Carbon fiber cloth performance improvement via hybrid materials (Fe₂O₃, FeCo₂O₄, and conducting polymer) addition for energy storage applications

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HIGHLIGHTS

- Carbon fiber cloth, iron oxides & conducting polymers are effective, abundant materials for supercapacitor electrodes.
- This review focused on how iron oxides and conductive polymers affect carbon fiber cloth supercapacitor electrodes.
- Previous research found FeCo₂O₄ and conductive polymers improved carbon fiber cloth supercapacitor electrodes.
- The outlook offers insights into improving supercapacitor energy storage using modified carbon fiber cloth electrodes.

ABSTRACT

Carbon fiber cloths (CFCs) are essential materials extensively studied and utilized in numerous applications, including supercapacitors (SCs), batteries, solar cells, and catalysis. CFC is gaining significant research attention as an inexpensive choice for (SC) electrode materials, mainly owing to its peculiar adaptability, which makes it suitable for conveyable or flexible devices. In fact, this characteristic is not easily attainable with other carbon-based matrices. However, bare CFC electrodes face difficulties concerning their capacitive performance because of numerous factors, including markedly little surface space, poor electrochemical efficacy, and limited porousness. In this way, these factors reduce their efficiency as supercapacitor electrodes. To address this, the incorporation of transition metal oxides (TMOs) and conducting polymers (CPs) within the CFC is expected to be crucial in developing the electrochemical performance. This work thoroughly reviews the design and the modification of (CFC) that provide high-performance electrode supercapacitors. It emphasizes implementing effective approaches, such as active material loading, specifically focusing on iron oxides. The SCs have high working potentials and can effectively increase their energy density by iron oxides. According to the researchers' findings, combining CFC and FeCo₂O₄ has a high electrochemical performance and potential range in aqueous electrolytes. Additionally, this paper outlines and highlights the recent advancements in developing iron oxides-CFC and iron oxides/CP-CFC for supercapacitor applications. It explores their design approaches and electrochemical properties, offering insights into future opportunities for energy storage technologies.

1. Introduction

The need for sustainable renewable energy reserve systems has been maximized recently because of the importance of preserving natural resources and managing energy consumption. Hybrid automobiles and adjustable electronic devices have adopted new energy devices like supercapacitors, batteries, and fuel cells. These designed devices convert chemical energy to electrical energy through electrochemical reactivities [1]. This particular increasing interest in supercapacitors (SC), specifically electrochemical capacitors (ECs), is due to their exceptional electrochemical performance, characterized by increased specified power, accomplished cycling life, and fast charging and discharging rates [2]. Nevertheless, compared to batteries, the existing supercapacitors still exhibit lower specific energy levels [3,4]. To address this limitation, researchers have extensively studied two main approaches to enhancing the specific energy of supercapacitors: (i) creating developed supercapacitors offering highly effective capacitance and (ii) increasing the voltage window by carefully selecting the electrolyte [5,6]. The essential aspect for advancing highly performing supercapacitors lies in their specific selection of

electrode materials that evince exceptional conduction of electricity and possess distinctly bigger specific surface areas (SSA), high electrical conductivity, and strong electrochemical activity as electrodes for supercapacitors [7-12].

Researchers aim to foster the supercapacitors' performance and raise their energy by incorporating various nanomaterials into electrode designs and improving diffusion length. The diffusion length is expected to be improved through the nanostructuring of materials. Recent studies have broadly investigated a range of nanomaterials with particular architectures and developed supercapacitor electrodes. These include carbon-based materials, metal oxides, nitrides, and conductive polymers [9,13–20]. Furthermore, concerning these materials, carbonaceous matrices stand out, including graphene, carbon nanotubes [21], and porous carbon, because of their exceptional conductivity [22], cost-effectiveness, large surface area [23], great chemical constancy, and eco-friendly, see Figure 1 [24].

Although carbon nanomaterials are viewed as promising supercapacitor electrodes, their capacitance is often insufficient because of their intrinsic electric double-layer (EDL) mechanism, leading to disappointing performance [25]. To overcome this challenge, researchers have dedicated significant efforts to activate the desired capacitance in carbon materials [26]. In this vein, they have also promoted and elaborated on various approaches, such as structural design, surface adjustment [27], and fusion with materials with pseudocapacitive features [28]. These approaches are intended to reinforce the overall capacitance of carbon nanomaterials while also developing their performance in supercapacitor applications. Iron oxides have been increasingly observed as positive electrode materials for SCs owing to their notable capacity, extensive functioning window in unfavorable potential, and non-toxicity, as well as their earth-abundance and lower cost [29].

$FeCo_2O_4$ is a promising material for energy storage due to its impressive ability to undergo countless valency conditions and plenteous redox reactions, leading to a higher fixed capacitance. However, it lacks high conductivity and a considerable electrolyte ion diffusion distance (20nm), which resultantly lowers the effectiveness of the entire electrode material in the redox reaction. The protective feature of the layer that develops on the metal's surface during certain types of oxidation should be in a physical connection with the crystal composition of the inactive film. As a result, $FeCo_2O_4$ mostly shows lower capacitance and rate performance, preventing its widespread commercial use. Thus, developing effective strategies is crucial to overcome these limitations and improve the energy denseness and the rate performance of $FeCo_2O_4$ electrodes. An electrode's construction and morphology are crucial in figuring out its electrochemical conduct, as improving these two elements is likely to increase the accessibility of electrolyte ions to the electrode material, thereby improving its overall electrochemical performance [30–32]. Carbon fiber cloth (CFC) is a cost-effective carbon material that consists of numerous uniform carbon microfibers, typically ranging from 5 to 10μm in diameter. This material possesses exceptional conductivity and forms a three-dimensional (3D) network structure. Additionally, CFC exhibits remarkable mechanical flexibility and chemical stability. These unique characteristics make CFC a highly favorable material for serving as a scaffold and current collector in flexible electrode designs for energy harvesting and storage devices [33,34].

In addition, carbon fiber cloth (CFC) exhibits excellent conductivity and favorable chemical stability, which enable CFC electrodes to possess higher rates of capability along with an extended lifespan. However, the commercial utilization of CFC in supercapacitors (SCs) is ineffective due to its unsatisfactory capacitive properties. These limitations arise from factors such as small and limited surface space, little porosity, low electrolyte wettability, and limited electrochemical performance [35,36]. Thus, to address these deficiencies, establishing effective methods is crucial to attaining higher energy and power rates and increasing the activity of CFC-based electrodes. To summarize, carbon fiber cloth coatings can enhance electron conductivity, thus increasing the effectiveness of electrochemical reactions. Compared to the pristine $FeCo_2O_4$ system, combining $FeCo_2O_4$ with CFC leads to improved electrochemical performance, entailing specific capacitance and cycling constancy. Accordingly, the hydrothermal synthesis of $FeCo_2O_4$ offers a promising technique for producing nanostructured materials with controlled characteristics [37].

Recent research has focused on combining the spinel structure of metal oxides with carbon materials to maximize their potential. Enhanced electrode materials are highly desired due to the synergistic effects achieved through the combination. It is worth mentioning that these compound materials are composed of multiple carbon materials, with transition-metal compounds outperforming pure carbon materials [38]. Composite materials make building porous nanostructures of a highly defined surface space easier. These nanostructures offer higher electroactive sites, enabling quick electron transference and enhancing structural constancy [39,40].

The present review first briefly explains the characterization and limitations concerning CFC aimed at highly effective SC assembly along with the effective principles of SCs, which are equally reviewed. Then, it summarizes and discusses the latest establishments in the capacitive improvements of CFC, along with their application in SCs. Strategies, including progress in the enhancement of CFC surface via active iron oxide loading on CFC, then advanced to iron oxides and conducting polymer-based CFC, $FeCo_2O_4$ has been taken as active loading on CFC and is particularly highlighted. The third and last section of the study tackles the limitations, future potentials, and recommendations for enhancing the capacitance of the existing TMO/CP-based fiber-based supercapacitors.
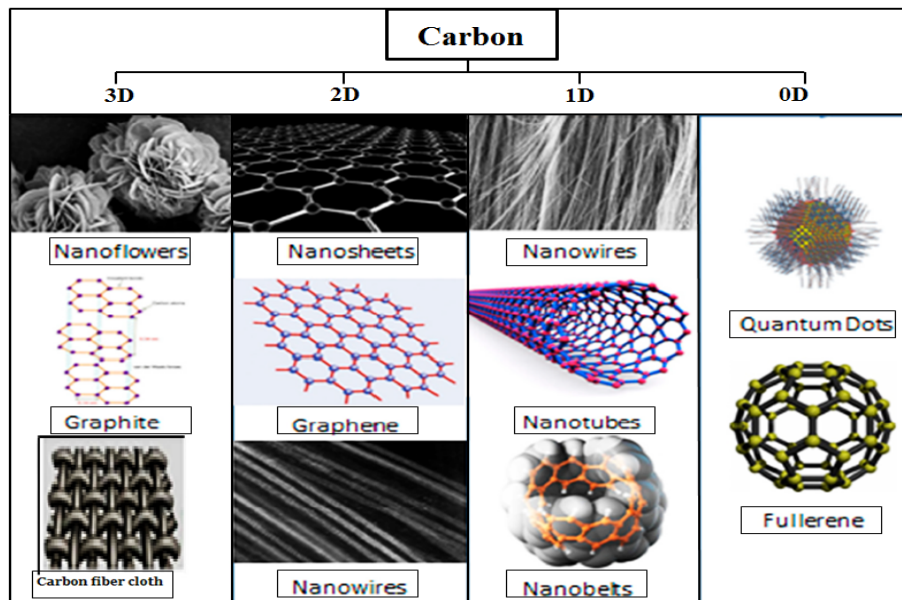
Figure 1: Three-dimensional (0D, 1D, 2D, and 3D) of carbon nanostructures in various forms [41]

2. Electrochemical performance of supercapacitor electrode materials

The overall electrochemical conduction of supercapacitors (SCs) can be determined through several variables, including definite capacitance, functioning voltage, corresponding sequential resistance, power denseness, and energy density, in addition to time constancy [42,43]. For the accurate evaluation of this SC's capacitive behavior, various techniques have been suggested for measuring three crucial variables: special-designed capacitance (Cs), functioning voltage (V), and corresponding sequential resistance (ESR). Power denseness (P) and energy density (E) are calculated according to these parameters. Cyclic voltammetry (CV), galvanic charge/discharge (GCD), and electrochemical-impedance spectroscopy (EIS) are commonly applied methods for evaluating these essential variables, which were mentioned earlier [43].

Conway et al. [44] calculated these fundamental parameters using the following Equations: 1, 2, 3, 4, and 5. The calculation of definite capacitances (F g^{-1}) can be figured via using CV curves as shown below [44]:

$$C = \frac{\int I dt}{m \, \Delta V} \tag{1}$$

where I represents the redox reaction current (in Amperes), dt symbolizes the time differential, m stands for the mass of the active material (in grams), and V is the voltage at discharging time (in Volts). The theoretical special-designed capacitance (Ct) of faradic electrochemical capacitor materials can be expressed as shown below :

$$C_t = \frac{nF}{\Delta V \, Mr} \tag{2}$$

The parameter 'n' symbolizes the moles of charges transmitted through the moles of active materials. 'F' stands for Faraday's constant, which has a value of 96485 C mol^{-1}. V denotes the voltage during the discharging process in volts (V), while Mr' symbolizes the molar mass of the active materials. The energy (E) reserved in a capacitor (Wh kg^{-1}) is directly proportional to the charge (Q) at every interface and the likely difference (V) across the capacitor. This relationship can be represented as shown below [44]:

$$Q = CV \rightarrow E = \frac{1}{2} QV \rightarrow E = \frac{1}{2} \times CV^2 \tag{3}$$

Here, Q stands for the charge with respect to Coulombs (C), C is the capacitance (F), and V is the likely difference in volts (V). This stored energy is proportional according to the capacitance of the capacitor. Equation (4) defines the cell's power density (P), energy density (E), and the time of discharging (t) in seconds as shown below [44]:

$$P = \frac{E}{t} \tag{4}$$

The cell's power density (P) (W kg^{-1}) is related to its energy density (E) (Wh kg^{-1}) and the discharging time (t) in seconds (s). According to a Nyquist plot of electrochemical impedance spectroscopy (EIS), the impedance (Z) is expressed as shown below [44]:

$$Z = Z' + jZ'' \tag{5}$$

where Z' stands for the actual part of impedance, and the imaginary aspect of impedance is represented as Z''. Here, 'j' is the imaginary unit, equal to the square root of -1.

3. Taxonomy of supercapacitor's storage

Understanding the specific charge storage mechanism in the Leyden jar, an early capacitor, was limited to the nineteenth century. During this time, Helmholtz [45] proposed a design explaining the dispensation of ions at the electrode/electrolyte interface. Subsequently, Gouy [46], Chapman [47], Stern [48], and Grahame [49] made further modifications to this model to enhance the understanding of its charge storage process. The first electric double-layer capacitor was credited to the patent of H. I. Becker [45] of General Electric Co. It utilized porosity features in carbon electrodes in an aqueous electrolyte functioning at a 2.5 V or less voltage. Later, Conway and Pell [50] presented the earliest pseudocapacitor employing a distinct charge storage mechanism compared to Becker's designed capacitor. Two main models of supercapacitors have received considerable attention in research, manufacturing, and commercialization: electric double-layer capacitors (EDLCs) and redox-based pseudocapacitors. The way these two models store electric charges sounds different. EDLCs operate through a non-Faradaic process, relying on the accumulated electrostatic charges on the interface between the electrode and the electrolyte, which includes carbon materials. The procedure for charge storage rests on constructing this specific electrical double layer. Furthermore, redox-based pseudocapacitors utilize Faradaic redox reactions for charge storage. This affects the transfer of charges through the double layer, resulting in a Faradaic current flowing straight through the cell, which incorporates transition metal oxides and hydrogens (like ruthenium oxide, manganese oxide, and nickel oxide), conducting polymers (such as polyaniline and polypyrrole), and suitable electrolytes [51]. The taxonomy of supercapacitors, including EDLCs and pseudocapacitors, can be visualized in Figure 2. Furthermore, the comparison between EDLCs and pseudocapacitance is presented in Table 1.
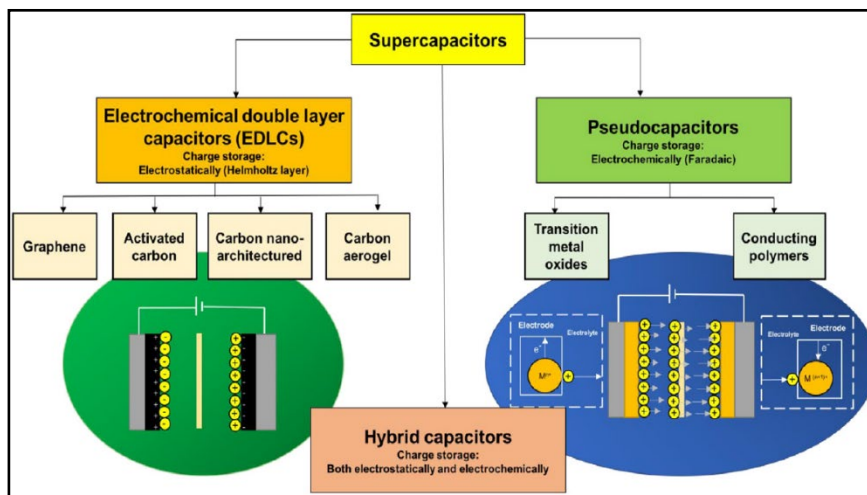

Figure 2: Supercapacitor types are classified according to the ruling mechanism of charge storage and the typical material used [51]

Table 1: EDLC and pseudocapacitance Comparison [52]

EDLC	Pseudocapacitance
Non-Faradaic	Involves Faradaic process (es)
20-50 $\mu F/cm^2$	For a single-state process, the specific capacitance is typically around (2000 $\mu F/cm^2$). On the other hand, for a multi-state, overlapping process, the specific capacitance ranges from (200 $\mu F/cm^2$) to (500 $\mu F/cm^2$).
The specific capacitance (C) generally remains relatively consistent with potential, with the exception of passing in the zero charge potential.	The specific capacitance (C) of RuO_2 is relatively constant with potential, meaning its variation is insignificant or small. However, in the case of a single-state process, a noticeable and significant maximum value is observed in the specific capacitance.
Highly reversible charging/discharging	In overlapping, multi-state processes such as hydrogen (H) behavior at platinum (Pt) electrodes, the specific capacitance can exhibit multiple maxima. This indicates that the capacitance can reach distinct peak values at different potentials. Although the process is generally reversible, there is an inherent limitation in the electrode kinetics rate due to the presence of Faradaic leakage resistance.
Unlike non-electric electrostatic capacitors, electric double-layer capacitors (EDLCs) have a limited voltage range in which they can operate effectively. In other words, there are restrictions on the maximum voltage that can be applied to an EDLC without compromising its performance or risking damage. This limitation sets EDLCs apart from non-electric electrostatic capacitors, which do not have such restrictions on their voltage extent.	Has hindered voltage extent
Displays the mirror-image of voltammograms	Displays the mirror image of voltammograms.

4. Carbon fiber cloth in supercapacitors

4.1 Characterization of CFC

One of the most notable advantages of (CFC) compared to variant carbon materials, like carbon nanotubes (CNTs), graphene, and activated carbon, is its exceptional mechanical potency coupled with preferable flexibility and mechanical completeness. While thin films based on CNTs or graphene are typically prepared through vacuum filtration, they often exhibit insufficient mechanical strength. On the contrary, it is possible to directly utilize CFC as an independent and flexible electrode for supercapacitors (SCs). Moreover, CFC might be incorporated into small appliances of compact sizes and various shapes. These functioning characteristics make the CFC a perfect candidate for transportable and wearable electronics, where flexibility and mechanical durability are crucial factors, see Figure 3. In a study accomplished by Han et al. [53], it was observed that CFC elucidated a remarkable tensile strength of 18.2 MPa, indicating its ability to withstand high levels of mechanical stress. Furthermore, the mechanical features of CFC were found to be minimally affected by concrete chemical etching and electrochemical actuation. Another research by Yu et al. [54] involved the fabrication of a higher-rate fiber-shaped SC using activated carbon cloth. This fiber-shaped SC was interwoven within a dragonfly knot and attached to a glove, demonstrating the weavability and knottability of CFC. Most importantly, the fiber-shaped SC kept its high performance even under the conditions of entwining and knotting, highlighting the effective flexibility of CFC. Additionally, CFC depicts two crucial factors for its functioning as an electrode material: high conductivity rates and favorable chemical stability. These properties contribute to the increasing capability and long lifespan of CFC-based electrodes. Overall, the combination of CFC's mechanical strength, flexibility, weavability, knottability, conductivity, and chemical stability makes it a highly desirable material for various applications, particularly in portable and wearable electronics. The utilization of commercial CFC in supercapacitors (SCs) for various applications is hindered by its unsatisfactory capacitive properties, as discussed in studies conducted by Wang et al. [55] and Wang et al. [56]. These limitations are primarily attributed to CC's small specific surface space, inadequate porosity, deficient electrolyte wettability, and insufficient electrochemical performance. In order to attain high rates of energy and power from SCs together, it becomes crucial to promote potent techniques to reduce the deficiencies associated with CFCs. Efforts should focus on enhancing the specific surface areas of CFC, improving its porosity to facilitate electrolyte penetration, enhancing electrolyte wettability, and boosting its electrochemical activity. By addressing these challenges and finding suitable solutions, improving highly performing supercapacitors by enhancing their capacitive properties and unlocking their full potential is possible.
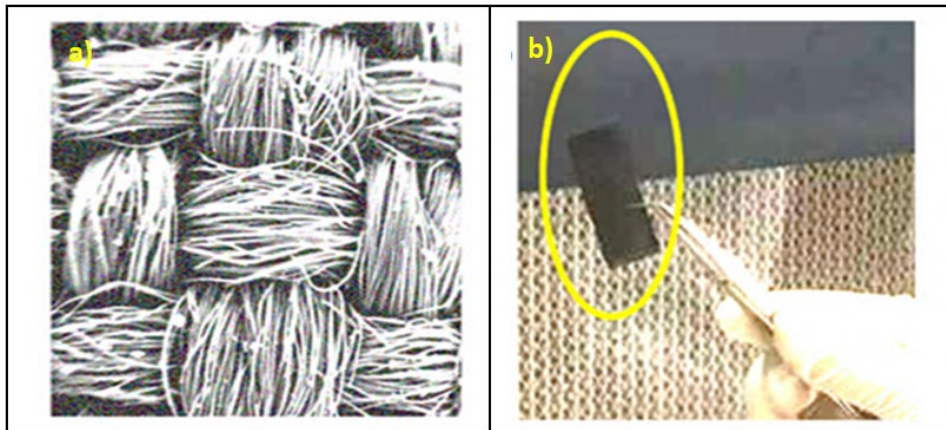

Figure 3: a) SEM image of CFC, and b) photographic image of CFC

4.2 CFC mechanism of energy storage

The energy storage process of (CFCs) is closely tied to this electrical double layer (EDL) phenomenon observed in supercapacitors (SCs). In an EDL capacitor, the charge accumulation develops at the electrode and electrolyte interface. This is facilitated by the adsorption of electrolyte ions onto the surface of the electrode material. In the case of CFCs, when an EDL capacitor is gathered via a potency that does not override the voltage window (breakdown voltage) of the electrolyte, the negative charges accumulate on the cathode, attracting electrolyte cations [57]. Conversely, the electrolyte anions are drawn from the lack of electrons on the anode. Understanding the capacitance mechanism within (CFCs) has evolved over time. Initially, Helmholtz [45] proposed that capacitance was credited solely for the charges' accumulation at the interface between the electrode and electrolyte. However, the subsequent models introduced by Gouy [46] and Chapman [47] explained that charges were not only localized at the interface but rather dispersed throughout the electrolyte's dispersed layer see Figure 4.

Stern [48] integrated the Helmholtz and Gouy-Chapman models to further refine the understanding. According to Stern's model, the double-layer capacitance arises from two distinct regions: (i) The Helmholtz layer, where the accumulation of charge materializes at the electrode and electrolyte interface. The thickness of the layer is equivalent to that of the solvent molecule. (ii) The diffuse layer is the point at which charges are dispersed through the electrolyte's thermal fluctuation.
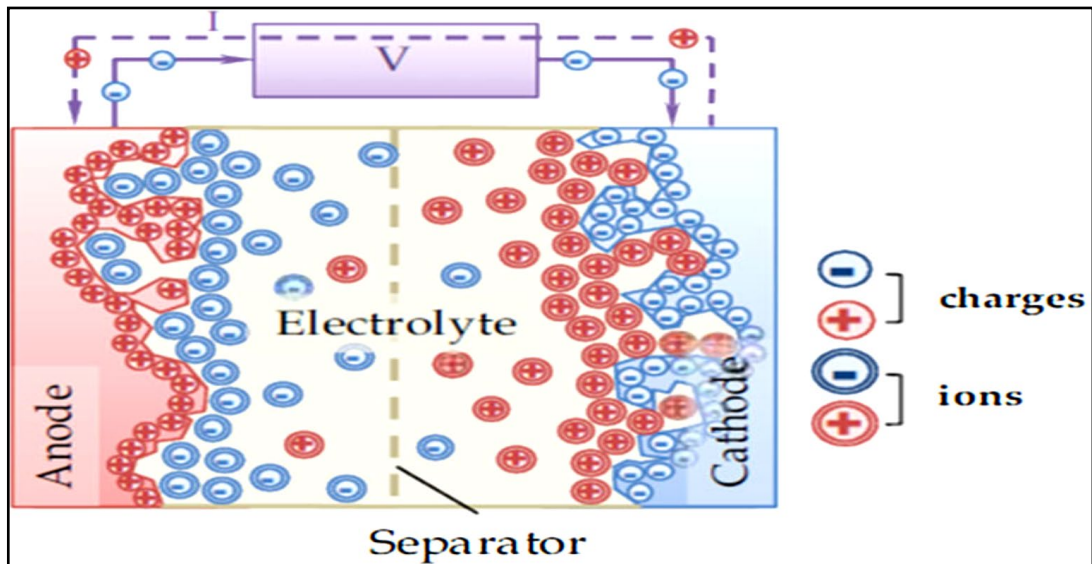
Figure 4: The accumulation of charge on the electrolyte results in electrolyte ions' adsorption on the anode and cathode surfaces [58]

This layer extends beyond the Helmholtz layer and contains scattered charges. By incorporating both the Helmholtz and diffuse layers, the Stern model provides a more comprehensive understanding of the double layer capacitance, considering both localized charge accumulation and charge dispersion throughout the diffuse layer. These models evolve the understanding of CFCs' charge storage process and capacitance, shedding light on the complex behavior at the electrode and electrolyte interface. The parallel double layer capacitance (C_{dl}) at the interface of electrode and electrolyte can be represented as the series combination of the Helmholtz capacitance, C_H, and the diffuse layer capacitance, C_{diff}, according to the following Equation 6 [59]:

$$\frac{1}{C_{dl}} = \frac{1}{C_H} + \frac{1}{C_{diff}} \leftrightarrow C_{dl} = \frac{(C_H \times C_{diff})}{(C_H + C_{diff})} \tag{6}$$

Concerning an electric double-layer capacitor (EDLC), the charge storage mechanism does not affect the electrode material's structure. As a result, EDLCs can achieve a higher number of lifecycles than batteries, as the electrochemical kinetics of their reactions limit the number of lifecycles [59,60].

As discussed earlier, the inadequate capacitive features of bare (CFC) are likely because of its insignificant surface space, lower electrochemical activity, and low porosity, as studied by Ye et al., [61]. Thus, to reduce the aforementioned limitations, varied techniques have been adopted for handling the structural shortcomings of CFC. Among these techniques are increasing the surface area, introducing surface operative groups, and optimizing pore distribution. These methods can be broadly categorized into two groups: surface modification of carbon fiber surfaces (CFC) and adding metal oxides such as $FeCo_2O_4$. This study focuses on the addition of iron oxides to CFC.

4.3 Improvement in CFC Performance

4.3.1 Active iron oxides loading on CFC

The successful use of cost-effective carbon-derived materials in energy storage relies on finding effective and scalable processes and establishing techniques. Recent studies have investigated CFC applicability within supercapacitors and found that CFCs serve as excellent supports for various pseudo-capacitive materials, for example, metal oxides, chalcogenides, and phosphides. More specifically, the considerable incorporation of transition metal oxides (TMOs) onto carbon materials with electrical conduction is due to their higher theoretical capacity and reversibility, making them suitable for Faradaic supercapacitor electrodes [62,63]. Binary TMOs, consisting of one single transition metal ion and one electrochemically active or inactive metal ion, have received significant attention. These binary TMOs reveal different crystal constructions, for example, spinel, scheelite, $CaFe_2O_4$-type, and more. Binary TMOs generally demonstrate higher electrical conductivity and electrocapacitive activity than single metal oxides, making them desirable electrode materials for supercapacitors [64–68]. By combining CFCs with binary TMOs, the overall efficiency of supercapacitors might be largely increased. These CFCs act as effective supports, offering a large surface area and further facilitating the efficient application of effective materials. This combination enables the improved energy storage capabilities, making it suitable for practical applications [69,70]. In order to enhance the catalytic conditioning of spinel oxides, which is often hindered by low electronic conductivity, mixing or supporting them with conducting carbon materials is common. This ensures fast electron transport within the nanocomposite structure. Nanocomposite supercapacitor electrodes are composed of multiple materials, typically chosen from the two types of supercapacitor materials mentioned earlier. This combination aims to exploit the finest features offered by every material, aiming for synergistic effects that can lead to improved electrode performance [71]. One common approach to achieve satisfactory capacitance is to load active materials onto conducting carbon. This strategy adds additional pseudocapacitance

and expands the operating voltage range. For example, Fe_2O_3, known for its considerable theoretical capacitance around 3625 F/g and appropriately functioning voltage window, has been fused into CFC-based electrodes [65].

Zhang et al. [66] conducted a synthesis study where they effectively planned the structure of a three-layered core-shell sandwich. This structure consisted of carbon nanotubes and Fe_2O_3 carbon arrays, backed by a substrate of CFC. The carbon array and nanotubes served multiple purposes, including extending the surface area, enhancing conductance, controlling effective materials, improving energy storage implementation, and ensuring long-term stability. Furthermore, they acted as surface-protective conductive layers for Fe_2O_3, preventing the incorporation of Fe-based intermediate oxides and hydroxides.

The electrode, comprised of carbon nanotubes and Fe_2O_3 at carbon arrays backed by a substrate of CFC, exhibited a particular capacitance of approximately 787.5 F/g. This remarkable performance establishes it as a successful negative electrode material for highly conductive supercapacitors.

Chen et al. [67] presented in their research the utilization of Fe_2O_3 backed by carbon cloth acting like a negative electrode for supercapacitors. They fabricated Tetsubo α-Fe_2O_3/C nanoarrays of vacuous structures composed of Fe_2O_3 nanocrystals and carbon nanoparticles supported on CFC. This unique structure provided sufficient mesopores between the Fe_2O_3 and carbon nanoparticles, promoting active electron and ion transfer in addition to increasing the effective points available for energy storage. The electrode demonstrated a definite supercapacitance of approximately 430.8 mF/cm^2 (391 F/g) at a 1 mA/cm^2 current density. Further, it exhibited favorable cycling constancy, keeping 88.9% of its capacitance succeeding 2500 cycles.

The Fe_2O_3/C nano-arrays supported on CFC were further utilized to design an asymmetric supercapacitor serving as the negative electrode, while MnO_2 became the positive electrode. The mechanism achieved an energy density of 0.64 mWh/cm^3 at a 14.8 mW/cm^3 power density. Such outcomes highlight the prospect of the CFC-supported Fe_2O_3/C nano-arrays acting like a favorable electrode material, producing supercapacitors with substantial performance.

Another study by Li et al. [68] presented the incorporation of porous Fe_2O_3 nanospheres onto activated carbon cloth (ACC) to perform a supercapacitor electrode. This electrode demonstrated an excellent super capacitance equivalent to 2775 at $1 mA/cm^{-2}$. This conductivity surpassed previously reported Fe_2O_3-reinforced carbon fiber cloth electrodes. Several factors influence the specific supercapacitor performance of Porous Fe_2O_3 nanospheres on ACC. First, the mixture of a considerable surface area (99.1 m^2/g) and porosity of Fe_2O_3 provided ample effective points to store energy. Second, ACC's particularly good electrical conductivity enabled efficient electron transport in the electrode. Finally, the lower diffusion barrier of Fe_2O_3 and the presence of displayed surface electronegativity further improved supercapacitor performance. Furthermore, the porous Fe_2O_3 nanosphere-ACC electrode offered outstanding stability, maintaining 95% of its capacitance after 4000 cycles. This underscores its durability for long-term usage. The electrode was used to construct a symmetric supercapacitor, although further details about its performance were not provided in the given information. Overall, the study highlights the promising potential of porous Fe_2O_3 nanospheres incorporated on activated carbon cloth as a supercapacitor electrode with considerable performance.

In a work by Song et al. [72], a hierarchical $CoFe_2O_4$ core-shell microsphere electrode grown on a carbon fiber cloth (CFC) substrate was laid and integrated via a mild hydrothermal method. The resulting products, labeled as CFC/$CoFe_2O_4$-1 h, CFC/$CoFe_2O_4$-4 h, CFC/$CoFe_2O_4$-8 h, and CFC/$CoFe_2O_4$-12 h, were cooled at room temperature, rinsed with water repeatedly, dried at $60°C$, and then strengthened at $300°C$ for 3 hours. These specific cobalt ferrite spheres synthesized in this process exhibited three phases: nanospheres, microspheres, and core-shell microspheres. The SEM images reveal the formation of CFC/$CoFe_2O_4$-1 h nanospheres. A thick layer of CFC/$CoFe_2O_4$-4 h nanospheres on the surface of CFC. The nanosphere measures around 100nm. The morphology of CFC/$CoFe_2O_4$-8 h microspheres, with a large diameter of approximately 1μm. As observed on their surfaces, microspheres consist of nanospheres and nanoparticles. The rough surface of the microsphere causes irregular microsphere formation after temperature lowering. Further heating causes cobalt ferrite nanoparticles to develop and collect on microsphere surfaces, eventually creating a shell over time. The final core-shell microsphere is a perfect sphere. The shell thickness is approximately 500nm. The latter possessed larger capacitances due to the energy-storing core-shell structure of cobalt ferrite. Hierarchical $CoFe_2O_4$ core-shell microspheres formed on CFC have outstanding electrochemical characteristics due to their nanoparticles, which improve the electrode and electrolyte surface area and charge storage capacity. The core-shell microsphere structure enhances CFC hydrophilicity and stabilizes the material by protecting the core layer cobalt ferrite microsphere, preventing degradation to the internal structure. This particular CFC/$CoFe_2O_4$ core-shell microsphere electrode, functioning as a positive pseudocapacitor electrode, manifested impressive capacitance performance. Specifically, at an actual density of 1 A g^{-1} in 3 M KOH, it exhibited a capacitance of 1280.5 F g^{-1}. The electrode also showed good cyclic constancy, reserving 95.8% of its capacitance following 2000 cycles at the actual density of 1 A g^{-1} in 3 M KOH. The maximum density of energy achieved was 84.6 Wh kg^{-1} at a power density of 1334 W kg^{-1}. The researchers further utilized the CFC/$CoFe_2O_4$ electrode in a supercapacitor with aqueous flexible asymmetric properties (AFAS). AFAS, known for its low cost, rising capacity, and plain manufacturing process, represents an advantageous model for the succeeding generation of highly effective supercapacitors. The remarkable effectiveness of the CFC/$CoFe_2O_4$ electrode suggests its capacity to project highly effective flexible supercapacitors.

Developing $FeCo_2O_4$ electrodes has provided a productive and practical technique for achieving high energy density levels and supercapacitor performance. Additionally, the inherent flexibility of polymer conductivity makes them advantageous for flexible supercapacitors. In this context, polypyrrole (PPy) can be an outstanding "shell" structure overlaying other nanomaterials' surfaces. Munhoz et al. [73] investigated electrodes for supercapacitors, binder-free flexible CFC from polyacrylonitrile (PAN) textiles. In order to create the finished activated carbon cloth (ACC), the fibers were thermally oxidized, CO_2 activated, and then subjected to a spontaneous deposition of iron oxide. In order to use ions as electrodes for supercapacitors without time-consuming and expensive binders, an acidic aqueous electrolyte (H_2SO_4 2mol L^{-1}) was studied.

Capacitances of up to 116.8 F g^{-1} were achieved. A study by Huang et al. [71] focused on the effectively designed structured polypyrrole nanowire arrays (NWAs) on carbon fiber cloth (CFC) surfaces. To achieve this, pyrrole was electropolymerized on a carbon cloth substrate in a 0.2 M phosphate buffer solution, forming PPy and CFC. The study concluded that the coordinated arrays of nanoarchitecture placed exactly on conducting substrates offer a novel approach to expediting Faradic reactions for charge storage in high-performance pseudocapacitor electrodes. The well-structured PPy NWAs electrode illustrated a fantastic capability rate and an increasing definite capacitance of 699 F/g at 1 A/g. Furthermore, it sequentially maintained 92.4% and 81.5% of its capacitance at 10 A/g and 20 A/g. The PPy NWAs demonstrated the ability to attain a higher power density of 0.65 kW/kg at an energy density of 164.07 Wh/kg.

Combining $FeCo_2O_4$ and polymer on the CFC substrate in the form of a nanocomposite enhances the electrochemical properties of the electrodes and further improves their performance in supercapacitors. The use of $FeCo_2O_4$ electrodes has proven to be a functional and applicable approach for achieving high rates of energy density and performance in supercapacitors. The flexibility of conducting polymers adds to their advantages for flexible supercapacitors, with polypyrrole (PPy) serving as a positive "shell" structure that can cover the surface of other nanomaterials. Wu. et al., [74]. Investigated the interface between the electrolyte and electrode using a straightforward chemical reduction procedure in the study of low-crystallinity Fe_2O_3 nanorod arrays built on CFC (D-Fe_2O_3/CC). Then, PPy was electrochemically deposited on the surface of low-crystallinity Fe_2O_3 to create a metal oxide/polymer core-shell nanocomposite (D-Fe_2O_3@PPy/CC). The D-Fe2O3/CC surface was made rougher by the $NaBH_4$ treatment, which favored the Faradaic reaction brought on by ion diffusion in the bulk phase. Electrodes deposited in 30, 60, 120, and 180 seconds. After 30s of PPy electrodeposition, no change was observed see Figure 5a. When the electrodeposition time reached 60s, nonuniform particles were embedded on the electrode and the nanostructure covered the CC fiber see Figure 5b. With 120s of PPy electrodeposition, the nanostructure was uniformly coated see Figure 5c. When the electrodeposition increased to 180s, the nanorod or nanosheet structure disappeared and PPy aggregated on the electrode see Figure 5d.
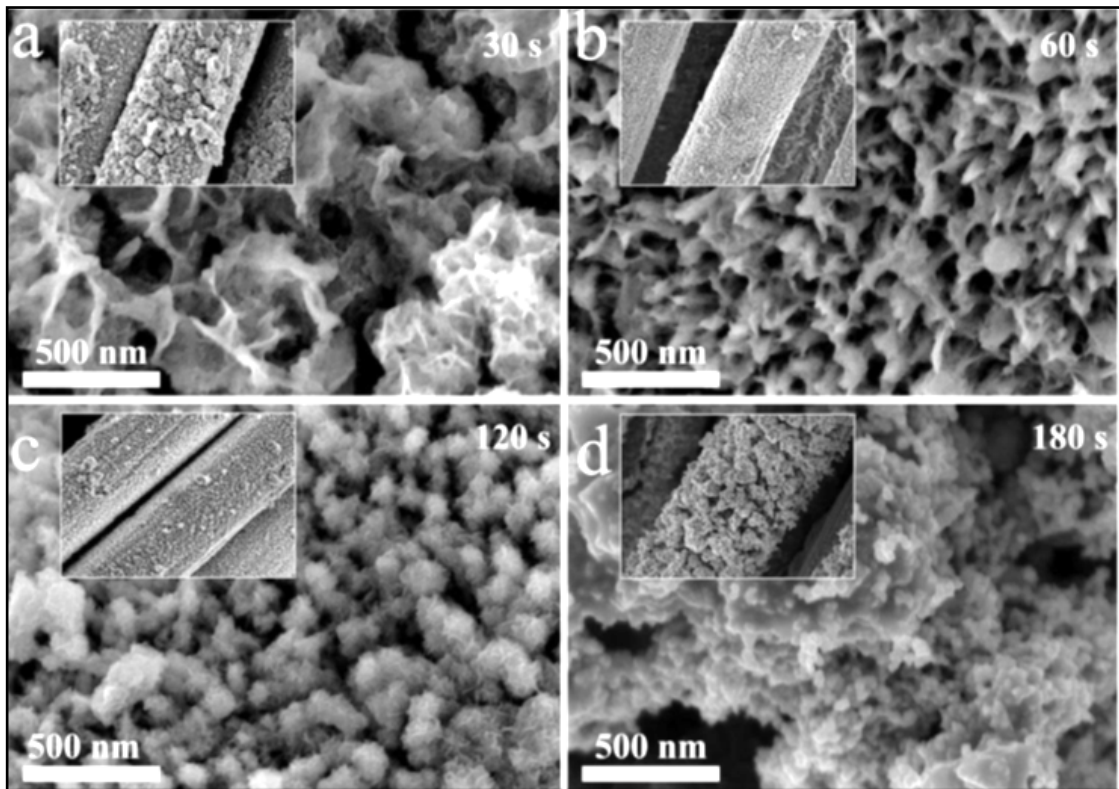

Figure 5: SEM photos with different electrodeposition timings of D-Fe_2O_3@PPy/CC: a) D-Fe_2O_3@PPy-30s, (b) D-Fe_2O_3@PPy-60s, (c) D-Fe_2O_3@PPy-120s, and (d) D-Fe_2O_3@180s [74]

The charge storage on or near the surface of the electrode was improved by the development of a PPy layer on the surface of D-Fe_2O_3. This D-Fe_2O_3@PPy/CC electrode produced an increased capacitance of 615 mF compared to the pure Fe_2O_3/CC electrode, which had a capacitance of 123 F g^{-1} at 1 mA cm^2. The D-Fe_2O_3@PPy/CC electrode showed superior cycling stability, retaining 79% capacity at 10 mA cm^{-2} after 5000 cycles, surpassing Fe_2O_3/CC (42% and D-Fe_2O_3/CC 24%) electrodes see Figure 6 (a-c).
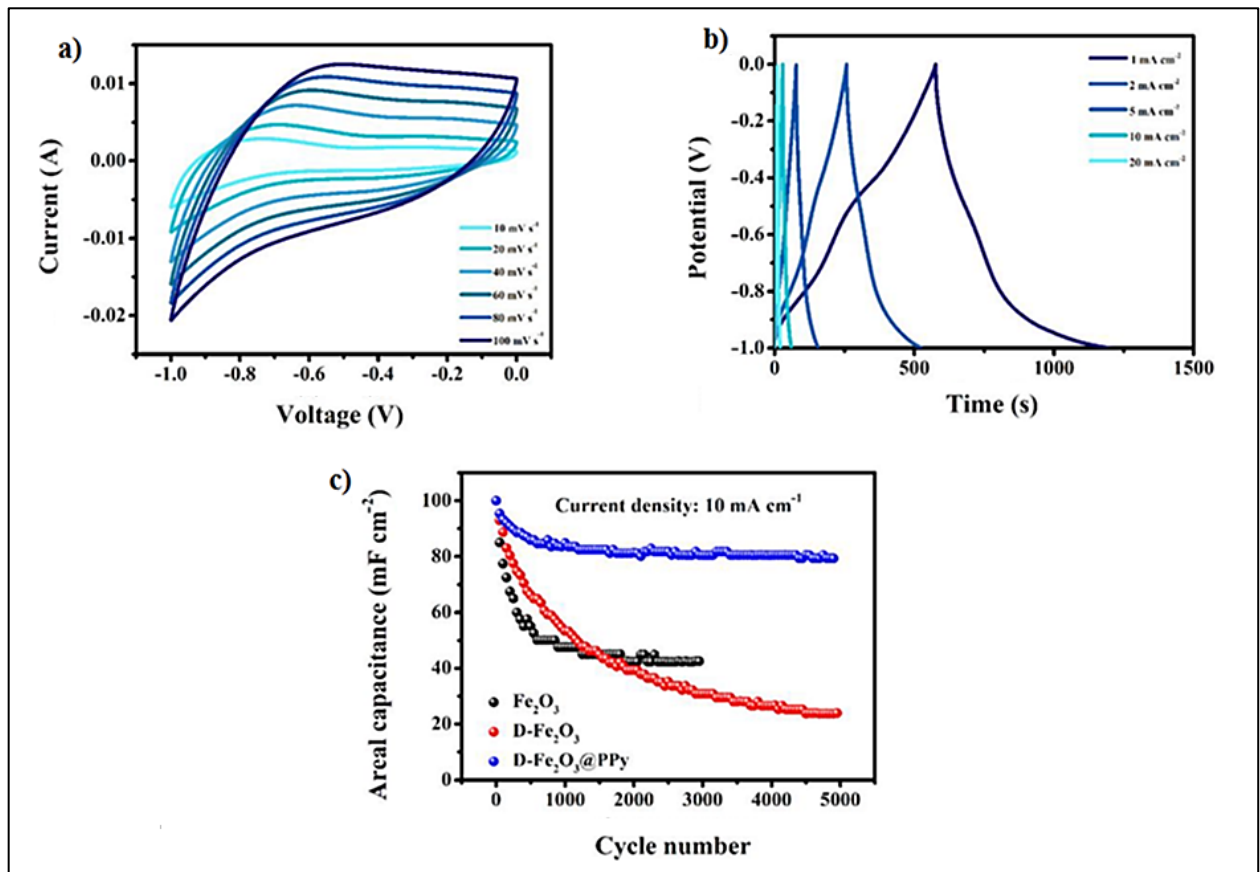
Figure 6: a) Cyclic voltammetry (CV) of D-Fe$_2$O$_3$@PPy-120 s at different scan rate, b) charge and discharge voltage (CDV) curves at 1 different current densities, c) cycling performance at 10 mA cm^{-2} of electrodes [74]

In a study conducted by Wang et al. [16], hierarchical T-Fe$_2$O$_3$/polypyrrole (PPy) nanoarrays (NAs) were fabricated on conductive CFC using a self-sacrificing molding within the situ vapor-phase polymerization route under temperate conditions, see Figure 7. The resulting electrode, composed of T-Fe$_2$O$_3$/PPy NAs on carbon cloth, exhibited an increasing areal capacitance of 382.4 mFcm^{-2} at a current density of 0.5 mAcm^{-2} and appeared great reversibility, with a capacitance retention of 97.2% after 5000 cycles. Positively, when integrated into a solid-state asymmetric supercapacitor (ASC) with MnO$_2$ electrodes, the T-Fe$_2$O$_3$/PPy NAs-based device achieved a considerable energy density of 0.22 mWhcm^{-3} at a power density of 165.6 mWcm^{-3}. The formation of T-Fe$_2$O$_3$/PPy NAs on conducting carbon cloth involves the fabrication of highly ordered sacrificial ZnO nanoarrays upon the carbon cloth using a low-temperature hydrothermal method see Figure 7. These ZnO nanoarrays are then absorbed in an aqueous Fe(NO$_3$)$_3$ solution to develop tectorum α-Fe$_2$O$_3$ nanoarrays. Finally, the 3D, hierarchically nanostructured T-Fe$_2$O$_3$/PPy NAs are obtained by encapsulating the T-Fe$_2$O$_3$ NAs within PPy shells through a straightforward in situ vapor-phase polymerization process.

He et al. [75] studied core/shell heterostructure electrode design and production for supercapacitors. They synthesized graded hybrid FeCo$_2$O$_4$@polypyrrole core/shell nanowires through a hydrothermal method. This approach evinced promising results in increasing the supercapacitors' electrochemical characteristics. In their research, the FeCo$_2$O$_4$/polypyrrole core/shell nanowires were used as anodes for flexible supercapacitors. These nanowires revealed a definite capacitance of 2269 F g^{-1} at 1 A g^{-1} and retained 79.2% of the specific capacitance at 20 A g^{-1}. This demonstrates their ability to maintain high-level capacitance even at higher rates of current densities. Furthermore, the researchers manufactured a moldable asymmetric supercapacitor (ASC) by integrating the FeCo$_2$O$_4$/polypyrrole anode into an activated carbon (AC) cathode. This ASC achieved a notable energy density of 68.8 Wh kg^{-1} at 0.8 kW kg^{-1} and manifested an extended cycle lifespan with 91% capacity retention over 5000 cycles. The FeCo$_2$O$_4$ nanowires were precisely developed on CFC, serving as the "core" material, needless for binder additives see Figure 8. This approach ensured increasing electrical conduction and mechanical constancy. The conductive polypyrrole (PPy) acted as the "shell," appropriately enhancing conductivity and ion accessibility. Ultimately, this study presented a successful synthesis method for hierarchical core/shell nanowires by combining FeCo$_2$O$_4$ and polypyrrole on CFC to develop the electrochemical functioning of supercapacitors. The study findings are summarized in Table 2, which provides an overview of the literature survey on Fe oxides with carbon-based flexible conductive substrates.
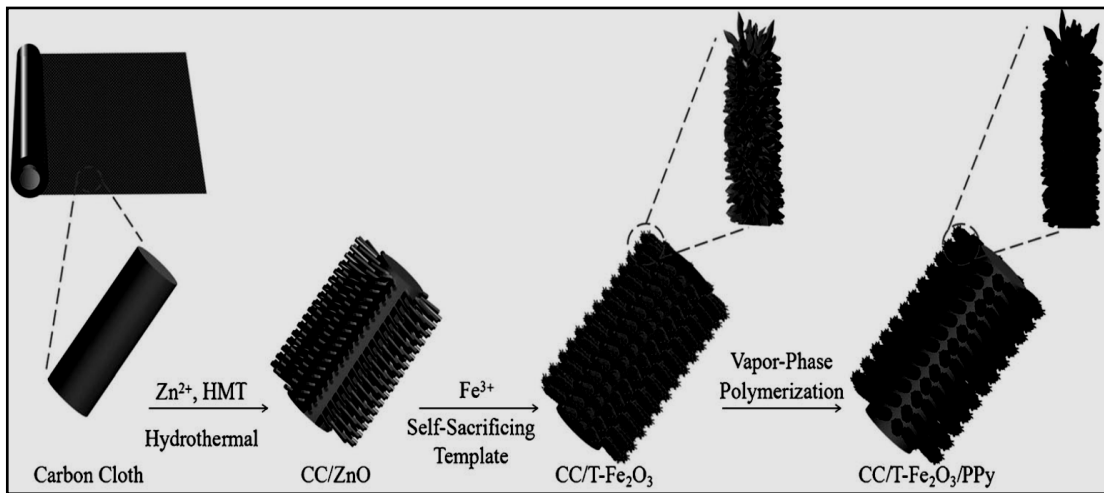
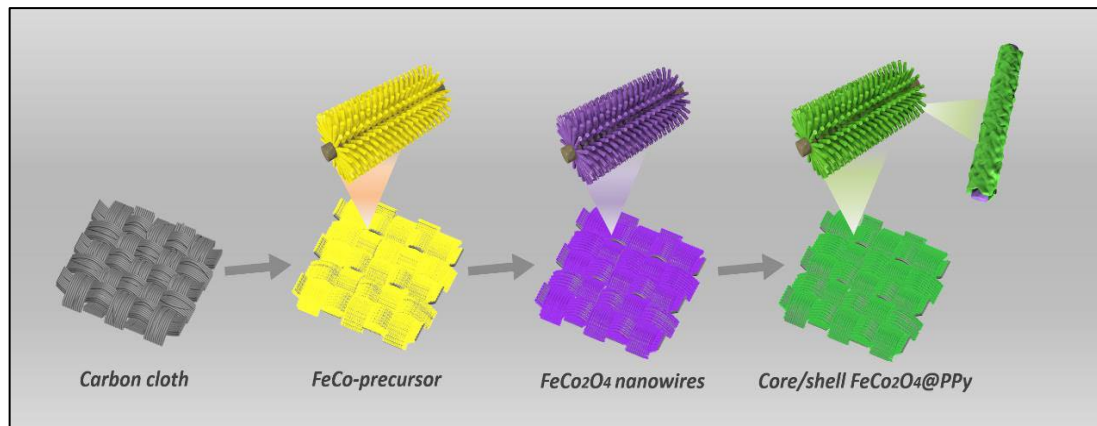**Figure 7:** Schematic illustration of synthesizing T-Fe$_2$O$_3$/PPy nanowire arrays (NAs) on carbon cloth (CC) [16]

Figure 8: Schematic exposition of the fabrication process of FeCo$_2$O$_4$@PPy on CFC [75]

FeCo$_2$O$_4$, which belongs to the MCo$_2$O$_4$ category (where M represents any metal), is a commonly used electrode material for supercapacitors. It has shown great potential due to its excellent electrochemical properties. This is because of the favorable conductivity and the existence of Fe and Co, which provide rich oxidation states for efficient redox reactions. Additionally, the earth's crust contains more elemental Fe than other transition metals, making it a cost-effective option suitable for large-scale production [76].

Among the available metals, iron is particularly interesting as a substitute for cobaltites in spinel structures. It possesses desirable characteristics such as its benign nature, abundance, and low cost. The studies by Pendashteh et al. [77] and Mohamed et al. [78] have elaborated on employing FeCo$_2$O$_4$ as an electrode material in supercapacitors.

Pendashteh et al. [77] attained a particular capacitance of 407 F g^{-1} at a scan rate of 10 mV s^{-1}, while Mohamed et al. [78] obtained higher rates of capacitance of 433 F g^{-1} at a current density of 0.1 A g^{-1}. These findings highlight the potential of FeCo$_2$O$_4$ serving as a significant electrode material in manufacturing applicable supercapacitors.

5. Future research direction of energy storage technologies

The typical synthesis of iron oxides/CP-based CFC is assumed to address the drawbacks of each component. Still, more developments in super capacitive performance are required to make these materials suitable for flexible and expandable energy storage mechanisms:

1) Developing new and improved electrolytes is another research area for increasing supercapacitors' performance. Conventional aqueous electrolytes, organic electrolytes, and ionic liquids are some of the electrolytes being studied for their potential use in high-performance supercapacitors

2) Another area of research for enhancing the performance of supercapacitors is the application of new and superior binder and conductive additives. These additions can enhance the electrode materials' mechanical stability and electrical conductivity, resulting in better performance.

3) Integration with other energy storage technologies: Combining supercapacitors of iron oxide (FeCo$_2$O$_4$)/(CPs)-based CFC with other energy storage technologies, such as batteries and fuel cells, is another area of research to increase the performance of supercapacitors. This combination can improve energy density, power density, and cycling stability.

4) More research and development are required to optimize the efficiency and cost-effectiveness of supercapacitor energy storage technology for particular applications.

Table 2: A summary of the performance of the CFC with different electrodes materials

Electrode materials	Potential range (V)	Electrolyte	Nanostructures	Specific capacitance	Cycling stability	Ref.
Fe_2O_3	-1.3 to 0 V	2 M KOH	Three-layer sandwiched core-shell	787.5 F g^{-1} at 5 mV s^{-1}	92% after 7000 cycles	[66]
α-Fe_2O_3	-1.0 to 0 V	1M Na_2SO_4	Nanoarrays are hollow structure	391 F/g at 1 mA/cm^2	88.9% after 2500 cycles	[67]
Fe_2O_3	-0.8 to 0 V	3M $LiNO_3$	Porous and nanospheres	2775 at 1mA cm^{-2}	95% of after 4000 cycles	[68]
$CoFe_2O_4$	0-0.6 V	3 M KOH	Core-shell microsphere	237.8 F g^{-1} at 1 A g^{-1}	95.8% after 2000 cycles	[72]
Fe_2O_3	-0.1-1 V	2mol L^{-1} H_2SO_4	Microparticle precipitates	116.8 F g^{-1}	cycles 1200	[73]
Polypyrrole	-0.8 to 0.4 V	5 M LiCl	Nanowire arrays	699 F/g at 1 A/g	80.1% after 5000 cycles	[71]
low-crystallinity Fe_2O_3/ polypyrrole	-0.1 to 0 V	1 M Na_2SO_4	Nanorod	640 F g^{-1} at 1 mA cm^{-2}	%79.3 5000 cycles	[74]
α-Fe_2O_3/ polypyrrole	-0.8 to 0 V	3 M KOH	Hierarchical Tectorum	382.4 mFcm^{-2} at 0.5 mAcm^{-2}	97.2% after 5000 cycles	[16]
$FeCo_2O_4$ & Polypyrrole	0 to 0.5 V	2 M KOH	Nanowires core/shell heterostructure	2269 F g^{-1} at 1 A g^{-1}	91% over 5000 cycles	[75]

6. Conclusion

Carbon fiber cloths (CFC) are highly promising materials for supercapacitor electrode fabrication owing to their eco-friendly, biocompatible, low toxicity, high mechanical strength, and excellent electrical conductivity. However, their limitations lie in their low surface area and porosity; resultantly, the pristine CFC is unsuitable for supercapacitor electrodes. To overcome this, various strategies have been developed to enhance their performance and enable them to function effectively as electrodes for supercapacitors by incorporating the pseudocapacitances materials on the CFC substrate as nanocomposites. This paper reviewed the mentioned drawbacks and current knowledge to overcome them in research on the effect of iron oxides and conductive polymers (CPs) on CFC performance. The article emphasized the influence of different types of iron oxide and its combination with conducting polymers with different electrolytes and morphologies, the indicator of the mode of supercapacitor modification based on CFC. There are different types of electrodes: CPs-CFC, iron oxides-CFC, and iron oxides/CPs-CFC. Based on the available information in this review, it is noted that the $FeCo_2O_4$/CPs-CFC with CFC based is used as nanocomposites because of their demonstrated high specific capacitance, good rate capability, and excellent cycling stability, good potential window, and low cost. However, there is a progressively need to use $FeCo_2O_4$ with different types of CPs and carbon materials structures. This review brings further research to fully explore new possibilities with these materials and improve their performance for energy storage applications.

Author contributions

Conceptualization, A. Radhi, S. Al-Rubaiey, and Sh Al-Rubaye; methodology, A. Radhi, S. Al-Rubaiey, and Sh Al-Rubaye; validation, A. Radhi, S. Al-Rubaiey, and Sh Al-Rubaye; formal analysis, Sh. Al-Rubaye; writing—original draft preparation, A. Radhi, S. Al-Rubaiey, and Sh Al-Rubaye; writing—review and editing, A. Radhi, S. Al-Rubaiey, and Sh Al-Rubaye; supervision, A. Radhi, and S. Al-Rubaiey; project administration, A. Radhi, S. Al-Rubaiey, and Sh Al-Rubaye. All authors have read and agreed to the published version of the manuscript.

Data availability statement

The data supporting this study's findings are available on request from the corresponding author.

Conflicts of interest

The authors declare that there are no conflicts of interest.

References

[1] M. Rajkumar, C.-T. Hsu, T.-H. Wu, M.-G. Chen, C.-C. Hu, Advanced materials for aqueous supercapacitors in the asymmetric design, Prog. Nat. Sci.: Mater. Int., 25 (2015) 527–544. https://doi.org/10.1016/j.pnsc.2015.11.012

[2] W. Wu, L. Yang, S. Chen, Y. Shao, L. Jing, G. Zhao, H. Wei, Core–shell nanospherical polypyrrole/graphene oxide composites for high performance supercapacitors, RSC Adv., 5 (2015) 91645–91653. https://doi.org/10.1039/C5RA17036B

[3] W. Du, Y.-L. Bai, J. Xu, H. Zhao, L. Zhang, X. Li, J. Zhang, Advanced metal-organic frameworks (MOFs) and their derived electrode materials for supercapacitors, J. Power Sources, 402 (2018) 281–295. https://doi.org/10.1016/j.jpowsour.2018.09.023

[4] B.Y. Guan, A. Kushima, L. Yu, S. Li, J. Li, X.W. Lou, Coordination polymers derived general synthesis of multishelled mixed metal-oxide particles for hybrid supercapacitors, Adv. Mater., 29 (2017) 1605902. https://doi.org/10.1002/adma.201605902

[5] J. Liu, J. Jiang, C. Cheng, H. Li, J. Zhang, H. Gong, H.J. Fan, Co_3O_4 nanowire@MnO_2 ultrathin nanosheet core/shell arrays: a new class of high-performance pseudocapacitive materials, Adv. Mater., 23 (2011) 2076–2081. https://doi.org/10.1002/adma.201100058

[6] H.-J. Qiu, L. Liu, Y.-P. Mu, H.-J. Zhang, Y. Wang, Designed synthesis of cobalt-oxidebased nanomaterials for superior electrochemical energy storage devices, Nano Res., 8 (2015) 321–339. https://doi.org/10.1007/s12274-014-0589-6

[7] N. Agnihotri, P. Sen, A. De, M. Mukherjee, Hierarchically designed PEDOT encapsulated graphene-MnO_2 nanocomposite as supercapacitors, Mater. Res. Bull., 88 (2017) 218–225. https://doi.org/10.1016/j.materresbull.2016.12.036

[8] M.A.A. Mohd Abdah, N.H.N. Azman, S. Kulandaivalu, Y. Sulaiman, Asymmetric supercapacitor of functionalised electrospun carbon fibers/poly (3,4- ethylenedioxythiophene) /manganese oxide//activated carbon with superior electrochemical performance, Sci. Rep., 9 (2019) 16782. https://doi.org/10.1038/s41598-019-53421-w

[9] T. H. Ko, D. Lei, S. Balasubramaniam, M.-K. Seo, Y.-S. Chung, H.-Y. Kim, and B.-S. Kim, Polypyrrole-decorated hierarchical $NiCo_2O_4$ nanoneedles/carbon fiber papers for flexible high-performance supercapacitor applications, Electrochim. Acta, 247 (2017), 524-534. https://doi.org/10.1016/j.electacta.2017.07.047

[10] Q. Gui, L. Wu, Y. Li, and J. Liu. Scalable Wire-Type Asymmetric Pseudocapacitor Achieving High Volumetric Energy/Power Densities and Ultralong Cycling Stability of 100 000 Times, Adv. Sci., 6 (2019) 1802067. https://doi.org/10.1002/advs.201802067

[11] T. Zhai, S. Sun, X. Liu, C. Liang, G. Wang, and H. Xia, Achieving Insertion-Like Capacity at Ultrahigh Rate via Tunable Surface Pseudocapacitance, Adv. Mater., 30 (2018) 1706640. https://doi.org/10.1002/adma.201706640

[12] R. Wang, Y. Han, Z. Wang, J. Jiang, Y. Tong, and X. Lu, Nickel@Nickel Oxide Core–Shell Electrode with Significantly Boosted Reactivity for Ultrahigh-Energy and Stable Aqueous Ni–Zn Battery, Adv. Funct. Mater., 28 (2018) 1802157. https://doi.org/10.1002/adfm.201802157

[13] Ali J. Saloum, Basma H.Al-Tamimi, Saad B.H., Preparation of Graphene Nanosheets from Graphite Flakes via Shear Assisted Exfoliation, Eng. and Technol. J., 39 (2021) 1663-1668. http://doi.org/10.30684/etj.v39i11.2219

[14] H. Wang, C. Xu, Y. Chen, and Y. Wang, MnO_2 nanograsses on porous carbon cloth for flexible solid-state asymmetric supercapacitors with high energy density, Energy Storage Mater., 8 (2017) 127-133. https://doi.org/10.1016/j.ensm.2017.05.007

[15] Y. Zeng, M. Yu, Y. Meng, P. Fang, X. Lu, and Y. Tong, Iron-Based Supercapacitor Electrodes: Advances and Challenges, Adv. Energy Mater., 6 (2016) 1601053. https://doi.org/10.1002/aenm.201601053

[16] L. Wang, H. Yang, X. Liu, R. Zeng, M. Li, Y. Huang, and X. Hu, Constructing hierarchical tectorum-like α-Fe_2O_3/PPy nanoarrays on carbon cloth for solid-state asymmetric supercapacitors. Angew. Chem. Int. Ed., 56 (2016) 1105–1110. https://doi.org/10.1002/anie.201609527

[17] V. Strauss, K. Marsh, M. D. Kowal, M. El-Kady, and R. B. Kaner. A Simple Route to Porous Graphene from Carbon Nanodots for Supercapacitor Applications, Adv. Mater., 30 (2018), 1704449. https://doi.org/10.1002/adma.201704449

[18] B. Liu, S. Sun, R. Jia, H. Zhang, X. Zhu, C. Zhang, J. Xu, T. Zhai, and H. Xia, Oxygen-Deficient Homo-Interface toward Exciting Boost of Pseudocapacitance, Adv. Funct. Mater., 30 (2020) 1909546.https://doi.org/10.1002/adfm.201909546

[19] J. Yan, S. Li, B. Lan, Y. Wu, and P. S. Lee, Rational Design of Nanostructured Electrode Materials toward Multifunctional Supercapacitors, Adv. Funct. Mater., 30 (2020) 1902564. https://doi.org/10.1002/adfm.201902564

[20] K. Zheng, Y. Zeng, S. Liu, C. Zeng, Y. Tong, Z. Zheng, T. Zhu, and X. Lu, Valence and surface modulated vanadium oxide nanowires as new high-energy and durable negative electrode for flexible asymmetric supercapacitors, Energy Storage Mater., 22 (2019) 410-417. https://doi.org/10.1016/j.ensm.2019.02.012

[21] A. K. Mohammed, A. M. Al-Dahawi, and Q. S. Banyhussan, Effect of adding additional Carbon Fiber on Piezoresistive Properties of Fiber Reinforced Concrete Pavements under Impact Load, Eng. Technol. J., 39 (2021) 1771-1780. https://doi.org/10.30684/etj.v39i12.1942

[22] M. Yu, D. Lin, H. Feng, Y. Zeng, Y. Tong, and X. Lu, Boosting the Energy Density of Carbon-Based Aqueous Supercapacitors by Optimizing the Surface Charge, Angew. Chem. Int. Ed., 56 (2017) 5454-5459. https://doi.org/10.1002/anie.201701737

[23] K. Song, Y. Jiang, X. Pang, Y. Li, and J. Liu, Electrodepositing a 3D porous rGO electrode for efficient hydrogel electrolyte integration towards 1.6 V flexible symmetric supercapacitors, Chem. Comm., 55 (2019) 8282-8285. https://doi.org/10.1039/C9CC03699G

[24] Y. Wu, Z. Liu, X. Zhong, X. Cheng, Z. Fan, and Y. Yu, Amorphous Red Phosphorus Embedded in Sandwiched Porous Carbon Enabling Superior Sodium Storage Performances, Small, 14 (2018) 1703472. https://doi.org/10.1002/smll.201703472

[25] A. Borenstein, O. Hanna, R. Attias, S. Luski, T. Brousse, and D. Aurbach, Carbon-based composite materials for supercapacitor electrodes: a review, J. Mater. Chem. A, 5 (2017) 12653-12672. https://doi.org/10.1039/C7TA00863E

[26] C. Teng, Y. Han, G. Fu, J. Hu, H. Zheng, X. Lu, and J. Jiang, Isostatic pressure-assisted nanocasting preparation of zeolite templated carbon for high-performance and ultrahigh rate capability supercapacitors, J. Mater. Chem. A, 6 (2018) 18938-18947. https://doi.org/10.1039/C8TA05726E

[27] Y. Qing, Y. Jiang, H. Lin, L. Wang, A. Liu, Y. Cao, R. Sheng, Y. Guo, C. Fan, and S. Zhang, Boosting the supercapacitor performance of activated carbon by constructing overall conductive networks using graphene quantum dots, J. Mater. Chem. A, 7 (2019) 6021-6027. https://doi.org/10.1039/C8TA11620B

[28] B. Yao, S. Chandrasekaran, H. Zhang, A. Ma, J. Kang, L. Zhang, X. Lu, F. Qian, C. Zhu, and E. B. Duoss, 3D-Printed Structure Boosts the Kinetics and Intrinsic Capacitance of Pseudocapacitive Graphene Aerogels, Adv. Mater., 32 (2020) 1906652. https://doi.org/10.1002/adma.201906652

[29] Zeng, Y., M. Yu, Y. Meng, P. Fang, X. Lu, and Y. Tong, Iron-based supercapacitor electrodes: advances and challenges, Adv. Energy Mater., 6 (2016) 1601053. https://doi.org/10.1002/aenm.201601053

[30] J. Zhao, Z. Li, M. Zhang, A. Meng, and Q. Li, Direct Growth of Ultrathin $NiCo_2O_4$/NiO Nanosheets on SiC Nanowires as a Free-Standing Advanced Electrode for High-Performance Asymmetric Supercapacitors, ACS Sustain. Chem. Eng., 4 (2016) 3598-3608. https://doi.org/10.1021/acssuschemeng.6b00697

[31] S. Ajeel, and A. Radhi, Optimization of Mild Steel Anodizing Using Box-Wilson Experimental Design, Eng. Technol. J., 32 (2014) 2830–2845. https://doi.org/10.30684/etj.32.11A.18

[32] X. He, Q. Liu, J. Liu, R. Li, H. Zhang, R. Chen, and J. Wang, Hierarchical $NiCo_2O_4$@NiCoAl-layered double hydroxide core/shell nanoforest arrays as advanced electrodes for high-performance asymmetric supercapacitors. J. Alloys Compd., 724 (2017) 130-138. https://doi.org/10.1016/j.jallcom.2017.06.256

[33] K. Jost, D. Stenger, C. R. Perez, J. K. McDonough, K. Lian, Y. Gogotsi and G. Dion, Knitted and screen printed carbon-fiber supercapacitors for applications in wearable electronics, Energy Environ. Sci., 6 (2013) 2698-2705. https://doi.org/10.1039/C3EE40515J

[34] Z. Wang, Z. Ruan, W. S. Ng, H. Li, Z. Tang, Z. Liu, Y. Wang, H. Hu and C. Zhi, Integrating a Triboelectric Nanogenerator and a Zinc-Ion Battery on a Designed Flexible 3D Spacer Fabric, Small Methods, 2 (2018) 1800150. https://doi.org/10.1002/smtd.201800150

[35] W. Wang, W. Liu, Y. Zeng, Y. Han, M. Yu, X. Lu and Y. Tong, A Novel Exfoliation Strategy to Significantly Boost the Energy Storage Capability of Commercial Carbon Cloth, Adv. Mater., 27 (2015) 3572-3578. https://doi.org/10.1002/adma.201500707

[36] W. Wei, L. Haiwei, K. Parvez, and X. Zhuang, Nitrogen-Doped Carbon Nanosheets with Size-Defined Mesopores as Highly Efficient Metal-Free Catalyst for the Oxygen Reduction Reaction, Angew. Chem. Int. Ed., 53 (2014) 1570–1574. https://doi.org/10.1002/anie.201307319

[37] R. Piticescu, A. M. Motoc, A. I. Tudor, C. F. Rusti, R. M. Piticescu, and M. D. Ramiro-sanchez, Hydrothermal Synthesis of Nanostructured Materials for Energy Harvesting Applications, Int. J. Mater. Chem. Phys., 1 (2015) 31-42.

[38] R. Rajagopalan, S. Al- Rubaye, Z. Wu, E. Wang, Y. Liu, C. Wu, W. Xiang, B. Zhong, X. Guo, S. X. Dou, and H. K. Liu, A novel high voltage battery cathodes of Fe^{2+}/Fe^{3+} sodium fluoro sulfate lined with carbon nanotubes for stable sodium batteries, J. Power Sources, 398 (2018) 175–182. https://doi.org/10.1016/j.jpowsour.2018.07.066

[39] A. Al-Keisy, R. Mahdi, D. Ahmed, K. Al-Attafi, and W. H. A. Majid, Enhanced Photoreduction Activity in BiOI1-xFx Nanosheet for Efficient Removal of Pollutants from Aqueous Solution, Chemistry Select., 5 (2020) 9758 –9764. https://doi.org/10.1002/slct.202000805

[40] S. Al-Rubaye, R. Rajagopalan, C. M. Subramaniyam, Z. Yu, S. X. Dou, and Z. Cheng, Electrochemical performance enhancement in MnCo2O4 nanoflake/graphene nanoplatelets composite, J. Power Sources, 324 (2016) 179–187. https://doi.org/10.1016/j.jpowsour.2016.05.081

[41] S.Z. Al Sheheri, Z.M. Al-Amshany, Q.A. Al Sulami, N.Y. Tashkandi, M. Hussein, and R.M. El-Shishtawy, The preparation of carbon nanofillers and their role on the performance of variable polymer nanocomposites, Des. Monomers Polym., 22 (2019) 8–53. http://doi.org/10.1080/15685551.2019.1565664

[42] W. Wu, D. Niu, J. Zhu, Y. Gao, D. Wei, C. Zhao, C. Wang, F. Wang, L. Wang, and L. Yang, Hierarchical architecture of Ti$_3$C$_2$@PDA/NiCo$_2$S$_4$ composite electrode as high performance supercapacitors, Ceram. Int., 45 (2019) 16261–16269. http://doi.org/10.1016/j.ceramint.2019.05.149

[43] Y. M. Lian, W. Utetiwabo, Y. Zhou, Z.-H. Huang, L. Zhou, F. Muhammad, R.-J. Chen, and W. Yang, From upcycled waste polyethylene plastic to graphene/mesoporous carbon for high-voltage supercapacitors, J. Colloid Interface. Sci., 557 (2019) 55–64. https://doi.org/10.1016/j.jcis.2019.09.003

[44] B. E. Conway, Electrochemical Supercapacitors. Scientific Fundamentals and Technological Applications, Kluwer Academic Plenum Publishers, New York 1999.

[45] H. Helmholtz, Ueber einige Gesetze der Vertheilung elektrischer Ströme in körperlichen Leitern mit Anwendung auf die thierisch-elektrischen Versuche, Ann. der Phys. Und Chemie., 165 (1853) 211–233. https://doi.org/10.1002/andp.18531650603

[46] M. Gouy, Sur la constitution de la charge électrique à la surface d'un électrolyte, J. Phys. Théorique Appliquée, 9 (1910) 457–468. https://doi.org/10.1051/jphystap:019100090045700

[47] D. L. Chapman, LI. A contribution to the theory of electrocapillarity, Philos. Mag. Ser., 6 25 (1913) 475–481. https://doi.org/10.1080/14786440408634187

[48] O. Stern, Zur Theorie Der Elektrolytischen Doppelschicht, Zeitschrift für Elektrochemie und Angew. Phys. Chemie, 30 (1924) 508–516. https://doi.org/10.1002/bbpc.192400182

[49] D. C. Grahame, The Electrical Double Layer and the Theory of Electrocapillarity, Chem. Rev., 41 (1947) 441–501. https://doi.org/10.1021/cr60130a002

[50] B. E. Conway, Transition from 'Supercapacitor' to 'Battery' Behavior in Electrochemical Energy Storage, J. Electrochemical Society, 138 (1991) 1539. https://doi.org/10.1149/1.2085829

[51] M. Amirul Aizat Mohd Abdah, N. Hawa Nabilah Azman, S. Kulandaivalu, and Y, Sulaiman, Review of the use of transition-metal-oxide and conducting polymer-based fibres for high-performance supercapacitors, Mater. Des., 186 (2020) 108199. https://doi.org/10.1016/j.matdes.2019.108199

[52] P. Forouzandeh, V. Kumaravel, and S. C. Pillai, Electrode Materials for Supercapacitors: A Review of Recent Advances, Catalysts, 10 (2020) 969. https://doi.org/10.3390/catal10090969

[53] Y. Han, Y. Lu, S. Shen, Y. Zhong, S, Liu, X. Xia, Y. Tong, and X. Lu, Enhancing the Capacitive Storage Performance of Carbon Fiber Textile by Surface and Structural Modulation for Advanced Flexible Asymmetric Supercapacitors, Adv. Fun. Mater., 29 (2019) 1806329. https://doi.org/10.1002/adfm.201806329

[54] D. Yu, S. Zhai, W. Jiang, K. Goh, L. Wei, X. Chen, R. Jiang, and Y. Chen, Transforming Pristine Carbon Fiber Tows into High Performance Solid-State Fiber Supercapacitors, J. Adv. Mater., 27 (2015) 4895-4901. https://doi.org/10.1002/adma.201501948

[55] W. Wang, W. Liu, Y. Zeng, Y. Han, M. Yu, X. Lu, and Y. Tong, A Novel Exfoliation Strategy to Significantly Boost the Energy Storage Capability of Commercial Carbon Cloth, J. Adv. Mater., 27 (2015) 3572-3578. https://doi.org/10.1002/adma.201500707

[56] G. Wang, H. Wang, X. Lu, Y. Ling, M. Yu, T. Zhai, Y. Tong, and Y. Li, Solid-State Supercapacitor Based on Activated Carbon Cloths Exhibits Excellent Rate Capability, Adv. Mater., 26 (2014) 2676-2682. https://doi.org/10.1002/adma.201304756

[57] H. Ji, X. Zhao, Z. Qiao, J. Jung, Y. Zhu, Y. Lu, L. L. Zhang, A. H. MacDonald, and R. S. Ruoff, Capacitance of carbon-based electrical double-layer capacitors, Nat. Commun., 5 (2014) 3317. https://doi.org/10.1038/ncomms4317

[58] A. Davies, and A. Yu, Material advancements in supercapacitors: From activated carbon to carbon nanotube and graphene, Can. J. Chem. Eng., 89 (2011) 1342–1357. https://doi.org/10.1002/cjce.20586

[59] F. Beguin, E. Frackowiak, Supercapacitors: Materials, Systems, and Applications, Wiley-VCH Verlag GmbH & Co. KGaA, Boschstr. 12, 69469 Weinheim, Germany (2013) 69-162.

[60] Y. Zhang, H. Feng, X. Wu, L. Wang, A. Zhang, T. Xia, H. Dong, X. Li, and L. Zhang, Progress of electrochemical capacitor electrode materials: A review, Int. J. Hydrogen Energy, 34 (2009) 4889–4899. https://doi.org/10.1016/j.ijhydene.2009.04.005

[61] D. Ye, Y. Yu1, J. Tang, L. Liu, and Y. Wu, Electrochemical activation of Carbon Cloth in Aqueous Inorganic Salts Solution for superior capacitive performance, Nanoscale, 8 (2016) 10406-10414. https://doi.org/10.1039/C6NR00606J.

[62] M. Yu, Y. Zeng, Y. Han, X. Cheng, W. Zhao, C. Liang, Y. Tong, H. Tang, X. Lu, Valence-Optimized Vanadium Oxide Supercapacitor Electrodes Exhibit Ultrahigh Capacitance and Super-Long Cyclic Durability of 100 000 Cycles, Adv. Funct. Mater., 25 (2015) 3534–3540. https://doi.org/10.1002/adfm.201501342

[63] H. Ji, X. Liu, Z. Liu, B. Yan, L. Chen, Y. Xie, C. Liu, W. Hou, G. Yang, In Situ Preparation of Sandwich MoO_3/C Hybrid Nanostructures for High-Rate and Ultralong-Life Supercapacitors, Adv. Funct. Mater., 25 (2015) 1886–1894. https://doi.org/10.1002/adfm.201404378

[64] X. Wang, P. Xu, P. Zhang, and S. Ma, Preparation of Electrode Materials Based on Carbon Cloth via Hydrothermal Method and Their Application in Supercapacitors, Materials, 14 (2021) 7148. https://doi.org/10.3390/ma14237148

[65] X. Chen, K. Chen, H. Wang, and D. Xue, Composition design upon iron element toward supercapacitor electrode materials, Mater. Focus, 4 (2015) 78–80. https://doi.org/10.1166/mat.2015.1213

[66] Z. Zhang, H. Wang, Y. Zhang, X. Mu, B. Huang, J. Du, J. Zhou, X. Pan, and E. Xie, Carbon nanotube/hematite core/shell nanowires on carbon cloth for supercapacitor anode with ultrahigh specific capacitance and superb cycling stability, Chem. Eng. J., 325 (2017) 221–228. https://doi.org/10.1016/j.cej.2017.05.045

[67] D. Chen, S. Zhou, H. Quan, R. Zou, W. Gao, X. Luo, and L. Guo, Tetsubo-like α- Fe_2O_3/C nanoarrays on carbon cloth as negative electrode for high-performance asymmetric supercapacitors, Chem. Eng. J., 341 (2018) 102–111. https://doi.org/10.1016/j.cej.2018.02.021

[68] J. Li, Y. Wang, W. Xu, Y. Wang, B. Zhang, S. Luo, X. Zhou, C. Zhang, X. Gu, and C. Hu, Porous Fe_2O_3 Nanospheres Anchored on Activated Carbon Cloth for High-Performance Symmetric Supercapacitors, Nano Energy, 57 (2019) 379–387. https://doi.org/10.1016/j.nanoen.2018.12.061

[69] T. Y. Wei, C. H. Chen, H. C. Chien, S. Y. Lu, and C. C. Hu, A cost-effective supercapacitor material of ultrahigh specific capacitances: spinel nickel cobaltite aerogels from an epoxide-driven sol–gel process, Adv. Mater., 22 (2010) 347-351. https://doi.org/10.1002/adma.200902175

[70] Y. Wang , C. X. Guo, J. Liu, T. Chen, H. Yang, and C. M. Li, CeO_2 nanoparticles/graphene nanocomposite-based high performance supercapacitor, Dalton Transactions., 40 (2011) 6388-6391. http://dx.doi.org/10.1039/c1dt10397k

[71] Z. Huang, Y. Song, X. Xu, and X. Liu, Ordered Polypyrrole Nanowire Arrays Grown on Carbon Cloth Substrate for High Performance Pseudocapacitor Electrode, ACS Appl. Mater. Interfaces, 7 (2015) 45 25506–25513. https://doi.org/10.1021/acsami.5b08830

[72] K. Song, X. Wang, J. Wang, B. Zhang, and R. Yang, Hierarchical structure of $CoFe_2O_4$ core-shell microsphere coating on carbon fiber cloth for high-performance asymmetric flexible supercapacitor applications, Ionics, 25 (2019) 4905–4914. https://doi.org/10.1007/s11581-019-03030-4

[73] M. G. C. Munhoza, A. C. Rodrigues-Siqueli, B. C. S. Fonseca, J. S. Marcuzzo, J. T. Matsushimad, G. F. B. Lenz e Silva, M. R. Baldan, G. Amaral-Labat. Electrochemical Properties of Iron Oxide Decorated Activated Carbon Cloth as a Binder-Free Flexible Electrode, Mater. Res., 25 (2022). https://doi.org/10.1590/1980-5373-MR-2022-0142

[74] C. Wu, Z. Pei, M. Lv, D. Huang, Y. Wang, and S.Yuan, Polypyrrole-Coated Low-Crystallinity Iron Oxide Grown on Carbon Cloth Enabling Enhanced Electrochemical Supercapacitor Performance, Molecules, 28 (2023) 434. https://doi.org/10.3390/molecules28010434

[75] X. He, Y. Zhao, R. Chen, H. Zhang, J. Liu, Q. Liu, D. Song, R. Li, and J. Wang, Hierarchical $FeCo_2O_4$@polypyrrole core/shell nanowires on carbon cloth for high-performance flexible all-solid-state asymmetric supercapacitors, ACS Sustainable Chem. Eng., 6 (2018) 14945–14954. https://doi.org/10.1021/acssuschemeng.8b03440

[76] Y. Wang, S. Li, J. Sun, Y. Zhang, H. Chen, and C. Xu, Simple solvothermal synthesis of magnesium cobaltite microflowers as a battery grade material with high electrochemical performances. Ceram. Int., 45 (2019) 14642−14651. https://doi.org/10.1016/j.ceramint.2019.04.183

[77] A. Pendashteh, J. Palma, M. Anderson, R. Marcilla, Nanostructured porous wires of iron cobaltite: novel positive electrode for high-performance hybrid energy storage devices, J. Mater. Chem. A. 3 (2015) 16849–16859. http://doi.org/10.1039/C5TA02701B

[78] S.G. Mohamed, C.-J. Chen, C.K. Chen, S.-F. Hu, R.-S. Liu, High-Performance Lithium-Ion Battery and Symmetric Supercapacitors Based on $FeCo_2O_4$ Nanoflakes Electrodes, ACS Appl. Mater. Interfaces., 6 (2014) 22701–22708. https://doi.org/10.1021/am5068244