

## Review article

# Advanced materials for energy storage devices.

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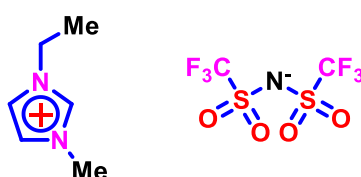
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**ABSTRACT:** This review examines high performing energy storage devices for high-power applications including heavy electric vehicles, energy-efficient cargo ships and locomotives, aerospace and stationary grid system. Such devices require systematic design and fabrication of composite nanostructured carbon-based material and conductive polymers. Electrochemical capacitors based on nanostructured carbon can complement or replace batteries in electrical energy storage and harvesting applications whenever high power delivery or uptake is needed. Composite device of pseudo-capacitive polymeric materials and nanostructured carbon with the latest generation of nanostructured lithium electrodes has brought the energy density of electrochemical capacitors closer to that of batteries without compromising its specific power density, high capacitance and lifetime cycling stability. Energy storage devices' widespread applications in industrial, hybrid electric vehicles and commodity electronics could be facilitated through careful selection of electrolyte-electrode system. Good understanding of charging mechanism is key to improving device's performance. Charging mechanism includes sequential ion desolations in pores smaller than the solvated ions through ion exchange or ion adsorption. This leads to higher capacitance for such storage devices. This has opened the door to designing advanced high-energy density devices with fast charging and discharging times using a variety of electrolytes and nanostructured carbon-polymer composite.

**KEYWORDS:** Electrochemical capacitors; Pseudo-capacitors; Energy density; Power density; conducting polymers.

### GRAPHICAL ABSTRACT:



### Introduction

World energy consumption has been continuously increasing in the past few decades due to high population growth. There are strong demands for superior energy storage and conversion devices to meet basic requirements of human life. Traditional energy storage materials and devices are based either on Lithium-ion battery or porous carbon (electric double layer). Supercapacitors and/or pseudocapacitors, based on conducting polymers, gained entry

into the energy storage system in order to improve electrochemical performance of device. Li-ion batteries (LIB) were introduced in 1991 by the Sony corporation and have transformed portable electronic devices since that time [1]. Though new generations of Li-ion batteries are capable of powering electric vehicles to a limited driving range while charging, it is still far from approaching the goal of ~500 Km. Several drawbacks are associated with Li-ion batteries including reactivity of the Lithium

metal electrodes leading to dendrites formation that may affect the cycle life of the battery. The specific energy density of current state-of-the-art LIBs is below the U.S. Department of energy vehicle technologies program's long-term target for the secondary batteries [2]. Similarly, the volatile organic electrolytes of LIB have raised safety concerns. Addressing these drawbacks in LIB led to the development of liquid electrolyte and solid polymer electrolyte (SPE) systems that inhibit dendrite growth and improve its practical specific energy capacity, energy density and power efficiency.

Interest in carbon-based materials such as graphene has grown tremendously in recent years since its isolation by Novoselov and co-workers in 2004 as a single-atom-thick layer of carbon [3]. A large number of publications have discussed applications of graphene in electrochemical energy-storage devices (EESDs). The properties of graphene vary significantly in terms of morphology, lateral dimensions, number of layers and defects. The presence of defects affects the quality of the end material and, consequently, its electrochemical features [4]. Common synthetic methods include mechanical exfoliation, liquid phase exfoliation, reduction of graphene oxide, bottom-up self-assembly by granulation or balling and chemical vapor deposition of hydrocarbons [5]. One commonly employed method is the reduction of graphene oxide (GO) to yield reduced graphene oxide (RGO). The GO is a highly defective form of graphene with a disrupted  $sp^2$ -bonding network. Reduction of Graphene oxide restores the  $\pi$ network which is the characteristic of conductive graphene [4]. This method allows production of bulk quantities of graphene with high yield at low to medium quality. Graphene-based

materials used in EESD include GO-composites or RGO-composite. Such composite systems incorporate either conductive polymer or metal oxide into the graphitic network to enhance its electronic conductivity by several order of magnitude, improve the poor cycling behavior and capacity fading. Graphene is an excellent matrix in the synthesis of functional nanomaterials for enhanced electronic conductivity. The nanocomposite of reduced graphene and conducting polymers such as polyaniline (PANI) exhibits excellent electrochemical properties for advanced energy storage devices. Such composites greatly improve the specific capacity, energy density, rate capability and cyclic performance. Some of the unique properties of graphene include good mechanical flexibility, large surface area and high thermal and chemical stability.

Carbon-based super capacitors have been well-suited to high power application due to its non-faradaic charge storage mechanism (electric double layer) which allows rapid rates of charge and discharge. Charge accumulation induced by electrostatic force on carbon-based electrode materials is generally accepted as the storage mechanism of electric double layer capacitors (EDLC). Such carbon materials vary in morphology, porosity and size distribution. Commonly employed carbon-based electrode materials include carbon sphere, activated carbon, carbon nanotube (CNT) and reduced graphene.

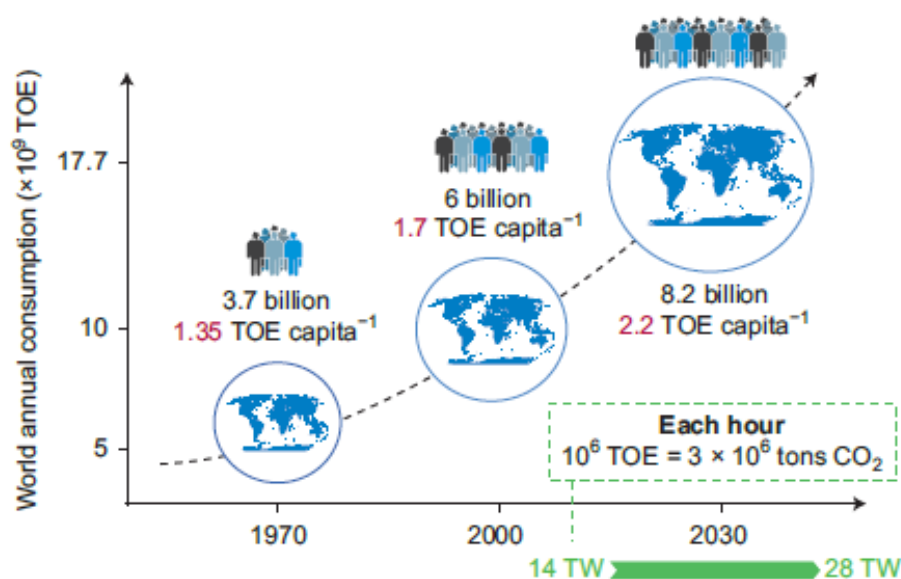
The pseudocapacitors, on the other hand, rely on the fast and reversible faradaic redox reaction between electroactive polymers or metal oxides and electrolyte ions. Conducting polymers and transition metal

oxides and hydroxides are being explored as successful electroactive materials in pseudocapacitors. They possess higher capacitance and superior energy density but are inferior in terms of power density than carbon-based electric double layer capacitors [5]. Quite a lot of research publications focused on composite electrode materials consisting of the superior and excellent specific surface area (SSA) of carbon-based material and conductive polymers. Such composite electrodes maximize the synergy of rapid rates of charge and discharge of carbon-based materials and fast redox reaction of electroactive materials (conductive polymers) to deliver superior and advance energy storage devices.

## 2. Advanced polymer materials for li ion battery

Lithium ion batteries cover a wide range of applications including portable electronics, electric vehicles and stationary grid, requiring power as low as 10 watt hours and up to megawatt hours.

The cost associated with producing energy storage and conversion devices is driven by the relative abundance of materials, fabrication processes, and large energy cost of battery manufacturing and recycling. The world's energy needs up to 2050 is clearly depicted on Fig.1.



**Fig. 1** Past, present and forecast of the world's energy needs up to 2050. With the changing lifestyles of an increasing number of inhabitants, our energy rate demand will double from 14 TW (2010) to 28 TW (2050). TOE = ton of oil equivalent. Map: © Macmillan Mexico/Haide Ortiz Ortiz, Mario Enrique Ramírez Ruiz [6].

The choice of electrolyte in battery technology will determine many aspects of material design, device operation and stability. The operational voltage range is fundamentally limited by the stability of the electrolyte, which inevitably will break down at a given potential. This limitation affects

the device energy density, which is proportional to the square of the cell voltage. For example, changing electrolyte system from aqueous to organic electrolyte in EDLC device results in an increase in maximum potential from 1.0 V to 2.5-2.7 V. Factors that must be considered for selection of

electrolyte include conductivity, electrochemical and thermal stability, and of course toxicity [7]. The maximum stable potential window with an aqueous electrolyte is 1.5 V. For batteries that go beyond powering hand-held devices new strategies are needed for identifying electrolytes with larger potential windows while retaining the good conductivity of  $\text{Li}^+$  ( $> 10^{-3} \text{ Scm}^{-1}$ ) and designing higher capacity anodes that are safe and capable of being charged at fast rates.

Combination of this strategy with alternative cathode host design involving electrode morphology that reduce the size of the active particles and replacing the cathode hosts by materials that undergo displacement reactions with higher capacity such as Sulfur are essential to take us to a portable rechargeable battery that can displace the internal combustion engine by powering electric vehicles, cargo ships and locomotives.

Composite systems of carbon and metal oxides or conducting polymer are to be exploited to deliver advanced polymer-based battery material for superior energy storage. Porous Si-C composite particles using a polymeric binder is an attractive alternative for industrial applications due to its higher electrical conductivity and higher capacity of Silicon. The annealing of carbon black at temperature above  $\sim 2000 \text{ }^\circ\text{C}$  results in graphitization of carbon with higher conductivity. The larger particles can then be transformed into spherical granules through granulation or balling using liquid binder by means of propylene ( $\text{C}_3\text{H}_6$ ) decomposition at  $\sim 700 \text{ }^\circ\text{C}$ .

This ensure formation of permanent bonds on drying and sintering through surface

adsorption of larger-molecular weights hydrocarbon products of intermediate steps of  $\text{C}_3\text{H}_6$  decomposition. It includes styrene, toluene, ethylbenzene, naphthalene and biphenyl products which aided the hierarchical bottom-up assembly to form a rigid spheres with open interconnected internal channels for a stable and reversible capacity over five times higher than that of the state-of-the-art anode ( $1,950 \text{ mAhg}^{-1}$ ) [8].

Fig. 2 shows a schematic diagram for the hierarchical bottom-up assembly of Si-C nanocomposites. The working electrodes were prepared from active material, C-Si composite granules, polyvinylidene fluoride binder for carbon electrode and 10 wt% polyacrylic acid for Si-containing electrode. The commercial electrolyte was composed of 1M  $\text{LiPF}_6$  salt in an ethylene carbonate/diethyl carbonate/dimethyl carbonate/vinylene carbonate mixture. Lithium metal foil of 1 mm thick was used as counter electrode.

Electrochemical performance of device showed specific reversible capacity of  $1,950 \text{ mAhg}^{-1}$  at C/20. This excellent gravimetric capacity is as a result of the theoretical capacity of Si ( $4,200 \text{ mAhg}^{-1}$ ). The specific capacity of Si nanoparticle alone was estimated at  $3,670 \text{ mAhg}^{-1}$ . The volumetric capacity was determined to be  $1,270 \text{ mAhcm}^{-3}$  at C/20 while its gravimetric capacity is nearly 18 times higher than that of the annealed carbon black.

There is 15 % irreversible capacity losses in the first cycle as shown in Fig. 3a. This is related to the solid-electrolyte interphase (SEI) formation. This device offers exceptional potential in energy storage applications. It provides new avenues for

electrode materials with enhanced conductivity, power, gravimetric and volumetric capacity for critical applications such as low emission hybrid electrical vehicles, energy-efficient cargo ships, aerospace and power-grid applications [8].

In a related development for large-scale advance stationary energy storage, sodium-sulfur battery (zebra cell) with high electrochemical performance has been commercialized in Japan and developed in the US by GE Corporation. Sodium has larger theoretical capacity than lithium making it more attractive than Lithium [9].

An affordable, safe, and scalable battery system, which uses organic polymers as the charge-storage material in combination with inexpensive dialysis membrane that separates the anode from cathode by retention of non-metallic, active (macro-molecular) species, and an aqueous sodium chloride solution as the electrolyte has been fabricated [10].

The scalable polymer battery consists of two components: a redox-active moiety and a unit enhancing water solubility to prevent precipitation in all used redox states. The cathode material contains TEMPO radical as the redox-active moiety, while the anode material uses a 4,4,9-bipyridine derivative (viologen). The water-solubility of both polymers is enhanced by a quaternary ammonium cation moiety. The cathode material was prepared by free radical copolymerization of 2,2,6,6-tetramethylpiperidin-4-yl-methacrylate and amine. Fig. 4 shows the scheme of this large scale, environmentally friendly polymer-

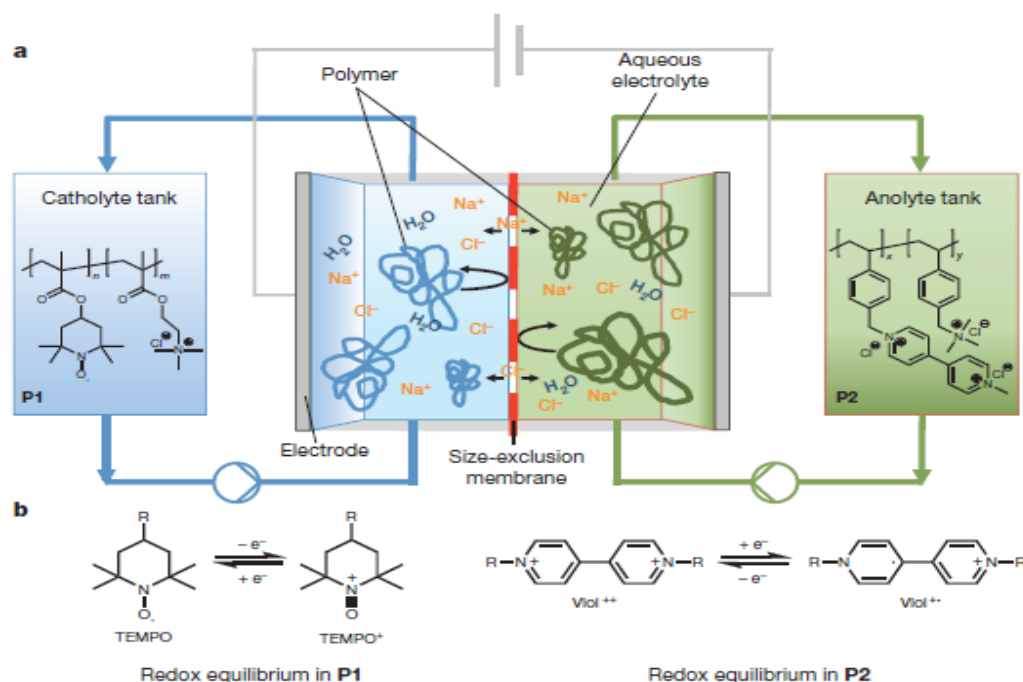
based redox battery for stationary energy storage.

In addition to TEMPO and viologen redox-active units, a large number of potential conducting polymer with redox-active moieties might help to further boost cell voltage and cycling stability of future polymer-based RFBs. This new framework typifies a new battery principle, which could lead to the production of economically energy-storage devices that are safe, metal-free, and efficient materials [10].

### **3. Carbon-based energy storage materials.**

Electrical double layer capacitors (EDLC) also known as supercapacitors with high power density and excellent cycling stability are the crucial alternatives in energy storage devices with the potential to meet increasing energy demands and environmental concerns. Porous carbon materials such as activated carbon, carbide-derived carbon, ordered mesoporous carbons, carbon aerogels, and carbon nanotubes remain the most common and important electrode candidates for EDLC [11].

The first patent describing the concept of an electrochemical capacitor was filed in 1957 by Becker [12]. who used carbon with a high specific surface area (SSA) coated on a metallic current collector in a sulfuric acid solution. In 1971, NEC (Japan) developed aqueous-electrolyte capacitors under the energy company SOHIO for power saving units in electronics, and this application can be considered as the starting point for electrochemical double layer capacitors (EDLC) in commercial devices [13].



**Fig. 2** Working principle of a polymer-based RFB, **a**. Schematic representation of a polymer-based RFB consisting of an electrochemical cell (which determines the power density) and two electrolyte reservoirs (which determine the storage capacity). The anolyte and catholyte cycle are separated by a semipermeable size-exclusion membrane, which retains the redox-active macromolecules while allowing small salt ions to pass. During the charging/discharging process, a solution of the redox-active polymers P1 and P2 is continuously transported from the electrolyte reservoirs to the electrochemical cell, where the redox reactions take place. **b**. Fundamental electrode reactions of P1 (TEMPO radical) and P2 (viologen)<sup>[10]</sup>.

Other applications in mobile electronics, electric vehicles, trams, trains and aerospace systems bolstered further research in supercapacitors.

The mechanism of EDCL that store charge electrostatically using reversible adsorption of electrolytes ions onto active materials that are electrochemically stable can be viewed from the perspective of charge separation which occurs on polarization at the electrode–electrolyte interface, producing what Helmholtz described in 1853 as the double layer capacitance  $C$ :

$$C = (\epsilon_r \epsilon_0 A) / d \quad (1)$$

where  $\epsilon_r$  is the electrolyte dielectric constant,  $\epsilon_0$  is the dielectric constant of vacuum,  $d$  is the effective thickness of the double layer (charge separation distance) and  $A$  is the electrode surface area. Also capacitance can be viewed practically from the perspective of

stored energy,  $E$ , in accordance with the following energy equation;

$$E = (1/2) CV^2 \quad (2)$$

In this regard  $C$  is the cell capacitance, and  $V$  is the operating voltage.

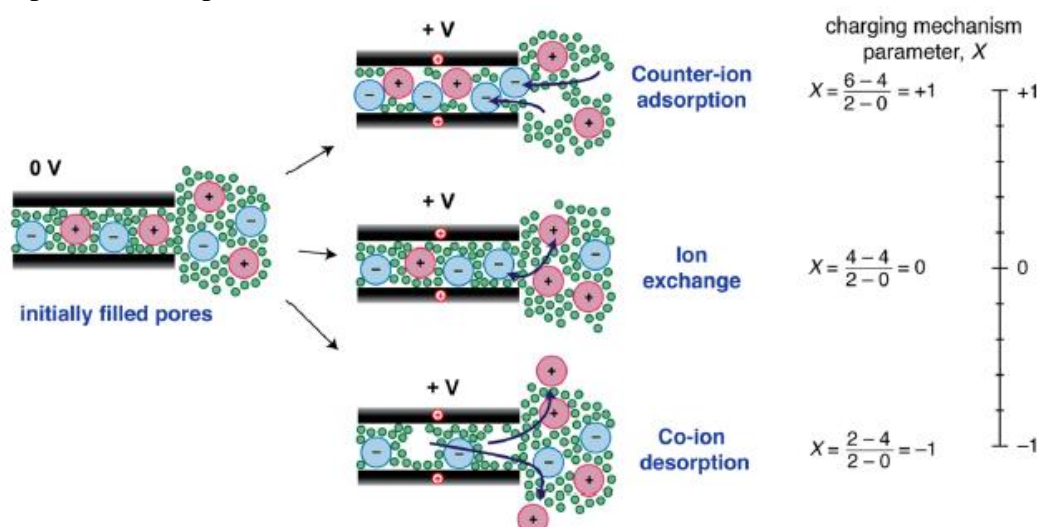
In addition to the traditional view of charging mechanism (adsorption of counter-ions) of carbon materials, other mechanisms have been suggested by Force and coworkers that include simultaneous co-ions desorption from the carbon pores as the counter-ions are adsorbed. Another mechanism proposed by Force and his team is that charging is driven purely by desorption of co-ions [13].

Charging may involve a combination of the different mechanisms. Understanding the charging mechanisms helps to tailor the energy storage device by choice of the correct electrolyte–electrode combination. More importantly, the charging mechanism

will affect the capacitance and similarly the energy density in accordance with our energy equation above. The mechanism also, have significant impact on the power that supercapacitors can offer, and optimizing the mechanism may improve the power performance of such energy storage device [13]. The different charging mechanism of supercapacitors are depicted in figure 3 below.

As already noted, one or a combination of these mechanisms may operate in any supercapacitor. The specific mechanism(s) in

any device is driven by thermodynamics and kinetics conditions. The charging mechanism which operates under thermodynamic conditions is one that minimizes the increase in free energy ( $\Delta G$ ) associated with charging. This, in turn will minimize the voltage increase per unit charge [13]. Counter-ion adsorption is disfavored here due to decrease in entropy for ions entering a pore and also unfavorable enthalpic terms associated with the packing of ions of the same charge inside the carbon pores [14].



**Fig.3** Different possible charging mechanisms for carbon pores that are initially filled with electrolyte: counter-ion adsorption, ion exchange, and co-ion desorption. The different charging mechanisms may be described by the charging mechanism parameter,  $X$ , which can assume the value of  $-1$  for co-ion desorption,  $0$  for ion exchange and  $+1$  for counter-ion adsorption [13].

Ion-exchange mechanism is favored thermodynamically by reduction in enthalpic penalty of ions packing and corresponding reduction in entropic penalty. In the same vein, charging by co-ion desorption increases entropy and minimize enthalpic penalty. Kinetically, the charging mechanism depends on the relative rates of in-pore motion of the anions and cations. Controlling the diffusion rates of the different in-pore ions will control the kinetics charging

mechanism and thus improve capacitance. [13].

The electrochemical performances of supercapacitors are scalable and mainly controlled by the structural properties of electrodes materials. Carbon Nanotube (CNT) have shown anisotropic microstructure, porous networks, high electric conductivity and large mechanical strength, which make them prime candidates as supercapacitor electrodes [12]. Specific capacitance of  $35 \text{ F g}^{-1}$  was obtained from

large-scale free-standing single-walled carbon nanotubes (SWCNT) film with high electric conductivity. Energy density of  $43.7 \text{ Wh kg}^{-1}$  was obtained. The capacitive performance was improved by incorporating a conducting polymers such as poly aniline (PANI). Among various conducting polymers, polyaniline (PANI) is considered to be one of the most promising active materials because of its relatively large specific pseudocapacitance, high conductivity and low cost of aniline monomers. The composite PANI- CNT showed improved electrochemical performance. A large specific capacitance of  $233 \text{ F g}^{-1}$  was achieved and high energy density of  $131 \text{ Wh kg}^{-1}$  [12].

Nanostructured carbon with large surface area are employed to maximize electrode performance. These materials are highly porous and its electrochemical performance improved upon incorporating functional groups including oxidative groups such as carboxylate, ketone, or hydroxyl groups. The surface modifications increase capacitance, accessibility to the electrolyte, and

electrochemical activities. Introducing heteroatoms such as Nitrogen into the carbon lattice was also reported to enhance the pseudocapacitance, rate performance, and cycling stability of supercapacitors owing to the increased surface wettability, electrical conductivity, and electron-donor tendency of carbon materials [12].

Carbon nanofibers (NFs) from a polymer precursor prepared by electrospinning are distinct from the others in that they have various different fiber morphologies (e.g., hollow, porous surface fiber and ribbon) aligned randomly. Electrospinning is advantageous in making polymer NFs with controlled fiber diameter, fiber alignment, and shape of the fibrous mat. It does not involve a tedious separation and dispersion process and use of harsh chemicals or catalysts. [15].

In one study [16] an effective method to prepare carbon nanofibers (N-CNFs)/polymer composite film grown on a silicon using a multistep method was developed. The synthetic method is shown on Fig.4.

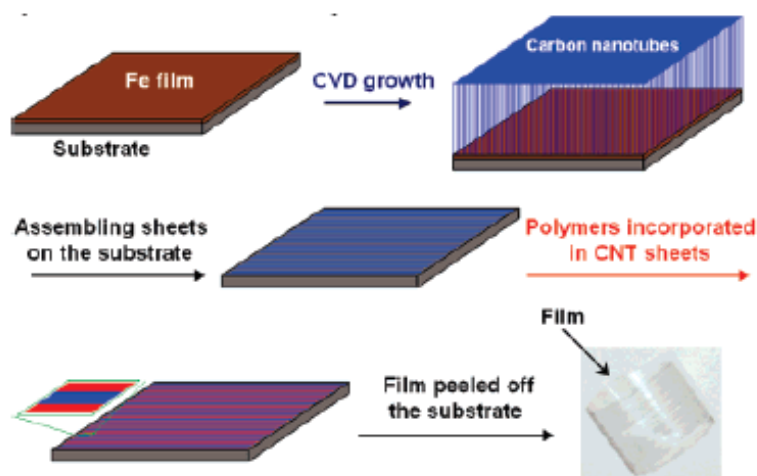


Fig. 4 Synthesis of aligned CNT/ Polymer composite film [16].

Chemical vapor deposition (CVD) process was used to grow the CNT onto silicon to

obtain uniform sheet of CNT which were then pulled and stabilized on glass. Spin-



coating the polymer solution onto CNT sheets produced the composite CNT-Polymer film. This was followed by evaporation of solvent. Control of film thickness can be achieved by varying the concentration of polymer solutions and coating times. Transparent and flexible films were made and readily peeled off the substrate. The CNT-Polymer composite films show high optical transparency, robust flexibility, and excellent conductivity [16].

#### **4. Polymer-based energy storage device.**

The EDLCs (based on carbon) store charge electrostatically, similar to a traditional electrolytic capacitor, in a double Helmholtz layer at the interface between its electrodes and electrolyte. Conducting polymers (pseudocapacitors), on the other hand, is a type of electrochemical capacitor where energy is stored in a Faradaic redox system as in batteries. The archetypical EDLC electrode material is activated carbon, which has high power performance but a limited energy density. Pseudocapacitors, store charge through redox reaction, but do so superficially, leading to a high energy density relative to EDLCs while allowing for better power performance and lifetime cycling relative to batteries. Pseudocapacitors based on conducting polymers offer low cost, high specific energy and power, high conductivity, lightweight and enhanced flexibility over other pseudocapacitive materials [15]. Pseudocapacitors (or electrochemical capacitors) bridge the performance gap between electrolytic capacitors and rechargeable batteries. Electrolytic capacitors, often modeled as the parallel plate capacitor, store energy as a polarized electric field between two

electrodes separated by a dielectric material. Electrolytic capacitors have superior cycling times and cycle efficiency, though they are limited by their low energy density [16].

Electrochemical capacitors have a lower energy density relative to batteries, but a power density more comparable to capacitors, making them useful in applications where a large amount of charge needs to be rapidly distributed. The device configuration of an electrochemical capacitor is shown in figure 5; composed of nanostructured conducting polymer-carbon electrodes. Some conducting polymers emerged to the forefront of pseudocapacitor device development which include polyaniline(PANI), polypyrrole (PPy), polythiophene (PT), and poly(3,4-ethylenedioxythiophene) (PEDOT). Common characteristics of these conducting polymers include their delocalized  $\pi$ -electron system, accessible redox states and controllable physical properties which make these conjugated polymers ideal candidates for advance energy storage materials and device fabrications.

Conductivity of conjugated polymer is significantly improved by doping. The crystal structures of doped and un-doped PEDOT illustrate the interrelation between chain alignment and charge mobility. Crystalline un-doped PEDOT is monoclinic with polymer chains extending along the b axis and  $\pi$ - $\pi$  stacking parallel to the c axis, whereas doped PEDOT crystallizes in the orthorhombic system and forms lamellar structures [16]. Several dopant ions including triflate tosylate, PF6-1, ClO4-1 and PSS have shown these characteristics. Doping also promotes quinoid-like structures in doped PEDOT chains that prefer more rigid, planar

chain orientation. Undoped PEDOT is characterized by folded chains that act as shorts stifling charge carrier mobility, and sterically prevent  $\pi$ - $\pi$  stacking within and between chains [16] and results in poor conductivity.

Despite the high capacitance of pseudocapacitors, they lack power due to faradaic processes that make ion transport sluggish compared to electrostatic adsorption in EDLCs [18, 19]. High conductivity of a pseudocapacitive material is crucial for improving charge transfer kinetics at the electrode [20]. Improving electrochemical performance of conducting polymer with respect to conductivity and capacitance, it must possess charge carriers, charge mobility, facile kinetics, and readily available solvated counterions. Electron insertion into the conduction band via n-doping (reduction), and/or removing an electron from the valence band via p-doping (oxidation) increase charge carrier concentration [21].

When a polymer is doped or undergoes ionization, the equilibrium geometry of the ionized state is lower than that of the ground state [22]. This results in lattice deformation which in turn causes the HOMO energy to shift up and the LUMO energy to shift down, creating new energy bands in the band gap that are delocalized over the polymer chain and result in a charge "island" [22]. The more a polymer chain is ionized ("doped"), the more these islands overlap and delocalized over the entire material giving rise to conducting polymer's ability to conduct electricity [23]. Doping adds new energy levels to the band gap and thus, increase electronic conductivity. Doping level in conducting polymer vary from one polymer

to the other. In general, it is usually less than one dopant per one polymer chain and are dictated by how closely the charge island can be spaced along the polymer chain. Strong electron affinity of a dopant is necessary to achieve high doping level [24].

Another important factor in enhancing the conductivity of conducting polymer is carrier mobility ( $\mu$ ); poor charge carrier mobility leads to insulating behavior that stifles charging and discharging cycles, thereby nullifying the capacitance of an electrochemical cell. Charges must travel along (intra-chain mobility) and between (inter-chain mobility) polymer chains. Facile intra-chain mobility is promoted by the conjugated  $sp^2$  carbon system that creates a resonance stabilized and delocalized  $\pi$  system along the polymer backbone by which the charge carriers freely move along the chain [26-28]. Conjugation also facilitates inter-chain charge mobility by encouraging  $\pi$ - $\pi^*$  stacking between chains in the bulk material [29-31]. Fast redox reaction is key during charging and discharging a pseudocapacitor. Counterions must be able to intercalate and deintercalate along the polymer chain in order to perform fast redox reactions and counterbalance the charge generated on the polymer electrode [32]. High conductivity in a conducting polymer and low internal cell resistance are paramount to fast kinetics. A polymer such as PPy is characterized by a high energy density (400–500 F  $cm^{-3}$ ) and tightly packed polymer chains in the solid-state [33]. Too high of a packing density adversely limits electrolyte accessibility and reduces capacitance [34]. Chain length has a tremendous impact on mobility; the longer the polymer chains, the greater the degree of

$\pi$ -delocalization in the system and opportunities for  $\pi$ - $\pi^*$  stacking [30]. Controlling chain length also minimizes hopping [35,36].

In general, increasing the degree of crystallinity and chain alignment, and producing a defect free, homogeneous long chain polymer results in superior pseudocapacitance [37]. Control of pore structure is a suitable technique for inducing high surface area and inducing facile kinetics

[38]. One synthetic strategy introduces thermally decomposing compounds such as benzoyl peroxide, azoisobutyronitrile, and ammonium bicarbonate into the conducting polymer as porogens. Controlled heating determines the rate of decomposition and the pore structure. Porous PANI is more capacitive than solid PANI, which exhibits a more rectangular shaped cyclic voltammogram and lower internal resistance [39].



**Fig.5** Electrochemical capacitors. **a** Schematic of a commercial spirally wound double layer capacitor. **b**, Assembled device weighing 500 g and rated for 2,600 F (Photo courtesy of Batscap, Groupe Bolloré, France.) **c**, a small button cell, which is just 1.6 mm in height and stores 5 F. (Photo courtesy of Y-Carbon, US.) Both devices operate at 2.7 V [17].

The ability of a conducting polymer pseudocapacitor to undergo hundreds of thousands of charge/discharge cycles with neither chemical nor physical degradation is

highly desirable for lifetime cyclic stability. There are several causes for low cycling stability in conducting polymer pseudocapacitors. The adherence of a

polymer to a current collector has been shown to greatly affect cycling stability. For example, depositing polypyrrole on a functionalized exfoliated graphite surface increases adherence and leads to 97% capacitance retention after 10 000 cycles at 6 A/g [40]. Poor cyclability and large leakage current are major obstacles for industry [41]. Degradation in device performance after extensive number of charge/discharge cycles is indicative of possible structural deterioration at the molecular scale (polymer composition, conformation, and chain alignment) or at the nanoscale (hierarchical architecture and morphology) [42].

Extended cyclability can also be imparted by depositing a thin carbonaceous shell onto the conducting polymer electrode; this physical buffer suppresses structural deformation during cycling and leads to 95% capacitance retention for PANI and 85% for PPy electrodes after 10 000 cycles [43]. Many studies report high gravimetric capacitance utilizing conducting polymer modified coral-like monolithic carbon and chelating dopants (451 F/g for PPy) [44].

Finally, it is important to also consider the role of ionic liquid as we strive to deliver advanced polymer energy storage device. Ionic liquid are low temperature molten salts, that is, liquids composed of ions only. The archetype of ionic liquids is formed by the combination of a 1-ethyl-3-methylimidazolium(EMI) cation and an N,N-bis(trifluoromethane)sulphonamide (TFSI) anion. The structures are shown below. This combination gives a fluid with an ion conductivity comparable to many organic electrolyte solutions and an absence of decomposition or significant vapour pressure up to ~300–400 °C [45].

The unique properties of ionic liquids may help to solve the safety problem of organic electrolytes as they are practically non-flammable, that is, a significant safety asset. The replacement of the conventional, flammable and volatile, organic solutions with ionic-liquid as the conducting electrolyte system may greatly reduce thermal runaway and lead to a superior conducting polymer-based pseudocapacitors. See Fig.8 for electrolyte solution.

## 5. Summary

As we aim to design advanced energy storage devices, it is important that we address significant challenges posed by the structural complexity of porous carbon electrodes, sluggish charging and discharging times of pseudocapacitive polymeric materials and safety of organic liquid electrolytes. In this perspective, we have reviewed that ideal electrode structure would be achieved by controlled modification of pore sizes. Composite carbon-polymer electrodes may serve as model systems to probe structure-property relationships.

Improving the power performance of energy storage devices requires systematic tailoring of device charging mechanism in the choice of electrode–electrolyte combination. The device charging mechanism have a significant effect on the power that storage device can offer. Different performances are expected from energy storage devices depending on whether ion adsorption, ion exchange and ion desorption mechanisms are in operation. Further work is needed to establish the optimal mechanism for high power application.

Implementation of advanced energy storage system in electric vehicle and other high-

power applications has been slowed by safety concerns surrounding the use of organic electrolytes. Unpredictable events such as short circuits or local overheating has led to an exothermic reaction of the electrolyte with electrode materials. Ionic-liquid-based electrolyte may help to solve the problem. This provides supercapacitors and lithium battery with level of safety that is required for large scale operation. The thermodynamic and kinetic stabilities of these wide array of ionic liquids with respect to the electrode materials should be the focus of further research.

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