-step activated carbon was 226 F/g, 1.4 times as high as that for the traditional two-step method. However, it was worth noticing that one-step activated carbon, only retained 80% of the initial capacitance in the $EMIMBF_4$ electrolyte, which presented a fleet deterioration and relative narrow potential window.

3 Carbon/metal-oxides composite electrodes

At present, the electrodes of most commercial supercapacitors are composed of carbon that is at low cost and has excellent resistance to corrosion. These carbon-based supercapacitors are characterized by superior cyclic stability and long service lifetime due to no chemical change occurring during the charge/discharge processes [18, 19, 32–36]. However, their maximum capacitance is limited by the pore size distribution and the positive electrode surface area, and their low energy density cannot satisfy the need of energy storage devices for solar power plants, wind farms, and even vehicles [37–39]. In order to enhance the specific capacitance and the energy density, metal oxides, especially transition metal oxides, are being considered as the particular materials for supercapacitor elec-

trodes. But metal oxides are not appropriate to be adopted alone as the supercapacitor electrodes for practical intentions attributed to the following reasons such as the low conductivity of most metal oxides except for RuO2 and the high resistivity of metal oxides leading to a large IR loss at a high current density, etc [40]. Thus, it is reasonable to develop carbon/metal oxides composite electrodes, which combines the pros and obtunds the cons of both the components. In such electrodes, the carbon nanostructures play a significant role in the physical support of metal oxides and offer the channels for charge transport. The electronic activities of metal oxides that are the core sources storing the charge and energy help to high specific capacitance and high energy density. A synergistic effect of carbon/metal-oxides composite electrodes is expected [41].

Xu Ma *et al.* [42] fabricated RuO_2/activated carbon (RuO_2/AC) composite electrodes for high-performance capacitive deionization (CDI). In this CDI process, salt ions were removed by a mixed EDL capacitive-faradaic process. Due to its high cost, RuO_2 was electrodeposited onto inexpensive AC though cyclic voltammetry to optimize production of the composite electrode RuO_2/AC. As demonstrated, the RuO_2/AC composite electrode had the highest specific capacitance of 60.6 F/g, which was almost twice as high as that of the AC electrode. This improvement was primarily attributed to the contribution of RuO_2, which participated in faradaic redox responses to store Na^+ ions, while AC maintained a high specific surface area with 576 m^2/g for capacitive electrosorption. The electrochemical measurements further proved that the electrical resistance was effectively decreased by the electrodeposition of RuO_2 in the composite electrode, ensuring fast charge transport during capacitive applications. Furthermore, as evidenced, the RuO_2/AC composite had a hopeful salt adsorption capacity of 11.26 mg/g 3.7-fold higher than that of initial AC. In general, RuO_2/AC composites are promising electrode materials as cathodes in CDI, and new opportunities for constructing novel composite electrodes utilizing the faradaic ion storage to achieve high-performance CDI are provided.

Juan A *et al.* [43] fabricated diverse configurations of electrodes made from MnO_2 and graphene nanoplatelets (GNP) by aqueous electrophoretic deposition (EPD) processes onto graphite paper. The electrodes were prepared either sequentially, continuously depositing the suspension of each material or synchronously, from suspensions of mixtures of the two materials, MnO_2 and GNP. The deposition of the MnO_2 particles on to the deposited in advance GNP electrodes denoted as GNP+MnO_2, enhanced the specific capacitance (422 F/g) of the deposited oxide, as was shown in Figure 3. The specific capacitance of the electrodes except for the GNP+MnO_2 electrode increased with the enhancement of the MnO_2 content based on the rule of mixtures. The symmetric supercapacitor cell assembled with two equal GNP+MnO_2 electrodes was the best performant in terms of the specific energy, exhibiting a maximum value of 9.2 Wh/kg and specific power up to 1.8 kW/kg for 0.1 and 10 A/g respectively. The highest specific energy values are favorably achieved in cells built with electrodes produced by depositing first a layer of graphene nanoplatelets and subsequently MnO_2.

A. Elmouwahidi *et al.* [44] synthesized carbon xerogel-TiO_2 composites (CTiX) by sol-gel techniques. Composites demonstrated a homogeneous and 3D mesoporous structure, where both phases similarly and intimately distributed. Due to the interactions between both phases, all the composites showed a high dispersion of anatase TiO_2 nanoparticles on the carbon support though samples were carbonized up to 900°C. These nanoparticles were decreased in part, with an oxygen surface distribution highly relied on the TiO_2 content. The attained composite materials possess specific surface areas varying from 423 to 539 m^2/g and an extremely well-developed micro/mesoporosity with an entire pore volume ranging from 0.361 to 0.480 cm^3/g. Moreover, a two-electrode symmetric supercapacitor based on the carbon xerogel-TiO_2 composites displayed a high electrochemical performance attaining high capacitances up to 137 F/g at 0.250 A/g for 20% TiO_2 composite and a high retention capacitance up to 66-80% at 20 A/g as well as high density 20.15 Wh/kg at a power density of 138.11 W/kg in the voltage range of 0 V to 1.1 V. It is worth noticing that the sample with a combination of low hydrophobicity and an abundant micromecropore network with a moderate content in TiO_2 reveals the best performance for energy storage.

The utilization of binary metal oxides-particularly spinel, represented by AB_2O_4-as pseudocapacitive electrode including two transition metals A and B such as ZnMn2O4, has also been gaining increasing attention due to their multiple available oxidation states and richer redox processes [45]. In 2018, Mozaffar Abdollahifa *et al.* [46] successfully synthesized carbon-coated $ZnMn_2O_4$ utilizing a novel solution combustion approach which adopted polyethylene glycol as a multifunctional structure-directing agent. In that work, polyethylene glycol served not only a pore-structure directing agent but also as a precursor to form a carbon shell on oxide particles. The role of the carbon shell was to inhibit crystallite growth and improve the electronic conductivity of oxide powder. Diverse mesoporous structures could be formed, and the specific surface area could be signifi-

cantly increased by conformal carbon coating by controlling the molecular weight and the number of the polymer in the combustion solution. From the measurements, carbon-coated ZnMn2O4 electrodes possessed specific capacitances up to 150F/g and cycle stability revealing no capacitance fade after 10,000 cycles at 60% of full capacity with over 99% coulombic efficiency. It is the first time that carbon-coated ZnMn2O4 exhibits ideal capacitor performances in an aqueous neutral electrolyte. This research elucidates a novel powerful synthesis avenue capable of fabricating conductive mesoporous crystalline oxide-based nanomaterials for energy storage applications.

Wenbin Fu *et al.* [47] prepared hierarchical electrodes by integrating N-C nanowire/metal oxide (Fe_2O_3 and MnO_2) nanocomposites into carbon fabric for warble aqueous asymmetric supercapacitors (ASCs) with a safe aqueous electrolyte. Both Fe_2O_3 and MnO_2 nanosheets were capable of being uniformly coated onto the N-C nanowires to form distinct coaxial nanostructures. In such nanostructured electrodes, the N-C nanowires offered rapid and efficient pathways for electrons, while short diffusion paths within nanosized metal oxides capacitated fast ion transport, contributing to greatly intensive behavior at high rates. Consequently, both the negative electrode N-C/Fe_2O_3 and active electrode N-C/MnO_2 revealed high areal capacitance and excellent rate capability in 5 M LiCl aqueous electrolyte. Moreover, solid-state ASCs assembled by utilizing an aqueous gel electrolyte operated at 1.6 V and delivered more than 60 mF/cm^2 during around 50 s charging/discharging time and over 30 mF/cm^2 for around 5 s discharge. These N-C nanowire/metal oxide composite electrodes render it possible for applications in safe wearable energy storage devices.

Similar to pure carbon, the bimetallic Ni-Co sulfides have problems in the rapid charge and discharge ability and sustained cycle stability, limiting their practical applications in energy storage [48]. In order to address the above concern, Qidi Chen [49] adopted a popular strategy to synthesize the distinct sandwich-like graphene oxide (rGO)/$CoNiS_x$/N-C nanocomposite, in which supersmall bimetallic $CoNiS_x$ nanocrystallites embedded in N-doped carbon were grown on the rGO. Profited by the multiple structural, morphological and compositional pros, the nanocomposite displayed importantly enhanced electrochemical performance as an advanced electrode material for supercapacitors. Compared with rGO/$CoNiO_x$ and rGO/$CoNiS_x$ nanocomposites, the rGO/$CoNiS_x$/N-C nanocomposite achieved a high specific capacitance with 1028.2 F/g at 1 A/g and outstanding rate capability with 89.3% capacitance retention at 10A/g as well as great cycling stability with 93.6% capacitance retention more than 2000 cycles, as was shown in Figure 4. Moreover, the asymmetric supercapacitor (ASC) device based on the rGO/$CoNiS_x$/N-C nanocomposite was able to deliver a high energy density of 32.9 Wh/kg at a power density of 229.2 W/kg with desirable cycling stability. These electrochemical consequences evidently reveal the great potential of the sandwich-like rGO/$CoNiS_x$/N-C nanocomposite for applications in high-performance supercapacitors.

However, in recent several years, it is found that transition metal oxides are not only limited by their poor cycling stability, low power density, and poor conductivity but also restricted by their non-transparent feature which greatly influences their real applications in apparent electronics [50]. Experimental studies on non-transition metal oxides have begun to come into focus. Rudra Kumar *et al.* [51] synthesized porous indium oxide hollow spheres (PIOHS) of 1-2 μm in diameter utilizing a cost-effective hydrothermal approach followed by the calcination. The metal and carbon precursor was mixed in aqueous solution to build a solid sphere comprising of carbon and indium nanoparticles at high temperature and pressure in the hydrothermal chamber followed by high-temperature calcination contributing to the formation of hollow porous spheres of crystalline In_2O_3 nanoparticles by the successful removal of carbon. The formation of mesoporous hollow spherical morphology was guided by the in situ formation and removal of carbon mesosphere template. This approach helped the synthesis of mesoporous metal oxide hollow spheres with the pro of template-assisted approach without numerous drawbacks involved in traditional template synthesis such as the difficulty in template production, the possibility of product destruction after template removal, multiple steps included and the uneconomic process included in the complete mean. From the measurements, the specific surface area was tested as 128 m^2/g and the electrode composed of PIOHS indicates maximum specific capacitance of 320 F/g at 1 A/g current density during electrochemical research. The synthesized material revealed a 56% rate capability at 10 A/g with 86% cycling stability after 3500 cycles at 5 A/g. Additionally, the full cell asymmetric supercapacitor was demonstrated with PIOHS as a cathode with a specific capacitance, energy density and power density of 30.84 F/g, 10.96 Wh/kg and 80 W/kg, respectively at 0.1 A/g current density. These superior electrochemical performances of the fabricated full-cell device are primarily due to the high surface area, unique 3D porous hollow architecture and better charge transfer kinetics of PIOHS.

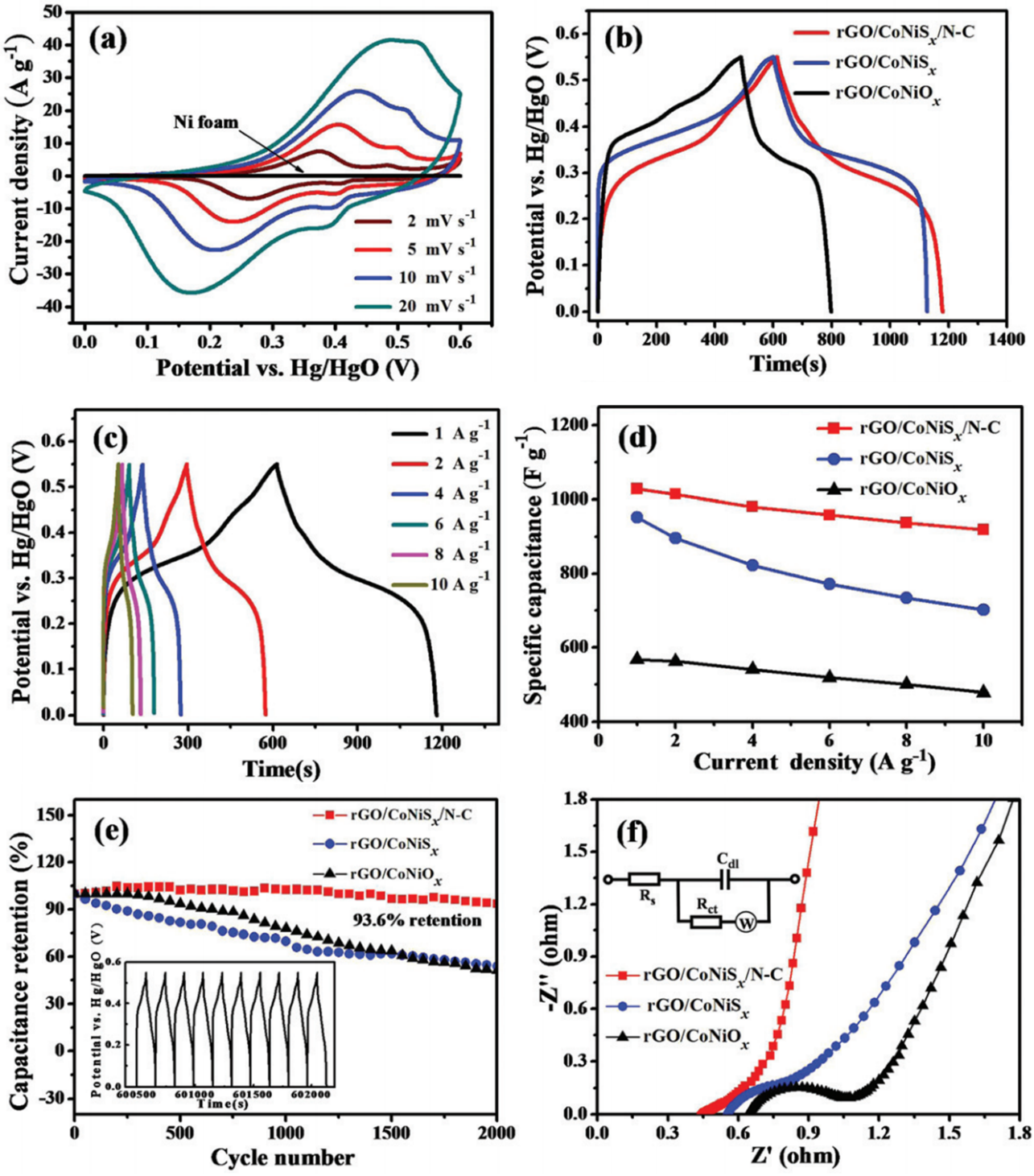

Figure 4: (a) CV curves of the rGO/CoNiS$_x$/N–C electrode recorded at different scan rates; (b) charge and discharge curves of the three electrodes at a current density of 1 A/g; (c) GCD curves of the rGO/CoNiS$_x$/N–C electrode at different current densities; (d) the calculated capacitance as a function of the current density; (e) cycling performance of the three electrodes at a high current density of 6 A/g; and (f) Nyquist plots of the three electrodes.

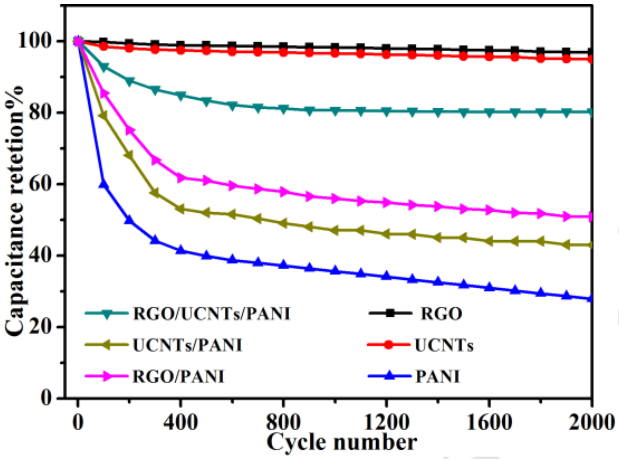

Figure 5: Cycling stabilities of rGO, UCNTs, PANI, rGO/PANI, UCNTs/PANI and rGO/UCNTs/PANI electrodes.

4 Carbon/conducting-polymers composite electrodes

Conducting polymers (CP) are organic polymers that conduct electricity via a conjugated bond system along the polymer chain. During the past two decades, the conducting polymers are widely explored for supercapacitor application due to their reversible faradaic redox property, high charge density and lower cost in contrast to the expensive metal oxides [52–59]. CPs mainly contain polyaniline (PANi), polypyrrole (PPy), and polythiophene (PTh). Pure PANi cannot satisfy the needs of practical application since its poor cycling stability of the supercapacitor contributes to its specific capacitance reducing rapidly [60]. Pure PPy owns a lot of merits such as easy synthesis, relatively high capacitance property and high cycling stability while it is easily affected by preparing approach, substrate, dopant, template and so on. Pure PTh is mainly limited to rapid loss of power density, thus inferior to PANi and PPy [61–66]. Hence, it is essential to develop CPs-based composites for the purpose of improving electrochemical properties. Carbon materials as supercapacitors electrodes possess cyclic stability, considerable specific surface areas, etc, covering the shortage of pure CPs [67, 68]. Many investigations have also demonstrated that as compared to these pure CPs, carbon/CP material composites exhibit more excellent electrochemical properties. Currently, diverse carbon/CP nanocomposites have been extensively investigated.

Shiyong Wang *et al.* [69] produced a free-standing and flexible 3D reduced Graphene/PANI (rGN/PANI) composite film by vacuum filtration of the rGN and PS mixed solution, and subsequently, the PS microspheres were removed after PANI nanowire array was deposited on. This novel structure was able to significantly increase the positive surface area of the electrode and offer high interfacial area and short ion diffusion path as well as fast electrical pathways, thus making full use of positive materials. In addition, with the high conductivity of graphene and a strong π electron interaction between 3D rGN and PANI nanowires, the ion-diffusion and charge-transfer resistance of the composite film were reduced. Therefore, the specific capacitance and cycling stability of the flexible composite film were improved greatly compared to pure polyaniline. Adopted as a supercapacitor electrode, the maximum specific capacitance was as high as 740 F/g at a current density of 0.5 A/g and the specific capacitance maintained 87% of the initial after constant charge-discharge 1000 cycles at the current density of 10 A/g. In addition, a maximum energy density was capable of reaching to 65.94 Wh/kg at a power density of 0.2 kW/kg. It is believed that these flexible and low-cost composite films may be regarded as a potential candidate for application in energy storage systems.

Yanping Huang *et al.* [70] prepared reduced graphene oxide /unzipped carbon nanotubes/ polyaniline (rGO/UCNTs/PANI) through an in-situ polymerization approach. The rGO/UCNTs composite formed a conductive carbon skeleton with a 3D structure, subsequently the PANI dispersed in the rGO/UCNTs skeleton. The existence of UCNTs discouraged the stacking of rGO and provided larger space for deposition of PANI. Moreover, UCNTs also offered more transport paths and shortened the transmission distance for the electrolyte electrons or ions. On the other hand, PANI brought in the pseudocapacitance and facilitated the capacitance and energy storage capacity of the nanocomposite. RGO and UCNTs were able to moderate the structure destruction of PANI, contributing to the enrichment of cycling stability. Finally, the rGO/UCNTs/PANI composite demonstrated a specific capacitance of 359.3 F/g at 1 A/g, higher than that of rGO, UCNTs, PANI, UCNTs/PANI and rGO/PANI, as was shown in Figure 5. The capacitance of the composite still maintained 80.5% of its original value after 2000 cycles, and the composite presented an energy density of 7.4 Wh/kg and a power density of 189.0 W/kg. This excellent performance is due to the special 3D structure, which aids carbon materials and polymers rise above their cons. It is worth noticing that 3D carbon nanomaterial is superior to 1D or 2D carbon nanomaterial while building composite capacitance material with PANI.

The utilization of aluminum foils and CNTs are quite common in recent years, thanks to its relatively

low cost and abundance [71]. Combined with neutral aqueous electrolytes, composite electrodes based on aluminum foils and CNTs can effectively improve energy density [72]. Alptekin Aydinli *et al.* [73] prepared and electrochemically characterized vertically aligned carbon nanotube/polyaniline (VACNT/PANI) nanocomposite supercapacitor electrodes in Na_2SO_4 electrolyte (aqueous electrolyte). VACNTs were grown on Al foils and PANI layers were electrodeposited on the top of these VACNTs, combining the capabilities of VACNTs and PANI. Among the produced electrodes, nanocomposite with the thickest PANI layer though 15 electrodeposition cycles revealed significant performance during CV, galvanostatic charge-discharge, electrochemical impedance spectroscopy measurements. The specific capacitance of these electrodes was figured out as 16.17 mF/cm^2 at a current density of 0.25 mA/cm^2. However, the cyclic performance was found to be lowest perhaps due to the degradation of the PANI under atmospheric conditions. Moreover, the increased amount of PANI electrodeposition cycles reduced the VACNT content of the nanocomposites and consequently caused the degradation of adhesion between components of the nanocomposites. As discussed above, the VACNT/PANI nanocomposite supercapacitor electrode is a hopeful energy system with its remarkable properties through short electrodeposition cycles.

Sowmya *et al.* [74] prepared four multilayered electrode systems based on the activated carbon/polyaniline (AC/PANI) composites utilizing the potentiodynamic technique. In each of the multilayered electrodes, PANI varied merely with respect to its dopants, respectively including sulphuric acid, camphor-10-sulphonic or p-toluene sulphonic acid. As was shown in Figure 6, there was electropolymerization of aniline on the AC surface but their morphology was found to be various in the SEM figures. It is cleared that AC offers sites for the electroactive polyaniline to form the composites. The merged layers indicate that good contact between the layers might have contributed to better ionic mobility during charge/discharge cycling. The highest specific capacitance of 549.5 F/g was finally attained for the multilayered symmetrical supercapacitor based on M2 type multilayer electrode. Its specific capacitance, specific energy and specific power were also found to be higher than the other multilayered ones. The time constant was found to be 0.24s. These multilayered systems are among the ideal candidates for supercapacitors.

Ji Won Lee *et al.* [75] synthesized pitch-based activated carbon/tubular polypyrrole (AC/PPy) composites with diverse tubular polypyrrole (T-PPy) contents as positive electrode materials for supercapacitors. The ACPPy composites produced in the presence of SDS revealed higher specific capacitances than AC or T-PPy electrodes due to the addition of T-PPy to ACs importantly improving the specific capacitance of the carbon electrode. Furthermore, the ACPPy electrodes displayed significantly improved cycling stability and the electrochemical performances of ACPPy composites. The composite material had a high specific capacitance of 82.3 F/g, whereas excessive amounts of T-PPy decreased the specific capacitance by blocking the pore network structure in composite materials with higher T-PPy contents. The specific capacitance of the ACPPy stabilized at a similar value after 1000 cycles.

5 Carbon/Metal-oxides/conducting-polymers composite electrodes

Plenty of researchers have investigated composites consisting of carbon-based materials and conducting polymer as electrode materials for supercapacitors before. Metal oxides such as RuO_2, MnO_2 and Fe_2O_3 are regarded as ideal electrode materials and taken into account for pseudocapacitors since metal oxides provide superior specific energy and electrochemical stability as compared with carbon-based and polymer materials [76–85]. Thus, recently, the rapid advancement of worldwide research on the performance of supercapacitors has upgraded the study of electrode material for supercapacitors to another level whereby ternary composites consisting of the carbon-based material, conducting polymer, and metal oxide are renowned in further enhancing the supercapacitive performance of the composites [86].

Nur Hawa Nabilah Azman *et al.* [87] prepared poly(3,4-ethylene dioxythiophene)/graphene oxide/manganese oxide (PEDOT/GO/MnO_2) ternary composite as an electrode material for supercapacitor. In order to research the supercapacitive properties, the ternary composite was sandwiched together and separated by filter paper soaked in 1 M KCL. The ternary composite revealed higher specific capacitance of 239.4 F/g, in contrast to the binary composite (PEDOT/GO) of 73.3 F/g. The addition of MnO_2 acting as a spacer in the PEDOT/GO contributed to improving the supercapacitive behavior via maximizing the utilization of electrode materials by the electrolyte ions. Furthermore, as was shown in Figure 7, the PEDOT/GO ternary composite respectively revealed a specific energy and specific power of 7.9 Wh/kg and 489.0 W/kg, and achieved 95% capacitance retention whereas PEDOT/GO only retained 79% af-

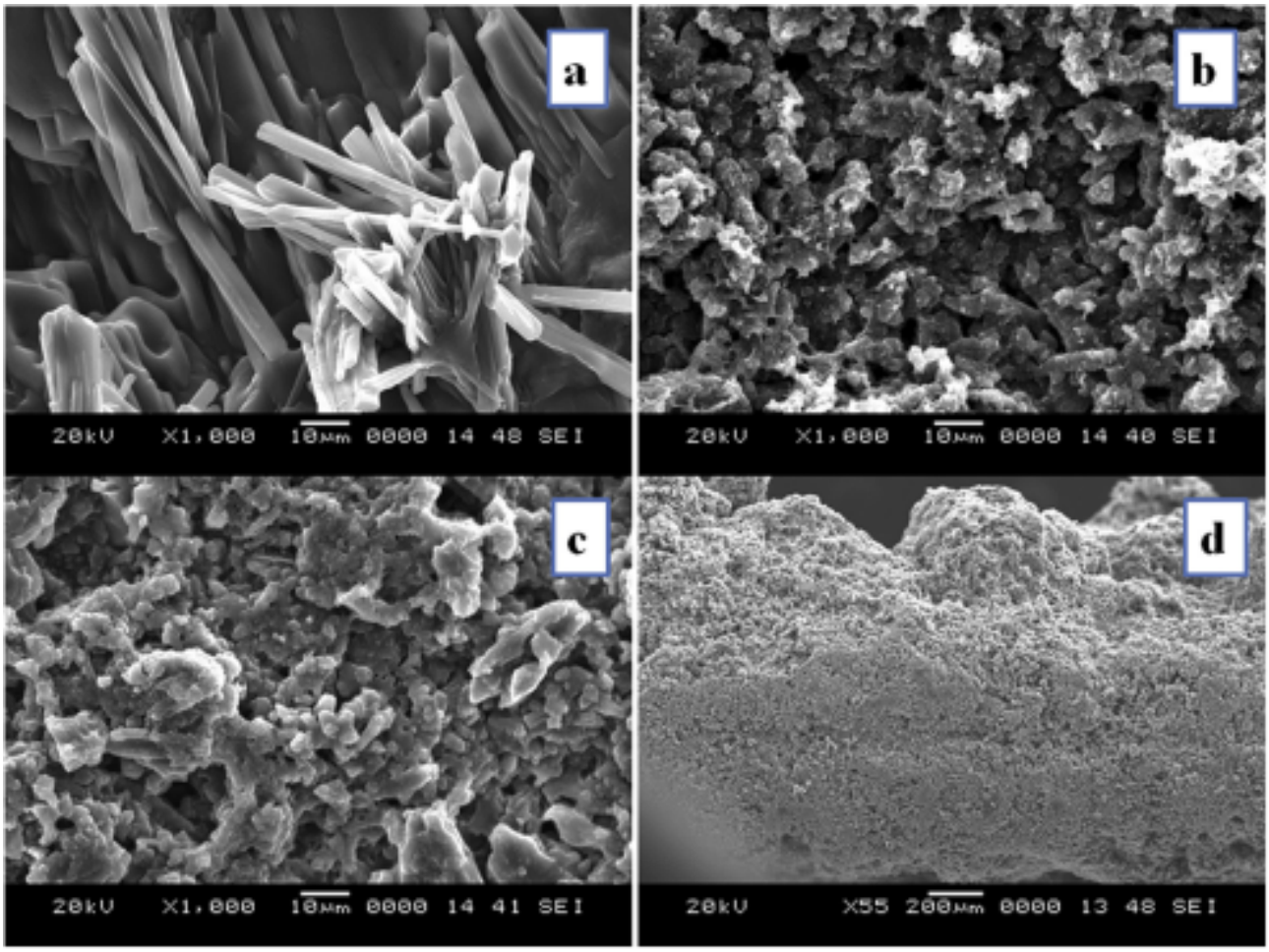

Figure 6: Scanning electron micrographs of single layered (developed using a) camphor-10-sulphonic acid b) p-toluene sulphonic acid c) sulphuric acid) and d) multi-layered activated carbon-polyaniline composite electrode materials.

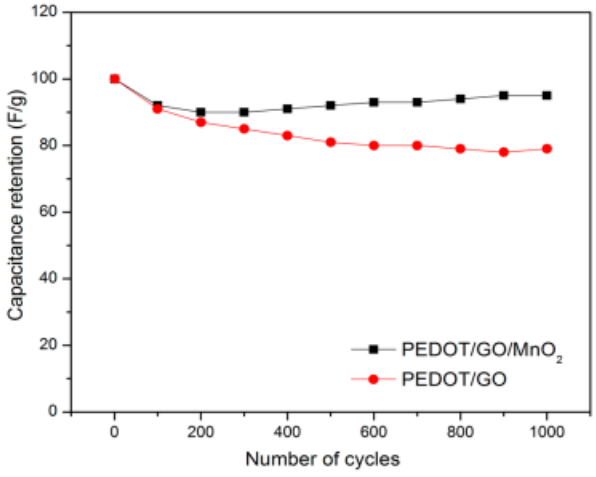

Figure 7: Stability test of PEDOT/GO/MnO2 and PEDOT/GO.

ter 1000 cycles owing to the synergistic composite, showing excellent cycling stability.

Jie Chao *et al.* [88] synthesized MoS_2/polyaniline/reduced graphene oxide hierarchical nanosheets (MoS_2/PANI/rGO HNSs) with the novel structure of sandwiched MoS_2/PANI nanosheets array vertically align on rGO as supercapacitor electrode in 1 M H_2SO_4. In constructing MoS_2/ PANI/rGO HNSs, PANI chains were intercalated into MoS_2 interlayers building sandwiched nanosheets, which invents adequate and intimate hetero-interface between PANI and MOS_2 layers, consequently improve the electronic and ionic conductivity between two contiguous S-Mo-S layers. The sandwiched MoS_2/PANI nanosheets array vertically aligned on rGO nanosheets forming indicated and tighten MoS_2/PANI/rGO contact which could effectively enhance the surface area and improve the structural stability of the electrode material. The rGO nanosheets built a conducting network enabling rapid electrons and ions transport in the entire electrode. Therefore, outstanding conductivity and superhigh reactive surface area were obtained and contributed to supe-

rior supercapacitance. In the three electrode system, the MoS_2/PANI/rGO-300 HNSs revealed a capacitance of 330.7 F/g at the current density of 10 A/g at first cycle and had capacitance retention around 81.9% after 40,000 cycles. Integrated as MoS_2/PANI/rGO-300 symmetric supercapacitor, it displayed a capacitance of 97.8 F/g at the current density of 2 A/g at first cycle. After 20,000 cycles, 84.2% of original capacitance was maintained. These outstanding electrochemical properties allow the MoS_2/PANI/rGO-300 HNSs to be a promising electrode material for high-performance supercapacitor.

Li Wang *et al.* [89] prepared 3D kenaf stem-derived macroporous carbon (3D-KSCs)/rGO/PANI nanocomposites as an integrated electrode for supercapacitors. The agglomeration of rGO on the electrode surface could be effectively controlled to attain a 3D-KSCs electrode coated with well-dispersed rGO. The 3D-KSC with macroporous structure loaded numerous layered rGOs on the 3D-KSC surface, increasing the efficiency of rGO and 3D-KSCs. PANI arrays were polymerized on the 3D-KSCs/rGO surface vertically and consistently. The 3D-KSCs/rGO/PANI supercapacitor electrode revealed outstanding performances. For instance, as was shown in Figure 8, the gravimetric capacitance was up to 1224 F/g, and the capacitance maintained 87% after 5000 cycles under 1.0 A/g, which is much higher than that of 3D-KSCs/PANI and other reported rGO-based and PANI-based supercapacitors. These excellent performances can be attributed to the following aspects. On the one hand, the 3D-KSCs/rGO/PANI combine the hierarchical porous architectures of 3D-KSC and the high specific surface area and good conductivity of rGO as well as the good electroactivity and high pseudocapacitance of PANI. On the other hand, it not only offsets the cons of rGO and PANI such as reunion effect and poor stability but also raises the efficiency of materials and mechanical strength. However, the growth of PANI by electrodeposition takes a long time, which poses a certain challenge to the extensive use of 3D-KSCs/rGO/PANI and large-scale practical fabrication.

As a novel class of porous crystalline materials, metal-organic frameworks (MOFs) are formed by linking inorganic with organic components via covalent coordination linkages and are hence attracting increased great attention owing to their remarkable surface areas and easily tunable pore size. However, compared with transition-metal oxides, the capacitance of MOFs is usually lower due to their poor electrical conductivity for electrolyte diffusion [90, 91]. To address this problem, Linghao He *et al.* [92] synthesized a novel multicomponent hybrid of copper metal-organic framework-derived (MOF-derived) copper oxide/mesoporous carbon embedded with polyaniline and reduced graphene oxide through in situ polymerization approach. The hybrid was hereafter denoted as CuOx/mC/PANI/rGO and utilized as supercapacitor electrodes for the first time. This efficient conductive network could enhance the ion-diffusion process and rapid redox response at the electrode/electrolyte interface. Varying the pyrolysis temperatures, the ternary CuO_x/mC/PANI/rGO attained at 700°C revealed the highest capacitance of up to 534.5 F/g along with excellent cycling stability. The as-attained CuO_x/mC/PANI/rGO exhibited three preponderances in that work, in contrast to other MOF-related electrode materials for supercapacitors. First, PANI had a unique structure endowed by uniformly and highly ordered interface layer on the surface of CuO_x/mC frameworks with high specific surface area and excellent electrochemical activity. Next, the addition of rGO formed an efficient conductive network, which improved the ion diffusion at the electrode/electrolyte interface owing to its good conductivity and large surface area. Last but not least, adopting PANI led to environmental stability and convenient operation. These findings might broaden the applications of metal-organic framework-derived composites as high-performance supercapacitors.which much higher than that of 3D-KSCs/PANI and other reported rGO-based and PANI-based supercapacitors. These excellent performances can be attributed to the following aspects. On the one hand, the 3D-KSCs/rGO/PANI combine the hierarchical porous architectures of 3D-KSC and the high specific surface area and good conductivity of rGO as well as the good electroactivity and high pseudocapacitance of PANI. On the other hand, it not only offsets the cons of rGO and PANI such as reunion effect and poor stability but also raises the efficiency of materials and mechanical strength.

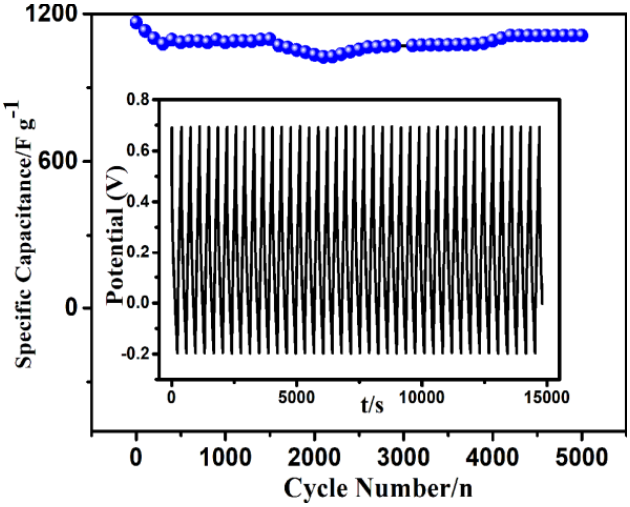

Figure 8: Cyclic stability of 3D-KSCs/rGO/PANI at 1 A/g.

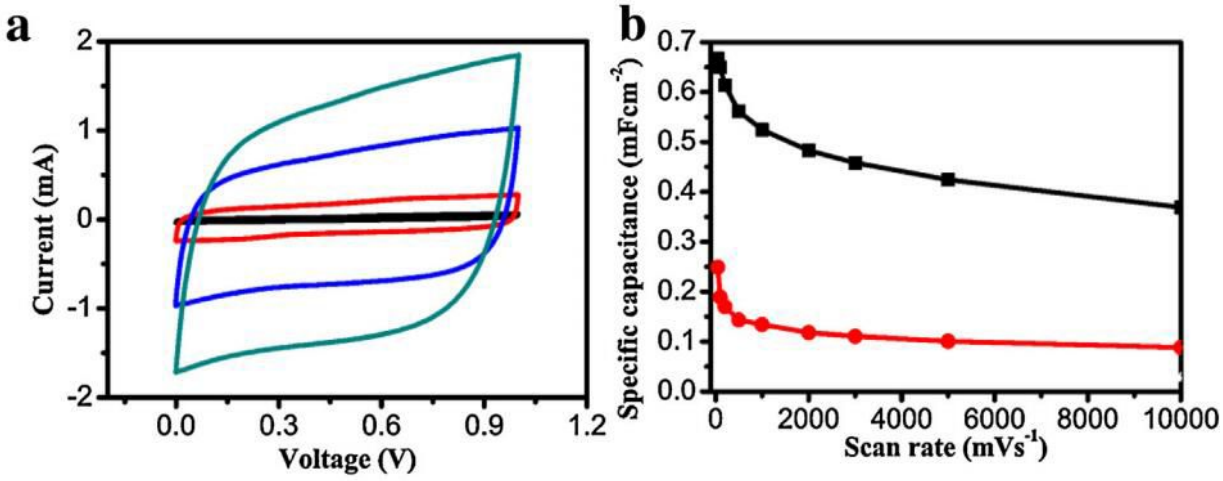

Figure 9: Electrochemical performance of the VOG-10 EDLC in PVA-KOH gelled electrolyte. (a) The CV curves of the device with scan rates of 100 mV/s (black curve), 1000 mV/s (red curve), 5000 mV/s (blue curve) and 10,000 mV/s (green curve). (b) Comparison of the capacitance of EDLCs based on VOG-10 electrode based on flat substrate (red curve with filled circles) and VOG-10 on 3D silicon nanocone substrate (black curve with filled squares) at different voltage scan rates.

However, the growth of PANI by electrodeposition takes a long time, which poses a certain challenge to the extensive use of 3D-KSCs/rGO/PANI and large-scale practical fabrication.

6 Combination with other materials

Chemical vapor deposition (CVD) grown 2D graphene for supercapacitors has the shortcoming that it can fabricate merely a few layers, which cannot offer high capacitance per unit area [93–95]. To address this issue, Baogang Quan *et al.* [96] combined Si nanocone with vertically oriented few-layer graphene, which is directly deposited on metalized Si nanocone arrays, to attain 3D graphene/Si composite electrodes. The well-defined 3D electrode was synthesized to solid-state graphene supercapacitor, revealing superior rate capability, large areal capacitance and cyclic stability. As Figure 9a shows, all the CV curves illustrate nearly symmetrical rectangular shapes, indicating an ideal capacitive behavior and a good capability. The specific capacitances were attained depending on various voltage scan rates, which are listed in Figure 9b. The electrode with 10 min of chemical vapor deposition (CVD) growth of graphene endowed with a specific capacitance of 667.2 uF/cm^2, which was several times larger than previously reported data (120 uF/cm^2 and 238 uF/cm^2). These excellent performances can be attributed to the following reasons. Firstly, the silicon nanoarrays can effectively enhance the surface area, improving the loading amount of positive materials per unit area on the Si chip. Next, the graphene directly deposited on the current collectors by CVD possesses excellent electric contact, which decreases the contact resistance between the graphene and the current collectors.

Aleena Rose *et al.* [97] prepared graphene oxide/polyaniline/polyvinyl alcohol (GO/PANI/PVA) composite nanofibers via electrospinning approach. The average size of the composite nanofibers ranged from 89 to 97 nm. The electrochemical performance of the GO/PANI/PVA electrode reached a maximum specific capacitance of 438.8 F/g, more than that of PANI/PVA with 143.3 F/g. The reason for the high current value for PANI/PVA composite might be due to the existence of anodic peak arising from the pseudocapacitive behavior of PANI. Incorporation of graphene oxide contributed to the electrical double layer capacitance suppressing faradaic current and simultaneously increasing the area under the curve, thus increasing the overall specific capacitance of the GO/PANI/PVA composite. A comparison chart illustrating the performance of GO/PANI/PVA nanofibers with that of other GO-based composites is offered in Figure 10. It is worth noticing that PANI/GO-based nanofibers acquired through blending with traditional polymers should be significant research directions for the preparation of high-performance supercapacitor electrode materials.

Biomass-derived O/N-co-doped porous carbons have also become the most competitive electrode materials for supercapacitors due to their renewability and sustainability. An alternative approach to activation is the hydrothermal assistant, which involves hydrothermal treatment of

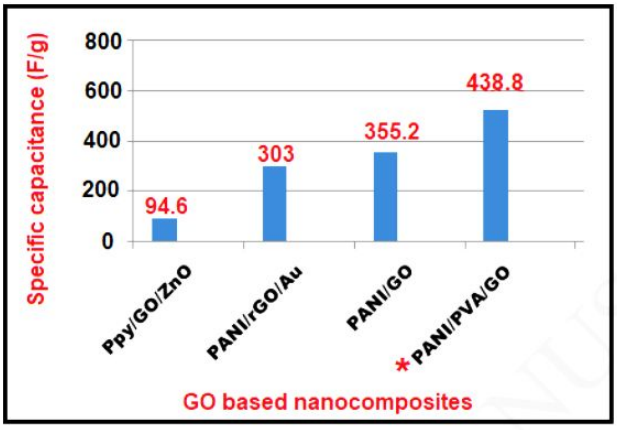

Figure 10: Specific capacitance of PANI/PVA/GO nanofibers in comparison to that of different GO based composites.

plant biomass in the presence of alkaline followed by simultaneous pyrolysis and activation [98]. Bei Liu *et al.* [99] prepared O/N-co-doped hierarchical porous carbons by directly pyrolyzing PF leaves. Under optimal pyrolysis temperature at 700°C, the resultant PF leaf-derived hierarchical porous carbon displayed a graphene-like nanosheet structure, a moderate specific area with 655 m^2/g, a relatively low pore volume with 0.44 cm^3/g, a high O, N contents of 18.76% at O and 1.70% at N, and a hierarchical porous structure. Profited from these characteristics, such O/N-co-doped porous carbon nanosheets exhibited a high gravimetric capacitance of 270 F/g at 0.5 A/g and high volumetric capacitance of 287 F/cm^3 at 0.5 A/g. Furthermore, the symmetric supercapacitor provided a high volumetric energy density of 14.8 Wh/L at 490 W/L as well as high stability about 96.1% of capacitance retention after 10000 cycles at 2 A/g. With a view to the abundance and renewability of the PF plant, the O/N-co-doped porous carbon electrodes should have extensive application prospect in supercapacitors.

Xiaomei Dong *et al.* [100] presented a Fe_2O_3 or FeS decorated, N and S co-doped hierarchical porous carbon hybrid. The specific area, morphology and doping elements could be conveniently controlled through adjusting the hydrothermal reaction between waxberry and iron sulfate. The FeSN-C and N-C electrodes in a 6 M KOH aqueous electrolyte was conducted at a scan rate of 1000 mV/s, and exhibited higher specific capacitance than N-C electrode, indicating that the capacitive behavior of carbon materials could be improved by iron and sulfur doping. The constructed supercapacitors with the as-prepared carbon materials were capable of revealing excellent capacitive performance with an ultrafast charging or discharging rate (<1 s), superlong cycle life (>50 000 cycles, 80 A/g), ultrahigh volumetric capacitance (1320.4 F/cm^3, 0.1 A/g), and high energy density (100.9 Wh/kg, 221 Wh/L). The excellent performance might be due to hierarchical porous architecture with shorted diffusion pathway, multi-doped heteroatoms offering outstanding conductivity and electrochemical reactivity, and small amounts of the iron salts residue enabling fast redox reaction. Exhibiting the superior performance, the Fe_2O_3 or FeS decorated, N and S codoped hierarchical porous carbon hybrids may arise its behavior from the N and S codoping on the surface of the carbon microspheres and nanosheet composites coupled with the fast redox response of Fe_2O_3 or FeS.

7 Conclusions

To help facilitate the research and development of electrodes for supercapacitors, this article offers a comprehensive overview of recent progress concerning advanced carbon-based electrodes. Diverse types of carbon-based electrodes exploited and reported in the literature are summarized and classified into pure carbon electrodes, carbon/metal oxides composite electrodes, carbon/metal oxides/conducting polymers composite electrodes as well as carbon electrodes based on other materials. Pure carbon-based supercapacitors have excellent cyclic stability and long service lifetime, while their maximum capacitance is restricted by the positive electrode surface area and the pore size distribution and their energy density are too lower to fulfill the need of energy storage devices. In order to improve the specific capacitance and the energy density, a composite electrode, combined with metal oxides and conducting polymers, etc, covers the shortage of pure carbon electrodes and further enhances its electrochemical performance. Overall, combining various materials to form composites has been a significant trend to own a positive synergistic effect for the carbon-based electrodes.

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