Development of High Performance Electrochemical Capacitor: A Systematic Review of Electrode Fabrication Technique Based on Different Carbon Materials

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Increasing demand for energy requirement has attracted considerable attention among researchers to develop efficient energy storage device. Among energy storage devices, electrochemical capacitor (EC) has great potential for its capability to deliver more power than batteries and store more energy than conventional capacitors. The electrode or active material is the most crucial factor in determining the device properties. Recently, carbon based materials play significant roles as electrode materials and possesses remarkably significant achievements toward the development of sustainable energy storage applications. Electrode fabrication technique is another important factor to be considered. Hence, this article reviews the electrode fabrication techniques for EC based on different types of carbon as electrode materials, and their EC performances measured by techniques such as cyclic voltammetry and charge discharge characteristics are also discussed.

Background.— Nowadays, sustainable energy sources are important and have been utilized in many applications due to the decreasing availability of fossil fuels.[1] Renewable resources such as solar[2] and wind power[3] have the ability to generate electricity, and thus offers high potential for future energy demands. However, these kinds of sources provide limited energy consumption due to the continuous utilization of energy for up to 24 h a day. To overcome this matter, energy storage devices are introduced to achieve an effective level in the cycle of renewable energy sources.[4] A lot of efforts have been put in researching and developing more efficient energy storage system that is more novel, low-cost, environmentally friendly, and better performance to meet the market requirement.[5] Batteries, fuel cells, and electrochemical capacitors (ECs) are among those devices for the newly introduced electrochemical energy storage and conversion.[6]

ECs provide the necessary power for acceleration and additionally allow for recuperation of brake energy in hybrid electric vehicle.[7–9] Moreover, ECs are constructed and/or assembled much like a battery and their function is also similar. Function of both batteries and ECs are to store electrical charges. In a basic form, ECs consist of two symmetric electrodes immersed in an electrolyte with a dielectric separator between the electrodes. ECs are generally classified into three types, which are electrochemical double layer capacitor (EDLC), pseudocapacitor, and hybrid capacitor.[8,10,11] The general principle and mechanism of these types of ECs will be discussed in this manuscript.

Commonly, fabrication of ECs consists of electrode preparation and cell assembly. Studies about the electrode fabrication technique of ECs are important to successfully produce high performance ECs. Notably, selection of electrode materials has become an essential factor to verify the properties and performances of ECs.[12] Also, simple procedures to fabricate ECs will reduce the fabrication complexity and reduce the number of process steps in fabricating the device.[13] Typically, cyclic voltammetry (CV) and charge discharge analysis are commonly conducted to determine electrochemical performance of ECs. Fabrication of high performance ECs with high operating voltage, high energy density and power delivery, and longer charge discharge cycle lifetimes must be developed to significantly enhance the potential of energy storage technology.[14]

Advantages of EC.— As we know, batteries are the most common energy storage device, batteries have short life cycle

and powers of batteries are below than 100 W kg^{-1}.[15] However, batteries are useful and suitable for energy storage over long time application more than 100 s, while conventional capacitors for short time storage less than 0.01 s. Meanwhile, conventional capacitor possesses high power density more than 10^3 kW kg^{-1} and also long life cycle, but their energy density is low about 70 mWh kg^{-1}. Hence, ECs have been developed for the cases which required large energy density (Wh kg^{-1}), high power density (W kg^{-1}), and long life cycle, more than 100,000.[15]

As compared to other energy storage devices, ECs have some advantages such as high power density, high energy density, long life cycle, fast charge and discharge rate, a wide thermal operating range, low weight, flexible packaging, and low maintenance.[16–21] According to Pandolfo et al., ECs have the capability to rapidly charge and discharge at power density exceeding 1 kW kg^{-1}.[22] Also, ECs show intermediate energy storage devices that bridge the critical performance gap between higher energy density of battery and high power density of conventional capacitor.[23–25]

Principle and mechanism of EC.— ECs are generally categorized into three different types which are electrical double layer capacitors (EDLCs), pseudocapacitors and hybrid capacitors. EDLCs are electrical energy storage devices that undergo the electrostatic or physical separation of charge at the interface between electrode and electrolyte.[26,27] The negative electrode attracts the positively charged cations and the anions are accumulated in the pores of the positive electrode during charging process. These two parallel regions of charge are called electrical double layer interface.[28,29]

As shown in Figure 1, when the system is connected to power supply, the surface of electrodes is charged and attract ion of opposite charge. Importantly, the major difference of EDLCs compared to other types of ECs are no redox reaction is involved in the energy storage process, and the charges are stored only at the surface of carbon.[30,31] The calculation of capacitance (*C*) can be described in Equation 1:[23]

$$C = \frac{\varepsilon A}{d} \qquad [1]$$

where ε is the electrolyte dielectric constant, *A* is the surface area accessible to ions, and *d* is the distance between the center of the ion and the carbon surface in the order of angstroms. According to the Equation, increasing the specific surface area and reducing distance between ions and the electrode surface are the two approaches can be taken in order to enhance the charge storage of EDLCs as effectively.[23] Therefore, a morphological property of the porous carbon electrodes

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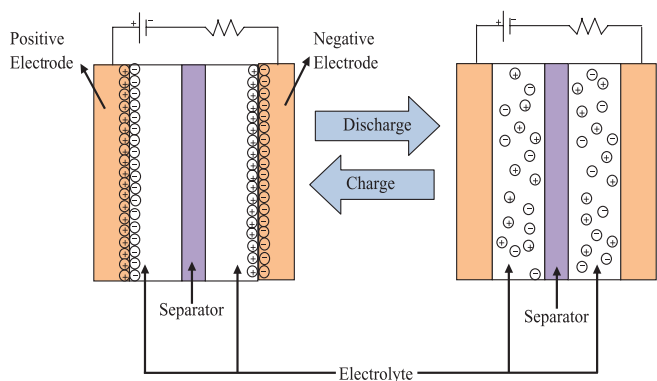zE-mail: asyadi@utem.edu.my

Figure 1. Mechanism of charge discharge process for EDLC.

Figure 2. Energy storage mechanism for pseudocapacitor.

such as the surface and pore size distributions are the factor that correlated with double layer capacitance.[32] The power density or the charge discharge time for EDLCs will determined how fast the ions transport within the electrode particles.[33] The energy (E) of ECs can be calculated using Equation 2 in below;[8]

$$E = \frac{1}{2}CV^2 \qquad [2]$$

Where C is the value of capacitance in Farads and V is the operating voltage which depending on the electrolyte stability window.[8,31] Meanwhile, the power (P) can be calculated by using the following Equation;[8]

$$P = \frac{V^2}{4Rs} \qquad [3]$$

where Rs is represented the equivalent series resistance (ESR) for ECs. In order to enhance the power density, it is necessary to utilize the materials with high capacitance and low resistance. SI unit for energy density and power density is Wh kg^{-1} and W kg^{-1}, respectively.

Other types of EC are pseudocapacitors that store energy using highly reversible surface redox (faradaic) through the transfer of charge between electrode and electrolyte interface. Typically, there are several process involves in pseudocapacitors such as electrosorption, reduction and oxidation reaction, and also intercalation processes. As compared with EDLC, the pseudocapacitors show relatively less cycling stability due to faradaic reaction mechanism, thus it decreases other properties such as life cycle.[35] For high performance of pseudocapacitors, utilization of suitable electrode material is important to ensure fast and reversible redox reactions on the surface or subsurface.[36] Typical electrode material for pseudocapacitors including transition metal oxides such as ruthenium oxide (RuO2), magnetite (Fe$_3$O$_4$), Nickel(II) oxide (NiO), and manganese (IV) oxide (MnO$_2$) and electronically conducting redox polymers such as polyanilines, polypyrroles, and polythiophenes. Electrical charge storage mechanism for pseudocapacitors is shown in Figure 2.[37]

Furthermore, there is another special type of capacitor system besides both EDLCs and pseudocapacitors called 'hybrid' capacitors. Hybrid capacitors are the combination of one rechargeable battery electrode (as energy source) with the double layer electrode (as power source) in the same of ECs cell.[38] Therefore, hybrid capacitors offer the advantages of both high power density of EDLCs and high energy density of batteries but relatively low life cycles. These capacitors can be applied in energy storage, energy management and power conversion.[39]

Electrode material: Why carbon?.— Carbon materials have been playing a significant role in the development of energy storage device especially ECs. Generally, carbon materials composed of carbon atoms and have only one kind of element. Carbons materials however have largely diverse structures, properties, and also consist of different allotropes such as graphite, diamond, fullerenes, and nan-
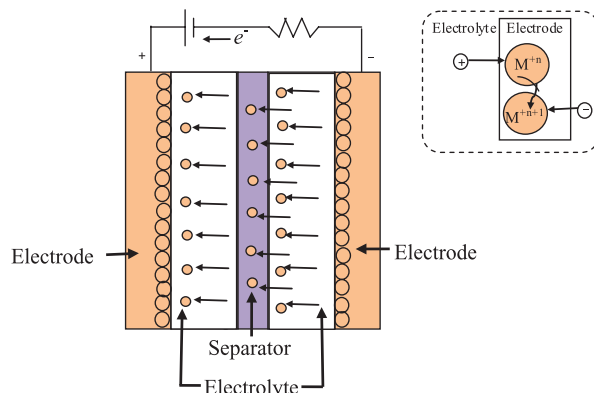
otubes. Diamonds have three dimensional structures, graphite two dimensional, whereas carbon nanotubes (CNTs) have one dimensional structure. Nowadays, a great interest from researchers about using carbon materials based electrode for EC because of their accessibility, relatively low cost, and versatile existing forms such as powders, fibers, felts, composites, mats, monoliths, and foils. Apart from that, carbon materials are environmentally friendly, chemically stable in different solutions and have the capability to perform in a wide range of temperatures.[28]

On the other hand, the specific gravimetric capacitance (C_{sp}) of a porous carbon (expressed in F g^{-1}) is proportional to the surface area of electrode in (m^2 g^{-1}).[40] Generally, carbon materials posses high surface area in the range of 1,000 to 2,000 m^2 g^{-1}.[12] Pore size distribution of porous carbons also give the influences to the performance of carbon based ECs such as the relationship between power density and energy density, and the dependence of performance on frequency. In addition, ionic conductivity and voltage stability of the electrolytes however become others important parameters that determine the energy stored in a carbon based ECs.[41] In this review article, carbon materials that have been used as electrode material for ECs will be discussed. And, to be included is the electrode preparation technique based on different carbon materials to study which technique is preferable for better electrochemical performance.

Electrode Fabrication Technique Toward High Performance EC

Standard component of EC.— As explained in previous section, a typical of EC unit cell consists of two electrodes immersed in an electrolyte and there is one porous separator between the two electrodes. Standard cell of EC is illustrated in Figure 3 where it is composed
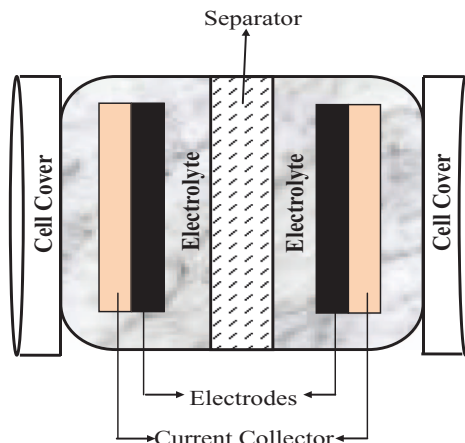

Figure 3. Common symmetric electrode cell component for EC.

of two symmetric electrode materials, separator, electrolyte, and current collectors. From the figure, current collectors are mainly utilizing metal foil or carbon filled polymers and their function is to supply the electrical current to the system. The separator and electrodes are impregnated in the electrolyte, which allows ionic current to flow between the electrodes while preventing electric current from discharging the cell. Moreover, separator between two electrodes also prevents the charge from directly moving between the two electrodes.[42] According to Ghosh et al., the active material used as electrode, nature of electrolyte and interface between electrodes and electrolytes are the several parameters that influence the performance of ECs.[43] And, in many laboratory practices, there are several types of cell for ECs are being used such as coin cell, button cell, teflon cell, and button cell.

Usually, in the performance evaluations of the ECs, three-electrode cells are used to test the cell and also to investigate the performance of single electrode. Three electrode cells consist of working electrode (materials to be tested), a reference electrode (to be operational in the electrolyte), and a counter electrode (designed to avoid any interference with the working electrode). When using acidic aqueous solution, current collectors of working electrode can be titanium, counter electrode is platinum or carbon and reference electrode is saturated calomel electrode (SCE) or a silver/silver chloride electrode (Ag/AgCl). Basically the same configuration is used when using neutral aqueous solution but Ni is preferred for the current collector and the counter electrode. In alkaline aqueous solutions, a mercury/mercury oxide electrode (Hg/HgO) is used as the reference electrode. For non-aqueous electrolyte solutions case by case approach is required depending on the composition of electrolyte.[40,41]

However, two-electrode cells are recommended for the evaluation of the cell performance. Energy density, power density, and the life cycle of the cell can be easily estimated by using this system. Value of capacitance should be based on the sum of active materials in two electrodes. Also, the capacitance of single electrode measured in a two-electrode cell does not coincide with that in a three-electrode cell because of various factors, such as the difference in sizes between the solvated cation and anion, the different potential changes of positive and negative electrodes during charge/discharge measurements, and others.

The most common techniques for electrochemical testing are CV, galvanostatic potentiometry, rotating disk electrochemistry and impedance spectroscopy. In CV testing, CV curves are rectangular when the capacitance is simply originated from EDLCs. However, when the pseudocapacitance is added, the point of the potential for capacitance calculation should be chosen case by case carefully because the CV curve is not always rectangular.[40,41]

Electrode fabrication technique based on different carbon materials.— Electrode as the active materials are the main component of ECs due to capacitance and charge stored depend on the types of electrode material used.[8] It is important to fabricate electrodes which are comparable to commercially available ECs because electrodes are the active components that will determine the charge storage performance of ECs.[45] Recently, high surface area and porous carbon materials as well as noble metal oxides are used as electrode material for commercial productions of ECs. However, carbon materials have been widely used as electrode materials for EDLCs.[46] High surface area of carbon material such as activated carbon, CNTs, and carbon aerogels are commonly used as electrode materials for EDLCs.[47]

The energy, power efficiency and lifetime of ECs are also depends on the electrical contact resistance between the electrodes and current collectors.[48] Electrode surface area, electrode area specific differential capacitance, electrode volumetric capacitance, the frequency behavior of the impedance, the shape of the CV trajectory and the ESR are the basic measures of ECs performance.[49] The next section will describe about the several types of carbon materials such as CNTs, activated carbons, carbon aerogels, carbon blacks and graphene that have been used to fabricate the high performance of ECs.

Activated carbon.—Activated carbons are especially attractive as electrode material or active ingredient for ECs in order to provide high capacitance license due to high surface area, relatively low cost electrode material, and lightweight compared to among different carbon materials.[50] There are two types of activated carbons; activated carbon particles/powder and activated carbon fiber cloth. Generally, activated carbons can be obtained from natural sources such as fruit shell like coconut shell, wood, pitch, coke or from synthetic precursors such as selected polymers. Activated carbons will undergo carbonization process and also derived from carbon-rich organic precursors by heat-treatment in inert atmosphere.[51] According to Pandolfo et al., activated carbons are also obtained from carbonized phenolic resins or petroleum cokes. Moreover, conductive carbon blacks or graphite are also mixed with activated carbons for utilization in commercial ECs.[22]

Although the activated carbons able to store less total energy, but they have large percentages of big pores that can deliver high energy at high rate and make them to be more suitable as high power of ECs.[52] However, the activated carbons are difficult to handle when in powder form. Thus, conductive agents (carbon black) and polytetrafluoroethylene (PTFE) binders are always required.[53] For EC application, high C_{sp} can be achieved by choosing a suitable high surface area of material with BET surface area more than $1,000 \text{ m}^2 \text{ g}^{-1}$. For example, EC with C_{sp} of 120 F g^{-1} is achievable with proper techniques of electrode fabrication.[54]

Sun et al. investigated electrochemical performance of ECs by using activated carbons as electrode material and Cu (II) containing ionic liquid was used as electrolyte. For the preparation of electrode, activated carbon powders (85 wt%) were mixed with graphite (10 wt%) and polyvinilidene fluoride (PVDF) (5 wt%) as binder material. All the mixtures were stirred adequately, and then pressed to form round electrodes. The round electrode has 10 mm in diameter and 0.2 mm in thickness. The current collector (stainless steel), electrode, separator (polypropylene) and electrolyte solution were assembled in sequence as a sandwich and enveloped in a cell. When Cu (II) containing ionic liquid was used as electrolyte, average C_{sp} decreased with increasing current intensity, from 225 F g^{-1} at 1 mA cm^{-2} to 210 and 178 F g^{-1} at 2 and 5 mA cm^{-2}, respectively. Also, high specific energy of about 45 Wh kg^{-1} is attributed to the faradaic pseudocapacitance resulting from the diffusion-controlling, reversible redox reaction of Cu^{2+}/Cu^0 ion pairs.[55]

Kalpana et al. used a poly (o-anisidine-co-metanilic acid) (PASM) /activated carbons as an electrode material for ECs. The PASM were deposited on stainless steel that was coated with activated carbons. For the preparation of activated carbons electrode, 70 wt% of activated carbons with specific surface area of $700 \text{ m}^2 \text{ g}^{-1}$ were mixed with 25 wt% acetylene black and 5 wt% N-methylpyrroli-dine binder. The mixtures were then pressed on a stainless steel grid current collector with geometrical area 1 cm^2 and kept in an oven at $200°C$ for 30 min. Electrochemical testing such as CV and galvanostatic were carried out and the resulted a C_{sp} of 373 F g^{-1} at a power density of 0.22 kW kg^{-1} was obtained for PASM/AC at a 5 mV s^{-1} scan rate. However, pulverization may occur during charge and discharge due to thickness and instability of electrodeposited coating. Smaller particle size of PASM may overcome this problem to reduce pulverization and a maximum C_{sp} as high as 576 F g^{-1} was obtained.[56]

Furthermore, Gamby et al. studied about the several of activated carbon from PICA Company that have been used as electrode materials to compare their performance. Ni foam was used as current collector and 50 μm thick polyethylene sheets were used as separator. The electrode material was prepared by mixing 95% of activated carbon with 5% of binder (carboxymethylcellulose and PTFE). After drying process, active materials are laminated on each side of the current collector to make 600 μm thick electrodes. As shown in Figure 4, a 4 cm^2 test cell with PTFE plates and stainless steel clamp was used to improve the contact inside the cell. Then, the cell is immersed in electrolyte and placed in an argon filled sealed box. The PICACTIF SC carbon was found to be an interesting active material for ECs with a C_{sp} as high as 125 F g^{-1}.[57] As we can see from all previous experiments, activated carbon are always required mixing process with conductive agents and binder material to form slurry and then
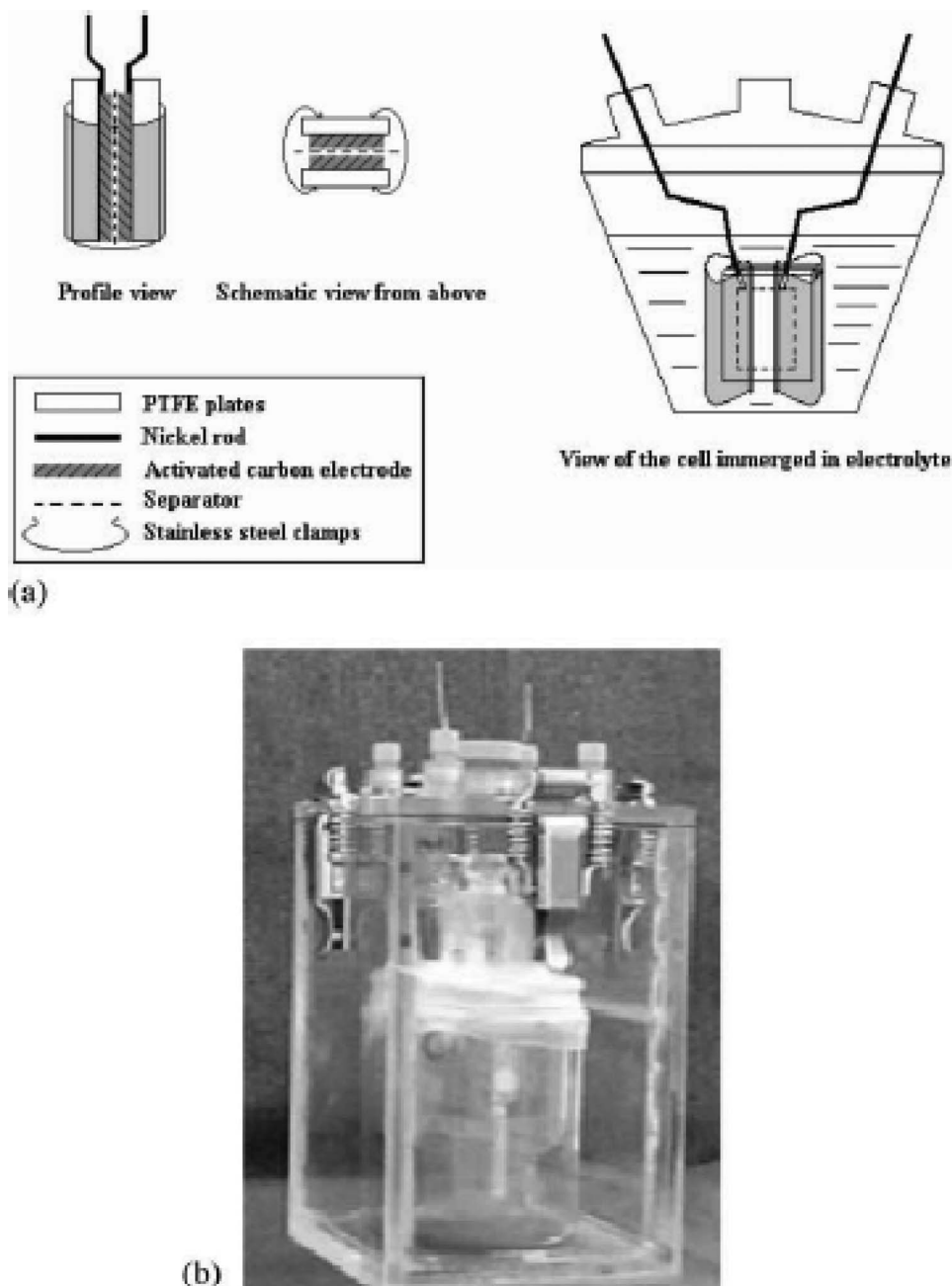
Figure 4. a) Schematic view of 4 cm^2 test cell; b) 4 cm^2 test cell in sealed box.[57]

coating or pressing on the current collector in order to fabricate the ECs electrode.[53]

Carbon aerogel and xerogel.—Carbon aerogels have large amounts of mesopores and considered as promising materials for EC. Usually, the size of primary particles carbon aerogels are about 4–9 nm and interconnected with each other to form a network forming interparticle mesopores.[40] According to a method proposed by Pekala, carbon aerogels were derived from pyrolysis of a resorcinol – formaldehyde (RF) gel.[58] Moreover, sol-gel process with a subsequent drying procedure to extract the pore liquid is use to produce aerogels. The particle sizes are controlled by the catalyst concentration and the degree of dilution determines the density of the material.[59] The advantages of carbon aerogels for EC application are high surface area, great electrical conductivity and low density are the several advantages for using in EC application.[59,60]

Li et al. studied on preparation and performances of carbon aerogel electrodes for the application of ECs. The mass ratio 9:1 of carbon aerogel/graphite was mixed with 5 wt% PTFE (60%) that used as a binder material. All the mixtures were then pressed to form disk like working electrode. Carbon aerogels as electrode materials for ECs were characterized using CV and charge discharge analysis. Result of CV testing indicated a maximum C_{sp} of carbon aerogels electrode was 110 F g^{-1}. Meanwhile, a maximum C_{sp} of about 28 F g^{-1} was obtained through galvanostatic charge discharge testing.[46]

Liu et al. investigated the performance of resorcinol–formaldehyde-based carbon aerogels in EDLCs. The preparation of carbon aerogels electrodes consist of mixing carbon aerogels, PVDF and carbon black in a weight ratio of 80:10:10. Also, N-methyl-pyrrolidone (NMP) is used to wet the mixture. The mixtures were homogenized in a mortar and finally rolled into a thin film. A 10 mm

circular electrode were punched out and pressed onto Ni foam under about 10 MPa for 30 s. Sandwich-type capacitors were prepared with a pair of the carbon aerogel electrodes are separated with a piece of polypropylene membrane as a separator and immersed in 1 M Et_4NBF_4–AN solution as the electrolyte. From the CV testing, highest C_{sp} of 147 F g^{-1} was exhibited at a scan rate of 5 mV s^{-1} while the galvanostatic charge discharge testing give the value of C_{sp} about 152 F g^{-1}.[62]

As we discuss before this of about common traditional coating process of slurry on the conducting foil to fabricated the EC electrode, Hwang and Hyun however developed a cost-effective process for synthesizing resorcinol-formaldehyde (RF) aerogels via ambient drying to make optimal carbon aerogels for EDLCs and electrosorptive applications. Carbon aerogel was prepared by pyrolysis of RF aerogels. Pyrolysis of the RF aerogels was carried out under continuous nitrogen flow in a tube furnace. It was heated to 300°C using a heating rate of 2°C min^{-1} and held there for 2 h. The furnace was then heated up again to 800°C by heating rates of 3°C min^{-1} and maintained for another 1 h. Diamond saw was used to cut carbon aerogel into a disk of 1 mm thickness. After cleaning and drying, the carbon aerogel electrode was activated at 450°C in hot air environment for 1 h in order to modify surface functionality and improve the affinity with the electrolyte. The C_{sp} has been improved to 220 Fg^{-1} when carbon aerogel electrodes activated at 450°C in air environment for 1 h.[63]

Carbon black.—Carbon blacks are widely used as conductive fillers for ECs application due to their electrically conductive properties. Usually, carbon blacks are applied for conductivity improvement in polymer engineering and electrochemical industry. It is consisting of composition more or less spherical particles (primary particles) that have diameter in the size range of 10–75 nm to form aggregates (fused primary particles) with size of diameter in 50–400 nm. For EC application, the aggregates form a compact one-, two- or three-dimensional network of the conducting phase when the carbon blacks homogeneously dispersed and mixed with the matrix such as activated carbon, binders, and other additives. Microstructure of carbon blacks are similar like graphite and usually very pure and also considered to be ''amorphous''.[50] Generally, the surface areas of carbon blacks are considered to be more accessible than other forms of high surface area carbon. According to Pandolfo et al., EC electrodes have been produced from high surface area blacks (containing a binder) with C_{sp}s of up to 250 F g^{-1}.

Kossyrev fabricated the electrodes for EC by using traditional coating and inkjet printing on a conventional current collector or directly on a separator membrane. Traditional coating involved casting of carbon black ink containing 2 wt% of solids on top of a 25 μm thick conductive vinyl current collector. The solids in ink constituted of 10 wt% of PTFE binder and 90 wt% of SC3 carbon black which were ultrasonically dispersed in isopropyl alcohol solvent. Also, thin carbon black electrodes are produces directly on separator membranes by inkjet printing. One or both sides of membranes were deposited with carbon black electrodes of around 1 μm thickness. For inkjet printing, 2 to 4 wt% of SC3 carbon blacks were ultrasonically dispersed in n-methylpyrrolidone (NMP) solvent and 4 wt% PVDF binders were used. The produced inks were stable over a few days inside the inkjet cartridges. Hence, the utilization of carbon black, SC3 gives a C_{sp} of 115 F g^{-1} by using an organic electrolyte and a surface area of around 1800 m^2 g^{-1}. Examples of supercapacitor electrodes (1 cm × 1 cm), which were inkjet-printed on one side of cellulose separator membrane, and one or both sides of polypropylene (PP) separator membrane is shown in Figure 5.[64]

Nasibi et al. used mechanical pressing as a fast and easy method to fabricate carbon black electrodes. Electrode fabrication technique involves the mixing process of carbon black with PTFE binder (10 wt%) in ethanol to form a paste and then proceed with pressing process onto Ni foil. This work was obtained high specific capacitance of about 33.58 F g^{-1} C_{sp} in 2 M KCl electrolyte and also the carbon black electrode shows a good cycling performance.[65]
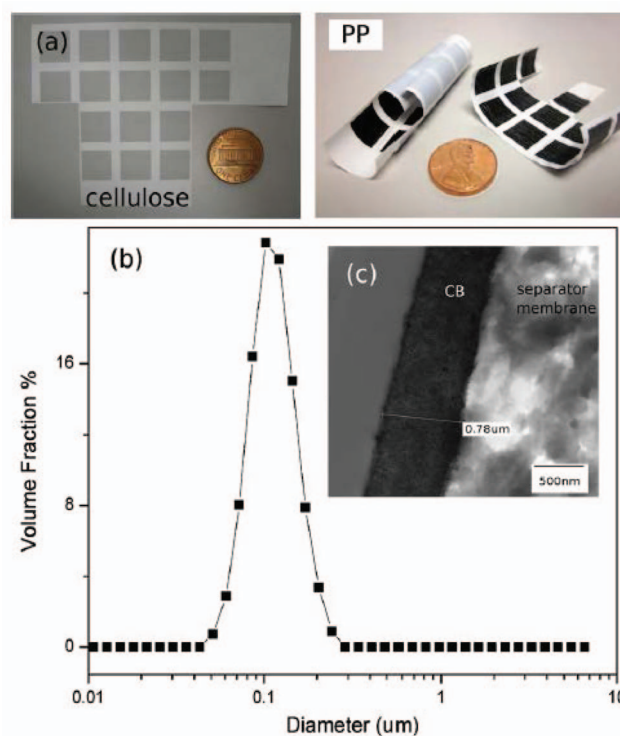

Figure 5. (a) Examples of supercapacitor electrodes (1 cm × 1 cm), which were inkjet-printed on one side of cellulose separator membrane, and one or both sides of polypropylene separator membrane. (b) Particle size distribution of inks containing 4 wt% SC3 carbon black in NMP solvent. (c) TEM image of cross-section of SC3 carbon black electrode (PP) on separator membrane.[64]

Graphene.—Graphene based ECs are attracting a lot of research attention because they have special structure and excellent performance. Graphene consists of a one atom thick 2D single layer of sp^2 bonded carbon and it is necessarily to modify or doped graphene to enhance its electrochemical properties. Also, graphene has been considered as the basic construction material for carbon materials in all other dimensionalities. On the other hand, graphene has unique properties including high thermal (~ 5,000 W m^{-1} K^{-1}), high electrical conductivity (10^8 S m^{-1}), high transparency (absorbance of 2.3%), great mechanical strength (breaking strength of 42 N m^{-1} and Young's modulus of 1.0 TPa), inherent flexibility, high aspect ratio, and large specific surface area (2.63 × 10^6 m^2 kg^{-1}).[5,64] There are four synthesize technique of graphene in the application of ECs which are mechanical exfoliation from bulk graphite, arc discharge, chemical vapor deposition (CVD) and epitaxial growth, and reduction of graphite oxides.[23,65]

Stoller et al. used chemically modified graphene (CMG) to demonstrate an ultracapacitor cell performance. CMG materials are made from 1 atom thick sheets of carbon and it was synthesized by suspending graphene oxide sheets in water and then reducing them using hydrazine hydrate. The individual graphene sheets agglomerate into particles approximately 15–25 μm diameters during reduction. Fabrication of graphene based electrode consisting of mixing process the CMG particles with PTFE binder (3% by weight). The mixtures were then homogenized in an agate mortar, then, rolling the CMG/PTFE mixture into 75 μm thick sheets formed into electrodes, and punching out in 1.6 cm diameter disks. Schematic of test cell and fixture assembly is shown in Figure 6, and this ultracapacitor gives the result of C_{sp}s about 135 and 99 F g^{-1} in aqueous and organic electrolytes, respectively.[68]

Wang et al. used a gas-solid reduction process to prepare the graphene materials and used it as electrode for supercapacitor. The electrodes were fabricated by mixing graphene with 10 wt% PTFE binder. The two graphene electrodes were separated by a thin
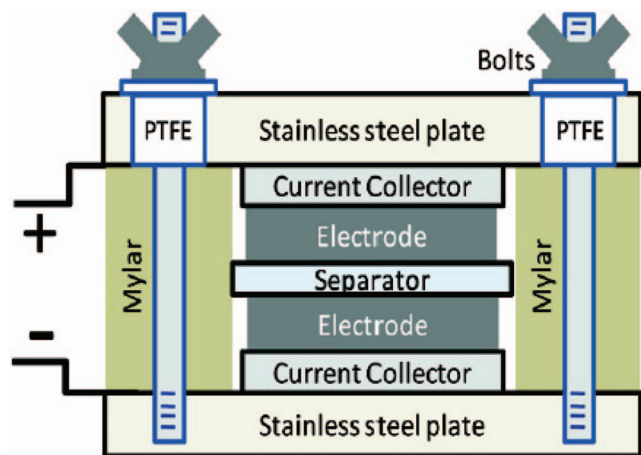
Figure 6. Schematic of test cell assembly for graphene based electrode.[68]

polypropylene film in 30 wt% KOH aqueous electrolyte solutions. The presence of heteroatoms and functional groups in graphene material is supposed to contribute some pseudocapacitance. However, the linear current with the increase of voltage indicates that there is little faradaic for this supercapacitor. In addition, CV shape shows a rectangular shape with various scan rates and even at a high scan rate of 50 mV s^{-1}. In this work, a maximum C_{sp} of 205 F g^{-1} was obtained with a measured power density of 10 kW kg^{-1} and energy density of 28.5 Wh kg^{-1} in an aqueous electrolyte. Schematic diagram of the graphene-based supercapacitor device shown in Figure 7 depicts the experimental arrangement used to assemble the supercapacitor devices.[69]

Hsieh et al. fabricated graphene based ECs to see the influence of their physiochemical properties on the performance of the resulting capacitors. Two types of graphene which are graphene nanosheets and graphene oxides electrodes were used as EC electrodes to compare the capacitive performance. They used Hummer's method to prepare graphene oxide powders while the graphene nanosheet powders were synthesized by chemically reducing the resulting graphene oxides powders. Commercial carbon paper (CP) has been chosen as the substrate as an alternative for use as an electrode in the EC. Graphene nanosheets and graphene oxides were sprayed and coated over the CP substrate forming flexible electrodes. The specific discharge capacitances of a single electrode in the capacitors were calculated based on the results of charge–discharge cycling. In this work, the discharge capacitances are 158.2 and 17.3 F g^{-1} for graphene oxide and graphene nanosheet capacitors respectively at the discharge current of 5 mA.[16]

Meanwhile, Yan et al. fabricated high performance of EC electrodes based on highly corrugated graphene sheets (HCGS). HCGS have been prepared by a rapid, l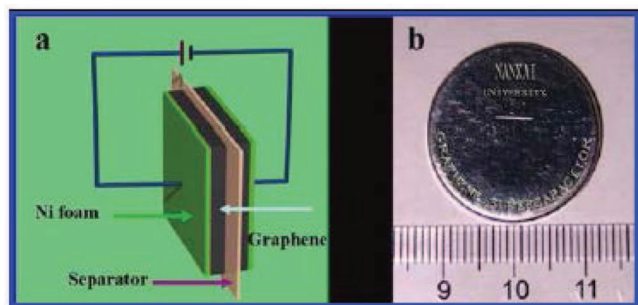ow cost and scalable approach through the thermal reduction of graphite oxide at 900°C followed by rapid cooling using liquid nitrogen. For the fabrication of EC electrode, HCGS were mixed with carbon black and PTFE binder and dispersed in an ethanol. The resulting slurry was then coated onto Ni foam substrate. The maximum C_{sp} of 349 F g^{-1} at 2 mV s^{-1} is obtained for the HCGS electrode in 6 M KOH aqueous solution. The electrode shows excellent electrochemical stability along with an approximately 8.0% increase of the initial capacitance after 5,000 cycles. These features make the present HCGS material a quite promising alternative for next generation of high-performance supercapacitors.[70]

On the other hand, Xu et al. also successfully fabricated supercapacitors using an hierarchical graphene/polypyrrole (GNS/PPy) nanosheet composites as electrode materials by an in situ chemical polymerization method. Sheet-like PPy with a thickness of 20–50 nm was grown on GNS/PPy composites by adjusting the concentration of the pyrrole. The presence of the sheet-like GNS in the synthesis causes the formation of the structure process. The electrode was prepared by mixing 5 mg of active materials with 5 mg PVDF. 1 mL of absolute ethanol was then added to the mixtures and sonicated for 1 h to obtain a homogeneous suspension. 10 mL of the homogeneous suspension was dropped onto the glassy carbon electrode and dried in an oven before the electrochemical test. The fabricated supercapacitor was exhibited good electrochemical capacitance as high as 318.6 F g^{-1} at a scan rate of 2 mV s^{-1}.[71]

Carbon nanotubes.—CNTs were first discovered in 1991 and attracted great interest among scientists around the world. CNT posses outstanding properties such as small dimensions, high strength, and remarkable physical properties that make them as a very unique material with a whole range of promising applications.[72] The structure of CNT consists of all sp^2 carbons arranged in graphene sheet which rolled up to form seamless hollow cylinders of graphitic carbon molecules.[73] Also, CNTs have excellent stiffness, strength, and thermal conductivity which exceed all other known natural and synthetic materials due to their seamless structure, small diameter and to the resilience of individual carbon-carbon bonds.[74] Among others carbon materials, CNTs have been recognized as highly potential electrode carbon materials for EC[75] because of their remarkable electrical charge storage ability[13] high accessible surface area,[76] low mass density,[77] excellent electrical conductivity,[78] great chemical stability[79] and interconnected network structure.[80] As compare with activated carbon, CNTs show excellent electrical conductivity, mesoporosity, and electrolyte-accessibility.[81] There are two major groups of CNTs which are single walled CNTs (SWCNTs) and multi walled CNTs (MWCNTs).[82–84]

Technically, CNT based ECs are binder-free and binder-enriched.[85] Although the CNTs are mechanically and electrically tight when mixed with polymeric binders, it may contain impurities which can degrade its electrochemical performance.[86] The binder is required to attach the CNTs to current collectors and tend to increase equivalent series resistance (ESR). Also, CNTs are mixed with conductive binder will lead to low contact resistance between CNTs and current collector. This process drastically modifies the properties of CNTs electrode and leading to undesirable performance of the ECs. Currently, many researchers try to develop binder-free for ECs electrode that will enhance the performance of EC in term of charge storage ability and specific capacitance.[87] Thus, the electrochemical performance of CNT based ECs are known to be closely related to many factor such as CNT dispersion/orientation, electrical contact between the electrodes and current collector, and fabrication procedures.

In recent years, ECs based on CNT electrode have been reported using either aqueous or organic electrolytes. In 1996, Niu et al. first introduced the idea to produce double layer capacitor using entangled MWCNT and prepared sheet type CNT electrode by the filtration of a dispersed CNT solution. This technique required no binder and reported a maximum C_{sp} of 113 F g^{-1} with respect to the unit cell in 38 wt% H$_2$SO$_4$ solution. However, the pre-treated with nitric acid increase the parasitic resistance.[88] Meanwhile, Ma et al. fabricated several types of block-form porous tablets of carbon nanotubes to use as polarizable electrodes in EC. These tablets are prepared by using molded mixtures comprising CNTs and phenolic resin powders

Figure 7. Graphene-based supercapacitor device. (a) Schematic diagram of graphene-based supercapacitor device. (b) An optical image of an industry grade coin-shaped graphene-based supercapacitor device.[69]

capacitors. EC with a specific capacitance of about 15 to 25 F cm^{-3} are obtained by using these polarizable electrodes.[89]

There are several reports on the preparation of CNT based EC by mixing with binder material. Frackowiak et al. investigated the electrochemical characteristics of an MWCNT pellet electrode prepared by pressing a mixture of CNT with a binder and achieved the C_{sp} ranged from 4 to 135 F g^{-1} in 6 M KOH.[90] In 2001, An et al. investigated the key factors determining the performance of supercapacitors by using SWCNT as the active material. The SWCNTs electrode consisted of 70 wt% of randomly entangled and cross-linked SWCNTs were mixed with 30 wt% polyvinylidene chloride (PVDC) as the binder material. They achieved result of C_{sp} of 180 F g^{-1} in 7.5 M KOH.[91] In same year, Zhang et al. also prepared MWCNT electrodes by molding the CNT with a PTFE binder material and reported a C_{sp} of 18.2 F g^{-1}.[92] Nowadays, CVD appears as a promising technique for production high quality CNTs at large scales that is achieved by pyrolytic decomposition of hydrocarbon gases at elevated temperatures in the range of 600–1,200°C.[93] There are two major technique used to fabricated CNTs based EC electrodes using CVD process; transfer technique[94] and direct growth technique.[13]

(a) CNT: Transfer technique.— Technically, transfer technique is easily defined as transfer of CNTs from non-conducting substrate such as silicon (Si) substrates to the conductive substrate by cut-paste or printing technique to prepare CNT electrode. CNT based ECs are usually made by first growing CNTs on the Si substrate using CVD process when certain reaction parameters such as reaction temperature and the right variety source of gases are carefully selected.[94] Unfortunately, Si substrate itself cannot be directly utilized as a conductive substrate for CNT electrode because Si is an intrinsic semiconductor. Therefore, transfer technique of CNTs grown from Si substrate to the conducting foils can be utilized in order to prepare CNT electrode. Zhang et al. reported the fabrication of an aligned CNT electrode by a simple cut-paste method, by which the microstructure of the aligned CNT array would not be damaged. They used ferrocene–xylene CVD system to grow 800 μm vertically aligned CNTs on a silica substrate. Then, aligned CNT arrays were removed from the silica substrate with razor blade, and then pasted onto Ni foam current collector to obtain a CNT fur electrode. The CNT fur electrode obtained a C_{sp} of 14.1 F g^{-1} at current density 50 mA g^{-1} by using 7 M KOH as electrolyte.[95]

The same Zhang and co-workers also examined the electrochemical properties of a 500 μm aligned CNTs array electrode in an organic electrolyte by using same cut-paste method and exhibited the C_{sp} of 24.5 F g^{-1}. This result showed the improvement value of specific capacitance when using organic electrolyte compare previous work using aqueous electrolyte.[96] After one year, Zhang et al. fabricated aligned CNT electrode in ionic liquid at 60°C by using cut-paste method. Aligned CNTs on silica substrate was prepared by CVD as previously reported. For aligned CNT electrode preparation, a 1.0 mm high aligned CNTs were removed from substrate and paste on a Ni foil current collector. The C_{sp} calculated from the discharge slope measured at 0.05 A g^{-1} was 27 F g^{-1} which is higher than that achieved at aqueous and organic electrolyte.[97]

Meanwhile, Honda et al. fabricated EDLC by transfer procedure using printing technique a vertically aligned MWCNT sheet from a Si substrate to an aluminum (Al) sheet as a current collector. MWCNTs grown by CVD technique were transferred to Al sheet, and coated homogeneously with a slight amount of electrically conductive cement, phenolic glue containing 5 wt% graphitic carbon thickness to maintain their original vertical alignment even on the Al sheet. From this work, MWCNT sheet electrode provides a discharge capacity of 10–15 F g^{-1} of the aligned MWCNTs even at an extremely high current density at 200 A g^{-1}. Also, the fabricated EDLC also performed outstanding power density up to 125 kW kg^{-1} while maintaining a reasonable energy density of 2.2 Wh kg^{-1}.[98] The same Honda and co-worker also investigated several relationships among the specific capacitances of aligned MWCNT electrodes and their major properties by using same transfer methodology technique like previously work. They found that the rate capability of the aligned MWCNT is

outstanding 300–500 A g^{-1} irrespective of MWCNTs length. Moreover, CV at an extremely high scan rate of 50 V s^{-1} exhibited rapidly responsive charge–discharge currents without a significant distortion for either MWCNT electrode.[99] Furthermore, Honda et al. successfully prepared vertically aligned double-walled CNT (DWCNT) sheet by transfer technique from a Si substrate to an Al sheet as a current collector for application to a high-performance electrode for an EDLC. The vertically aligned DWCNT was grown using a thermal catalytic CVD technique. It was shown that C_{sp} of the DWCNT (44 F g^{-1}) electrode was four times larger than that of the MWCNT (10 F g^{-1}) electrode due to decrease in the wall layer number of CNTs enhances the capacitance.[100]

Lu et al. reported a new class of EC by utilizing transfer technique of vertically aligned CNT and ionic liquids was used as the electrolytes. Vertically aligned CNT arrays were grown by vacuum CVD on SiO$_2$ (silicon dioxide) / Si wafers. The CNT array was physically removed from the Si wafer using a commercially available double-sided conducting tape. A gold layer was deposited to the (upper) tips of the resultant CNT and used as current collector. Also, plasma etching was used in this work and played an important role in opening the end tips of CNT. The amorphous carbon layer that covers the CNT film can be properly removed without damaging the CNT. With the underlying gold layer, the resultant plasma-etched aligned CNT electrode can be used directly without the incorporation of an insulting polymer binder. The aligned CNT electrode showed butterfly shape of CV. They recorded that C_{sp} of aligned CNT electrode was found to be 440 F g^{-1} (1 V) at 5 mV s^{-1}.[25] On the other hand, Guittet et al. grew vertically aligned CNT using CVD in Si Substrate and then transfer the CNT onto copper foil tape as current collector in electrochemical cell and multiples parameter of CNT arrays were compared. They found that C_{sp} of the vertically aligned CNT electrodes of about 60 F g^{-1} in 1 M Et$_4$NBF$_4$-PC higher two or three times than that obtained with graphite electrode which is 20 F g^{-1}.[101]

(b) CNT: Direct growth technique.— Currently, direct growth technique of CNTs onto conducting substrate using catalytic CVD (CCVD) has becoming so effective and useful to fabricate the electrode for energy storage devices especially EC. This technique has the advantage of simplifying the electrode assembly and thus reduces the fabrication process. The metal alloy substrate/foil can directly act as a current collector and simplifies the conventional electrode assembly process which is typically associated with active materials composed of conductive and adhesive additive on the current collector. By this technique, binder material and conductive additive which could increase internal resistance and give adverse effect on capacitance performance is not incorporated in the device structure. Also, binder materials bring impurities into the electrodes and degrade electrochemical performance. Direct growth technique also gives better electrical contact between CNT and current collector.[13,102] Considering the connection of the CNT to the current collector, this technique is attractive due to the direct contact between CNT with current collector and exhibits one-step process. Current CNT growth methods require purification which results in the degradation of CNT and involve higher cost. To overcome this issue, direct growth technique is the best solution to reduce the cost and simultaneously produce high purity CNTs.

Chen et al. directly grew CNT on graphite foil using CVD. Ni catalyst particles were deposited on the graphite foil by magnetron sputtering and then CNT were grown in a pressure of 5–9 Torr maintained by flowing acetylene and nitrogen gases with a total flow rate of 110 sccm for 1 h at 660°C. The sample also treated in 15 wt% HNO$_3$ aqueous solution for 6 h to ensure that the CNT grew directly on the graphite foil. EDX was employed to examine the position of the Ni catalyst on as-grown and acid-treated. The result showed both before and after acid treatment, the Ni content is higher at the bottom area than at the tip area. CV measurement was done and the result of rectangular-shaped CV suggests that the CNT electrode is an excellent candidate for EDLC. The average C_{sp} can be obtained by integrating oxidation currents in the CV curve. The results of C_{sp} are as high
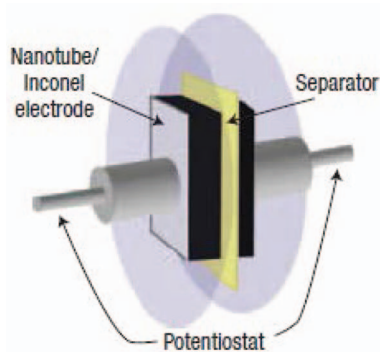
Figure 8. The experimental arrangement used to fabricate and measure the EDLC properties of the CNT–Inconel electrodes.[102]

as 115.7 F g^{-1} and 146.6 F g^{-1} at potential scan rates of 100 and 25 mV s^{-1}, respectively.[85] Talapatra et al. reported the direct growth of aligned CNT on a metallic alloy (Inconel 600) using vapor-phase catalyst delivery. They was used a ferrocene–xylene CVD system for the growth of vertically aligned CNT and obtained the value of C_{sp} for EC calculated from the discharge slope at 2 mA was found to be 18 F g^{-1} The experimental arrangement used to fabricate and measure the EC properties of the CNT-Inconel electrode is shown in Figure 8.[103]

Furthermore, Gao et al. *g*rew aligned CNT arrays with lengths up to 150 µm on Inconel 600 by pyrolysis of iron (II) phthalocyanine (FePc) in the presence of ethylene. The C_{sp}s recorded at 1 mVs^{-1} and 1,000 mVs^{-1} were 83 F g^{-1} and 47 F g^{-1}, respectively.[102] This indicates that the aligned CNT electrode for supercapacitor application has an excellent rate capability. On the other hand, Zhang et al. investigated electrochemical capacitive properties of CNT arrays directly grown on glassy carbon and tantalum (Ta) foils to fabricate supercapacitor electrodes. The CV curve showed rectangular shaped and C_{sp} obtained at 0.5 A g^{-1} of the CNT on glassy carbon and Ta are 27 and 28 F g^{-1}, respectively. Also, no obvious degradation was observed after the CNT electrodes were cycled for 10,000 times.[104] Shah et al. reported on the fabrication of EDLC electrodes with aligned CNT directly grew on Inconel using an air assisted CVD technique. The CV was rectangular in shape within a selected range of potential, suggesting that the integrated CNT-current collector systems have very rapid current response on voltage reversal with low ESR. The C_{sp} of the CNT used for EDLC electrodes increased with decreasing CNT lengths and ranged from 10.75 F g^{-1} to 21.57 F g^{-1}.[19]

Kavian et al. reported direct growth of MWCNT by using CVD on pure aluminum (Al) foils for preparation of supercapacitor electrode. CV analysis was performed on the CNT electrodes in an organic electrolyte and 1 M H_2SO_4 electrolyte at scan rate of 100, 50, and 20 mV s^{-1} resulting a high value of the C_{sp} about 54 F g^{-1} in aqueous electrolyte and 79 F g^{-1} in organic electrolyte.[105] Meanwhile, Kim et al. demonstrated vertically aligned CNT directly grew on Ta substrate via water assisted CVD and evaluated CNT properties for electrochemical capacitor applications. For electrochemical measurement, almost ideal rectangular CV shape was observed at the scan rate of ∼ 1 V s^{-1}, and specific capacitance was retained (94% retention) even at a high discharge current density of 145 A g^{-1}. Also, power density and C_{sp} estimated from CV curve are about 60 kW kg^{-1} and 13 F g^{-1} respectively.[87] At same year, Kim et al. grew vertically aligned CNT on stainless steel by water assisted CVD. Electrical measurement confirmed that the CNT were electrically connected to the stainless steel.[106] Kim et al. also fabricated high performance supercapacitor based on vertically aligned CNT and non aqueous electrolyte such as ionic liquid and conventional organic electrolyte. CNT were grown directly on carbon paper via CVD method. CV analysis showed the CNT based supercapacitor had excellent capacitive properties. According to Kim's work, C_{sp}, power density, and energy density of the supercapacitor measured in ionic liquid were 75 F g^{-1}, 987 kW kg^{-1}, and 27 Wh kg^{-1}, respectively. Both high power and energy density

could be attributed to the fast ion transport realized by the alignment on CNT and the wide operational voltage defined by the ionic liquid. Also, electrochemical oxidations of the CNTs have been improved the C_{sp} and energy density of about 158 F g^{-1} and 53 Wh kg^{-1}. This could be attributed to the fast ion transport through aligned structure of CNTs.[107]

Meanwhile, Azam et al. investigated direct growth of vertically-aligned SWCNT on conducting substrates using ethanol CVD to fabricate EC. Direct growth technique using alcohol CCVD (ACCVD) was employed to fabricate vertically aligned SWCNT electrode onto conducting SUS 310S foil in which binder material was not incorporated in the structure of EC.[108] Electrochemical analysis using KOH electrolyte was performed by using CV and galvanostatic charge-discharge measurements and obtained a maximum 52 F g^{-1} C_{sp}. Also, Azam et al. fabricated an EC that achieved very high C_{sp} of up to 584 F g^{-1} (at 1 mV s^{-1}) using ionic liquid as electrolyte.[13] During ACCVD, the lack of amorphous carbon was attributed to the OH$^-$ radical present in ethanol, which preferentially reacts with carbon molecules that have dangling bonds effectively etches away those carbon atoms that are most likely to produce amorphous carbon. Direct growth of SWCNT on pure metal, however, results in inevitable degradation of the foils, such as melting at the CVD growth temperature, thus, metal alloy foils are suitable use as conducting foil because of their durability under CVD conditions, and their corrosion resistivity, especially during high-applied potential electrochemical measurements.[109]

Important point of the review.—Carbon material being used as electrode, the fabrication technique, types of cell assembly, and findings of the performance of ECs are summarized in Table I. Figure 9 shows the process flow diagram for various electrode fabrication techniques. Most of the fabrication techniques undergone deposition or coating on conducting foil from slurry obtained by mixing the carbon materials with a binder and conductive materials. From one point of this review, Kalpana and co-workers were successfully obtained high C_{sp} of about 573 F g^{-1} using activated carbon as electrode material.[56] However, this technique leads to pulverization during charge discharge due to thickness and instability during coating process. Hence, small particles size of PASM may overcome this problem and achieved high specific capacitance.

Significant achievement of the C_{sp} was obtained through CNT direct growth technique. Azam et al. was successfully obtained highest C_{sp} of about 584 F g^{-1} by using direct growth of CNT onto conducting foil.[13] The capacitance performance achieved by Azam's work is almost similar to that of Kalpana work, but the fabrication technique simplifies the conventional electrode assembly by avoiding binder, reduces the process steps, which in theoretical can attribute to the optimum charge storage performance.

Application of EC (Current Market Availability, Potential Application, Future Prospective)

This section discusses several applications that uses EC as energy storage which reveal how charge/discharge time and cycle life differences affect the applicability of the technologies. EC are energy storage device with high power delivery and uptake and with an exceptional cycle life. They are used when high power demands are needed, such as for power buffer and power saving units and also of great interest for energy recovery. EC are many used in automotive engineering, railway traction, telecommunication systems, industrial, medical and consumer electronics.[1]

Currently, EC also used for energy management and conservation applications such as in seaport crane. One important function of EC in this application is to capture energy that would otherwise be wasted as heat in the repetitive up and down movement of heavy shipping containers. Also, EC allow a size reduction in the primary power source usually a diesel engine. EC are also applicable for hybrid electric vehicles such as metro trains and tramways. In this application, EC will allow store the energy obtained from regenerative braking and

Table I. Summary of carbon material based electrodes, the fabrication techniques, types of cell, and the electrochemical performances.

(a) ACTIVATED CARBON

Reference	Electrode preparation technique	EC cell assembly	Performance of EC

[55]	**Procedures:**
	• **Mixing** process (activated carbon powder (85 wt%) + graphite (10 wt%) + binder PVDF (5 wt%)) → **stirring** process → **pressing** process to form round electrodes (diameter = 10 mm, thickness = 0.2 mm).
		-EC component:
		• Electrode: **activated carbon**.
		• Conducting foil: **stainless steel**
		• Electrolyte: **Cu(II)-containing ionic liquid.**
		• Separator: **polypropylene**
		
		-EC cell assembly: in sequence as a sandwich and enveloped in a cell.
		
		-EC cell testing (Three-electrode cell):
		• Working electrode and counter electrode: two activated carbon electrodes (area =1 cm^2)
		• Reference electrode: SCE
			-CV testing:
			• Using pure [EMIm]BF$_4$ electrolyte:
			  ✓ CV curve: rectangular shape
			• Using [EMIm]BF$_4$/Cu(II) electrolyte:
			  ✓ Redox reaction of Cu(II) during charge/discharge process
			• Average specific gravimetric capacitance (C_{sp}):
			  ✓ [EMIm]BF$_4$ (**108 F g^{-1}**) and [EMIm]BF$_4$/Cu(II) (**225 F g^{-1}**)
			  ✓ Faradic pseudocapacitance-contribution to the total capacitance of EC.
			• Average C_{sp} decreased with current intensity increases
			  ✓ **225 F g^{-1} (1 mA cm^2)**
			  ✓ 210 F g^{-1} (2 mA cm^2)
			  ✓ 178 F g^{-1} (5mA cm^2)
			• High energy density using [EMIm]BF$_4$/Cu(II)
			  ✓ 45 Wh kg^{-1}
			
			- Galvanostatic charge/discharge testing:
			• Using pure [EMIm]BF$_4$
			  ✓ triangular shape-excellent capacitive properties
			• Using [EMIm]BF$_4$/Cu(II)
			  ✓ charge/discharge times are extended

[56]	**Procedures:**
	• **Mixing** process (activated carbon (70 wt%) + acetylene black (25 wt%) + N-methylpyrrolidine binder (5 wt%)) →**pressing** the mixture on a stainless-steel grid current-collector (geometrical area = 1 cm^2) → kept in an **oven** at 200°C for 30 min
	• The o-anisidine and metanilic acid copolymer were deposited on stainless-steel that was coated with activated carbon
		-EC component:
		• Electrode: **activated carbon + poly(o-anisidine-co-metanilic acid) (PASM)**
		• Conducting foil: **stainless steel**
		• Electrolyte: **1.0M H$_2$SO$_4$** that contained dissolved o-anisidine and metanilic acid in a 3:1 mole concentration of 0.1 M
		
		-EC cell assembly: A glass cell was fitted with a ground glass joint suitable for the introduction of the working electrode
		
		-EC cell testing (Three-electrode cell):
		• Working electrode: activated carbon + PASM
		• Counter electrode: Platinum foil
		• Reference electrode: SCE
			-CV testing:
			• Activated carbon electrode: rectangular shape CV curve without diffusion-controlled current peaks
			• PASM/SS: one redox peak
			• PASM/activated carbon: capacitive behaviour synchronizing both double-layer and redox reaction.
			  ✓ Combined effect of the double-layer and redox capacitive behaviour → capacitance is higher than the individual electrodes
			• C_{sp} at 5 mV s^{-1} **:**
			  ✓ **373F g^{-1}**
			• Power density
			  ✓ 0.22 kW kg^{-1}
			
			- Galvanostatic charge/discharge testing:
			• At 5 mA cm^{-2} current density over a potential window of 1V for up to 2000 cycles.
			• CV (PASM/AC) recorded at 2, 5, 10, 20, and 50 mV s^{-1} scan rates after 2000 cycles show acceptable reversible behaviour
			• Maximum C_{sp} at a 5 mA cm^{-2} current density:
			  ✓ **576 F g^{-1}**

[57]	**Procedures:**
	• **Mixing** process activated carbon (95 wt%) + carboxymethylcellulose and PTFE binder (5 wt%) → **drying** process → active material is **laminated** on each side of current collector (600 μm thickness electrode)
		-EC component:
		• Electrode: **activated carbon**
		• Conducting foil: **Nickel foam**
		• Electrolyte: **TEAMS 1M in 1.7M in acetonitrile and TEAMS 1M in propylene carbonate (PC)**
		• Separator: **polyethylene sheets**
		
		-EC cell assembly:
		  ✓ 4 cm^2 test cell with PTFE plates and stainless steel clamp → improve contact inside cell
		  ✓ Cell immersed in electrolyte and place in an argon filled sealed box.
			-Specific Cpacitance:
			  ✓ PICACTIF SC carbon give high C_{sp} (**125 F g^{-1}**)

Table I. (*Continued.*)

(b) CARBON AEROGEL

Reference	Electrode preparation technique	EC cell assembly	Performance of EC

[46]	**Procedures:**
	• **Mixing** process (carbon aerogel/graphite (9:1) + binder PTFE (5 wt %)) → **pressing** process to make disk like working electrode
		-EC component:
		• Electrode: **carbon aerogel**
		• Electrolyte: **6MKOH**
		
		- **EC cell testing** (Three-electrode cell)
			-CV Testing
			• C_{sp}
			  ✓ **110.06 F g^{-1}**
			• CV curve: rectangular shape (ions can occupy some pores within the electrode to participate in the formation EDLC).
			
			- **Galvanostatic charge/discharge testing:**
			• Specific capacitance C_{sp}
			  ✓ **25 Fg^{-1}**
			• Good cycling stability.

[62]	**Procedures:**
	• **Mixing** process (carbon aerogel + PVDF + carbon black)(weight ration 80:10:10 → N-methyl-pyrrolidone (NMP) to wet the mixture → **homogenized** in a mortar → rolled into thin film → **Punching** process (10mm circular electrodes were punched out and pressed onto nickel-foam under about 10 MPa for 30s).
		-EC component:
		• Electrode: **carbon aerogel**
		• Conducting foil: **Nickel foam**
		• Electrolyte: **6M H$_2$SO$_4$**
		• Separator: **polypropylene**
		
		-EC cell assembly:
		  ✓ Sandwich-type capacitors
		
		- **EC cell testing** (Three electrode cell)
			-CV testing
			• 5 mV s^{-1} (**147 F g^{-1}**)
			• Rectangular shape → idea capacitive behaviour
			
			-Charge discharge testing
			• Specific capacitance decreased when current density increased
			  ✓ 0.3 A g^{-1}(**152 F g^{-1}**) and 20 A g^{-1} (**101 F g^{-1}**)
			• Energy and power at 0.3 (A g^{-1})
			  ✓ Energy: 27.5 Wh kg^{-1}
			  ✓ Power:171 W kg^{-1}
			• Exhibit excellent cycle stability from the 1st to the 500th.

[63]	**Procedures:**
	• RF aerogels were heated to 300 °C using a heating rate (2°C min^{-1}) and held there for 2h,→ heated up to 800 °C by heating rates of 3°C min^{-1} and maintained for another 1h.
	• The volumetric/linear shrinkage upon pyrolysis was measured.
	• Synthesized carbon aerogels were cut into a disk of 1mm thickness, using a diamond saw.
	• After cleaning and drying, the carbon aerogel electrodes were activated at 450 °C in hot air environment for 1h to modify surface functionality and improve the affinity with the electrolyte.
		-EC component:
		• Electrode: **carbon aerogel**
		• Conducting foil: **graphite disk**
		• Electrolyte: **organic (1MEt$_4$NBF$_4$–AN)**
		• Separator: **polypropylene**
		
		-EC cell assembly:
		  ✓ The carbon aerogel electrodes were pressed by stainless steel screws to minimize contact resistance.
		  ✓ Cell assembly was placed in a Teflon cell
		
		- **EC cell testing** (Three electrode cell)
			-CV Testing
			• Specific capacitance C_{sp}
			  ✓ **220 F g^{-1}** ph 5.5 → activated at 450 °C in air for 1h.

(c) CARBON BLACK

Reference	Electrode preparation technique	EC cell assembly	Performance of EC
[64]	**2 Procedures:** 1. **Traditional coating** • Casting process of carbon black ink containing 2 wt % of solids on top of a 25 μm thick conductive vinyl current collector→The solids in ink + PTFE binder (10 wt %)(60 wt % PTFE dispersion in water) + of SC3 carbon black (90 wt %), which were ultrasonically dispersed in isopropyl alcohol solvent. 2. **Thin carbon black electrodes produced directly on separator membranes by inkjet printing** • One or both sides of membrane were deposited with carbon black electrodes of around 1 μm in thickness. Cellulose	**-EC component:** • Electrode: **carbon black** • Conducting foil: **conductive vinyl (traditional coating), expanded graphite (Cellulose separator), no current collector (PP)** • Electrolyte: **organic (1MEt$_4$NBF$_4$–AN)** • Separator: **cellulose, PP** **-EC cell assembly**: • Sandwiche 30 μm thick cellulose separator between two 1.35 cm in diameter carbon black electrodes and used KOH. • The utilized HS test cell was an alternative solution to assembling a supercapacitor in a coin cell.	**- CV Testing** • C_{sp} of the newly developed (SC3) carbon black ✓ **115 F g^{-1}**

Table I. (*Continued.*)

Reference	Electrode preparation technique	EC cell assembly	Performance of EC
	separator (30 μm thick) or polypropylene (PP) separator (25 μm thick) typical pore size of 0.21 μm by 0.05 μm) were used. • 2 to 4 wt % of SC3 carbon black were used. Carbon black was ultrasonically dispersed in NMP solvent + binder PVDF (4 wt %).		
[65]	**Procedures:** • **Mixing** process (carbon black + PTFE (10 wt %) mixed in ethanol to form a paste → **pressing** process onto nickel foil	**-EC component:** • Electrode: **carbon black** • Conducting foil: **Nickel foam** • Electrolyte: **2M KCl** • Separator: **cellulose, PP**	**-CV Testing** • Specific capacitance C_{sp} ✓ **33.58 F g^{-1}** • Good cycling performance

(d) GRAPHENE

Reference	Electrode preparation technique	EC cell assembly	Performance of EC
[68]	**Procedures:** • Graphene was synthesized by suspending graphene oxide sheets in water and then reducing them using hydrazine hydrate. During reduction, the individual "graphene" sheets agglomerate into particles approximately 15–25 μm in diameter. • **Mixing** process (CMG particles consisting of agglomerated graphene sheets + binder PTFE (3% by weight) 60% dispersion in H2O, Sigma Aldrich) → The mixture was **homogenized** in an agate mortar → **rolling** process (CMG/PTFE mixture into 75 μm thick sheets → **punching** process (1.6 cm diameter discs).	**-EC component:** • Electrode: **graphene** • Conducting foil: **conductive vinyl Film (aqueous), Al foil with conducting carbon coating (organic)** • Electrolyte: **aqueous electrolyte (5.5M KOH), two organic electrolyte systems (TEA BF$_4$ in acetonitrile (AN) solvent and TEA BF$_4$ in propylene carbonate (PC) solvent)** **-EC cell assembly:** • Cell assembly was supported in a test fixture consisting of two stainless steel plates fastened together using threaded bolts. • Spacers were placed between the SS plates to electrically isolate the plates, provide a hermetic seal, and maintain a consistent, even pressure on the cell.	**-CV testing:** • Specific capacitance C_{sp} ✓ **100 F g^{-1}** • Rectangular shape (good charge propagation within the electrode) • Graphene material works well with current commercial electrolytes, good electrical conductivity, has very promising charge storage capability. • Low variation of specific capacitance for increasing voltage scan rates → good charge propagation
[69]	**Procedures:** • **Mixing** process (graphene+binder PTFE (10 wt %). Two electrodes were separated by a thin polypropylene film in 30 wt % KOH → the mixture of graphene and PTEF was **homogenized** in water by being sonicated for 30 min, and then dried for 18 h at vacuum oven at 120 °C to make water completely evaporate.	**-EC component:** • Electrode: **graphene** • Conducting foil: **Nickel foam** • Electrolyte: **KOH** • Separator: **polypropylene** **-EC cell assembly:** • Electrodes pressed on a Ni foam current electrode → separated by a PP film → sandwiched in a stainless steel (SS) cell with a pressure.	**-CV testing** • Specific capacitance C_{sp} ✓ **205 F g^{-1}** **-Galvanostatic charge discharge testing:** • Good stability, lifetime and a very high degree of reversibility in the repetitive charge-discharge cycling.

[16]	**Procedures:**
	• The procedure for preparing graphene oxide (GO) powders was based on a modified Hummers' method.
	• The graphene nanosheet (GN) powders were synthesized by chemically reducing the resulting GO powders.
	• Both GO and GN powders were immersed into a liquid mixture, (composed of 5% Nafion (ionic conducting media, binder for adhesion between graphene and CP substrate) and 95% solvent (isopropyl alcohol + water) → forming the graphene slurry → An airbrush was used to spray the graphene slurry onto the CP substrate → GO/CP and GN/CP composite layers were then dried in an oven at 105 °C overnight.
		-EC component:
		• Electrode: **graphene**
		• Conducting foil: **Stainless steel**
		• Electrolyte: **1M H$_2$SO$_4$**
		
		-EC cell testing (three electrode cell):
		• Counter electrode: Pt wire
		• Reference electrode: Ag/AgCl
		• Working electrode: pressing the carbon paper onto the stainless steel foil as the current collector.
			-CV Testing:
			• **CV curve:**
			   ✓ Nafion/CP: no double layer current
			   ✓ GN/CP: minor double-layer current
			   ✓ GO/CP: improved double-layer current and an obvious pair of redox peak at 0.3–0.5 V.
			
			-Charge Discharge Testing:
			• C_{sp} at discharge current 1 mA
			   ✓ **219.7 Fg^{-1}** (GO/CP)
			   ✓ **18.1 F g^{-1}** (GN/CP)
			• C_{sp} at discharge current 5 mA
			   ✓ **158.2 F g^{-1}** (GO/CP)
			   ✓ **17.3 F g^{-1}** (GN/CP).

Table I. (*Continued.*)

Reference	Electrode preparation technique	EC cell assembly	Performance of EC
[70]	**Procedures:** • Synthesis of HCGS and TEGS 　✓ Thermal reduction of graphite oxide at 900°C followed by rapid cooling using liquid nitrogen. • **Mixing** process (HCGS+ carbon black+ PTFE) in a mass ratio of 75:20:5 and dispersed in ethanol→ **Coating** process (slurry was coated onto the nickel foam substrate with a spatula→ **drying** process at 100 °C for 12 h in a vacuum oven.	**-EC component:** • Electrode: **graphene** • Conducting foil: **Nickel foam** • Electrolyte: **6M KOH** **-EC cell testing:** • Working electrode: Ni foam coated with HCGS (TEGS) • Counter electrode: platinum foil • Reference electrode: Hg/HgO	**-CV Testing:** • Specific Capacitance C_{sp}: 　✓ HCGS = **349 F g^{-1}** 　✓ TEGS =**183 F g^{-1}** **-Charge discharge Testing:** • Specific Capacitance C_{sp}: 　✓ **227 F g^{-1}** at 1 Ag^{-1}
[71]	**Procedures:** • Graphene oxide (GO) was prepared from graphite flakes by the modified Hummers method. • Sheet-like PPy with a thickness of 20 −50 nm grown on the surface of the composites of the GNS/PPy polymerized at an early stage due to the dominated role of the sheet-like GNS and residue glucose in the synthesis process. • **Mixing process** (5 mg of active materials + 5 mg PVDF binder) → **Adding** 1 mL of absolute ethanol to the mixtures and sonicated for 1 h to obtain a homogeneous suspension→ 10 mL of the as prepared suspension was dropped onto the glassy carbon electrode→**Drying process** in an oven.	**-EC component:** • Electrode: **graphene/polypyrrole (GNS/PPy)** • Electrolyte: **1M H$_2$SO$_4$** **-EC cell testing (three electrode cell):** • Counter electrode: Pt wire • Reference electrode: SCE	**-CV Testing:** • Specific capacitance C_{sp} 　✓ 2 mV s^{-1} **(318.6 F g^{-1})** 　✓ The capacitance retained ~95% (132.9 F g^{-1}) after 1000 cycles at a scan rate of 100 mV s^{-1}

(e) CNTs (TRANSFER TECHNIQUE)

Reference	Electrode preparation technique	EC cell assembly	Performance of EC
[95]	**Procedures:** **1.CNT Growth** • Use ferrocene-xylene CVD system to grow VA-CNT array on a silica substrate. **2.Transfer technique to prepare electrode** • **Removed** an 800 μm long aligned CNT array from the silica substrate with a razor blade→ **cast** onto nickel foam (cleaned with distilled water before use) a graphite milk consisting 32 wt. % graphite, 55 wt. % ethanol, and 8 wt. % binder using a blade. The graphite milk on the nickel foam was 50 μmin thickness→ **pasted** the CNT array onto the nickel foam to prepare a CNT fur electrode→ **drying** process in an oven at 110°C for 2 h.	**-EC component:** • Electrode: **CNT** • Conducting foil: **Nickel foam** • Electrolyte: **7M KOH** **-EC testing(three electrode system):** • Reference electrode: Hg/HgO • Counter electrode: activated carbon	**-CV testing:** • Specific capacitance C_{sp} 　✓ **14.1 F g^{-1}** 　✓ Rectangular shape→ ideal capacitive behavior
[96]	**Procedures:** **1.CNT Growth** • Use ferrocene–xylene CVD system to grow VA-CNT array on a silica substrate. **2.Transfer technique to prepare electrode** • Removed a 500 μm aligned CNT array from the silica substrate with a razor blade. A layer of graphite milk (50 μm in thickness) was cast on to a nickel foil→ CNT was pasted onto nickel foil→ drying process in an oven at 120°C for 1h.	**-EC component:** • Electrode: **CNT** • Conducting foil: **Nickel foil** • Electrolyte: **1M Et4NPF6 in propylene carbonate** **-EC testing (three electrode system):** • Reference electrode: platinum • Counter electrode: activated carbon	**-CV testing:** • Specific capacitance C_{sp} 　✓ **24.5 F g^{-1}** 　✓ Rectangular shape • Further improvements in performance may be achieved by improving the paste technique or growing CNT directly on current collectors, such as Al and Cu foils.

Table I. (*Continued.*)

Reference	Electrode preparation technique	EC cell assembly	Performance of EC
[97]	**Procedures:** **1. CNT Growth** • Use ferrocene–xylene CVD system to grow VA-CNT array on a silica substrate. **2. Transfer technique to prepare electrode** • Removed a 1.0mm high aligned CNT from the substrate with a razor blade→ pasted on a nickel foil current collector by graphite milk→ drying process in an oven at 120 °C for 1 h.	**-EC component:** • Electrode: **CNT** • Conducting foil: **Nickel foil** • Electrolyte: **Ionic iquid** **-EC testing (three electrode system):** • Reference electrode: platinum • Counter electrode: activated carbon	**-CV testing:** • Specific capacitance C_{sp} ✓ **27 F g^{-1}**
[98]	**Procedures:** **1. CNT Growth** • A thin Fe-metal layer was deposited on a Si substrate using an electron beam, followed by heat treatment to form catalytic minute particles in a helium atmosphere. • MWCNTs were then grown on the particles in a CVD furnace, with acetylene acting as the carbonaceous source gas. **2. Transfer technique to prepare electrode** • Resulting VA-MWCNT was transferred to an Al current collector coated homogeneously with a slight amount of electrically conductive cement, phenolic glue containing 5 wt. % graphitic carbons to maintain their original vertical alignment even on the Al sheet. • The electrodes were dried at 150°C for 24 h under a reduced pressure before cell assembly.	**-EC component:** • Electrode: **CNT** • Conducting foil: **Aluminium sheets** • Electrolyte: **propylene carbonate (PC)** • Separator: **Cellulose** **-EC cell assembly:** • Coin-type cell made of stainless steel. The parts were fixed by a spring to add a constant load (ca. 5 kg) in the cell. • Packed cell in a thin envelope made of laminated Al films, which were sheets of Al foil coated with insulating polymer layers. **-EC testing (three electrode system):** • Reference electrode: platinum • Counter electrode: activated carbon	**-Galvanostatic charge discharge testing:** • no IR drop (internal resistance)→good high-rate performance • provided a discharge capacity of **12 F g^{-1}** even at an extremely cell provided a discharge capacity high current density of 200 A g^{-1} • Power=**125 kW kg^{-1}**, energy density= **2.2 Wh kg^{-1}**.

[99]	**Procedures:**
	
	1. CNT Growth
	• A thin Fe-metal layer was deposited on a Si substrate using an electron beam, followed by a heat-treatment to form catalytic minute particles in a helium atmosphere.
	• MWCNTs were then grown on the particles in a CVD furnace, with acetylene acting as the carbonaceous source gas
	2. Transfer technique to prepare electrode
	• The resulting VA-MWCNT forest was transferred to an Al current-collector sheet coated homogeneously with a slight amount of electrically conductive cement to also maintain its original vertical alignment on the Al sheet.
	• The electrodes were dried at 150°C for 24 h under a reduced pressure before cell assembly.
		-EC component:
		• Electrode: **CNT**
		• Conducting foil: **Aluminium sheets**
		• Electrolyte: **propylene carbonate (PC)**
		• Separator: **Cellulose**
		
		-EC cell assembly:
		• Coin-type cell made of stainless steel. The parts were fixed by a spring to add a constant load (ca. 5 kg) in the cell.
			-CV testing:
			• Specific capacitance C_{sp}
			    ✓ CNT 10 (**8.6 F g^{-1}**)
			    ✓ CNT 200 (**13.1 F g^{-1}**)
			
			-Galvanostatic charge discharge testing:
			• Neither of them showed any IR drop at the beginning of discharge, even at 10 A g^{-1}.

[100]	**Procedures:**
	
	1. CNT Growth
	• Vertically aligned DWCNTs were growth using thermal catalytic CVD technique.
	
	2. Transfer technique to prepare electrode
	• The resulting vertically aligned DWCNT was transferred to an Al current collector sheet coated homogeneously with a slight amount of electrically conductive cement (phenolic glue containing 5wt% graphitic carbon to maintain the original vertical alignment on the Al sheet.
		EC component:
		• Electrode: **CNT**
		• Conducting foil: **Aluminium sheets**
		• Electrolyte: **propylene carbonate (PC)**
		• Separator: **Cellulose**
		
		-EC cell assembly:
		• Coin-type cell made of stainless steel. The parts were fixed by a spring to add a constant load (ca. 5 kg) in the cell.
			-CV testing:
			• Specific capacitance C_{sp}
			    ✓ 31 F g^{-1} at 0V
			    ✓ **47 Fg^{-1}** at 2.5V
			
			-Galvanostatic charge discharge testing:
			• Capacitance for DWCNT (44 Fg^{-1}) is about four times larger than that for MWCNT (10 Fg^{-1}).
			    ✓ A decrease in the wall layer number of CNTs enhances the gravimetric capacitance.
			    ✓ Transfer methodology is highly beneficial for realizing extremely high rate capability of a DWCNT electrode.

Table I. (*Continued.*)

Reference	Electrode preparation technique	EC cell assembly	Performance of EC

[25]	**Procedures:**
	
	1. CNT Growth
	• Vertically aligned CNT arrays were growth by vacuum CVD on SiO2/Si wafers that were pre-deposited with 3-nm thick Fe catalysts.
	• The catalyst-coated substrates were inserted into a quartz tube furnace and remained at 450°C in air for 10min, followed by flowing a mixture gases of 48% Ar, 28% H2, and 24% C_2H_2 under 10–100 Torr at 750°C for 10–20 min to grow the aligned CNTs.
	
	2. Transfer technique to prepare electrode
	• A gold layer was deposited to the (upper) tips of the resultant CNT→CNT array was then physically removed from the silicon wafer using a commercially available double-sided conducting tape→ exposed side of CNT array was subjected to oxygen plasma etching → the amorphous carbon layer that covers the CNT film can be properly removed without damaging CNTs.
	• The resultant plasma etched ACNT electrodes can be used directly without the incorporation of an insulting polymer binder.
		-EC component:
		• Electrode: **CNT**
		• Conducting foil: **Aluminium sheets**
		• Electrolyte: **ionic liquid**
		• Separator: **PTFE membrane**
		
		-EC cell assembly:
		• Coin-type cell made of stainless steel. The parts were fixed by a spring to add a constant load (ca. 5 kg) in the cell.
		
		-EC testing (three electrode system):
		• Working electrode: **aligned CNT**
		• Auxiliary electrode: **platinum**
		• Quasi-reference electrode**: silver wire**
			-CV Testing:
			• Specific capacitance C_{sp}
			  ✓ **440 F g^{-1}**
			  ✓ high rate capability

[101]	**Procedures:** **1. CNT Growth** • CNT samples were grown using CVD on a silicon substrate with ethylene and hydrogen as the precursor gasses **2. Transfer technique to prepare electrode** • These samples were then transferred onto copper foil tape (current collector)	**-EC component:** • Electrode: **CNT** • Conducting foil: **Copper foil** • Electrolyte: **1M H$_2$SO$_4$, 6M KOH, Et$_4$NBF$_4$ in nonaqueous carbonate (PC).** • Separator: **PTFE membrane**	**-CV testing:** • Good rectangular and symmetric shape over a large range of scan rates. • Specific capacitance C_{sp} ✓ **60 F g^{-1}**

(f) CNTs (DIRECT GROWTH TECHNIQUE)

Reference	Electrode preparation technique	EC cell assembly	Performance of EC

[85]	**Procedures**
	• Nickel (Ni) catalyst was deposited on the graphite foil by magnetron sputtering.
	• CNTs were grown in a pressure of 5–9 Torr maintained by flowing acetylene and nitrogen gases with a total flow rate of 110 sccm for 1 h at 660°C
		-EC component:
		• Electrode: **CNT**
		• Conducting foil: **Graphite foil**
		• Electrolyte: **H$_2$SO$_4$**
		
		-EC testing (three electrode system):
		• Reference electrode: **SCE**
		• Counter electrode: **platinum**
			-CV Testing:
			• Specific capacitance C_{sp}
			  ✓ 115.7 F g^{-1} (100 mV s^{-1})
			  ✓ **146.6 F g^{-1}** (25 mV s^{-1})

[103]	**Procedures** • Used a ferrocene–xylene CVD system for the growth of VA-CNTs directly onto an Inconel 600 substrate. • A solution made by dissolving 1 g of ferrocene in 100 ml of xylene was injected into a preheated steel bottle (210°C) with a syringe pump. Constant pumping speed of 0.11 ml min^{-1} was maintained while injecting this solution into the bottle. An Ar/H^2 mixture (85% Ar) carried the xylene vapour containing the catalyst at 100 s.c.c.m. before entering the furnace. The furnace containing the Inconel substrates was maintained at 770°C.	EC component: • Electrode: **CNT** • Conducting foil: **Inconel 600**	**-CV Testing:** • Specific capacitance ✓ **18 F g^{-1}**

Table I. (*Continued.*)

Reference	Electrode preparation technique	EC cell assembly	Performance of EC

[102]	**Procedures:**
	• growth of aligned CNT on Inconel 600 substrates by pyrolysis of iron (II) phthalocyanine (FePc) in the presence of ethylene (C_2H_4)
	• Al_2O_3 film (20 nm) was sputtered onto the Inconel surface by the electron beam evaporation.
	• A quartz boat with about 100 mg FePc was placed in the region where the temperature was about 530–570°C→ Inconel 600 plate was put at the center area of the quartz tube as the substrate for the growth of CNT→ Mixture gas of Ar (300 cm^3 min^{-1}) and H_2 (40 cm^3 min^{-1}) was introduced to quartz tube→ C_2H_4 (50 cm^3 min^{-1}) was added when the temperature reached 800°C→ After 120 min, the quartz tube was naturally cooled down to room temperature→ taken out from quartz tube.
		-EC component:
		• Electrode: **CNT**
		• Conducting foil: **Inconel 600**
		• Electrolyte: **1M(Et)$_4$NBF$_4$ in propylene carbonate (PC)**
		• Separator: **Celgard-2400 polymer film**
		
		-EC cell assembly:
		• The cell was assembled in a glove box filled with Ar inert gas.
		
		-EC testing (three electrode system):
		• Reference electrode: **lithium metal plate**
		• Counter electrode: **activated carbon sheets**
			-CV Testing:
			• Specific capacitance C_{sp}
			  ✓ **47 F g^{-1}** (1000 mV s^{-1})
			  ✓ **83 F g^{-1}** (1 mV s^{-1})
			• After 1000 cycles→ only a slight decrease of specific capacitance can be observed→ excellent stability of the aligned CNT electrode.

[104]	**Procedures:**
	• GC and Ta foils were coated with 20 nm-thick Al_2O_3 buffer layers by e-beam evaporation (to enhance the CNTA growth efficiency).
	• CNTAs were growth in a 1 in. quartz tube furnace CVD system→ The substrates were put at the center of the quartz tube→ A mixture gas of 300 sccm Ar and 50 sccm H_2 was introduced into the quartz tube during heating→ When furnace had reached 800°C, a quartz boat with 100 mg iron (II) phthalocyanine was placed in the region where the temperature was about 550°C, and then 50 sccm C_2H_4 was added into the quartz tube→ After 2 h heating, CNT selectively grew in the direction normal to the substrate surface.
		-EC component:
		• Electrode: **CNT**
		• Conducting foil: **Glassy carbon (GC) and Tantalum foil (Ta)**
		• Electrolyte: **1M H_2SO_4**
		
		-EC testing (three electrode system):
		• Reference electrode: **saturated calomel electrode**
		• Counter electrode: **activated carbon sheets**
			-CV Testing:
			• Specific capacitance C_{sp}
			  ✓ CNT on GC (**27 F g^{-1}**)
			  ✓ CNT on Ta (**28 F g^{-1}**)
			• As current density rises to as high as 100 A g^{-1}, the capacity retention of CNTA electrodes is more than 50%→indicative of superior power performance.
			• No obvious degradation was observed after the CNT electrodes were cycled for 10,000 times,

[19]	**Procedures:**
	• Use WACVD for the growth of CNT
	• Furnace was heated to 790°C in an argon environment and a solution of ferrocene and xylene was continuously injected, vaporized, and blown (using Ar and H_2 (85%/15%) gas) into a quartz tube reactor containing the Inconel substrates. The flow rate of carrier gas was maintained at ~400 sccm.→ During the growth process, a small amount of air (~7.5 sccm) was mixed with the reaction environment to maintain the catalyst activity facilitating enhanced growth rate → The reaction time was controlled by adjusting the feeding time of the xylene/ferrocene solution→ The quartz tube reactor was cooled down to room temperature after growth time in the Ar environment.
		-EC component:
		• Electrode: **CNT**
		• Conducting foil: **Inconel 600**
		• Electrolyte: **6M KOH**
		• Separator: **Filter paper**
			-CV Testing:
			• Rectangular shape → the integrated CNT-current collector systems have very rapid current response on voltage reversal→ low equivalent ESR
			
			-Charge discharge testing:
			• Specific capacitance C_{sp}
			  ✓ 290 μm : **21.57 F g^{-1}**
			  ✓ 450 μm: **14.6 F g^{-1}**
			  ✓ 600 μm: **10.75 F g^{-1}**
			• Energy density: **2.3 to 5.4 Wh kg^{-1}**
			• Power density: **19.6 to 35.4 kW kg^{-1}**

[105]	**Procedures:**
	• MWCNTs were grown on the nickel-coated aluminium substrate by CVD
	• mixture of H_2/N_2 was fed to the reactor→ The furnace temperature was increased at approximately 15°C min^{-1} up to 600°C. → As the temperature was stabilized, the flow rate of the C_2H_2 reactant was adjusted to its value (100 cm^3 min^{-1}) and fed to the reactor together with the H_2/N_2 mixture for 10 min to grow MWCNT.
		-EC component:
		• Electrode: **CNT**
		• Conducting foil: **Aluminium foil**
		• Electrolyte: **1.0 M H_2SO_4 aqueous and an organic solution**
		• Separator: **Filter paper**
		
		- EC testing (three electrode system):
		• Reference electrode: **saturated calomel electrode**
		• Counter electrode: **A dimension stable anode (DSA)**
			-CV Testing:
			• Specific capacitance C_{sp}
			  ✓ Organic (**79 F g^{-1}**)
			  ✓ Aqueous (**54 F g^{-1}**)
			
			-Charge discharge testing:
			• In organic→ 2% decrease in the initial capacitance value after 500 cycles.
			• In aqueous→ 9% decrease in the initial capacitance after 500 cycles was recorded.

Table I. (*Continued.*)

Reference	Electrode preparation technique	EC cell assembly	Performance of EC
[87]	**Procedures:** • 10 nm of Al and 1 nm of Fe layer were deposited by e-beam evaporation. • The substrates were placed in the middle of quartz tube in a furnace→ While the furnace was heated, hydrogen (99.999%) and Ar (99.999%) were introduced at flow rates of 100 and 125 sccm, respectively→ Small amount of water vapor was introduced simultaneously by passing Ar through a DI-water bubbler at 0.75 sccm→ Once the temperature reached 800°C, ethylene started to flow at 50 sccm→ After typical 5 min of reaction time, the furnace was cooled down in the flow of Ar and samples were taken from the quartz tube near room temperature.	**EC component:** • Electrode: **CNT** • Conducting foil: **Tantalum foil** • Electrolyte**: H$_2$SO$_4$ aqueous and PC organic** **EC testing (three electrode system):** • Working electrode: **CNT onto Ta** • Reference electrode: **Ag/AgCl electrode** • Counter electrode: **platinum gauze**	**-CV Testing:** • Specific capacitance C_{sp} ✓ **13 F g^{-1}** **-Charge discharge testing:** • Only slight reduction of specific capacitance was observed, even when the current density was increased up to 145 A g^{-1}.
[106]	**Procedures:** • Growth of CNT on stainless steel (SS 304) by WACVD using an Al/Fe bimetallic catalyst. • 10-nm Al layer and a 1-nm Fe layer were deposited by e-beam evaporation→ substrates were placed in the middle of quartz tube→the tube was heated up to 800°C using a furnace in the flow of H$_2$ and Ar at 100 and 125 sccm, respectively→ Once the reaction temperature was reached, ethylene was introduced as a carbon source at the flow rate of 50 sccm→ small amount of water was introduced by flowing Ar through a bubbler at the rate of 0.75 sccm→ After growing CNTs for 20 min, the flow of ethylene and hydrogen was discontinued→ Argon flow through the water bubbler was stopped 5min later.→ the furnace was cooled down to room temperature in the flow of argon.	**-EC component:** • Electrode: **CNT** • Conducting foil: **Stainless steel (SS)** **-EC testing (three electrode system):** • Working electrode: **CNT onto SS** • Reference electrode: **Ag/AgCl electrode** • Counter electrode: **platinum mesh**	**-CV Testing:** • Presence of CNTs on the SS electrode→ improved the electrochemical properties such as redox current and electron transfer rate
[107]	**Procedures:** • Al layer (10 nm) was laid under the Fe layer to prevent the aggregation of Fe nanoparticles and to improve the adhesion between CNTs and CP. • Ethylene co-flowed with Ar and H$_2$ at a flow rate of 50, 125 and 100 sccm, respectively→ Introduced small amount of water vapour (increase catalyst lifetime)	**-EC Component:** • Electrode: **VA-CNT** • Electrolyte: **Ionic liquid and conventional organic** • Conducting foil: **Carbon Paper (CP)** • Separator: **PTFE** **-EC testing (three electrode system):** • Working electrode: **CNT** • Reference electrode: **3M Ag/AgCl** • Counter electrode: **platinum mesh**	**-CV testing:** • Specific capacitance C_{sp} ✓ ✓ Electrochemical oxidation CNT (158 F g^{-1})
[108]	**Procedures:** • Al (20 nm), and Co (0.5 nm), thin films deposited on the substrates by e-beam deposition. • Substrate transferred to CVD furnace and baked at 400 °C in static air for 10 min just before the CVD growth process. • Furnace evacuated using an oil-free scroll pump to around 0.1 Pa. Ar/H$_2$ (3% H$_2$) as the pretreatment gas injected (400Pa) concurrently with 4 min rapid heating process of the CVD furnace. • Ar/H$_2$ gas was continuously flowed for another 5 min annealing process→ mixed gas flow was stopped after the furnace temperature reached the TCVD of 750°C, and then ethanol vapor was immediately introduced into the furnace (flow rates110 – 130 sccm) → Internal pressure during CVD process was fixed to 3 kPa and 10 min	**-EC Component**: • Electrode Material: **VA-SWCNT** • Electrolyte: **6M KOH** • Substrate/Current Collector: **SUS 310S foil** • Separator**: 25-μm polypropylene**	**- CV testing:** • Specific capacitance C_{sp} ✓ **52 F g^{-1}** (5 mV s^{-1}) ✓ the device to have high rate capability, up to 500 mV s^{-1} **- Galvanostatic charge discharge testing** ✓ Capacitor operated at very rapid (less than 1s) charge-discharge performance

Table I. (*Continued.*)

| Reference	Electrode preparation technique	EC cell assembly	Performance of EC
[13]	**Procedures:** • Electron beam (EB-) deposited Al films (20 nm) were thermally oxidized (400°C, 10 min, static air), and Co (0.5 nm) as the catalyst. • Formation of Al–O: Deposited Al was first naturally oxidized at room temperature for 2 h. • The substrate was subsequently transferred to CVD furnace & baked at 400°C in static air for 10 min just before the CVD growth. • The furnace was then evacuated using an oil-free scroll pump to around 0.1 Pa. • Injected Ar/H_2 (3% H_2): 400 Pa, 4 min rapid heating process of the CVD furnace. • SWCNT growth: CVD parameter was fixed at 700°C, ethanol flow rates (100–130 sccm), 3 kPa pressure, and 10 min processing time.	**-EC Component**: • Electrode Material: **VA-SWCNT** • Electrolyte**: ionic liquid** • Substrate/Current Collector: **SUS 310S foil** • Separator: **25-μm polypropylene**	**-CV testing:** • Specific capacitance C_{sp} ✓ **584 F g^{-1}** (heat treatment) **-Charge discharge testing:** • At 50 Ag^{-1} current density, HT-SWCNT ECs were tested up to but not limited to 500 cycles→ only 12% capacitance loss
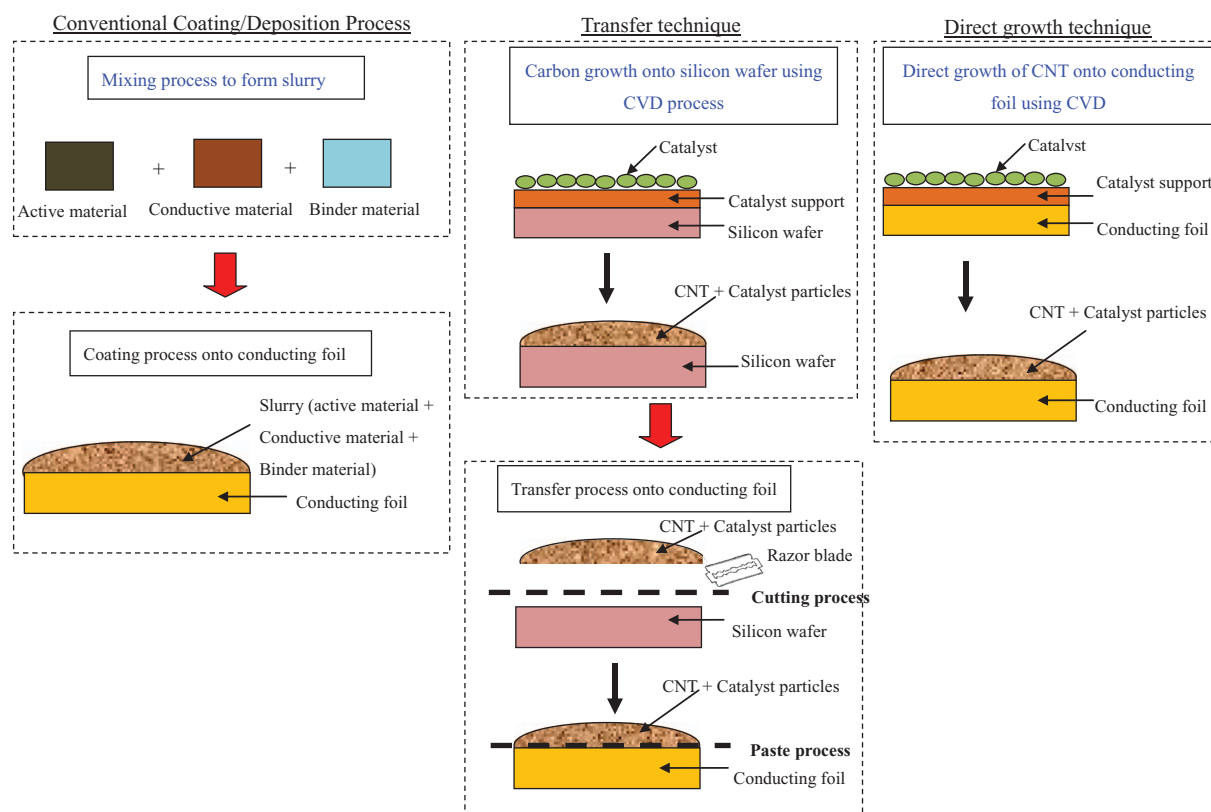
Figure 9. Schematic of process flow diagram for various electrode fabrication techniques.

this energy will be reused in the next acceleration phase and allow fast acceleration. For automotive applications, manufacturers are already proposing solutions for electrical power steering, where EC are used for load-leveling in stop-and-go traffic.[110]

The largest part of the EC sold nowadays are used in consumer electronic products, where they mainly serve as backup sources for memories, microcomputers, system boards, and clocks. In these applications there is a primary power source which normally supplies the load. In case of power outages due to disconnection or turn-off of the primary source, contact problems due to vibration or shocks, or a drop of the system voltage due to switching in of other heavy loads, the EC can supply the critical consumers. Hence, EC has the

strong capability to be used in many applications and technologies as key role in energy storage and harvesting, decreasing the total energy consumption and minimizing the use of hydrocarbon fuels.[7]

Summary

To conclude, there are various electrode fabrication techniques based on different types of carbon materials available for the development of electrochemical capacitors (ECs). However, it is important to note that the selection of materials and processing techniques to fabricate the EC will determine the performance of EC as energy

storage device. Carbon materials have been focused as a highly potential electrode material for EC due to their remarkable electrical charge storage ability. In this article, it was found that conventional technique; mixing the commercially available carbon material with conductive agent and binder material during the slurry preparation process is mostly selected. The binder materials used in the slurry could increase the internal resistance of EC and thus may negatively affect the electrochemical performance. Another approach of preparing the electrode is to synthesize carbon nanomaterial on Si wafer, and then the materials are transferred to conducting substrate by cutting and pasting (or printing) them onto conducting current collector, but again with the help of adhesive. To overcome this issue, direct growth technique of CNTs onto conducting foil has become an effective technique to simplify the electrode fabrication process, and importantly without the incorporation of binder and/or adhesive material. There are still many approaches from researchers trying to develop electrode fabrication technique that might enhance the EC performance from different aspects. Future research and development efforts to solve these matters are highly expected.

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