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CONCEPT

Ultrafast Electrochemical Capacitors with Carbon Related Materials as Electrodes for AC Line Filtering

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Abstract: High-frequency responsive electrochemical capacitors (ECs), which can directly convert alternating current (AC) to direct current (DC), are getting more essential for the rapid development of electronic devices. In order to satisfy the requirements of ECs with fast rate capability, appreciable capacitance density, numerous efforts have been made towards the preparation and design of electrode materials, which is a decisive factor in the performance of ECs. Carbon related electrode materials have been widely demonstrated to significantly increase the performance of ECs because of its light weight, high strength and high processability. In this concept, the latest advances in the rational design and controllable fabrication of carbon related electrode materials including planar two-dimensional materials, random three-dimensional materials, and vertical carbon materials are summarized. Moreover, the state-of-the-art progress on carbon-based ECs has been discussed from the viewpoint of structure of electrode and performance of ECs. Finally, this concept presents integrated perspectives on further design and preparation of carbon related ECs.

Introduction:

Alternating current (AC), as the main form of electrical energy distribution, has been widely used in electric power transmission and domestic power supply.[1-8] However, common electrical equipment, such as cell phones and most electronic circuits, needs to be driven by the direct current (DC) voltage to work normally, so the rectifier filter system used to convert AC to DC has become an essential part of the current circuit.[9] Among the rectifier filter system, the performances of the filter capacitor are important parameters, determining the conversion efficiency and DC quality.[10-14] Aluminum electrolytic capacitor (AEC) used to be regarded as a good choice for function in current ripple filtering because of its wide range of voltage, fast response capability, and low price. Unfortunately, with the rapid development of electronic products, wearable devices, electric vehicles, and other energy storage devices toward lightweight and miniaturization, the large size, and limited capacitance of AEC restrict its application in high-power devices.[10, 11] Instead, electrochemical capacitors (ECs) have received extensive attention as next generation filter capacitors owing to their fast rate capability, appreciable capacitance density, good flexibility, and excellent cycle stability.[14] However, in order to realize the requirement of integration of high energy density and high frequency response into a tiny AC line filtering circuit, ingenious designs and preparation of electrode materials with special structures are very essential.[7]

Electrode materials, which are used to transport ions and store charge, play an important role in ECs.[12] The ideal electrode materials applicable to AC line filtering should not only exhibit a good capacitive behavior with a phase angle being close to −90° at 120 Hz (beneficial to reduce the thermal loss), but also possess a high capacitance density, which contributes to DC with low ripple and downsize the device space. To this end, a myriad of electrode materials such as transition-metal-based materials,[15-18] polymer-based materials,[10, 11, 19] and carbon-based materials have been developed to meet the ion transport property and capacitance density.[1, 2, 20-25] To realize a high-frequency response in ECs, minimizing the resistance is essential, including the contact resistance (the interfaces of the electrode and current collector, electrolyte and electrode), the ohmic resistance (materials resistance), and ionic transport resistance in electrode pores.[26] To satisfy the large specific capacitance in ECs, the electrode material should have a large specific surface area. This requires the electrode material to have rich channels for ion transport and rich surfaces to store charge.[27] Among these, carbon materials are the most commonly used electrode material in ECs owing to its lightweight, conductivity, and diverse pore structures.

The structure of electrode material is very important to the performance of capacitor, which determines ionic transport kinetics and ionic available surface of electrode materials for storing charges. [12-14, 27, 28] Both of them are “factor of merits” to

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evaluate the performances of AC line filtering. Unfortunately, they are mutually exclusive. In this concept, we focused on the carbon materials-based electrode for ECs, summarized and classified the different electrode structure of carbon materials, analyzed and discussed the influence of several typical structure of carbon material on the performance of ECs, and proposed the prospect of carbon electrode structure design and preparation methods.

2. Carbon materials-based electrode

As shown in Figure 1, the structures of carbon materials-based electrodes for ECs can be divided into three types. The first one is planar two-dimensional material. The common feature of this class of materials is the planar stacking structure, which can reduce the volume of the electrode but impede the ion transport. Thus, the thicknesses of such materials are usually thin, only a few hundred nanometers. The typical examples include films composited of carbon black, carbon nanotubes (CNT), graphene and their compounds.[24-26, 29-35] The second is random three-dimensional materials. Compared with films, the random three-dimensional materials are no longer confined to the limitations of the planar space, and form three-dimensional channels. The three-dimensional channels not only help to quick ion transport, but also increase the surface area of electrode materials. The typical examples include graphene foam, graphene sponge, graphene nanowall, and so on.[36-41] However, it should be noted that the random structure is also difficult to achieve the maximum space charge storage density, and still slows down the migration of ions to some extent due to the tortuous random networks. In contrast, the third is vertical structure, being more ideal for the ultrafast electrode materials of ECs. The typical examples include vertical carbon nanotubes and vertical graphene.[42-52] This class of materials possess the strictly vertical structure, which is the shortest path for the ion transports. Meanwhile, by adjusting the pore size of the vertical structure, the ions accessible area could be easily regulated. On the whole, all the three structures exhibit the same physical and chemical properties, including high chemical stability, large specific surface area, adjustable porosity, and excellent electrical conductivity. However, different pore structures and specific surface area between these carbon materials and their compounds effect ion transport property and high-frequency response of ECs. In the following sections, we will discuss these different structure and different performance of carbon-based ECs in detail.

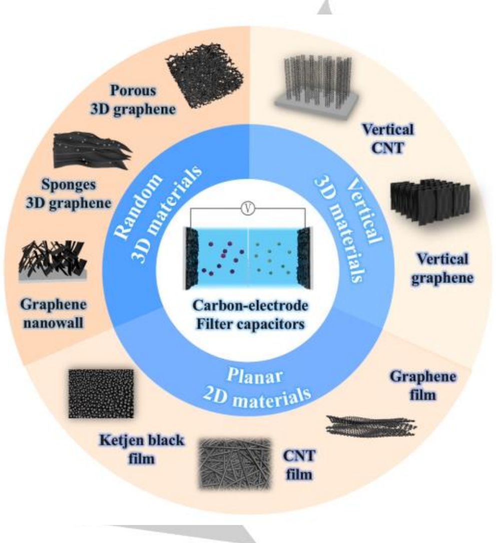

Figure 1. Schematic diagram of carbon-based capacitors with different structures.

2.1 Planar 2D carbon materials

Carbon powder materials such as carbon black powder, CNT powder, and graphene powder can be prepared in large quantities by physical or chemical methods. However, powder is difficult to be directly used as electrode material. The thin film assembled from powder can be a very suitable substitute for electrode material. Nazar and co-workers reported a versatile carbon nanotube-based ECs.[26] As is shown in Figure 2a, carbon nanotubes are connected together to form a continuous and porous network. As a result, the CNT-based film exhibited low interfacial resistivity and high specific capacitance. Kim et al. successfully fabricated an EC based on CNT films.[31] As shown in Figure 2b, because of its relatively large pore size and short pore length, the capacitor had high volumetric energy densities and fast-response capacitance. More importantly, as the thickness of CNT film increased, the area specific capacitance increased gradually, and reached 282 $\mu F \cdot cm^{-2}$ when the thickness was 298nm. (Figure 2c) In addition to form a continuous ion transport pathway with higher capacitance density, Kim and coworkers further fabricated an electrode material combined Ketjen black (KB) and CNT using vacuum filtration method (Figure 2d).[25] KB is one type of carbon black but with higher specific surface area and better electronic conductivity. As shown in Figure 2e, the open pore structure and the good electronic conductivity of KB benefit to the ECs exhibiting excellent areal capacitance of 574 $\mu F \cdot cm^{-2}$ at 120 Hz. However, the complicated micro-pores of KB also lead to a compromised frequency response capability with a phase angle of ~−80° at 120 Hz, which is inferior of that of pure CNTs electrode. Even so, this ECs based KB/CNT can smooth the pulsating signal to constant DC output. (Figure 2f) Except for carbon black and one-dimensional CNT, graphene sheets were also be used as electrode materials. In Figure 2g, Liu and co-workers reported a free-standing graphene nanomesh film with uniform and dense nanoholes for ECs applications, in which the size and density of the nanoholes could be well controlled.[34] Compared to graphene films, graphene mesh film with nanoholes can be better function as the ion diffusion and transport channels across the whole films. (Figure 2h) Due to the special structure produced efficient ion diffusion, and electron transport pathways, the ECs exhibits a high area capacitance of up to 306 $\mu F \cdot cm^{-2}$ at 120 Hz and ultrafast frequency response with a phase angle of −82.3°at 120 Hz. (Figure 2i)

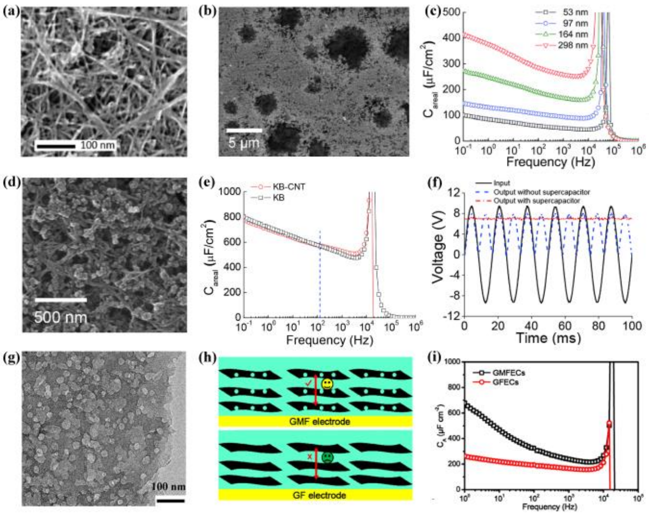

Figure 2. Planar carbon film electrodes. (a) SEM image of CNT films [26]. Copyright 2015 American Chemistry Society. (b) SEM image of CNT films large pore size. (c) Specific capacitance of CNT based electrode [31]. Copyright 2015

The Royal Society of Chemistry. (d) SEM image of the film of Ketjen black and CNT. (e-f) Specific capacitance and filtering performance of carbon black-based electrode [25]. Copyright 2017 Elsevier B.V. (g) SEM image of porous graphene. (h-i) Schematic diagram and specific capacitance of grapheme film and graphene mesh film [34]. Copyright 2018 Elsevier Ltd.

Although the area or volume specific capacitance of the 2D structure is good, its actual capacitance is not sufficient to fulfill the requirement of miniaturization of ultrafast ECs. Because of the densely assembled 2D structure, the capacitance will decrease significantly in the process of thickening. Therefore, the application of 2D structure in high-frequency capacitors is limited, and preparation of porous 3D structure is very important.

2.2 Random three-dimensional carbon materials

Thin films made of carbon black, CNT, and graphene powder are used as electrodes to improve the properties of capacitor. However, the discontinuous pore structures between horizontal layers of the film material significantly restricts the ion movement in the electrode. Hence, Balakrishnan and co-workers synthesized a porous carbon-sponge by freeze-drying method, which exhibited a typical complex hierarchical network with controllable macro and meso-pores as shown in Figure 3a.[38] The tunable size of pores in the macroporous carbon sponges lead to excellent ion mobility and fast ion transport, resulting in ultrafast frequency response with a RC time constant of 319 μs and a high specific capacitance of 172 $\mu F \cdot cm^{-2}$ at 120 Hz (Figure 3b). In Figure 3c, Fan and co-workers synthesized a flexible freestanding electrode composed of edge-oriented graphene grown on carbonized cellulous paper.[37] The edge-oriented graphene sheets provide rich large surface area, which is used to store charges, and the carbonized cellulous electrode exhibits great conductivity property, which is beneficial to high-rate response performance. As a result, this composite electrode has excellent properties with a high areal capacitance of 600 $\mu F \cdot cm^{-2}$, a good volumetric capacitance of 0.6 $F \cdot cm^{-3}$, a large phase angel of −83º, and a high specific capacitance of 0.55 $F \cdot g^{-1}$ at 120 Hz. It worth noting that the specific capacitance will be dramatically increased to 1.5 $mF \cdot cm^{-2}$ when the electrode materials stacked to 3 layers with thickness about 30 μm (Figure 3d). It can be seen that both pore structure and oriented graphene are beneficial to improve the performance of ECs. Based on this, Shi et al. design a kind of oriented 3D interconnected porous structure by electrochemical deposition of graphene oxide (GO) flakes.[40] As is shown in Figure 3e, most of the GO sheets are vertically aligned on the substrate, and some are connected together to form a quasi-vertical material with a porous structure, which make up a random graphene nanowall structure. Benefiting from this structure, the organic electrolyte can easily diffuse to the rich surface of the electrode material, resulting in a high phase angle together with a high areal specific capacitance. Hence, the ECs can efficiently smooth the leftover ripples for AC line filter application in electronics (Figure 3f). Similarly, Qu and co-workers prepared a negative electrode of quasi-vertical graphene by electrochemical deposition, and positive electrode is composed of PEDOT.[41] This ECs yield excellent specific energy density and show excellent filtering effect.

Although the random 3D structure can improve the capacitance compared with the 2D structure, the unsmooth pore structure makes it difficult for ions to adsorb to the entire surface of the material, which greatly limits its performance improvement. Therefore, it's very important to design three-dimensional materials with unobstructed channel structure and rich specific surface to improve the performance of capacitors.

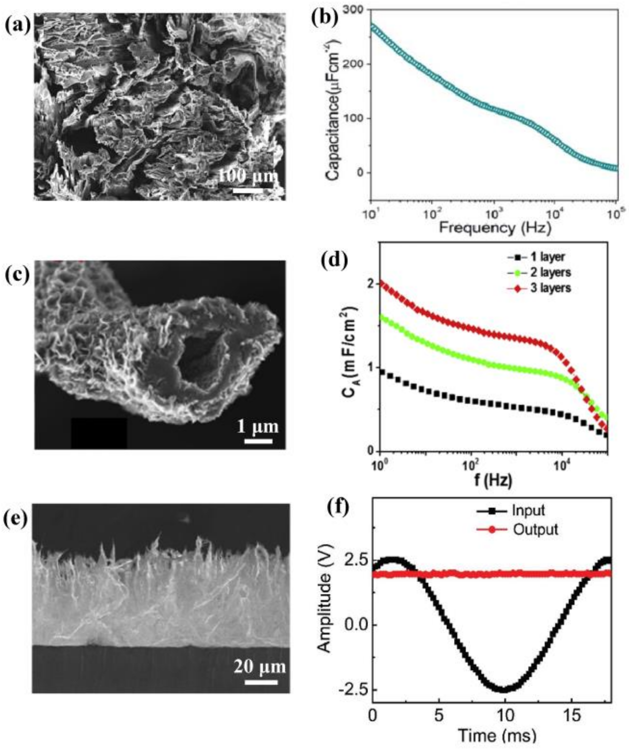

Figure 3. Random 3D carbon materials electrodes. (a) SEM image of carbon-sponges. (b) Specific capacitance versus frequency of carbon-sponges based electrode [38]. Copyright 2015 The Royal Society of Chemistry. (c) SEM image of edge-oriented graphene on carbonized cellulous. (d) Specific capacitance versus frequency of graphene-cellulous electrodes [37]. Copyright 2016 Elsevier B.V. (e) SEM image of 3D graphene prepared by electrochemical deposition. (f) Filtering performances of quasi-vertical graphene-based electrodes [40]. Copyright 2018 Wiley-VCH.

2.3 Vertical three-dimensional carbon materials

There are some works reported that pore structure and quasi-vertical channel facilitate ion transport.[37-41] Therefore, the design and preparation of graphene with strict vertical structure is of great benefit to the performance improvement of capacitors. In addition, interface conductivity also affects the performance of high-power energy storage devices. Compared to electrode materials constructed with reduced graphene oxide, carbon materials grown with chemical vapor deposition (CVD) behaves greater conductivity. Apparently, vertical CNT and vertical graphene directly synthesized with CVD seem to be the best candidates for the electrode material.

Tour et al. designed a three-dimensional (3D) structure composed of graphene and carbon nanotube for ECs application.[44] The structure of the 3D graphene-CNT composite is schematically illustrated in Figure 4a. Few-layers graphene and vertical CNT were grown on patterned nickel current collector by sequence (Figure 4b). The 3D composites are directly and intimately connected to nickel current collectors, providing good interfacial electrical conduction. Together with vertical open channel structure, electrolyte can readily penetrate into CNTs, thus enhancing the specific capacitance and frequency response. (Figure 4c) More interestingly, water-etching can significantly improve the capacitance and energy density, resulting in an excellent filtering performance. It is well known that growth of CNT is catalyst-assisted, whereas growth of vertical graphene by plasma enhanced CVD (PECVD) is catalyst-free. Miller et al. were the first to utilize directly grown vertical graphene as electrode materials of capacitor, showing certain advantages in terms of specific capacitance and fast response.[47] Subsequently, Fan et al. also used microwave assisted PECVD to grow vertical graphene on nickel substrate as electrode material, and the performance of the capacitor was significantly improved.[49] It is noteworthy that most of the graphene grown with PECVD is not strictly vertical, but random graphene nanowall structures in which the graphene sheets overlap each other. Considering that the morphology of vertical graphene directly affects the performance of capacitors, Zhang and co-workers recently developed an electric-field-assisted PECVD method to achieve the preparation of strictly vertical graphene.[53] By adjusting the electric field intensity and growth time, highly controllable vertical graphene was successfully prepared and used as electrode materials.[51] As shown in Figure 4d and 4e, vertically aligned graphene structure provide rich surface area and open channels for electrolyte flow, ion transfer, and charge storage. As a result, the vertical graphene-based ECs exhibit a remarkable specific areal capacitance of 886 $\mu F\cdot cm^{-2}$ and phases angels of 80.6° at 120Hz. In addition, the output voltage and energy density could also be improved to 2.5 V and 0.33 $mF\cdot V^2\cdot cm^{-2}$ when using organic electrolyte. Finally, vertical graphene-based ECs exhibit excellent filtering performance for smoothing arbitrary AC noise into DC signals (Figure 4f). It is worth mentioning that Miller et al. prepared electrode materials by uniformly coating a layer of carbon black on the vertical graphene grown by PECVD (Figure 4g and 4h).[52] Vertical graphene serves as an underlying architecture with an open microstructure and rich surface area, while uniform coating of carbon black induces the increasement of the specific surface area of the electrode material. In addition, with the coating time of carbon black changing from 1 s to 8 s, the phase angles of the carbon black/vertical graphene electrode material are maintained at −80° to −85°, higher than that of the vertical graphene electrode without carbon black deposition. It can be found in Figure 4i, when the deposition time of carbon black is 8 seconds, the specific capacitance of the ECs can reach 2.3 $mF\cdot cm^{-2}$ at 120 Hz, which means that the electrode material of carbon black/ vertical graphene structure has great potential to be used in filter capacitors.

Vertical 3D carbon material can provide strictly open channel and rich surface area for the shortest straight path of ions and abundant storage sites of charge, which is in favour of excellent electrochemical performances. Further design of microstructure in vertical carbon materials can be beneficial to improve the performance of ECs.

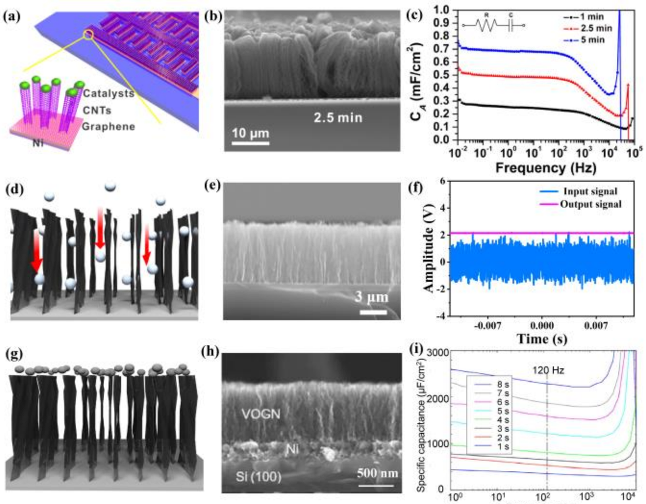

Figure 4. Vertical carbon materials electrodes. (a-b) Schematic diagram and SEM image of vertical CNT grown on graphene film. (c) Specific capacitance versus frequency of vertical CNT electrode [44]. Copyright 2012 American Chemical Society. (d-e) Schematic diagram and SEM image of vertical graphene arrays. (f) Filtering performance of vertical graphene electrode [49]. Copyright 2021 Wiley-VCH. (g-h) Schematic diagram and SEM image of vertical graphene coated with carbon black. (i) Specific capacitance versus frequency of vertical graphene coated with carbon black-based electrode [51]. Copyright 2018 The Electrochemical Society.

3. Conclusion and Perspective

According to the type of material, the carbon materials that make up the electrode are mainly conductive carbon black, carbon nanotubes, graphene, and their compounds. According to the preparation method, the electrode material can be prepared from carbon powder material by physical methods, such as film prepared by filtration, and porous structure prepared with freezing-drying method, or can be directly prepared by chemical vapor deposition method, such as graphene film grown with CVD, and vertical graphene grown with PECVD. The physical method is more flexible in the structure design of electrode materials, while the intrinsic properties of materials prepared by CVD are better. In terms of structure, the carbon related electrode is mainly divided into two-dimensional planar film, disorderly orientation composite material, and vertically aligned carbon material. Compared with material type and preparation method, structure design of electrode material has the most significant effect on performance of capacitor.

In this concept, we mainly discuss the influence of carbon electrode with different structure on capacitor performance. It should be emphasized that phase angle and specific capacitance are two of the most important parameters to evaluate an ultrafast EC. Therefore, we mainly compare the effects of carbon-based electrode with different structures on phase angle and specific capacitance. The phase angle is closely related to ionic transport in the pore structures of the material, and the specific capacitance is determined by the specific surface area of the material.

Meanwhile, the response rate of the capacitor is related to the conductivity and resistance of the electrode material.

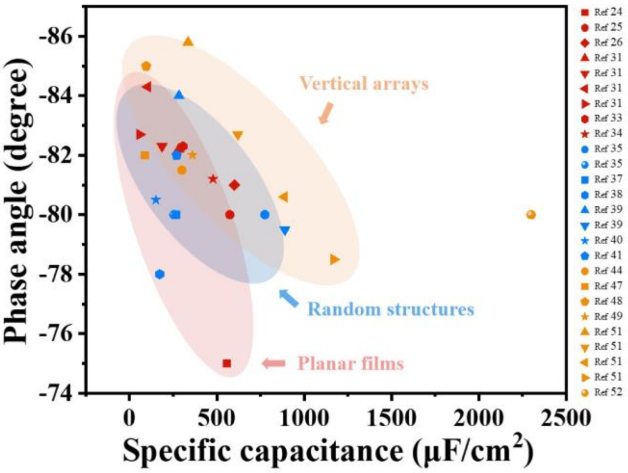

Figure 5. The specific capacitance and phase angel of carbon electrodes with different structure.

In the planar thin film electrode, the carbon material is tightly assembled layer by layer, so the transport path of the electrolyte in this structure is tortuous and long, and the effective area provided for charge storage is limited. Therefore, the specific capacitance of the thin film electrode is difficult to meet the requirements of the filtering capacitor. The disordered three-dimensional structure has more channels, which facilitate ion and charge transfer. However, it still falls into the dilemma of discontinuous pore structure and insufficient specific surface area of the electrode, so the specific capacitance has not been significantly improved. In contrast, the vertical structure of carbon electrode shows a significant advantage. Highly ordered and vertical nanostructures offer unobstructed channels for ion transport and numerous active sites and ion adsorption/desorption. As a result, vertical carbon materials-based electrodes yield a fast frequency response and considerable capacitance. In particular, their specific capacitance is greatly improved while maintaining a large phase angle. All of these results can be found in Figure 5 and Table 1. We prospect that the performance of vertical carbon related electrodes can be significantly improved when some microstructure subtly designed between the vertical channel.

Besides the carbon related electrode, some non-carbon-based electrodes are also used for constructing the ultrafast ECs with AC-line filtering performance. Such as conducting polymer materials[11,54-56] and transition-metal-based materials[57-59], are both pseudocapacitive materials that can store additional charge via faradaic processes. Thus, the capacitance density based on the non-carbon materials may be superior to that of carbon materials. But the sluggish kinetics of the redox reaction of the pseudocapacitance should be considered also. Balancing the trade-off between high capacitance and the high-frequency response of non-carbon materials is still fraught with challenge. Notably, the structure design principle mentioned in this concept for the carbon materials are applicable for the non-carbon materials. By contrast, electrochemical process of carbon materials is a double electric layer mechanism, which can easily realize the quick ion adsorption/desorption. In addition, carbon material is widely used as electrode because of its advantages of excellent stability, good electrical conductivity, simple preparation method. The design and selection of electrode materials should be considered comprehensively.

By ingenious design and controlled preparation, carbon-related ECs exhibit excellent performance in ECs applications. However, there are still some problems to be solved in the practical application of carbon-based capacitors. First, the structural stability of the vertical carbon material is very important, which depends on the repeatability of the preparation method. Only when the performance of carbon-based capacitors is stable will they be accepted by the market. Secondly, the large-scale preparation of carbon-based capacitors is also a serious problem. Only when the carbon electrode is prepared in batches can the carbon-based capacitor be widely used. Finally, another problem is related capacitor packaging. Packaging process also determines the performance of the capacitor. Therefore, an appropriate packaging technology is very key to improve the performance of the capacitor. In a word, carbon-based electrodes have great potential in capacitor field to solve the above problems.

Acknowledgements

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Keywords：carbon · electrochemistry · electrochemical capacitors · electrode material · line filtering

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Table 1. Performance of ECs with different carbon-based electrode structures.

Electrodes	C_A[a] [μF cm^{-2}] at 120 Hz	−Phase angle [°] at 120 Hz	E_A [μWh cm^{-2}] at 120 Hz	τ_0 [μs]	τ_{RC} [μs]	Voltage window [V]	Ref.
Carbon black	558	75			354		24
Ketjin black	574	80	0.625			2.8	25
CNT film [b]	601	81	0.0835		199	1	26
CNT film	282	82.2	0.245	501	181	2.5	31
CNT film	186	82.3	0.161	316		2.5	31
CNT film	104	84.3	0.0903	124		2.5	31
CNT film	58	82.7	0.0503	63		2.5	31
Porous graphene film	306	82.3	0.0272	160	320	0.8	33
NHG film [c]	478	81.2	0.0425	819	203	0.8	34
Carbon nanofiber aerogel	775	80	0.108			1	35
Carbon nanofiber aerogel	255	80	0.221			2.5	35
EOG/CCP [d]	265	80	0.0298	100		0.9	37
Carbon sponges	172	78	0.0538	371	319	1.5	38
VGO [e]	283	84	0.0252	238	1350	0.8	39
VGO	890	79.5	0.0791	1000		0.8	39
VGO	151	80.5	0.131	563	219	2.5	40
VGO	270	82	0.122	464	180	1.8	41
VCNT [f]	300	81.5	0.04167	820	195	1	44
VG [g]	87.5	82	0.0122	67	200	1	47
VG	95	85	0.0132		251	1	48
VG	360	82	0.0405	248	205	0.9	49
VG array	335	85.8	0.0465	383	95	1	51
VG array	620	82.7	0.0861	826	166	1	51
VG array	886	80.6	0.123	999	215	1	51
VG array	1170	78.5	0.163	1460	265	1	51
VG/carbon black	2300	80					52

[a] The C_A and E_A were calculated by the single EC unit rather than the single electrode; [b] CNT= carbon nanotube; [c] NHG= nitrogen-doped holey graphene; [d] EOG/CCP= edge oriented multilayer graphene/thin-graphite in carbonized cellulous paper; [e] VCNT= vertical carbon nanotubes; [f] VGO= vertical graphene oxide; [g] VG= vertical graphene

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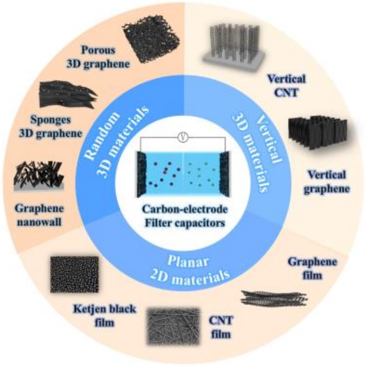
Entry for the Table of Contents



Carbon related electrode materials have been widely demonstrated to significantly increase the performance of ECs because of its light weight, high strength and high processability. The preparation method and structure design of carbon related electrode materials are very important to the performance of capacitors.

Shichen Xu received his B.S. degree from Northwest University in 2017. He is currently pursuing a PhD degree at the College of Chemistry and Molecular Engineering, Peking University in Beijing, China, under the guidance of Prof. Jin Zhang. His current research interest mainly focuses on electric-field-assisted growth of vertical graphene and its applications in thermal interface materials and electrochemical capacitors.

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