Abstract: Development of well-designed electrodes is the key to achieve high performance supercapacitors. Therefore, as one of the effective methods, a layer-by-layer (LBL) approach is often fruitfully employed for the fabrication of electrode material. Benefiting from a tunable parameter of the LBL approach, this approach has paved a way to design a highly ordered nanostructured electrode material with excellent performance. Conducting polymers (CPs) are the frontrunners in supercapacitors and notably, the LBL assembly of CPs is attracting extensive attention. Therefore, this critical review covers a comprehensive discussion on the research progress of CP-based composites with special importance on the LBL approach predominately for supercapacitors. Following a brief discussion on supercapacitors and CPs, the most up-to-date techniques used in LBL are highlighted.

Keywords: layer-by-layer assembly; supercapacitors; conducting polymers; carbon materials

1. Introduction

The 21st century has brought in a new revolution to our lifestyle. The advancement in technologies has provided remarkable insights all over the globe. In this period, a considerable amount of applications and technologies such as hybrid vehicles, solar cell, power smart grid, communication devices, artificial hearts etc. have been innovated. Meanwhile, ever-increasing demands for new technologies give a direct impact on energy consumption. The proliferation of technologies has raised the global fossil fuel consumption and there will be a day when the supply will be depleted. Driven by this energy crisis, there is a continuous need to develop energy storage and conversion technologies that are able to address this issue and able to respond to the increased energy demands [1,2]. Considering the above-mentioned concerns, rechargeable batteries and fuel cells are promising energy storage devices and being widely used to store energy on demand. Another leading candidate of energy storage technologies is an electrochemical capacitor also known as supercapacitor (SC) which is able to store charge higher than conventional capacitors and capable of delivering it faster than batteries [3].

Supercapacitor

The intense interest in the SCs is particularly for their high specific power (>10 kW·kg⁻¹), longer life cycle (>100,000 cycles), simple configuration and capable to charge and discharge within seconds [1,4,5]. Mainly, the SCs are an important key in overcoming the differences between conventional capacitors and batteries/fuel cell (bridge the gap) in terms of their specific power and specific energy, respectively [4,6]. As illustrated in Figure 1, the Ragone plot, a graph of specific energy plotted against specific power.
comprises the overall performance of various energy storage devices. In that plot, SCs lie in between the conventional capacitors and batteries demonstrating SCs have greater specific energy than conventional capacitors. However, the specific energy of SCs still needs to be improved to be comparable with the performance of batteries and fuel cells.

In general, SCs can be classified into three main classes: an electrochemical double layer capacitor (EDLC), pseudocapacitors, and hybrid capacitors (Figure 2). Each of these classes has its own unique charge storage mechanisms. In EDLC, the capacitances are derived from the charge separation at the electrode–electrolyte interface to form a thin electrochemical double layer. The formation of the double layer involves ion adsorption/desorption at the interface through electrostatic force without any faradaic reaction [4]. Mainly, the capacitance performance (100–200 F·g⁻¹) of EDLC is dependent on the porosity (>2 nm pore width) and surface area (>1000 m²·g⁻¹) of the electrode material while carbonaceous materials (Figure 3) are considered as promising EDLC electrode materials [8–11]. Nevertheless, despite having high specific power and excellent cycle life, EDLC suffers from poor specific energy (<12 Wh·kg⁻¹) and lower electrical conductivity which is about 0.1–1.0 S·cm⁻¹ [1,12,13].
In contrast to EDLC, a pseudocapacitor builds up charges via fast and reversible surface faradaic reaction and electrosorption between electrolyte and electrode active materials at the appropriate potential window (rarely exceeding 1 V) [13,14]. Viswanathan [15] has identified three types of faradaic processes taking place in pseudocapacitors that can result in capacitive behavior: (i) reversible adsorption, (ii) redox reaction of transition metal oxides/hydroxides, and (iii) reversible electrochemical doping-dedoping in conducting polymers (CPs). In comparison with EDLC, the specific capacitance and specific energy of pseudocapacitors are superior as a result of faradaic reaction which enables more charge to be stored on the electrode surface and the bulk of electrode material [12,16,17]. However, the pseudocapacitors usually have lower specific power (due to slower faradaic reaction) compared with EDLC which has faster kinetics since only the surface of the EDLC electrode material is in contact with electrolyte ions [13,18,19]. Additionally, due to the reversible redox reaction, the stability of pseudocapacitors deteriorates during the cycling process [20,21]. CPs and transition metal oxides/hydroxides (Figure 3) are the typical candidates for the pseudocapacitor [22–24].

![Figure 3. Schematic diagram of three different types of materials used as supercapacitor electrodes: CPs, carbon materials, and transition metal oxides/hydroxides.](image)

Another widely studied SC is the hybrid capacitor. Hybrid capacitors consist of a combination of EDLC and pseudocapacitor based electrodes [25,26]. As a matter of fact, the charge storage mechanisms of the hybrid capacitors (symmetrical and asymmetrical capacitors) are a combination of the faradaic and non-faradaic reactions. As a result, the hybrid capacitors provide synergistic effects of both electrodes to the resultant material. A mixed different type of transition metal oxides/hydroxides or doped CP is also used to construct the hybrid capacitor [27–29]. This review will focus on CP based SC prepared via layer-by-layer (LBL) assembly. As can be seen in Figure 4, the studies on LBL assembly and CPs for SCs has had a remarkable increasing trend in the number of articles published per year over the last decade.
2. Layer by Layer Assembly

2.1. Introduction

A high interest is centered on ultrathin films due to their aspiring usefulness in the field of optical, medical, electrical, and mechanical. In this regard, many efforts have been dedicated to constructing nanostructured functional materials with well-designed control of chemical compositions, surface properties, and size in one, two or three dimensions. Construction of such nanostructured functional materials is strongly influenced by the fabrication methods and characteristics of nanostructured materials. There are two different approaches used in the nanofabrication: top-down and bottom-up [30–32]. The top-down approaches involve breaking up bulk material into nano-sized particles, whereas bottom-up approaches refer to assembling the material by molecule-by-molecule (or atom-by-atom) growth [33]. The bottom-up approaches are more beneficial than the top-down approaches. The reason is that the former approach has a high chance of fabricating a nanostructured functional material with less surface imperfection, more homogeneous in chemical composition, and better short-range order in nanoscale dimensions [34]. Although a lot of substantial efforts have been devoted to developing an efficient and reliable bottom-up approach, assembling a single building block into desirable functional material remains a challenge. One of the examples of the bottom-up approach is self-assembly [35,36].

Self-assembly stands out as an extraordinary assembly in nanotechnology, material science, polymer science, and engineering. Self-assembly is a process where the molecules or macromolecules are organized spontaneously forming an organized structure as a result of specific interactions among the individual components. The uniqueness in this self-assembly process is that any materials from biological materials (e.g., DNA, proteins) to functional materials (e.g., carbon materials, polymers, clay minerals, and nanoparticles) can be assembled. Under self-assembly, there are three primary methods for fabricating ultrathin films in nanoscales, such as Langmuir–Blodgett techniques [37,38], self-assembled monolayers [39,40], and sequential adsorption of LBL assembly multilayers. There are certain limitations of the Langmuir–Blodgett technique and the self-assembled monolayers method that do not allow these approaches for practical applications. The requirement for expensive instrumentation and limitations for appropriate materials, namely amphiphilic molecules hinder its usage as a reliable multilayer assembler. Whereas, the self-assembled monolayers method is highly recommended for controlling surface properties, it is not applicable for multilayer fabrication [41]. Compared to these approaches, LBL assembly has been a versatile and reliable technique to construct multilayer films with the desired functions, morphologies, and structures to nanoscale precision. Compared with other bottom-up approaches, the LBL assembly has more advantages and surpasses the limitation set by other
methods as summarized in Figure 5. The LBL assembly is continuously developing advanced concepts and new materials which are also applicable for energy storage devices including SC. Additionally, the use of LBL assembled multilayer films for SC provides an excellent nanostructured building block which eventually increases conductivity and electrochemical performance [42].

![Figure 5. Characteristics and controllable properties of layer-by-layer (LBL) assembly method.](image)

### 2.2. Overview of Layer by Layer Assembly

The root of LBL assembly was initiated by Iler [43] as a study entitled “Adsorption of Colloidal Silica on Alumina and of Colloidal Alumina on Silica.” The author showed the possibility of adsorption of colloidal particles, namely alumina and silica on oppositely charged solid substrate. Though, it was only in 1966, Iler still introduced the deposition of multilayers via the LBL assembly method. Iler described in his study that multilayer films consisting of alternatively arranged opposite charged colloidal particles could be obtained on a glass substrate. He further added that the thickness of the resultant films could be controlled and estimated from the reflected color on the substrate surface [32]. However, this method did not draw significant interest until the early 20th century Decher and his coworkers established and reintroduced the concept [44–46]. Their pioneering work on sequential adsorption of polyelectrolytes on a charged surface triggered a high number of studies on this method later on [33,47–49]. Traditionally, the fundamental principle of this approach is depositing the alternative layer of oppositely charged polyelectrolytes commonly referred to as polyanion and polycation onto a charged solid or flexible substrate surface via electrostatic interaction. In this approach, first, the charged substrate is immersed in the oppositely charged polyelectrolyte solution which is then adsorbed onto the substrate. Successively, the substrate with the deposition layer is rinsed with deionized water to remove the weakly bound polyelectrolyte molecules on the surface. Then, once the surface charge is reversed, the substrate with the deposition layer is immersed in the second oppositely charged polyelectrolyte, followed by washing of the layers. The whole steps are then repeated to get a desired thickness and a number of layers as shown in Figure 6 [50].

Apart from frequently used electrostatic interaction, LBL multilayer films could also be assembled through other various interactions such as hydrogen bonding, covalent bonding, hydrophobic interactions and so on [51–54] which widen the potential applications. There are numerous reviews on LBL assembly focusing on interactions [54,55] or techniques producing LBL based films [56,57].
However, a review of LBL assembly emphasizing the preparation techniques for SC application has still not yet been extensively discussed. Thus, in this review, we highlight LBL assembled CPs for SCs.

![Diagram of LBL assembly](image)

**Figure 6.** Schematic illustration of LBL assembled multilayer films via electrostatic interaction: A simplified multilayer film assembled from negatively charged substrate with multiple immersion of polyelectrolytes in sequential order to allow the formation of \( n \) layers.

2.3. Techniques of Assembly

Constructing multilayer films through the LBL approach is an easy and straightforward procedure. However, the chosen technique to assemble LBL as well as the assembly process (e.g., deposition time, an intermediate step, yield) directly influences the properties of the resultant films (e.g., thickness, surface roughness, morphologies, homogeneity) [56]. In regard to this matter, different types of assembly techniques have been developed to construct multilayer films to meet the desired properties such as dipping, spin, spray and so on. Many of the assembly techniques are still new and have been intensely explored mainly for applications in the field of energy storage and conversion. In this section, the most common assembly techniques used to fabricate multilayer films for SC applications are reviewed.

2.3.1. Dip-Coating

Among the various assembly techniques, dip-coating assembly is a traditional way of constructing LBL based thin films. This method is also known as an immersive assembly. Conventionally, this construction relies on manually immersing substrates in the material solutions to form layers with alternate washing and drying as shown in Figure 7 [32,46]. The immersion time of the substrate in the material solution can vary from seconds to hours. Whereas, the rinsing/washing steps are not more than 10 minutes to eliminate the weakly adsorbed components. This straightforward approach provides precise control of the structure, size, homogeneity, thickness, and morphology by adjusting the immersion time and number of layers [58–60]. Ge, et al. [58] reported in their study that preparation of graphene/MnO\(_2\) via the dip-coating method is faster and easier compared with the conventional electrochemical method. In another work, Xu, et al. [59] reported a synthesis of graphene/cotton composite synthesis using a simple and scalable dip coating method that does not require a high-temperature treatment process and an organic surfactant.
Although it is a direct method for preparing layers, the monotonous steps, an excess of waste at each level, and high usage of material hinders its practical usage on a broad scope. Therefore, few procedures have been developed to change the slow diffusion kinetics to faster kinetics or to quicken the processing time, and or to move from manual assembly to automated assembly. For example, Sarker and Hong [61] fabricated graphene/PANI multi-layered films by an automated dipping robot. This automation approach allows one to accurately control the layers by fixing the immersion time and washing steps. Furthermore, it also aids the processability of the PANI and graphene oxide and repeatability of the process. Another interesting way of using this dip-coating approach is via a computerized automated slide stainer [62,63], automating the process of staining (dipping), rinsing, and drying. These automated assemblies control the material deposition by fixing the immersion times. However, quartz crystal microbalance is another type of automated assembly solely directing deposition by setting the adsorbed mass of the material on the substrate in which quartz crystals act as a substrate. This technique allows precise control over the architecture and size of the deposition [64]. Even though the automated assembly takes over the manual involvement, the time required for layer formation is still slow. Hence, the automated machine is often combined with some other steps to quicken the assembly times. Hyder, et al. [60] used an automated dipping robot with a rotating sample holder to fabricate PANI nanofiber/multiwalled carbon nanotube multilayered films. The equipped rotating sample holder expedited the layered assembly time. In another improvement, a computer-programmed slide stainer attached with a magnetic disk bar was used. Here, the purpose of the magnetic bar is to avoid the precipitation of solution (e.g., multiwalled carbon nanotube) during the assembly process period and support the formation of a uniform thin film with better quality [65]. The prominent part of these automated techniques is that it enables coating on various substrates, such as fused quartz, indium tin oxide slides, and glass slides [60,62].

On the other hand, the use of magnetic bars [66] and sonication [67] in the traditional dip-coating approach also aids to form a clear homogenous layer and yet accelerates the adsorption process [68,69]. Most of the studies reported that the dip coating method whether conventional or automated technique was carried out on a rigid substrate [60,62,70,71]. However, this method also can be achieved on flexible substrates [72,73] and particulate substrates [74,75]. Unlike the immersive assembly of the rigid or flexible substrate, an immersive assembly for solid particulate requires centrifugation followed by washing (Figure 8) [74,76].
2.3.2. Electrodeposition

Among the available methods, electrodeposition is an often used method for the fabrication of SC electrode materials. It is a well-established method for depositing materials by controlling the voltage \[77\] or current density \[78\] in an electrode setup. The CPs (e.g., polyaniline (PANI), poly(3,4-ethylenedioxythiophene) (PEDOT), and polypyrrole (PPy)), carbon-based materials (e.g., multiwalled carbon nanotube, graphene), and metal oxides/hydroxide are normally assembled by this technique \[79,80\]. In a standard electrodeposition method, the substrate acting as a working electrode (flexible or solid substrate) is connected in a three-electrode setup and immersed in the material solution. Then, it is coated by applying potential or current density (Figure 9). This approach is able to control the thickness, structure, surface area, and rate of deposition by applying the desired potential and current density. Therefore, the potential or current density is very crucial in the electrodeposition process. The advantage of this straightforward technique is that it involves mild processing conditions which are mostly conducted at room temperature, non-toxic chemicals, and minimum use of chemicals \[78,81,82\]. The most common electrolytes used in the electrodeposition are aqueous \[80,83–85\] and non-aqueous \[86,87\].

![Electrodeposition LBL assembly](image_url1)

**Figure 8.** Immersive assembly of the particulate substrate using a centrifugation process with alternate washing steps.

![Simple electrodeposition LBL assembly](image_url2)

**Figure 9.** Simple electrodeposition LBL assembly.
2.3.3. Spin Coating

Another most common LBL assembly method is spin coating [88]. Typically, in this method, the material is drop casted onto the rotating substrate as shown in Figure 10 or drop casted on a stationary substrate that will later be rotated. Deposition of materials using a spin coating technique is relatively faster in comparison with the time consuming immersive assembly. However, in the spin-coated thin film, the film at the edge of the substrate is thinner than the place where the solution has been cast. Still, this method is able to produce more homogeneous films due to the presence of strong electrostatic interactions between the layers. Commonly, the thickness of the prepared films is determined based on the speed of spinning. However, the available spin coaters are mostly aimed for planar substrates [89,90].

![Figure 10. Schematic illustration of the spin assembly.](image)

2.3.4. Spray Assembly

Spray assembly is another faster yet efficient method of constructing an LBL assembled thin film [91]. This approach was developed by Schlenoff, et al. [92] to overcome the drawbacks of the traditional dip-coating method. As described by its name, the films are assembled by spraying the solution materials on the substrate sequentially as illustrated in Figure 11. In this process, water is sprayed in between the spraying of the solution step to remove the loosely bound material. In the spray assembly, the morphology, chemical structure, and homogeneity of the prepared film can be tuned the same as in the dip coating method. Whereas, the thickness and morphologies of the film are controlled by spray orientation, spray duration, washing duration, spray flow rate, the sample to nozzle distance, and the solution material concentration. However, the film shows a regular morphology covering the substrate even without the washing step, but with alternating washing, the films grow thicker. It has been shown that after each washing the layer attaches itself stronger to subsequent layers due to rearrangement of the layers [56,93].

![Figure 11. Schematic illustration of the spray assembly.](image)
Similar to most other techniques, spray assembly has also been combined with other techniques to develop the spray assembly. The conventional spray assembly suffers from the growth of inhomogeneous films due to the usage of a nozzle. Therefore, spray assembly has been combined with spin assembly to reduce the use of the materials and support the growth of a uniform layer.

2.3.5. Chemical Bath Deposition (CBD)

Chemical bath deposition (CBD) has emerged as a method to deposit various metal-based thin films [94]. This process has attracted much interest due to the following; simple instrumentation, cheap chemicals as starting materials, low temperature, simplicity, low-cost method, and a reproducible, scalable, convenient technique. The CBD method is remarkably direct, economical, and simple. Layers are fabricated on the substrates by immersing the substrates in a suitable hot solution bath (Figure 12). Similar to the dip-coating method, it does not require any electrical field. The thickness and morphologies of the fabricated layers rely on the bath temperature and immersion time [95,96]. However, still, few studies have focused on the multi-layered thin film by this method for SC due to its drawbacks. The CBD process often results in the formation of precipitation in the bulk electrolyte which causes loss of material and solution [97].

2.3.6. Successive Ionic Layer Adsorption and Reaction (SILAR)

The straightforward and low-cost successive ionic layer adsorption and reaction (SILAR) method is often known as a modified CBD method. This technique is another way to create a multi-layered thin film for SC applications [98]. The SILAR method involves an anionic and cationic precursor. The schematic of the SILAR method is shown in Figure 13. In the SILAR method, the substrate is immersed sequentially in the anionic and cationic precursor solutions that are placed separately. After each immersion, the substrate is washed to remove the loosely bound particles. The thickness and deposition rate of the film can be easily controlled by adjusting the immersion cycle, similar to immersive assembly. Moreover, it is an efficient method to fabricate a uniform, robust, and large area thin film. Additionally, by using this approach, various types of substrates, rigid as well as flexible, can be coated [97,99].
conductivity. In the neutral insulating forms, CPs have very low metal-like conductivity behavior in the CPs. In order to make the CPs (in their neutral form) reach a high level of conductivity, a charge carrier (dopant) needs to be introduced into their chains, altering the band structure of the CPs [107]. The range of the conductivity of CPs can be tuned by controlling the amount of dopant incorporated into the polymer backbone. The formation of nonlinear defects by the dopants allows electrical transport in the polymer chains either by hole carriers or charge carriers [107–110].

Furthermore, the existence of an extended π-conjugated network alone is not sufficient for the metal-like conductivity behavior in the CPs. In the neutral insulating forms, CPs have very low conductivity. In order to make the CPs (in their neutral form) reach a high level of conductivity, a charge carrier (dopant) needs to be introduced into their chains, altering the band structure of the CPs [107]. The range of the conductivity of CPs can be tuned by controlling the amount of dopant incorporated into the polymer backbone. The formation of nonlinear defects by the dopants allows electrical transport in the polymer chains either by hole carriers or charge carriers [107–110].
3.1. Conducting Polymer-Based LBL Multilayers

SCs fulfill the requirement of energy storage devices with their high specific power and long life cycles. Here, it should be emphasized that the electrode material has a pivotal role in the significant development of the SC performances. In particular, the CP has appeared ubiquitously as a unique substitute electrode material for SC due to its prominent characteristics. Also, the remarkable versatility of LBL approach allows the fabrication of CP-based multilayers as suitable materials for SC. This review section will give an outlook on the performance of the CP-based LBL assembly as electrode materials for SC.

3.1.1. Conducting Polymer-Conducting Polymer Based LBL

Even though CPs are known for their outstanding pseudocapacitive characteristics, CP-based SCs still struggle to reach the theoretical specific capacitance values. As an example, PANI, PEDOT, and PPy have theoretical specific capacitances as high as ~2000 F g\(^{-1}\) \([111]\), ~200 F g\(^{-1}\) \([112]\), and ~620 F g\(^{-1}\) \([113]\), respectively. Therefore, as driven by the versatility of the LBL approach, significant interest is given in the construction of CPs multilayers to improve the performance of CP-based SCs (Table 1). Focusing on the electrochemical performances, the morphology of composites plays an important role. Aradilla, et al. \([82]\) reported the preparation of alternating layers (three-layered and five-layered) of PEDOT and poly(N-methylpyrrole) (PNMPy) via a potentiostatic method at 1.4 V (vs. Ag/AgCl) on steel sheets. The initial studies on LBL assembled multi-layered PEDOT/PNMPy films showed the synergistic effect of PEDOT and PNMPy generated at the interface. The as-prepared multi-layered nanocomposite film was found to be an effective material for SC applications with specific capacitance \(C_{sp}\) of 50 F g\(^{-1}\) and 63 F g\(^{-1}\) calculated from the cyclic voltammogram (CV) for three-layered and five-layered PEDOT/PNMPy, respectively. Comparable \(C_{sp}\) values were also reported from galvanostatic charge-discharge (GCD) tests for three-layered (42 F g\(^{-1}\)) and five-layered (53 F g\(^{-1}\)) PEDOT/PNMPy. In addition, the authors also discovered that the topography and morphology of the films affect the \(C_{sp}\). Even though the multi-layered film retains the structure of its individual CPs, an obvious variance in porosity and roughness was observed compared with PEDOT which explaining the significant difference of \(C_{sp}\) values.

Moreover, the resulting multi-layered film holding minimal structure deterioration in 200 consecutive oxidation-reduction cycles, indicated great cycling stability. Furthermore, the multi-layered PEDOT/PNMPy has low internal resistance (10.2 Ω) and low charge transfer resistance (2.8 Ω), thanks to its porous structure, which facilitated ion diffusion into the polymer matrix. Indeed, the highly porous multi-layered PEDOT/PNMPy showed excellent electrochemical behavior as anode and cathode in the symmetrical SC system. The as-obtained multi-layered SC has nearly two times higher \(C_{sp}\) (90 F g\(^{-1}\)) and 10% higher Coulomb efficiency compared to PEDOT (50 F g\(^{-1}\)). Briefly, the synergistic effect provided by PEDOT and PNMPy via LBL assembly has favored the fabrication of a more porous film, which directly influences the electrochemical performance.

Similarly, in another approach, Sowmya, et al. \([114]\) developed LBL assembled multi-layered PANI on stainless steel (SS) substrate using electrochemical polymerization for symmetrical SC. Specifically, an electrode comprised of successive layers of PANI doped with three different dopant ions i.e., camphor-10-sulfonic acid, p-toluene sulfonic acid, and sulfuric acid, were fabricated to enhance the performance of SC. The major advantage of this assembly is the use of different types of dopants with different anion sizes. As known, the size of the dopant anions has a great effect on the porosity of CP which is favorable for the fabrication of SC with high capacitance performance. The utilization of three different dopants potentially molds the structure of the material and the movements of ions within the material. The multi-layered electrode exhibits a spongy and large porous structure with a surface roughness of 71.0 nm. The close contact between the spongy PANI layers as well as the interactions of dopant anions in the three layers has resulted in good charge propagation. These intriguing properties gave a high \(C_{sp}\) (468 F g\(^{-1}\)) and electrical conductivity (1480 mS m\(^{-1}\)). The GCD stability test showed
that this electrode exhibited high specific capacitance (260 F·g\(^{-1}\)) with a negligible decrease after the 500th cycle.

In order to improve the properties of CP, particular attention has been paid to modifying the substrate to control the surface properties and to fabricate stable composites on the modified substrate. A particular study on electrochemical preparation of CP; for example polybithiophene [115,116], poly(3-methylthiophene) [117,118], poly(3-octylthiophene), PEDOT [119], PPy [120], and PANI [121] and its derivatives [122] on alkanethiol coated substrate disclosed that adsorption of alkanethiols directly influence the growing mechanism of CPs. An interesting study was carried out by Aradilla and coworkers [123], where two different CPs, PEDOT and PPy were assembled into a three-layered film (PEDOT|PPy|PEDOT) through the electrochemical LBL deposition method at a potential of 1.4 V. The central issue addressed in this study is the relationship between the octanethiol self-assembled monolayer and the electrochemical behaviour of the three-layered symmetric system. The as-formed PEDOT|PPy|PEDOT multilayer film on octanethiol treated steel substrate exhibited a higher ability to store charge (314 C·g\(^{-1}\)) than the multilayer on untreated steel (211 C·g\(^{-1}\)). Furthermore, the former displayed a higher \( C_p \) (150 F·g\(^{-1}\)), excellent Coulombic efficiency (99%), and good specific energy (15.7 Wh·kg\(^{-1}\)) with promising specific power (2136 W·kg\(^{-1}\)) in comparison to the latter. This is mainly due to the presence of octanethiol which manipulates the electrochemical activity of the three-layered system. However, the long-term cycling stability of pre-treated PEDOT|PPy|PEDOT multilayer film severely deteriorated upon 1000 oxidation–reduction cycles holding only 21 F·g\(^{-1}\). On the other hand, the \( C_p \) retention under GCD gave better value, 80 F·g\(^{-1}\) after 2000 consecutive cycles. Yet, this value is less comparable with untreated PEDOT|PPy|PEDOT multilayer film (87 F·g\(^{-1}\)). Likewise, the pre-treated and untreated multilayer films delivered a nearly constant \( C_p \) at different scan rates (10–100 mV·s\(^{-1}\)) and the difference of \( C_p \) between both layered films is negligible. Thus, the authors assumed octanethiol has a substantial impact on the electrochemical activity of three-layered film, yet not on stability improvement. They also demonstrated that octanethiol tuned the roughness, porosity, and thickness of the system.

### Table 1. Conducting polymer-conducting polymer-based layer-by-layer assembly.

<table>
<thead>
<tr>
<th>Material</th>
<th>( C_p ) at 100 mV·s(^{-1})</th>
<th>( E )</th>
<th>( P )</th>
<th>Stability</th>
<th>Electrolyte</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT/PNMPY/PEDOT</td>
<td>90 F·g(^{-1})</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.1 M LiClO(_4)</td>
<td>[82]</td>
</tr>
<tr>
<td>Multilayered PANI</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>polypropylene</td>
<td>[114]</td>
</tr>
<tr>
<td>Potentiodynamic</td>
<td>468 F·g(^{-1}) at 50 mV·s(^{-1})</td>
<td>24.4 Wh·g(^{-1})</td>
<td>0.08 W·g(^{-1})</td>
<td>93.5% over 500 cycles</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potentiostatic</td>
<td>12 F·g(^{-1}) at 3 mA cm(^{-2})</td>
<td>0.027 Wh·g(^{-1})</td>
<td>0.16 W·g(^{-1})</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Galvanostatic</td>
<td>15 F·g(^{-1}) at 3 mA cm(^{-2})</td>
<td>0.013 Wh·g(^{-1})</td>
<td>0.56 W·g(^{-1})</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEDOT/PPy/PEDOT</td>
<td>150 F·g(^{-1}) at 20 mV·s(^{-1})</td>
<td>15.7 Wh·kg(^{-1})</td>
<td>2136. W·kg(^{-1})</td>
<td>14% over 1000 cycles</td>
<td>0.1 M LiClO(_4)</td>
<td>[123]</td>
</tr>
</tbody>
</table>

#### 3.1.2. Conducting Polymer-Carbon Based LBL

A serious evolving issue in the use of CP in SCs is its poor cycling stability. The mechanical instability of CP is due to the volumetric swelling and shrinking caused by insertion and removal of counter ions during the charge/discharge cycling process [66,124]. This proves to be cumbersome for high rate electrochemical SC production. On the other hand, carbon materials, the prospective material in industrial applications are actively being explored as an electrode due to their large specific area and high chemical stability. In order to meet the requirements of high-performance SCs (e.g., high \( C_p \), cycling stability, specific power, and specific energy), carbon-based materials have been introduced as a new frontier in electrode materials by incorporating with CPs (Table 2). For instance, PANI and (graphene oxide) GO multilayer films were deposited on indium tin oxide
(ITO) substrate electrochemically, which produced a capacitance of 429 F·g⁻¹, two-fold higher than that PANI multilayer electrodes at 1 mA [100]. The author clearly stated that the extended active sites of the composites and the oxygenated groups in GO highly contributed to the $C_{sp}$ and cyclic stability. Long cycle stability of electrodes is essential in SC applications and the carbon material is well known for long-term stability. However, pseudocapacitive materials, due to the significant volume changes, shrinking and swelling during the repetitive charge-discharge process, have a shorter life cycle. Thus, in this feasible introduction of carbon material, GO with the pseudocapacitive material, PANI to form a multilayer thin film, the stability effectively improved from $\sim$100 F·g⁻¹ (PANI multilayer) to $\sim$350 F·g⁻¹ (PANI/GO multilayer) over 1000 cycles.

In another similar study, Lee, et al. [125] demonstrated a flexible LBL assembled thin film consisting of PANI and graphene nanosheets (PANI||GO)$_n$. With the basic root of electrostatic interaction, the electrodes were developed by a dip coating method in which the layers were arranged in alternating order, varying from 2–10 bilayers. The ultraviolet-visible (UV-vis) absorption spectra in this study showed the regular growth of multilayers, while ellipsometry recorded an increase in thickness (with approximate 19 nm in thickness) as a function of the number of bilayers. The different pH level of GO also has an influence on the thickness, composition, and morphology of multilayers due to the changes in the degree of ionization. Hence, the right pH level of GO is important to balance the surface charges in order to ease adsorption. Additionally, by performing thermal and chemical treatment on the multilayers, improvements on mechanical and electrical properties were noticed as a result of the restoration of the conjugated structure of the graphene nanosheets and changes in the conducting state of PANI. The thermally annealed (PANI||GO)$_{10}$ hybrid electrode’s gravimetric capacitance up to 375.2 F·g⁻¹ at 0.5 A·g⁻¹, which is almost three-times increase of an un-annealed electrode; however, with chemical treatment it leads to poor electrochemical results. It also offers acceptable electrochemical cyclic stability (90.7%) over 500 cycles at 3.0 A·g⁻¹, yet its specific power and specific energy still remain low.

Likewise, Sarker and Hong [126] also fabricated LBL assembled PANI-GO$_{30}$ on polyethylene terephthalate (PET) using the dip coating method and on further reducing the GO it enhanced the overall performances of multilayers in flexible SC devices. After treating the multilayer films at 100 °C for 3 h in hydroiodic acid solution, in a three-electrode system, the films displayed impressive $C_{sp}$ (529 F·cm⁻³ at a current density of 3 A·cm⁻³), and with 86% retention over 1000 cycles. In contrast, the PANI-rGO$_{30}$/ITO showed better pseudocapacitive performances (956 F·cm⁻³) but with a 21% loss in capacitance under the same experimental conditions. Furthermore, PANI-rGO$_{30}$/ITO outperformed the PANI-rGO$_{30}$/PET in the rate capability. That is, 44% of the $C_{sp}$ was retained from 3 A·cm⁻³ (956 F·cm⁻³) to 70 A·cm⁻³ (416 F·cm⁻³) as compared to PANI-rGO$_{30}$/PET with 26%. Mechanical flexibility is an important factor to consider in assembling a flexible SC device. The mechanical flexibility of PANI-rGO$_{30}$/PET is purported to be functioning in bending conditions in which the electrical resistance showed almost no changes up to 200 bending cycles. The same author, in another study, pointed out the importance of PANI and GO concentrations in assembling the multilayer. Also, they stated that among the pyrolysis and chemical treatment with hydroiodic acid or hydrazine, hydroiodic acid was found to be the best way to obtain rGO without damaging the PANI structure [61]. Choosing the right reduction method could help in developing high-performance SC. Tayel, et al. [127] also reported the fabrication of rGO/PANI composite by directly spray coating PANI onto rGO electrodes. The obtained electrodes showed high $C_{sp}$ (916 F·g⁻¹ at 5 mV·s⁻¹), excellent specific energy (127.9 Wh·kg⁻¹) and good rate capability (86% over 1000 cycles).

In 2016, Gupta and Price [128] primed highly conductive hybrid multilayer electrodes based on graphene nanosheets and CPs (PPy and PANI) via in-situ electropolymerization followed by electrochemical reduction of GO to form ErGO. The authors drop cast the GO dispersion onto the polymer film which subsequently undergoes electrochemical reduction. This is a simple and effectual method in producing LBL denoted as (PPy/ErGO)$_n$ and (PANI/ErGO)$_n$ with $n = 1, 2, 3, 4,$ and 5 bilayers. As a comparison, the electrochemical performance of (PANI/rGO)$_n$ up to $n = 5$
bilayer with three different rGO weight loadings (5%, 10%, and 15%) were discussed. In the second approach, the chemically prepared PANI was drop cast onto the substrate or the substrate was dipped into PANI solution before being dipped in rGO dispersion. As mentioned earlier, in this study the authors used two different approaches to prepare PANI and also to reduce GO. The authors aimed to highlight the importance of physicochemical and tailored interfacial properties on electrochemical activity by discussing two different approaches. All the prepared multilayers were demonstrated to be a pseudocapacitive electrode. These graphene–polymer hybrid multilayers exhibited excellent gravimetric \( C_{sp} \) in the range of 300–560 \( \text{F} \cdot \text{g}^{-1} \) at 1.0 \( \text{A} \cdot \text{g}^{-1} \) and 10 mV·s\(^{-1}\), lower internal resistance, and good cyclic stability (~90% over 1000 cycles at 1.5 \( \text{A} \cdot \text{g}^{-1} \)). Surprisingly the bilayer electrodes \((n = 1)\) showed extraordinary gravimetric \( C_{sp} \) compared to electrodes with \( n > 1 \), where the thickness directly affects the capacitive of the electrode. Furthermore, the authors also pointed out the role of rGO and ErGO and the importance of rGO mass loadings in multilayers. A higher rGO content in graphene–polymer hybrid multilayers aids in accumulating electrical charge at the interfaces. Additionally, the good contacts between polymer and graphene nanosheets provide a smooth path for electron transfer and give strong adherence. Also, compared with PPy, PANI has been found to have a less pronounced effect on the mechanical degradation from swelling and de-swelling.

Not to be forgotten, in a deposition involving CP, dopants play an important role in determining morphologies and benefitting charge carriers movements of the composite. De la Fuente Salas, et al. [78] described composites composed of multilayer PPy with three different counter ions namely, \( p \)-toluene sulfonic acid, benzene sulfonic acid, and sulfuric acid deposited on GO coated stainless steel for symmetrical SC. The multilayer was produced galvanostatically and the deposition mechanism is as shown in Figure 14. The choice of counter ions and order of deposition layers were decided for the following reasons:

- The \( p \)-toluene sulfonate ions with bigger size which densely pack inside PPy were chosen as the first layer. This criterion assists in increasing the capacitance and conductivity of the composite.
- The second layer with smaller sized counter ions (benzene sulfonate ions) form highly \( p \)-doped PPy as the smaller ions donate electrons easily.
- Complete dissociation of sulfuric acid (final layer) allows sufficient space for the ions to be electrostatically adsorbed onto the pore layer of the composites.

After forming the symmetrical SC, the multilayer electrode exhibited stable performance with \( C_{sp} \) as high as 341 \( \text{F} \cdot \text{g}^{-1} \) at a current density of 2 mA·cm\(^{-2}\), specific energy of 78 Wh·kg\(^{-1}\) and specific power of 6 kW·kg\(^{-1}\). The multilayer film with mesoporous structure effectively minimizes the loss of ions from the layer and thus lessens the \( C_{sp} \) drop at different scan rates.

\[
\text{GO-O} + \overset{\text{Anodization}}{\text{(pTS)}} \rightarrow \text{GO-O} \quad \begin{aligned}
\text{H}^+(\text{pTS})_n
\end{aligned} \rightarrow \text{GO-O} \quad \begin{aligned}

\text{H}^+(\text{pTS})_n
\end{aligned}
\]

Figure 14. Mechanism of polypyrrole (PPy) multilayer films deposition on graphene oxide [78].
Surfactants are often used to control the morphologies of the CPs. During the polymerization of a monomer in the presence of a surfactant, for example, sodium dodecylsulfate (SDS), hexadecyl-trimethylammonium bromide (CTAB) or dodecyl-trimethylammonium bromide (DTAB) are incorporated inside the CP as counter ions. It has been proven that CP formed with the aid of surfactants shows better properties [129]. In order to prepare electrodes with superior pseudocapacitive properties, PPy-pillared GO sheet (PPy-GO) composites were vacuum filtered [130]. The underlying importance of surfactants was detailed in this study. The author highlighted that mixed cationic surfactant and GO solution ensure the surfactants are sandwiched in between the GO layers, forming GO-surfactant multilayers. Upon polymerization followed by surfactant removal, PPy pillars between GO sheets were formed. The PPy-GO composite without any surfactants divided into two distinct morphologies, while in CTAB, the PPy fibers layered between the GO sheets were noticed whereas, the composites obtained in DTAB exhibited sphere-like PPy sandwiched between GO sheets. Consequently, both composites showed excellent pseudocapacitive behavior with 510 F·g⁻¹ and 528 F·g⁻¹, respectively. However, fiber-like PPy-GO composite shows better rate capability with ~70% retention at scan rates from 0.3 to 5 A·g⁻¹ than sphere-like PPy-GO composite with ~48%. This manifests the influence of morphology controlled by surfactants on the movement of ions in the composites.

An SC with high \( C_{sp} \), specific power and specific energy is highly desirable in energy storage devices. Shortening the diffusion length by altering the morphologies could boost the electric performances as well as mitigate the cycling degradation issues [131]. One dimensional (1D) nanomaterials (i.e., nanotube, nanorods, nanowires, and nanofiber) seems a fascinating forerunner of electrochemical SC for its interconnected network which can facilitate the ions and electrons diffusions across the interface in the absence of binder as well for its remarkable electronic properties [132,133]. The dip-coating method together with the reduction process followed by electropolymerization has been used to prepare rGO/PANI nanofiber [134]. The as-synthesized composite presents \( C_{sp} \) of 5.16 F·cm⁻² and 3.35 F·cm⁻² at a current density of 10 mA·cm⁻² and a scan rate of 10 mV·s⁻¹, respectively. These results are significantly higher than those for rGO sheets and PANI nanofiber. The impedance studies further displayed a smaller semicircle (decreased charge transfer resistance) with smaller internal resistance. This implies good electrical conductivities and excellent electrochemical properties.

A hollow or hierarchical structure in 3D (foams, aerogels, hydrogels or sponges) has drawn increasing attention compared to 1D nanomaterial as a result of the continuous electron transport pathway, a larger aspect ratio at the interface, and high surface area with greater pores contributing to mechanical stability and good electrolyte accessibilities [135]. Excitingly, this concept has been successfully applied in assembling multilayer electrodes for SC [76,136]. In particular, Luo, et al. [76] developed the rGO-PANI hybrid hollow spheres using sulfonated polystyrene (PS) microsphere as a sacrificial template (Figure 15). In this study, the authors prepared PANI chemically and later wrapped the PS with PANI aided by centrifugation. The obtained PANI:PS was dispersed in rGO to form a PANI/rGO, and later the entire process was repeated to form multilayers. They showed that an electrode with up to six bilayers has a higher \( C_{sp} \) than an electrode with eight bilayers. This is due to the respective hollow structure with different shell thickness. The optimized six bilayers of rGO-PANI hybrid hollow spheres showed comparatively a higher \( C_{sp} \) (456 F·g⁻¹ at 0.5 A·g⁻¹) and retention of capacitance of 83% after 1000 consecutive cycles. This higher stability is due to better accommodation caused by volume expansion during the cycling process.

An important criterion of graphene-based electrodes is their mechanical strength. Their exceptionally good mechanical strength enables the production of a GO or rGO based flexible or free-standing electrode a lot easier and more straightforward by a simple filtration process without the use of binder or additives. For example in 2015, a flexible 3D rGO/PANI was designed on a PS microsphere by a vacuum filtration followed by dilute polymerization, whereby aligned PANI nanowire array was grown on the PS-coated rGO film [136]. This 3D rGO/PANI produced a high \( C_{sp} \) of 740 F·g⁻¹ at 0.5 A·g⁻¹ capable to retain 87% of its capacitance after 1000 cycles compared to pure PANI (58%). More importantly, this electrode material exhibited maximum specific power and specific energy of 4 kW·kg⁻¹ and 65.94 Wh·kg⁻¹, respectively.
(Figure 16). This improvement in the capacitive performance is due to the increment in surface area that facilitates ion movement through the formation of the 3D porous structure after removal of PS. In addition, aligned PANI nanowires encourage a greater interfacial area and shorter diffusion path for the availability of the oxidation/reduction reaction. Other than the contribution of high electrical conductivity from rGO, PANI nanowires also provide a conductive pathway for ions and electrons.

![Diagram](image)

**Figure 15.** The illustration of the fabrication procedure of graphene—PANI hollow spheres (rGO-PANI HS) [76].

![SEM Images](image)

**Figure 16.** (a,b) Surface and cross-section scanning electron microscope (SEM) images of 3D rGN/PANI film, (c) CV curves at 20 mV s⁻¹ in 1 M H₂SO₄, (d) Galvanostatic charge/discharge curves at a current density of 0.5 A g⁻¹, (e) Variation of the specific capacitance with current density and (f) Ragone plots of rGN film, 3D rGN film, PANI and 3D rGN/PANI composite film [136].
Recently, Hong, et al. [137] also built binder-free 3D rGO/PANI nanocomposites. The complexation between negatively charged GO and branched polyethyleneimine (b-PEI) forms a stable GO/b-PEI complex on filter paper and then proceeds hydrothermally to produce the 3D rGO framework. The diffusion-driven LBL (dd-LbL) assembled GO/b-PEI complex at the liquid-liquid interface permits the continuous diffusion of b-PEI molecules at the interface which is responsible for the formation of a foam-like porous network structure. Subsequently, PANI nanoparticles were then directly grown on this 3D rGO nanosheets acting as a scaffold via in-situ polymerization. Worth mentioning, the concentration of aniline has a strong influence on the weight of nanocomposites and distribution of PANI on the rGO nanosheets. However, aggregation was noticed within the nanosheets when the concentration rose. After exceeding certain limits of concentration, PANI only covered the outline of the nanosheets. However, aggregation was noticed within the scaffold when the concentration rose. After exceeding certain limits of concentration, PANI only covered the outline of the scaffold. Commonly, the PANI grow in-situ on rGO as electrodes for SC has few interesting benefits: the interconnected and porous morphology of rGO facilitates electrolyte ion movements, the evenly distributed PANI-based pseudocapacitance on the rGO-based EDLC scaffold resulted in higher electrochemical performances, and good adherence between PANI and rGO could be formed without the necessity of binder. Thus, the as-assembled 3D rGO/PANI symmetrical electrode provides 401.5 F·g⁻¹ at a current density of 4.0 A·g⁻¹ and is able to retain 76.5% of its C_{sp} after 2000 cycles.

The most commonly used conductive template for SCs is nickel foam. The nickel foam serves as the best conducting backbone and platform for the growth of nanostructures. Furthermore, the 3D structure of nickel foam has a high specific surface area and open pores. It is worth noting, the microholes and hierarchically arranged irregular flow channels in the nickel foam provide an excellent ion transport network [138]. As an example, 3D nickel foam was used as a current collector by Yu, et al. [139] in the fabrication of PANI nanowire arrays on rGO foam. The prime strength of this study is growing rGO on nickel foam forming rGO foam, which appears to be the main hub for electrical conductance with a substantial interior surface area. Mainly, this approach avoids the necessity of a binder. Moreover, it has been verified that deposition of PANI nanowires on the top of rGO foam greatly enhances the C_{sp} (790 F·g⁻¹) with maximum specific energy and specific power of 17.6 Wh·kg⁻¹ and 98 kW·kg⁻¹, respectively. Simultaneously, this rGO foam/PANI composite overcomes the shortcoming of PANI by strengthening the stability with 80% capacitance retention after 5000 cycles.

### Table 2. Conducting polymer-carbon material based layer-by-layer assembly.

<table>
<thead>
<tr>
<th>Material</th>
<th>C_{sp}</th>
<th>E</th>
<th>P</th>
<th>Stability</th>
<th>Electrolyte</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI GO multilayer</td>
<td>504 F·g⁻¹ at 10 mV·s⁻¹</td>
<td>-</td>
<td>-</td>
<td>82% over 1000 cycles</td>
<td>1.0 M H₂SO₄</td>
<td>[100]</td>
</tr>
<tr>
<td>PANI GO multilayer</td>
<td>375.2 F·g⁻¹ at 0.5 A·g⁻¹</td>
<td>-</td>
<td>-</td>
<td>90.7% over 500 cycles</td>
<td>1.0 M H₂SO₄</td>
<td>[125]</td>
</tr>
<tr>
<td>PANI(rGO) on ITO</td>
<td>529 F·cm⁻³ at 3 A·cm⁻³</td>
<td>-</td>
<td>-</td>
<td>86% over 1000 cycles</td>
<td>1.0 M H₂SO₄</td>
<td>[126]</td>
</tr>
<tr>
<td>PANI(rGO) on PET</td>
<td>956 F·cm⁻³ at 3 A·cm⁻³</td>
<td>-</td>
<td>-</td>
<td>79% over 1000 cycles</td>
<td>1.0 M H₂SO₄</td>
<td>[126]</td>
</tr>
<tr>
<td>PANI/rGO</td>
<td>584 F·cm⁻³ at 3 A·cm⁻³</td>
<td>-</td>
<td>-</td>
<td>56.5% over 1000 cycles</td>
<td>1.0 M Na₂SO₄</td>
<td>[61]</td>
</tr>
<tr>
<td>rGO/PANI</td>
<td>916 F·g⁻¹ at 5 mV·s⁻¹</td>
<td>122.9 Wh·kg⁻¹</td>
<td>-</td>
<td>86% over 1000 cycles</td>
<td>6.0 M KOH</td>
<td>[127]</td>
</tr>
<tr>
<td>PPy/rGO</td>
<td>315 F·g⁻¹ at 10 mV·s⁻¹</td>
<td>-100 Wh·kg⁻¹</td>
<td>-1.5 kW·kg⁻¹</td>
<td>88–90% over 1000 cycles</td>
<td>1.0 M H₂SO₄</td>
<td>[128]</td>
</tr>
<tr>
<td>PANI/rGO</td>
<td>390 F·g⁻¹ at 10 mV·s⁻¹</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.0 M H₂SO₄</td>
<td>[78]</td>
</tr>
<tr>
<td>PANI/rGO</td>
<td>250 F·g⁻¹ at 10 mV·s⁻¹</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.0 M H₂SO₄</td>
<td>[78]</td>
</tr>
<tr>
<td>GO/PPy</td>
<td>332 F·g⁻¹ at 5 mV·s⁻¹</td>
<td>78 Wh·kg⁻¹</td>
<td>6 W·kg⁻¹</td>
<td>-</td>
<td>1.0 M H₂SO₄</td>
<td>[78]</td>
</tr>
<tr>
<td>PPy/sphere GO</td>
<td>510 F·g⁻¹ at 0.3 A·g⁻¹</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.0 M H₂SO₄</td>
<td>[130]</td>
</tr>
<tr>
<td>PPy/fiber GO</td>
<td>528 F·g⁻¹ at 0.3 A·g⁻¹</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.0 M H₂SO₄</td>
<td>[130]</td>
</tr>
</tbody>
</table>

*Translating from Chinese*
3.1.3. Conducting Polymer-Metal Oxides Based LBL

This segment summarizes the collection of works conducted by the group of researchers making use of CPs and transition metal oxides (TMOs) to fabricate electrode materials via LBL assembly. TMOs such as ruthenium oxides (RuO$_2$), manganese dioxide (MnO$_2$), iron oxides (FeO$_2$), vanadium oxide (V$_2$O$_5$), and cobalt oxides (Co$_3$O$_4$) have received a lot of interest as electrode materials for their intriguing properties such as high C$_{sp}$ and multi oxidation states that match the global demand for better SCs. With the upsurge in demand afforded for its easy fabrication method, compatibility with electrolytes, and chemical and environmental stability, TMOs are often integrated or layered with other pseudocapacitive or electrical double layer capacitive materials [140]. In this section, the contributions of CP supported TMOs serving as electrode materials in the electrochemical performances of SCs are discussed (Table 3).

Hong, et al. [141] prepared PEDOT layered with RuO$_2$. As a very demanding metal oxide for its metal-like conductivity [142], RuO$_2$ takes the center stage of energy storage devices. Hong and co-workers used platinum foil to grow PEDOT followed by deposition of RuO$_2$. PEDOT was electrically polymerized on the platinum foil from EDOT prepared in acetonitrile medium. After that, the authors covered the PEDOT surface with RuO$_2$ to improve the capacitive properties of the composite. Here, they used two different methods for ruthenized PEDOT electrodes; dipping-hydrolysis or electrolysis method. They discovered that after coating with RuO$_2$, the electrodes showed enhanced capacitive properties, especially, electrodes fabricated by the electrolysis method. The capacitive properties of the composite produced at different times were evaluated to understand the effect of polymer thickness on the capacitance. The obtained results showed that a thick polymer could impede the accessibility of ions, in which only the RuO$_2$ and outer portion of the polymer surface played the major role in contributing capacitance. Further studies were also conducted to address the relationship between the amount of RuO$_2$ and capacitance. It was shown that the micropores of the polymer are only able to hold a limited content of RuO$_2$. The optimized PEDOT/RuO$_2$ SC electrode exhibited a specific capacitance of 420 F·g$^{-1}$ (based on combined mass of polymer and metal oxide) and 930 F·g$^{-1}$ (based on mass of metal oxide alone) in aqueous 0.5 M sulfuric acid (H$_2$SO$_4$), which is almost two times higher than that of RuO$_2$ deposited on platinum foil (182 F·g$^{-1}$) with specific energy of 27.5 Wh·kg$^{-1}$.

The high rate performance of SC relies on the architecture of the active materials. Therefore, their morphologies are often tuned into nanostructures to provide high surface area and short ion/electron diffusion pathways for rapid charge/discharge [143]. However, the poor electrical conductivity of metal oxides is the only major flaw that hinders the use of metal oxide as the sole electrode material [144]. This drawback limits the electron movements and delays the oxidation/reduction reactions causing low specific capacitances and rate capabilities. Hence, combining with CP will mitigate the problem. Strikingly, in 2015, Wei, et al. [145] successfully electropolymerized PPy on the layer of Co$_3$O$_4$ nanoparticles where Co$_3$O$_4$ ethanol suspensions were drop cast onto carbon paper. Co$_3$O$_4$ is an inexpensive pseudocapacitive material with a high surface area and good reversible redox

### Table 2. Cont.

<table>
<thead>
<tr>
<th>Material</th>
<th>$C_p$</th>
<th>$E$</th>
<th>$P$</th>
<th>Stability</th>
<th>Electrolyte</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>* rGO/PANI nanofiber</td>
<td>5.16 F·cm$^{-2}$ at 10 mA·cm$^{-2}$</td>
<td>-</td>
<td>-</td>
<td>95% over 1000 cycles</td>
<td>1.0 M H$_2$SO$_4$</td>
<td>[134]</td>
</tr>
<tr>
<td>* rGO/PANI hollow spheres</td>
<td>3.35 F·cm$^{-2}$ at 10 mV·s$^{-1}$</td>
<td>-</td>
<td>-</td>
<td>85% over 1000 cycles</td>
<td>1.0 M H$_2$SO$_4$</td>
<td>[76]</td>
</tr>
<tr>
<td>3D rGO/PANI</td>
<td>456 F·g$^{-1}$ at 0.5 A·g$^{-1}$</td>
<td>-</td>
<td>-</td>
<td>87% over 1000 cycles</td>
<td>1.0 M H$_2$SO$_4$</td>
<td>[136]</td>
</tr>
<tr>
<td>3D rGO/PANI</td>
<td>401.5 F·g$^{-1}$ at 4 A·g$^{-1}$</td>
<td>-</td>
<td>-</td>
<td>76.5% over 2000 cycles</td>
<td>1.0 M H$_2$SO$_4$</td>
<td>[137]</td>
</tr>
<tr>
<td>rGO/PANI nanowire</td>
<td>790 F·g$^{-1}$ at 1 A·g$^{-1}$</td>
<td>17.6 Wh·kg$^{-1}$</td>
<td>98 kW·kg$^{-1}$</td>
<td>80% over 5000 cycles</td>
<td>1.0 M H$_2$SO$_4$</td>
<td>[139]</td>
</tr>
</tbody>
</table>

* three-electrode system.
properties [143, 146]. In this study, the authors prepared flower-like Co$_3$O$_4$ nanoparticles (f-Co$_3$O$_4$) through a facile solvothermal method and for comparison, ball-like Co$_3$O$_4$ nanoparticles (b-Co$_3$O$_4$) were also prepared. The f-Co$_3$O$_4$ showed well-defined redox peaks with wide current densities highlighting the capability to store more energy compared to the b-Co$_3$O$_4$ (Figure 17a). This is due to the high specific surface area and pore volume offered from its 2-dimensional petaloid nanosheets which enhance the accessibilities of OH$^-$ ions. As PPy was incorporated with f-Co$_3$O$_4$, the pseudocapacitive properties of PPy enhanced the specific capacitance of the composite to 398.4 F·g$^{-1}$ at a current density of 10 A·g$^{-1}$ with a longer discharge time than f-Co$_3$O$_4$ (40.9 F·g$^{-1}$) (Figure 17b,c). The Ragone plot (Figure 17d) demonstrated that PPy layered with f-Co$_3$O$_4$ exhibited the highest specific energy and specific power. The multilayer also maintained good cycling stability which was almost 100% over 1000 cycles at 50 A·g$^{-1}$.

Similarly, in another attempt, Co$_3$O$_4$ nanosheet arrays were hybridized with PPy which were designated as core and shell, respectively [147], in which both core and shell are known as good pseudocapacitive materials. First, the Co$_3$O$_4$ nanosheet arrays were prepared by a solvothermal and calcination method from a solution containing cobalt nitrate (II) hexahydrate and hexamethylenetetramine on nickel foam. The layer of PPy was then grown on the mesoporous Co$_3$O$_4$ nanosheet arrays by using the potentiostatic method (Figure 18a). It was proven that the existence of CP could improve the electrons and ion diffusion rate, resulting in the enhancement of...
electrical conductivity and specific capacitance. In this case, the interconnected Co$_3$O$_4$ nanosheet arrays act as an effective scaffold to support the growth of PPy with a highly accessible surface area (Figure 18b,c). This core/shell hybrid electrode is able to deliver a maximum specific areal capacitance of 2.11 F·cm$^{-2}$ at the current density of 2 mA·cm$^{-2}$ in a 1 M potassium hydroxide (KOH), a remarkable rate capability (65% retention when increased from 2 to 20 mA·cm$^{-2}$) as well as an outstanding long-term cycling stability (85.5% capacitance retention after 5000 cycles) (Figure 18e–h). In addition, the CV profiles of the core/shell electrode show that the electrode exhibited a reversible electrochemical process and ideal pseudocapacitive characteristics. It is clear that the overall electrochemical properties improvement is attributed to the synergetic effects of the PPy shell and Co$_3$O$_4$ core.

![Schematic diagram for the synthesis of mesoporous Co$_3$O$_4$@PPy hybrid nanosheet arrays on Ni foam](image)

**Figure 18.** (a) Schematic diagram for the synthesis of mesoporous Co$_3$O$_4$@PPy hybrid nanosheet arrays on Ni foam, (b–d) SEM and TEM images of the Co$_3$O$_4$@PPy hybrid composites after 5 min electrodeposition, (e) CV curves of the Co$_3$O$_4$@PPy hybrid electrode and Co$_3$O$_4$ electrode at a scan rate of 50 mV·s$^{-1}$, (f) CV curves of the Co$_3$O$_4$@PPy hybrid electrode and Co$_3$O$_4$ electrode at various scan rates, (g) CD curves of the Co$_3$O$_4$@PPy hybrid electrode and Co$_3$O$_4$ electrode with a current density of 2 mA·cm$^{-2}$ and (h) Areal capacitances of the Co$_3$O$_4$@PPy hybrid electrode and Co$_3$O$_4$ electrode at various current densities [147].
Stimulated by the high electrochemical performance of the transition metal oxides, Guo, et al. [148] demonstrated a green and fast tandem redox strategy to fabricate a sandwich-like structure of layered vanadium oxide/poly(3,4-ethylenedioxythiophene)/layered manganese oxide (LVO/PEDOT/LMO). The uniqueness of this method is that it involves two redox reactions in tandem; (i) LVO-catalyzed oxidizing polymerization of PEDOT on LVO nanosheets and (ii) reduction of KMnO₄ by PEDOT on nanosheets (Figure 19), where the cylinder-shaped LVO aerogel is the starting material. Moreover, this time-saving method is a green alternative to the currently available methods with the absence of toxic reducing or oxidizing agents. An asymmetric SC with LVO/PEDOT/LMO as a positive electrode and the activated carbon (AC) as a negative electrode sandwiched between a separator dipped in Na₂SO₄ aqueous electrolyte was assembled using a Swagelok-type cell. The detailed construction is shown in Figure 20a. The cyclic voltammetry (CV) and GCD curves are presented in Figure 20b,c. The assembled asymmetrical SC (LVO/PEDOT/LMO//AC) exhibited a superior specific capacitance of 41.8 F·g⁻¹ at a scan rate of 25 mV·s⁻¹ which is much higher than that reported for LVO/PEDOT//AC (34.2 F·g⁻¹) and LVO//AC (17.5 F·g⁻¹). A comparable specific capacitance for LVO/PEDOT/LMO//AC (59.2 F·g⁻¹), LVO/PEDOT//AC (39.2 F·g⁻¹), and LVO//AC (15.6 F·g⁻¹) electrodes was also extracted from the GCD curves at 1.2 A·g⁻¹. Furthermore, the LVO/PEDOT/LMO//AC asymmetrical electrode showed remarkable specific energy of 39.2 Wh·kg⁻¹ compared to the LVO/PEDOT//AC (28.9 Wh·kg⁻¹) and LVO//AC (10.8 Wh·kg⁻¹) electrodes. Additionally, the fabricated LVO/PEDOT/LMO//AC electrode offered excellent rate capability, 21.7 Wh·kg⁻¹ at 2.2 kW·kg⁻¹ with good cycling stability after 3000 cycles (93.5%). These results give further clear evidence of the tandem redox reaction on the performance of the layered material on the SC performance.

![Figure 19. Scheme and digital images showing the fabrication of (a) layered vanadium oxide (LVO) aerogel, (b) layered vanadium oxide/poly(3,4-ethylenedioxythiophene) LVO/PEDOT, and (c) layered vanadium oxide/poly(3,4-ethylenedioxythiophene)/layered manganese oxide LVO/PEDOT/LMO [148].](image)

<table>
<thead>
<tr>
<th>Material</th>
<th>Cₛ</th>
<th>E</th>
<th>P</th>
<th>Stability</th>
<th>Electrolyte</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>PEDOT/RuO₂</td>
<td>420 F·g⁻¹</td>
<td>27.5 Wh·kg⁻¹</td>
<td>-</td>
<td>-</td>
<td>0.5 M H₂SO₄</td>
<td>[141]</td>
</tr>
<tr>
<td>PPy/Co₃O₄</td>
<td>398.4 F·g⁻¹ at 10 A·g⁻¹</td>
<td>8.4 Wh·kg⁻¹</td>
<td>2.9 kW·kg⁻¹</td>
<td>100% over 1000 cycles</td>
<td>2.0 M KOH</td>
<td>[145]</td>
</tr>
<tr>
<td>PPy/Co₃O₄ nanosheet</td>
<td>2.11 F·cm⁻² at 2 mA·cm⁻²</td>
<td>-</td>
<td>-</td>
<td>85.5% over 5000 cycles</td>
<td>1.0 M KOH</td>
<td>[147]</td>
</tr>
<tr>
<td>V₂O₅/PEDOT/MnO₂</td>
<td>85.7 F·g⁻¹ at 0.5 mV·s⁻¹</td>
<td>21.7 Wh·kg⁻¹</td>
<td>2.2 kW·kg⁻¹</td>
<td>93.5% over 3000 cycles</td>
<td>1.0 M Na₂SO₄</td>
<td>[148]</td>
</tr>
</tbody>
</table>

* three-electrode system.
Figure 20. (a) Configuration of the asymmetric supercapacitors. (b) CV curves of asymmetric supercapacitors with a voltage window of 1.8 V at a scan rate of 25 mV·s\(^{-1}\). (c) Charge-discharge measurements of asymmetric supercapacitors at a current density of 1.2 A·g\(^{-1}\). (d) Ragone plots of the asymmetric supercapacitors calculated from charge-discharge curves based on the total mass of active materials. (e) Cycle performance of the asymmetric supercapacitors at 6 A·g\(^{-1}\). (f) Digital images of a green LED powered by two LVO/PEDOT/LMO//AC supercapacitors connected in series [148].

4. Conclusions: Summary and Perspectives

Supercapacitors are evolving devices in the world of energy storage technologies. They have piqued the interest of world researchers for the possibility of maximizing the diversity of materials and obtaining the best surface and electrochemical properties. Therefore, intense development of nanostructured material has been undertaken for use as electrode materials. Improving the material
preparation method helps to bridge the gap of specific energy. In this review, we covered the leading studies of CP composites for supercapacitor electrodes, based on the LBL approach. In the current research world, CP-based nanostructured material and its composites hold significant promise as electrodes for supercapacitor for their captivating properties. Combination of both pseudocapacitance and electrical double layer capacitance in a composite has become the forerunner of electrodes with excellent properties and LBL is one of the ways. The LBL approach offers straightforward, versatile, and low-cost methods for the preparation of supercapacitor electrodes with a variety of materials. The most common methods used to deposit CP composites onto supercapacitor electrodes include electrochemical deposition, spin coating, and so forth to enable fabrication of composites with different thickness, flexibility, structural diversity, composition, and morphology. Several important criteria need to be highlighted here in the preparation of LBL assembled CP based composites electrodes. Each layer can be optimized with different materials according to their functions. Also, there is no boundary in choosing the materials. The most important part is the thickness of the layer which can be altered to have control of the transport resistance. Based on the benefits highlighted above, the LBL assembled CP-based composites have a viable future as electrodes for supercapacitors. Several main aspects need to be considered for future research as listed below:

1. The main issue in fabricating a supercapacitor is the high cost. Fabricating more cost-effective LBL assembled CP-based composites needs to be considered.
2. Commonly, the electrode material for a supercapacitor suffers from high transport resistance. In order to achieve a supercapacitor with low transport resistance, an electrode material with minimum thickness is important.
3. An environmentally friendly approach and environmentally suitable materials are preferred. Overall we should pay more attention to the fabrication of LBL assembled CP-based composites in a more environmentally friendly approach.
4. More importance should be placed on the selection of electrolyte. Choosing the correct electrolyte for the electrode determines the performance of the supercapacitor.

In conclusion, the supercapacitor plays an important role in current energy storage technologies. Thus, it is very important to develop suitable electrode materials for supercapacitors for practical use in the future.

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Conflicts of Interest: The authors declare no conflict of interest.

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