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Carbon Nanotube-Polymer Composites for Energy Storage Applications

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Abstract

Renewable energy has attracted growing attention due to energy crisis and environmental concern. The renewable power is featured by its intermittent and fluctuating nature, which requires large-scale electrical energy storage devices for dispatch and integration. Among the current energy storage technologies (e.g., pumped hydro, fly-wheel, compressed air, superconducting magnet, electrochemical systems), electrochemical storage technologies or batteries that reversely convert electrical energy into chemical energy demonstrate extremely great potential in the stationary and transportation applications. Scale determines the device type. Redox flow batteries (RFBs), as one of the large-scale types, are capable of complying with power station. Meanwhile, portable smart electronic devices promote the development of small-scale energy storage systems, such as Li-ion batteries and supercapacitors. With delicate device configuration, materials play critical roles on pursuing advancing performance, in terms of electrode, current collector, and separator. Carbon nanotube (CNT)/polymer composites exhibit promising potentials in the above key entities, which integrate the merits of conductivity, mechanical strength, flexibility, and cost. Therefore, this chapter is devoted to the design and application of carbon nanotube/polymer composites in different kinds of energy storage systems.

Keywords: carbon nanotube, carbon nanotube/polymer composite, energy storage, lithium battery, supercapacitor, flow battery

1. Introduction

Electricity generation from renewable sources, such as solar and wind, has been increasing in the context of growing environmental concerns and constraints of the fossil fuels and hydro-

carbon reserves [1, 2]. The renewable power is featured by the intermittent and fluctuating nature, which requires large-scale electrical energy storage devices to dispatch and integrate the renewable power. Among the current storage technologies (e.g., pumped hydro, fly-wheel, compressed air, superconducting magnet, electrochemical systems), electrochemical storage technologies or batteries that reversely convert electrical energy into chemical energy demonstrate extremely great potential in the stationary and transportation applications. Among the electrochemical storage technologies, redox flow battery is one of the promising technologies for large-scale energy storage application. Meanwhile, portable smart electronic devices promote the development of small-scale energy storage systems, such as Li-ion batteries and supercapacitors. Key elements, such as membranes and electrodes, are crucial for their application in different batteries. Polymer/carbon nanotubes (CNTs)-composited materials have been successfully used in above-mentioned energy storage batteries. In the following sections, we introduce the application of polymer/CNT for different electrochemical storages.

2. Carbon nanotube/polymer-composited membrane for redox flow batteries

2.1. Redox flow battery

Redox flow batteries (RFBs) have widely received attention for both medium- and large-scale storage needs in the past decades. As schematically shown in **Figure 1**, a typical RFB system consists of two external reservoirs that store soluble charged/discharged electrolytes, two electrodes, and a membrane that effectively separates the anode and cathode electrolytes, while allowing the transport of non-active ions (e.g., H^+ , Cl^-) to complete the reaction and a flow circulation system. In RFB, the chemical energy is converted to electrical energy (discharge) or vice versa (charge) when liquid electrolytes are pumped from storage tanks to flow through electrodes [3, 4].

Unlike conventional batteries that store energy in electrode materials, RFB systems store energy in anolyte and catholyte solutions. As such, the most prominent advantage of RFB system is that the power and energy capacity of one RFB system can be designed separately. The power rating of the system is determined by the number of cells in the cell stack and the area of electrode, whereas the energy storage capacity is controlled by the concentration of the active redox couple species in electrolytes and the solution volume. As a result, it is possible to independently optimize the RFB's storage capacity and the power output for different applications. Both energy and power capacity of RFB can be easily increased by simply adding the volume of electrolytes and the numbers of cells in the stack, respectively. Consequently, the incremental cost of each additional energy storage capacity unit is lower than other types of battery technologies. In addition, the process of manufacturing a modular production of RFB stacks can be simplified by omitting the cell-making process, and thus, the cost would be reduced compared with solid-state batteries (e.g., Li-ion and NiMH). Furthermore, unlike practical solid-state battery, the simple design of RFB system can minimize the energy density loss resulted from negative impact of inactive materials because the volume of energy-bearing reactive electrolyte can be independently scaled up [5–7].

With the unique mechanism of the RFB system, there are some additional advantages of RFB systems over other battery systems: quick response, long cycle life, no high operational temperature, deep-discharge capacity, simple electrode reactions, low maintenance cost, safety.

2.2. History of RFB

The modern RFB system (iron-chromium RFB) was proposed in the 1970s by Lawrence Thaller at the National Aeronautics and Space Administration (NASA). Since then a number of other redox flow batteries have been invented and developed. Based on different redox couples used, these RFBs can be divided into the following: polysulfide/bromine flow battery (PSB), all vanadium redox flow battery (VRB), vanadium-bromine flow battery (VBB), vanadium-cerium flow battery (VCB), vanadium/iron redox flow battery (VIB), vanadium/air flow battery, zinc/bromine flow battery (ZBB), zinc-cerium flow battery (ZCB), iron/chromium flow battery (ICB), iron-titanium redox flow battery (ITB), soluble lead-acid battery, etc. Among these various RFBs, ZBB, ICB, VRB, and PSB have been demonstrated at a few hundred kW and even multi-MW levels for different applications [8]. Until now among these flow batteries, VRB is the most widely studied and successfully demonstrated one due to its low crossover of vanadium ions and good performances, which will be discussed in details.

2.3. Vanadium redox flow battery

The vanadium redox flow battery (VRB) proposed by Skyllas-Kazacos et al. shows great promise as a new, highly efficient, and reliable energy storage system for a wide range of applications such as solar cell and wind turbine generators, remote area power systems, emergency back-up applications, and uninterruptible power sources (UPS) [9]. The VRB employs V(II)/V(III) and V(IV)/V(V) redox couples in its anolyte and catholyte, respectively, and H₂SO₄ as the supporting electrolyte [10]. The ion-exchange membrane responsible for separation and proton transportation is crucial for a VRB. And the carbon felt usually used as the electrodes provides the electrochemically active surface for the redox reaction to take place. The electron exchange occurs at the electrodes in the aqueous phase according to the following reactions:

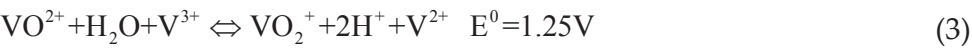
Cathodic side:



Anodic side:



Overall reaction:



Since invention, the VRB has received extensive attention around the world, especially in Japan, Europe, the USA, and China. Though many systems have been installed in a variety of fields, the practical application of the VRB is still hindered by the high cost and low energy density. Accordingly, developing a chemically stable, low-cost, and high-quality membrane is one of the promising ways to overcome these two challenges of VRB.

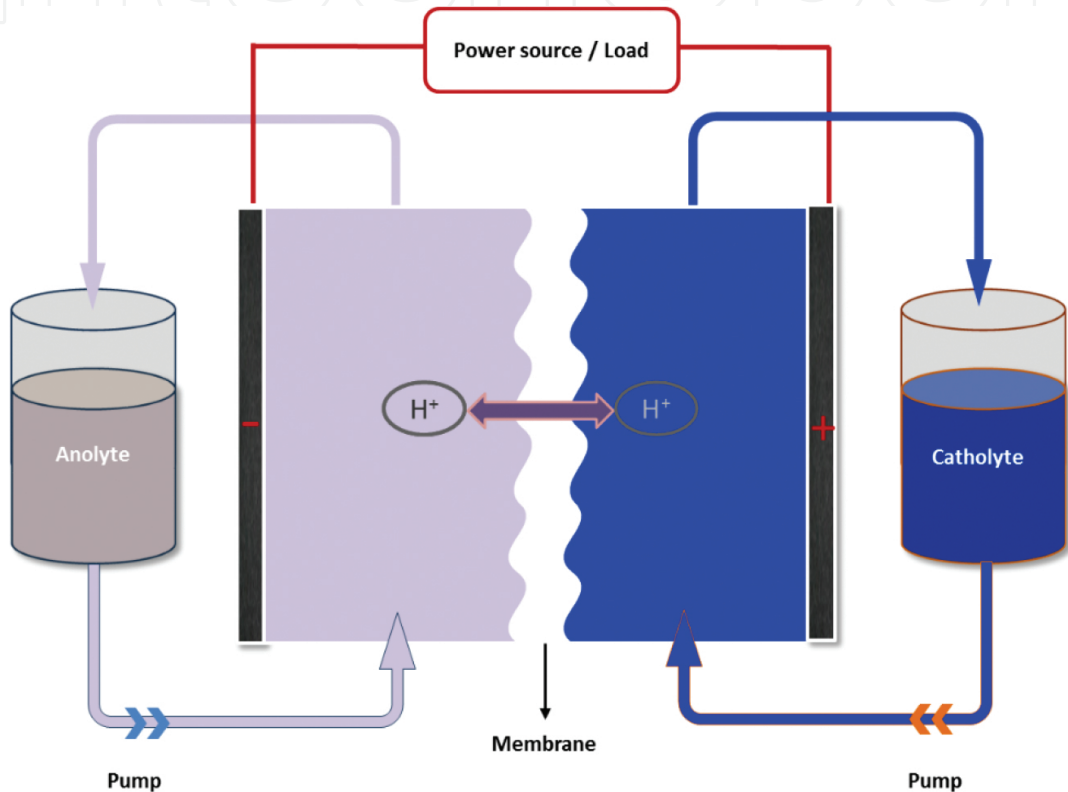


Figure 1. Schematic of vanadium redox flow battery.

2.4. Membranes for VRB application

In VRB, an ion-exchange membrane plays a critical role on separating the anode and cathode electrolytes effectively, namely, no migration or a very low permeability of vanadium ions, while allowing the transport of ions to complete the circuit during passage of current. An ideal membrane should possess high proton conductivity, good chemical stability, high tensile strength, low permeability for vanadium ions, and low cost [11]. Among ion exchange membranes, perfluorosulfonic acid (PFSA) membranes, such as Nafion (DuPont), are most commonly used due to their high chemical stabilities and proton conductivities. However, PFSA membranes usually suffer from high cost and especially high permeability of vanadium ions. To reduce the migration of V ions, many approaches such as doping of inorganic materials, surface modification, and layering have been employed to modify the Nafion

membranes. Although some important progress proceeds with lower vanadium species in modified Nafion than the pristine one, the cost is still far from afforded that limits the commercialization [12, 13]. It is therefore of equivalent significance to reduce the cost. Recently, non-perfluorinated polymers such as sulfonated poly(ether ether ketone) (SPEEK) and sulfonated poly(ether sulfone) (SPES) have been received wide attention for VRB application due to their low vanadium ion permeability and low cost [14]. The ion selectivity and mechanical strength are highly dependent on the degree of sulfonation (DS). SPEEK membranes with high DS possess high ion selectivity and low areal resistance, but poor mechanical property, high vanadium ions permeability, and stability. On the other hand, SPEEK membranes with low DS exhibit good mechanical strength and stability but poor ion selectivity and high areal resistance [15]. Consequently, it is important to reduce the vanadium ions crossover and increase the mechanical strength of SPEEK membranes, while keeping their high ion selectivity for VRB. One effective approach to address this issue is to embed inorganic nanoparticles/carbon nanostructures into the SPEEK matrix such as, WO_3 , graphene, rGO, and GO [16–18], which can significantly increase the mechanical strength and stability of the composite membranes with high DS SPEEK matrix.

CNT is well known as its good conductivity, high surface area, well-directed 1D conductive path, low cost, and good mechanical stability. Integrating their merits, CNT/polymer nanocomposites become promising candidates in membranes for VRB application. General strategies include co-casting and post-synthesis. Casting of CNT/polymer may require further surface modification on CNT to possess desirable functional groups/charge. Polymeric materials can also be synthesized on CNT architectures/frameworks by CVD or vacuum filtration through chemical/electrochemical polymerization.

CNT/polymer-composited membranes, such as CNT/Nafion and CNT/SPEEK, have been successfully used in fuel cell and shown not only good physical properties (e.g., mechanical strength, chemical stability, and ion selectively) but also good cell performances [19]. However, there are no reports about CNT/polymer membrane for VRB before 2015. In order to combine the good properties of CNT and SPEEK matrix and eliminate their individual disadvantages, Jia et al. firstly reported a novel SPEEK/short-carboxylic multiwalled CNT membrane for VRB application [20]. They introduced only 0.7 wt% CNT into SPEEK matrix using solution casting method. With the combination of functionalized CNTs with excellent electrocatalytic activity and the low cost of SPEEK membrane, this novel nanotube-polymer-composited membrane consequently exhibits good chemical strength, high ion selectively, and low vanadium permeability. Detailed study showed that the short-carboxylic multiwalled CNTs are well dispersed in the traditional SPEEK membrane due to the good interaction between short-carboxylic multiwalled CNTs and SPEEK matrix. In addition, the well dispersion of carbon nanotubes and good π - π interactions, electrostatic interactions, and van der Waals interactions between the aromatic groups of SPEEK polymer and the sidewall of CNTs increased the mechanical strength significantly (61.8 MPa) compared to a pure SPEEK membrane (39 MPa). Moreover, as shown in **Figure 2**, the carbon nanotubes used as an inner filler can dead or decrease the size of ion transport pathway significantly and thus restrain the vanadium permeability. Furthermore, the hydrophilic cluster formed by different $-\text{COOH}$, $-\text{OH}$ groups

on the side wall of CNTs will not only further decrease the ion transport pathway but also provide enriched proton transport pathways. Therefore, the permeability of vanadium ions through this composited membrane ($3.22 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$) is lower than that through the pure SPEEK ($4.03 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$) membrane and Nafion 212 membrane ($8.23 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$), which leads to a low self-discharge of the VRB cell and thus high Columbic efficiency. On the other hand, the inner proton transport pathway formed by various functional groups on the CNTs could enhance the proton selectivity and ion conductivity and thus enhance the voltage efficiency and energy efficiency of the VRB cell.

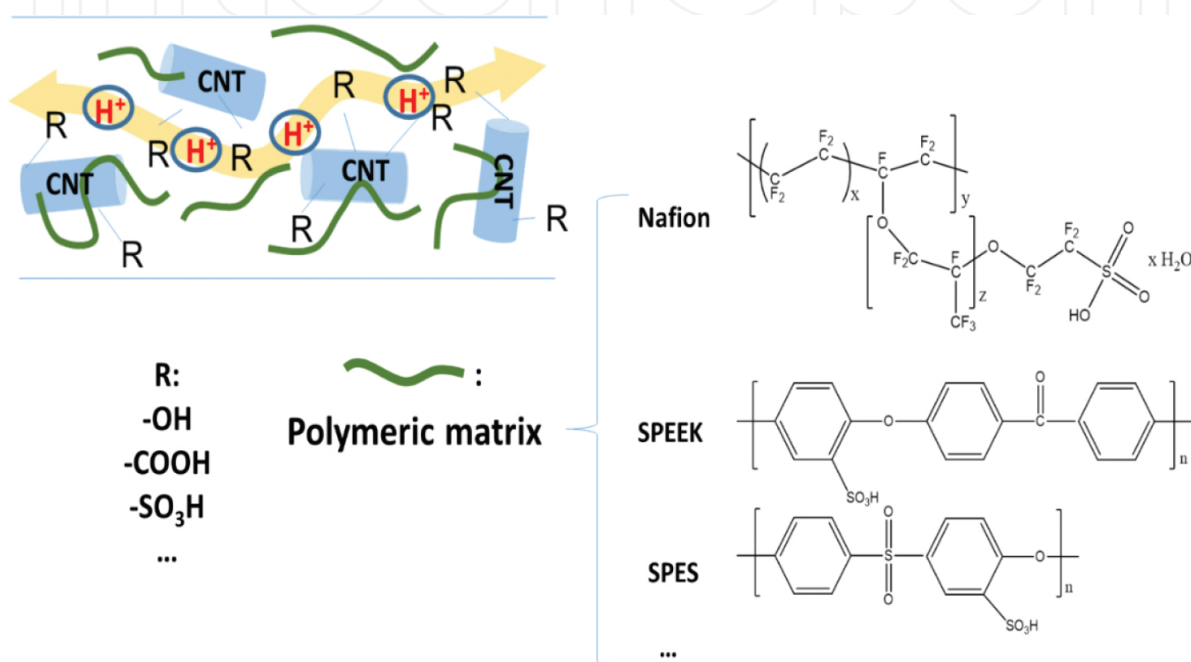


Figure 2. Mechanism of proton transport in polymer/CNT-composited membranes.

Although the cell performance of the VRB cell with SPEEK/CNT is better than those only with Nafion membranes or SPEEK membrane individually, the chemical properties of the SPEEK membrane should be further optimized. The chemical stability of the composited membranes could be optimized using stable matrixes such as Nafion, SPES, PBI, and SPEEK with low DS. In addition, the properties of polymer/CNT-composited membranes could be further controlled and optimized in different polymer matrixes via different designed R group-functionalized CNTs (e.g., CNT-OH, CNT-COOH, CNT-SO₃H, and CNT-NH₂). The advancing composited CNT/polymer membranes are always designed to pursuit the desirable performance of VRB. In addition, these polymer/CNT-composited membranes provide us suitable approaches to synthesize membranes and shine new light on novel membrane-electrode assembly for VRB.

2.5. Going beyond: toward other redox flow batteries

Non-aqueous redox flow batteries based on non-aqueous electrolytes have received widely studied recently. Although being far less developed than aqueous redox flow batteries, of the

non-aqueous redox flow batteries seem more attractive due to their wider electrochemical window (>2 V) and greater energy density. However, the lithium-conducting membranes and low power density are still the main challenges for their commercialization. Therefore, the lithium-conducting polymer (Nafion, Polyvinylidene difluoride, PEEK, Polybenzimidazole, PES, SPES, and SPEEK)/functionalized CNT-composited membranes such as CNT-SO₃Li/polymer, CNT-COOLi/polymer, and CNT-OLi/polymer are expected to be promising candidates for applications in the non-aqueous redox flow lithium batteries, redox flow lithium air batteries, and redox flow lithium sulfur batteries [21–23].

3. The application of CNT-polymer compositions in flexible Li-ion batteries

Because of the environmental contamination and energy crisis, energy storage systems have attracted much attention from research institutes and industries. Lithium ion batteries (LIBs) due to their high energy densities and long lifetime are the main commercial batteries, especially for portable devices [24, 25]. Among the possible candidates of lithium storage, carbon nanotubes (CNTs) have emerged as the promising ones. Their peculiar structure and unique properties, such as high electrical conductivity and tensile strength, make them well suited as a critical component in novel anode materials for enhanced lithium storage [26]. For example, it is possible to design free-standing and flexible electrodes using CNTs, which are important parts for the flexible batteries [27]. In addition, some organic active materials could work as electrodes in lithium ion batteries, which could realize much high capacity [28]. These materials have the minimal environmental footprint, lightweight, flexibility, and chemical tenability, which could guarantee its promising potentials in flexible LIBs.

3.1. The working mechanism of LIBs

The working mechanism of lithium ion batteries is demonstrated in **Figure 3**.

1. During the charging and discharging process, the lithium ions move between the anode and cathode via the electrolyte, which is typically a lithium salt such as LiPF₆ dissolved in organic solvent such as ethylene carbonate. The electrochemical reactions are expressed as reactions 1 and 2. The most common anode is graphite with a theoretical capacity of 372 mAh/g, and the cathode is LiCoO₂ with a theoretical capacity of 272 mAh/g [29]. The electrochemical properties of cathode and anode dramatically draw influence on the lithium storage properties. For example, lithium ions can only combine on every 2nd carbon hexagon in the graphite sheet which limits the amount of lithium ions to one for every six carbon atoms [30]. Thus, its theoretical capacity of graphite is 372 mAh/g.



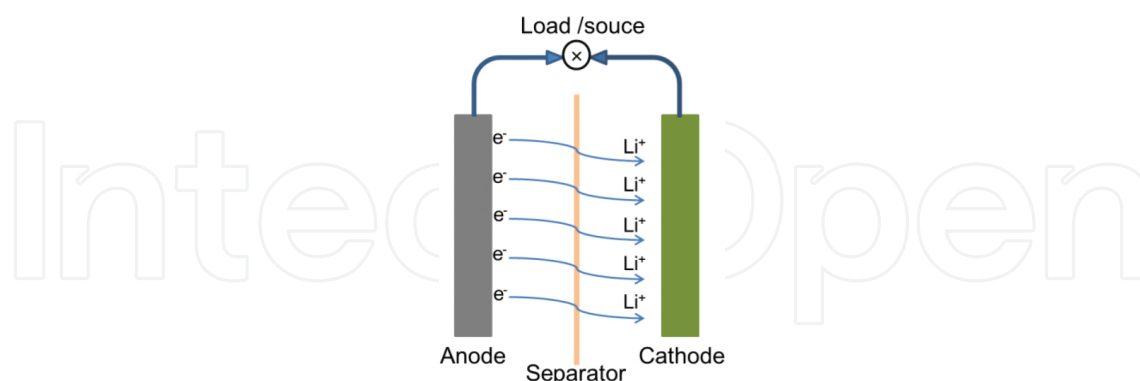
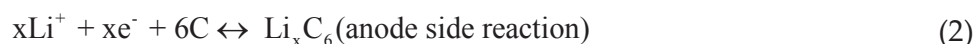


Figure 3. The basic structure of lithium ion batteries.

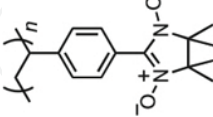
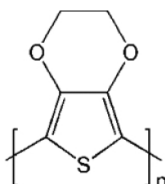
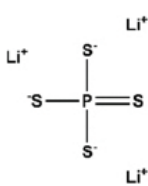
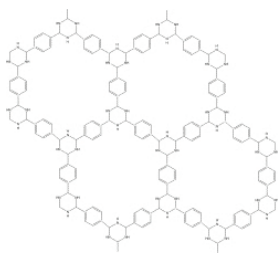
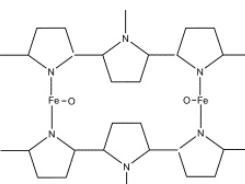
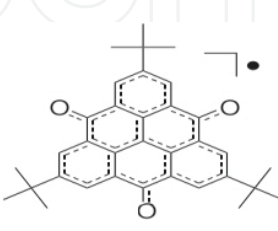
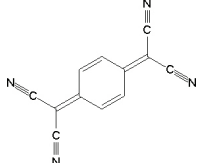
3.2. The significance of flexible Li-ion batteries

Flexible electronics will play more and more significant role in the future electronic markets, for example, flexible displays, sensors, batteries, etc. [31, 32]. Due to the characters of flexible devices, the corresponding energy storage systems should be flexible as well. Due to their high operation voltage, high energy density, and long life span, LIBs have been chosen as the most promising candidates for flexible electronics. Some concept and prototype flexible electronics have been demonstrated. However, there are lots of challenges to realize good flexible LIBs, for example, the package of the electrolytes and electrodes. As one key part in flexible LIBs, electrode with intrinsically flexible should be the best candidate [33].

3.3. The traditional organic polymer in LIB

Organic materials became more and more important in the LIBs due to their merits, such as renewable, designable, and flexible. various organic materials are used in LIBs, such as organic radical polymers [34–36], conducting polymers [37, 38], organosulfur compounds [39, 40], bipolar porous polymeric frameworks [41], layered compounds [42], trioxotriangulene derivatives [43], tetracyano quinodimethane (TCNQ) [44], pyrene-tetraone (PYT) [45], polyimide [46], and organic carbonyl compounds. Several reported organic compounds and their basic information in energy storage systems are shown in **Table 1**. Despite the rapid development of organic-based electrode materials, some critical obstacles still exist. For example, most organic electrodes suffer from the rapid capacity fading upon cycling due to the dissolution of active organic chemicals into organic electrolytes. And the power densities of these organic electrodes are relative low due to their poor electronic conductivity [47, 48]. In order to utilize these organic materials in flexible LIBs, CNTs were employed as free-standing conductive networks and current collectors [46, 49]. Current collector is the necessary component to support electrode materials and conduct electrons in the LIBs. The common current collectors are Cu and Al with high densities and smooth surface, which leads to low energy density and

poor adhesion. However, light and rough CNT-based current collectors could address these issues.

Polymers	Structures	Redox potentials (V)	Functions
Organic radical polymer (poly[4-(nitronyl nitroxyl styrene)] [35])		-0.61 and 0.72 V vs Ag/AgCl	Active material
Conducting polymer (poly(3,4-ethylenedioxythiophene)) [38]		1.25 V vs Ag/AgCl	Conductive additives for active material
Organosulfur compounds (lithium polysulfidophosphates) [39]		~2.2 V vs Li/Li ⁺	Active material
Bipolar porous polymeric frameworks (amorphous covalent triazine-based frameworks) [41]		2.8 and 4.2 V vs Li/Li ⁺	Active material
Layered compounds (polypyrrole-iron-oxygen (PPy-Fe-O) coordination complex) [42]		~1.5 V vs Li/Li ⁺	Active material
Trioxotriangulene derivatives (tri-tert-butylated TOT derivative) [43]		1.4 and 3.8 V vs Li/Li ⁺	Active material
Tetracyanoquinodimethane [44]		1.0 V vs. Li/Li ⁺	Active material

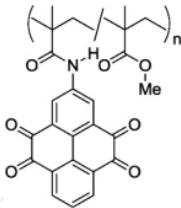
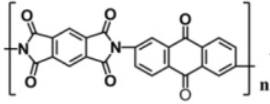
Polymers	Structures	Redox potentials (V)	Functions
Pyrene-tetraone (pyrene-4,5,9,10-tetraone) [45]		2.2 and 2.8 V vs. Li/Li ⁺	Active material
Polyimide (pyromellitic dianhydride (PMDA) and 2,6-diaminoanthraquinone (AQ) [46]		2.2 and 2.4 V vs Li/Li ⁺	Active material

Table 1. The reported several organic polymers in LIBs.

3.4. The methods of preparation of flexible CNT/polymer electrodes

Free-standing electrodes by combining CNTs and organic polymers have been widely developed towards multifunctional electrodes.

CNTs can be used as active anode materials, which are combined with conducting polymers to form as flexible electrodes. Chen et al. used aligned carbon nanotubes (ACNTs) and poly(3,4-ethylenedioxythiophene) (PEDOT) to produce flexible electrodes. In this composition, the ACNTs are the active anode materials and the PEDOT is used for enhancement of electrochemical activity and electronic conductivity of the electrode. PEDOT film was deposited onto the ACNT array using chemical vapor-phase polymerization. Cui et al. used PEDOT as conductive polymer for enhancement of electrochemical performance of Si nanowires. Electropolymerization is applied for generation of cation radicals and coupling of the radicals for chain growth. Although the previous methods achieved high electrochemical performance, the processes seem relatively complicated. Using vacuum or pressure filtration, free-standing CNT papers could also be produced [50]. This method is much facile, and the produced CNT papers also exhibit good mechanical properties.

On the other hand, CNTs can be mainly applied as the effective current collectors with organic polymers being employed as active material as either high-capacitance anode or cathode for the flexible electrodes. Lee et al. prepared a free-standing lumiflavine (LF)-single-walled carbon nanotubes (SWNTs) nanohybrids for fast and sustainable energy storage. The hybrid electrode was formed via interaction without disruption of their redox-active properties. The hybrid electrode could possess high conductivity and Li-ion accessibility. In addition, the structure could also prevent the dissolution of polymer into the electrolyte. During the preparation, the reassembly of bulk LF particles into molecular layers is significant for the improvement of stability and kinetics of Li storage in LF.

Li et al. developed one fabrication technique for SWNT/Nafion composite, which can be used as anode in Li-ion battery [51]. The battery exhibited reversible capacity of ~ 850 mAh/g after 15 cycles. Using this composite anode, they demonstrated the integration of electrode and separator to simplify device architecture and decrease overall weight.

Wang et al. prepared multiwalled carbon nanotubes (MWNTs) functionalized with a hyperbranched aliphatic polyester and two different poly(ethylene glycol)s by the reactions of carbonyl chloride groups on the surface of MWNTs and hydroxyl groups of polymers [52]. Due to the different electrode-electrolyte interfaces, the hyperbranched polymer-functionalized MWNT showed a significant improvement over linear polymer-functionalized MWNTs in lithium insertion/deinsertion capacity and cycle stability.

Wu et al. used the composite of polyimide derivative and SWNTs as electrodes for flexible LIBs. Before preparation of hybrid electrodes, they firstly synthesized an active polymer using a condensation polymerization of pyromellitic dianhydride (PMDA) and 2,6-diaminoanthraquinone (AQ). Then, the polymer was combined with SWNTs to form a binder-free flexible organic cathode film, which exhibited high capacity and good rate performance.

3.5. The perspective of CNT/polymer in flexible LIBs

CNTs, with high conductivity and good mechanical properties, are promising materials for flexible LIBs. On the other hand, some polymers with high conductivity can further enhance the performance of flexible LIBs by combining with CNTs. In addition, some polymers can work as active electrode materials with high specific capacities, which can also be used in flexible LIBs. The composites of CNT/polymer own the flexibility, high conductivity, high energy densities, which are suitable for flexible LIBs.

4. Carbon nanotube-polymer nanocomposites for supercapacitors

Among energy storage devices, supercapacitor possesses its unique merits of high power intensity and long lifetime. It can be categorized into electric double-layer capacitor (EDLC), pseudocapacitor, and newly evolving lithiumion capacitor [53]. With advantages on synergetic effects on electrochemical performance, CNT-polymer nanocomposites play significant roles on supercapacitors that integrate interfacial adsorption and redox reaction, hierarchical microstructure, conductivity, mechanical strength, and flexibility [54–57]. The following section focuses on current design and material synthesis of CNT-polymer nanocomposites in the pursuit of true performance matrices, that is, volumetric/areal performance.

4.1. Why supercapacitor in energy storage?

Comparing to lithium ion battery (LIB), supercapacitor enables fast/ultrasfast fully charging/discharging (in seconds) and much higher power delivery (>10 kW/kg) for shorter times [54]. It becomes an indispensable entity towards the development of sustainable and clean energy.

In supercapacitors, EDLCs represent the majority of commercially manufactured products. The electrode materials of EDLC are carbon allotropes (carbon onions, CNT, reduced graphene oxide (rGO), graphene (G), activated carbon, etc.) [58, 59]. The energy is stored at the electrolyte/carbon interface by charging the double-layer capacitance via reversible ion adsorption on the surface of carbon. In order to enhance the capacitance of carbon electrode, good electrical conductivity, high specific surface area (SSA), and electrochemical stability are the dominant factors attract great research interest.

Numerous endeavors have been devoted to increase energy density of supercapacitor. Organic electrolyte is applied to enlarge the voltage window (typically 0.8–1 V for aqueous electrolyte). On the other hand, pseudocapacitors chemically store charge via redox reaction at the surface/interface region. The electrode materials for pseudocapacitors include transition metal oxides/hydroxides and conducting polymers [e.g., polyaniline (PANI), polypyrrole (Ppy), and poly(3,4-ethylenedioxythiophene) (PEDOT), etc.]. To utilize their high capacitance and address the relative low conductivity, nanocomposites with conducting framework endowed with pseudocapacitive nanostructure are under intense study.

Most importantly, recent research focuses primarily on improving areal/volumetric energy densities of supercapacitor with mounting demand for compact and portable energy storage systems [60–62]. Though Ragone Plot provides a representative summary, the concern on the true performance matrices stems from the mass loading/packing density of active materials where the areal/volumetric properties turn to be realistic in device aspect ($C_a = C_g \times m$, $C_v = C_g \times \rho$, where m and ρ are the mass loading and packing density for the electrode respectively). Promising volumetric performances can be achieved in micro-/ultrathin configuration; however, they do not scale up linearly with thickness. The great challenge hence lies in the storage of large amount of energy with simultaneous promising areal/volumetric performances.

4.2. Current challenge and strategies for CNT-based electrode materials

Several merits of CNT deserve re-emphasis: its high conductivity, highly accessible outer surface, and its outstanding mechanical strength. The unique characteristics of CNT facilitate its role in supercapacitor as electrode, conducting additive, template/scaffold for nanocomposite electrode, platform for flexible/stretchable device [54–57]. However, the shortcomings are worthy of noting. The SSA of CNT is only in moderate level and is lower than activated carbon, mesoporous carbon, rGO, and G [63]. Also, its packing density needs to be improved considering areal/volumetric performances.

Recent research has explored numerous approaches to improve the performance of CNT-based electrodes from the angles of packing density, pores to enhance SSA, incorporation of redox nanostructures via surface functionalization [64–66]. The design of hierarchical CNT-based nanocomposites is now a general strategy to pursuit high performance. An integration of 1D (CNT) and 2D (GO, rGO, and G) carbon nanostructure becomes a greatly promising representative that serves further as scaffold for carbon-redox nanostructure hybrid electrodes [67–69]. Nevertheless, the central focus on areal/volumetric energy densities should not be override by the arts of material synthesis.

4.3. CNT-polymer nanocomposites for supercapacitors

Before focusing on CNT-conducting polymer nanocomposites, CNT-cellulose deserves certain lines. Victor et al. firstly demonstrated the fabrication of vertically aligned CNT-unmodified plant cellulose paper supercapacitor [70]. With however relatively low capacitance, this design started the concept of paper device with rationalization of active materials and triggered the development of ultrathin, flexible, and paper-like devices.

4.3.1. CNT-PANI

Conducting polymers generally possess high charge densities and relatively low costs. The redox reactions allow for high energy storage and reduced self-discharge; however, the power density may suffer from slow diffusion [71]. Conducting polymer-based composites with desirable pores and better conductivities hence seek better opportunities. PANI is one of the most promising candidates because of its multiple redox states, relatively high conductivity, environmental stability, and flexibility in terms of the synthetic methods and consequently the so-formed nanostructures.

From the device perspective, a binder-free structure is ideal to eliminate dead cell components, which benefits the areal/volumetric performance. Free-standing CNT-based frameworks via simple and facile ways therefore call for the demand. Meng et al. have prepared a CNT-PANI network starting from forming a free-standing CNT network [72]. Applying the in situ chemical polymerization of aniline monomer, a wholly uniform coating of ~50 to 90 nm of PANI was formed. A flexible all solid state symmetric device with ~23 wt% of PANI was further formed with H₂SO₄/PVA gel, giving a C_v of ~37 F cm⁻³ and correspondingly an E_v of ~2.4 × 10⁻³ Wh L⁻³. To construct the flexible supercapacitor, cellulose, the most abundant renewable organic materials in nature, is one attractive substrate material. Li et al. utilized ecofriendly bacterial cellulose (BC) paper by vacuum filtration that consists of ribbon-shaped ultrafine nanofibers as substrate for the BC-CNT-PANI paper electrode [73]. BC paper endows the device with porosity, high tensile strength, high water retention, and good contact between electrodes and aqueous electrolyte due to its hydrophilicity. CNT ink was then deposited on the BC paper with strong binding via hydrogen bonding and electrostatic interaction, followed by electrodeposition of PANI. The binder-free electrode showed an appreciable C_g of 656 F g⁻¹ in 1 M H₂SO₄. An optimal deposition time for the PANI coating indicates the critical value of thickness beyond which the pores in the paper are filled by PANI that blocks ion diffusion towards interior. This lightweight and cost-effective supercapacitor paper is a promising candidate for stretchable/flexible device. Hyder et al. utilized an electrostatic layer-by-layer (LBL) system to synthesize CNT-PANI films [74]. PANI nanofibers (~30 to 70 nm × 0.4–3 μm) were chemically polymerized, where the nanoscale concerns the redox reactions localizing in the thin surface layer, and meanwhile, the amine or imine surface groups were present. On the other hand, CNT surface was modified with carboxylic acid groups. The pH-dependence on surface charges for both entities facilitates the behavior like weak polyelectrolytes with controllable LBL film thickness and morphology, where high PANI content (58 wt%) can be achieved. The resulted film (e.g., 1.3 μm, 0.64 g cm⁻³) consisted of an interpenetrating nano-

porous network yielding excellent electrochemical performance: a C_v of $\sim 238 \text{ F cm}^{-3}$ in 1 M LiPF_6 (comparing to $\sim 180 \text{ F cm}^{-3}$ for LBL CNT film) and a C_v of $\sim 248 \text{ F cm}^{-3}$ in 1 M H_2SO_4 , and an E_v of $\sim 220 \text{ Wh L}^{-1}$ at 100 kW L^{-1} . Note that the mass loading of $0.15\text{--}0.23 \text{ mg cm}^{-2}$ was relatively low that was a direct consequence of LBL process, which lead to a C_a less than 0.1 F cm^{-2} .

Besides above, multifunctional design, for example, integrating advantageous mechanical strength, is making strides. Benson et al. reported a CNT-PANI fabric by electrodeposition of PANI on the CVD-formed CNT fabric ($15 \mu\text{m}$) [75]. The strong π - π interaction between CNT (benzenoid rings) and PANI (quinoid rings) resulted in strong chemical bonding and high interfacial shear strength. The electrode with $\sim 31 \text{ wt\%}$ PANI provided a C_a of $\sim 0.7 \text{ F cm}^{-2}$ and a C_v of 308 F cm^{-3} , which showed a 10-fold increase comparing to the initial CNT fabric. The synthesized nanocomposites demonstrated remarkable mechanical properties: a maximum tensile strength of 484 MPa and an elastic modulus of 19 GPa , which were comparable to CNT-epoxy composites, strong natural fibers and tissues, aerospace-grade metal alloys. This ultratough design may offer a solution to a system requires both structural and energy storage functions. Also, stretchable fiber-shaped supercapacitors find their applications in wearable device. Zhang et al. developed a superelastic (stretched by over 400% strain) symmetric supercapacitor by CNT-PANI nanocomposite sheets [24]. A prestrain method was employed to form the CNT sheet, followed by a layer of PANI coated via electropolymerization. At 50 wt\% of PANI, the electrode provided a length specific capacitance of 0.9 mF cm^{-1} and a C_a of $\sim 3 \text{ mF cm}^{-2}$. Most importantly, the device exhibited superior performance under dynamical test: $\sim 71\%$ retention after stretching at a strain of 300% for 5000 cycles, $\sim 90\%$ retention after bending for 5000 cycles, and $\sim 96\%$ retention at a high stretching speed of 30 mm s^{-1} . Very recently, a highly compressible all-solid-state supercapacitor was integrated by Niu et al., based on sponge-CNT-PANI electrodes [77]. The compression tolerance of the sponge is utilized, followed by a repeated "dipping and drying" strategy for CNT coating. Chemical polymerization of PANI was performed to form the porous hierarchical skeleton/skin architecture. The total mass loading of active materials was 6.3 mg cm^{-2} , with a contribution of 4.1 mg cm^{-2} from PANI. A layer of gel electrolyte $\text{PVA}/\text{H}_2\text{SO}_4$ was selected to overcome the contact between neighboring electrode materials at large compression strain. At the relaxed state, the supercapacitor showed a high C_a of 2.7 F cm^{-2} and a C_v of 3.4 F cm^{-3} , with 3% loss under 60% strain. It delivered an E_a of 0.01 Wh L^{-2} and an E_v of 0.12 Wh L^{-1} . The highly compressible supercapacitor will pave the way for advanced applications in the area of the compressible energy storage/compression-tolerant electronics.

4.3.2. CNT-Ppy

Ppy is another popular conducting polymer included in the work awarded 2000 Nobel Prize in Chemistry. A natural cellulose-Ppy all-polymer paper has been synthesized to achieve superior areal/volumetric performance of $\sim 5.7 \text{ F cm}^{-2}/236 \text{ F cm}^{-3}$ at $20 \text{ mg cm}^{-2}/290 \mu\text{m}$, where the scaling up facilities the practical applications [78]. Besides hierarchical structure, Ppy plays a role of nitrogen source for N-doped carbon materials, as demonstrated in Chen et al.' work [79]. The carbonization at $500\text{--}1100^\circ\text{C}$ of the Ppy-coated macroscopic-scale carbonaceous

nanofibers leads to the N-doped carbon nanofibers, where the incorporated heteroatoms favored the performance.

4.3.3. CNT-Nafion

Nafion is a state-of-art polymer electrolyte membrane as discussed in Section 2.4. Due to its ionic conductivity, it is a promising candidate for solid electrolytes in supercapacitor. Huang et al. sprayed CNT in diluted H_2SO_4 solution on both side of a Nafion membrane to construct a flexible solid state supercapacitor, where high H^+ mobility of protonated Nafion is fully utilized [80]. In a recent work by Daniel et al., Nafion 115 solution was dip-coated on the aligned CNT forest and covered its top to form a separating layer [81]. The symmetric EDLC without additional separator was then soaked in 1 M H_2SO_4 for much improved electrochemical performance comparing to its dehydrated state. In this design, Nafion acts as both separator and ionic conductor, brings promising mechanical strength, and favors operation at high temperature up to 60°C (~ 2.6 times enhancement on C_g).

4.4. Outlook

There is no doubt that the 3D hierarchical CNT-polymer architectures have made striking progress. Based on such scaffolds, more emerging advancing materials/device designs will be expected. One primary concern lies in the synthesis of newly discovered conducting polymers. Towards green chemistry and renewable resources, integration of CNT with other natural polymers than cellulose, like lignin currently under intense study, may be further explored [82]. Also, the control of macropores/mesopores/micropores will still be one of the focuses. In the ultrathin configuration, commonly obtained relatively low C_a with highly appreciated C_v urges the enhancement of the areal mass loading, where combination of multiple redox nanostructures with synergic effects may play significant roles. In the flexible/stretchable configuration, scaling up of the high C_v nanocomposites is still a challenge, which is also valid for ultrathick configuration. Furthermore, the stability of CNT-conducting polymer that puts influence on cycling stability warrants in-depth research. Above all, the understanding on fundamental interface chemistry and ionic transportation governs the development of energy storage [83].

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