



Advancements in Conducting Polymer-Based Asymmetrical Supercapacitors: Binary and Ternary Composite Electrodes and Future Directions

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Abstract:

Due to their benefits including high capacitance and rate capability, extended cycle life, and cheap processing cost of supercapacitors, have been thought one of the most viable options for addressing the issue of human sustainability. Research on the Asymmetrical Supercapacitor electrode materials is important, since it has a significant impact on the efficiency and the life cycle. In supercapacitors, conducting polymer (CP)-based materials have a great potential due to their distinct benefits, such as strong conductivity, flexibility, affordability, ease of synthesis, and others. This article provides an overview of recent developments in the study of CPs, such as binary composites based on CP, and ternary composite electrodes based on CP for supercapacitors. We conclude by providing a brief overview of future development directions for CP-based supercapacitors. It is highlighted how effective electrochemical impedance spectroscopy is at determining system parameters. It is observed that there are still problems with conducting polymer-based supercapacitors.

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1). Introduction

The two most urgent problems with human sustainable development are environmental pollution and a lack of energy. The development of effective and affordable energy storage technologies, including appropriate methods for material synthesis and preparation, is essential. The search for clean, renewable energies and energy efficiency are workable solutions to these issues. Numerous types of useful and efficient energy storage devices, including batteries, fuel cells, electrochemical supercapacitors, and others, have been studied as a result of technical advancements [1]. Despite the fact that the first patent for a supercapacitor design was issued in 1957, it wasn't until the middle of the 2000s that people began to realize how beneficial this technology might be for hybrid vehicles [2]. Supercapacitors, often referred to as ultra-capacitors or electrochemical capacitors, have an exceptionally high

power density of absorption or delivery (10 kW/kg) and may be fully charged or discharged in a couple of seconds [3]. The power/energy gap between conventional dielectric capacitors with high power output and batteries with considerable energy storage capacity can be exactly closed by them [4,5]. Among energy storage technologies, supercapacitors hold the most promise [6].

1.1). Introduction of the supercapacitor mechanism

The qualities of a supercapacitor mostly depend on the electrodes, which are immersed in the electrolyte. Electrodes, electrolyte, and a separator are the component parts of a supercapacitor. Depending on the changes in the storing technique, supercapacitors can be divided into two groups: electrochemical double layer capacitors (EDLCs) and pseudocapacitors. The energy storage mechanism of EDLCs is based on the electrostatic interaction between ions on the enormous surface area of active electrode materials and electrolytes. The much quicker charge-discharge process used in EDLC systems can complete over 100,000 cycles in a couple of seconds. A compact Helmholtz layer, a diffusional layer in the electrolyte, as well as a space charge layer in the electrode make up an EDLC, which has a thickness of about 1 nm. An EDLC's performance is governed by the electrochemical activity and kinetic properties of the electrode, so creating a high-performance EDLC requires electrode material with a large specific surface area, lots of porosity, and thus the proper pore distribution. Largeot et al. [4] studied the relationship in between ion and pore sizes in an EDLC and found that the highest double-layer capacitance is only possible when the pore and ion sizes are very close. Carbon-based materials, including carbon nanotubes, activated carbons, and similar materials, are considered to make the best electrode materials for EDLCs due to their distinctive properties, which include regulatory wide surface areas, porous architectures, high conductivity, and other properties [7-9]. Supercapacitors often have larger capacitance per kilogram storage capacity than EDLCs, but their kinetics are lower



because energy is stored in the majority of the electrode materials and the surface of the electrode materials in a pseudocapacitor, but solely along the surface of the electrode materials in an EDLC [11]. Supercapacitor electrodes composed of conducting polymers (CPs) (Pani.PPy, Polythiophene, etc.) demonstrated how far technology has come in recent years. They emphasised how crucial it is to pay special attention to the design and synthesizing of composite materials[13]. Examined recent advances in polymer-based hybrid nanostructure films/arrays used as supercapacitor electrodes in the context of design and manufacturing, which are crucial for enhancing the performance of supercapacitors.

1.2). Supercapacitor performance of metrics for electrode materials

To study the electrochemical behaviours of the electrode active materials, researchers frequently utilise a three-electrode setup.

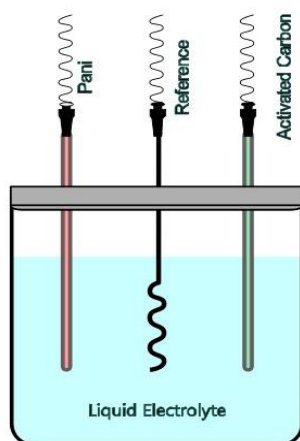


Fig. 1. Schematic of three-electrode configuration.

The schematic representation of a three-electrode setup in Fig. 3 shows the working electrode (WE), reference electrode (RE), counter electrode (CE), and electrolyte in that order. The working electrode can either have an active substance coating applied to it or be utilised plain. Saturated calomel electrodes and platinum electrodes are widely used as the reference electrode and counter electrode, respectively. Most electrolytes are composed of organic solvents and aqueous solutions. Because they are not likely to harm the environment when used as an electrolyte, aqueous solutions are chosen over used organic solvents. Supercapacitors' electrochemical capabilities are often assessed using galvanostatic charged discharge (GCD), cyclic voltammetry (CV). Researchers evaluate the electrochemical functionality of a supercapacitor using metrics generated from various methods, such as the

specific capacitance, cycle life, charge-discharge rate, etc. The specific capacitance can be calculated as from constant current charge-discharge curve using Eq. (1) [14]:

$$C = \frac{I \Delta t}{m \Delta V}, (1)$$

where m is the total mass of active materials, C is the specific capacitance, I is the charge current, t is the discharge period, and V is the potential window throughout the discharging process. All of the discharge current, active material mass, potential window, and discharge time parameters for the GCD method have an impact on the specific capacitance.

Fortunately, there are currently feasible synthesis techniques that have shown promising results. A polymeric stabiliser was used in order to provide a satiric effect on PANi chain formation and morphology modifications for the resultant PANi nanostructures useful for electrochemical applications [24]. PANi nanostructures' synthesis and properties (in combination improved and unadulterated forms) have been comprehensively studied in recent papers [22]. From careful observation, it is clear that the specific capacitance values of different PANi nanostructures depend on the synthesis techniques employed. However, it is difficult to link changes in the electrochemical behaviour of these nanostructures generally to characteristics like doping level, crystallinity, BET surface area, intrinsic oxidation state, and ordered mesoporosity. There are just a few study works that could independently resolve the aforementioned uncertainty (especially in terms of shape) in the contexts of polyaniline nanotubes and polyaniline nanofibers. We report a straightforward and effective one-step synthesis approach for PANi nanostructures, which are employed as working electrode materials in supercapacitors. The production of various PANi nanostructures, such as granular type PANi, PANi Nanifibers's, and PANi NanoTube's, is accomplished by making slight modifications to the conventional oxidative polymerization. The observed electrochemical properties of the three PANi nanostructures are described in terms of their , BET surface area, intrinsic oxidation state, crystallinity, doping concentration and ordered mesoporosity. The importance of this work is in the study between particular PANi granular capacitance values which were synthesised using the identical synthesis procedure, with the exception of very slight differences in the starting material concentration and reactant mixing. This study's production method makes it easier to create PANi nanostructures in liquid form as well.

2).Experimental procedure

2.1) Procedure for PANi Synthesis



Granules of green PANi were produced by chemical oxidative polymerization (COP) COP of aniline is historically used to make PANi. Rapid mixing polymerization involves great effort to maintain the reaction mixtures at low temperatures, frequently in the range of 0 to 4 C. PANi produced by this technique is heavily aggregated. Aniline solution was added drop by drop for an hour with an aqueous solution of 1 M HCl and ammonium peroxy disulfate (APS). The temperature of the reaction mixture was maintained between 0 and 4 C using an ice bath. The suspension was filtered to create a moist cake. The wet cake is then rinsed with water, methanol, and ultimately diethyl ether.

2.2) Supercapacitor active electrode material Characterization and testing

Cu K was employed as the x-ray source ($\lambda = 1.54$) for the XRD investigations, and Bruker's Model D8Advance System was used to record the X-ray diffraction (XRD) patterns with 2θ values from 10 to 60.

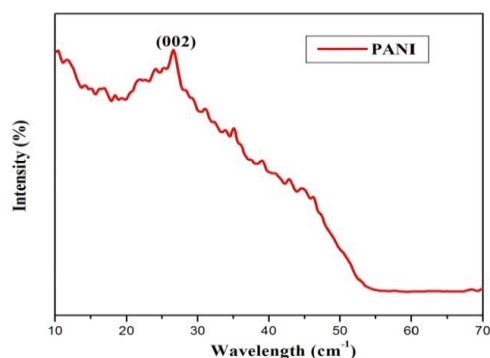


Figure 2. shows x-ray diffractograms spectra of granular PANi

The XRD peaks of pure PANi, APS, aniline, and PANi/APS composites made by doping during polymerization are shown in Figure 1. According to a review of the figure, the XRD pattern of PANi consists at 26.18 degrees of a broad band, a sharp peak of optimum efficiency at at about 19 degrees, and a sharp peak of second larger intensity at about 26 degrees. On PANi, there are a few other peaks with significantly lower intensities. The observed peak 2θ values are consistent with the JCPDS standard values (JCPDS No. 72-0634). PANi is seen in the XRD patterns of PANi-based composites. As the concentration of aniline and ASP in the composite rises, the band at roughly 19 degrees, which is the location of the unique peak of ASP, tends to dominate. The strength of this band increases as aniline and ASP concentrations rise in comparison to the band at about 26.18 degrees.

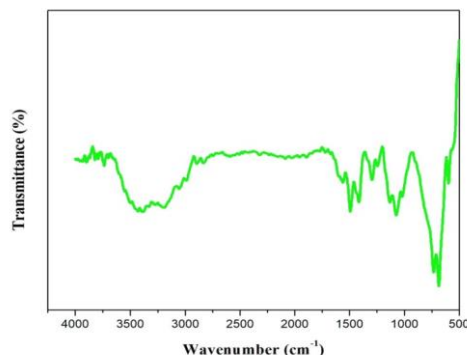


Figure 3. ECS-FTIR PANi's spectra

The ECS-FTIR PANi's spectra are shown in Figure 2. While the bands at 1588 and 1494 cm^{-1} are attributed to the ring stretching vibrations of quinoid (Q) and benzenoid (B), respectively, the bands at 1294 and 1136 cm^{-1} are created by the stretching vibrations of C-N-C and B-NH₁₄Q, respectively. The ratio of the areas of the peaks corresponding to the 1588 and 1494 cm^{-1} peaks can be used to determine the ratio of quinoid to benzenoid structure present in a PANi, which reflects the degree of oxidation of that PANi. The ECS-Q/B PANi's is 0.8. The electrode's capacity for additional aniline discharge and polyaniline deposition may decrease with continued aniline discharge and deposition.

2.3) Asymmetrical Supercapacitor Devices

ASCs typically consist of an electrolyte sandwiched between negative EDLC-based electrodes and positive pseudocapacitive electrodes. The arrangement of the two dissimilar electrodes with customised properties and geometries is of utmost importance and must be taken into serious consideration in order to create ASC devices that are light, durable, and dependable with remarkable functional qualities. Various device setups will be covered in the sections that follow.

2.4) Active material's thickness and electrode loading

Despite an increase in the active material film thickness on the electrode in an ECS, a significant decrease in specific capacitance has been routinely reported. This is mostly caused by the inefficient use of active materials in thick electrode films, which is closely related to the kinetics of ion transport in the film during charging-discharging cycles. It has been discovered that an increase in loading from 18.0 to 116.0 g/cm^2 is all that is necessary to cause a 55% reduction from the initial specific capacitance (330 F/g). By increasing the film thickness in proportion to the loading of active materials and figuring out the relationship between the loadings and the capacitance recorded, it is possible to optimise the electrode film thickness along with other

crucial characteristics, such as porosity and conductivity, to enable higher electrode specific capacitance. When the thickness of the film does not restrict the ion's kinetic movement, a compromise is considered to have been reached and is the optimal thickness.

2.5) Assembling and packaging of Asymmetrical Supercapacitors

Commercially, ECS are employed in packaged and assembled forms of single- or multiple-cell modules depending on applications like low voltage and high capacitance or high voltage and low capacitance. To reduce the losses in energy and power densities brought on by the usage of packaging and assembling materials, it is crucial to optimize the designs of construction and material selections for EC modules, where it obscures individual cells connected in series, parallel, or a combination of the two. ECs can be enclosed in a variety of ways. Thermal laminating is one patented technique. For generalized energy storage devices, various lamination packages are suggested, although they are not tailored for ECs. Additionally, attempts have been made to create multi-cell ECs by joining layer of bipolar electrodes that have been spirally wound, sandwiched with separators, and edge sealed in a spherical, oval, or square pattern. In addition to generating an average voltage of at least 5V, such a setup with bipolar electrodes could offer substantial surface areas for high capacitance. Over serial and/or parallel connections, it can serve as the building blocks in the creation of even bigger EC modules to address integrated high energy and power needs. Asymmetrical ECs with nickel hydroxide and nanoporous carbon acting as the positive and negative electrodes, respectively, in a potassium hydroxide electrolyte have been stated to be commercially available in particular. However, when using two distinct packages of cells as well as modules, quite considerable variances in energy and power losses are seen. Eliminating individual cell packages and connecting cells directly can both help reduce the module's weight and volume. In the case of symmetrical ECs, it has been shown that a bipolar electrode can be created by depositing active material sheets on both sides of the current collectors, resulting in a maximum specific energy of 1Wh/kg. Lighter and more highly conductive materials are preferred for current collector construction to reduce cell weight. These include foils made of materials like titanium and graphite. Although the total weight should be taken into account when building cells, there are additional considerations that must also be made

3). Results of Galvanostatic charge and discharge (GCD) and Cyclicvoltammogram (CV) for AC-PANi

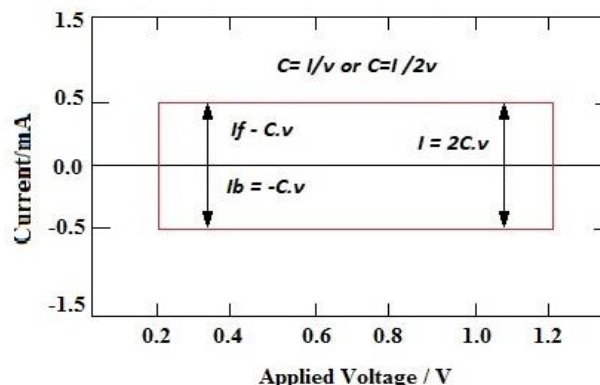
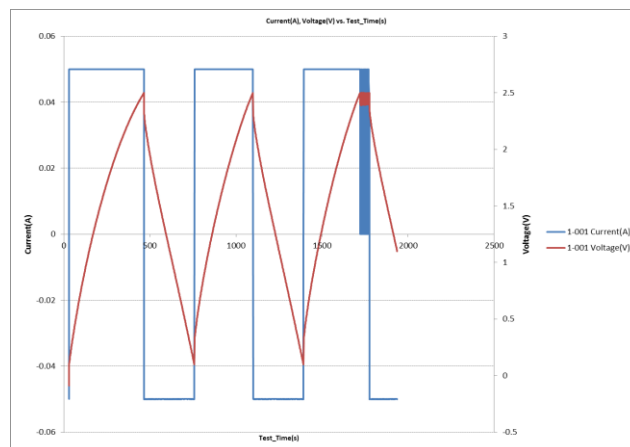


Figure. 4. (a) constant-current charge–discharge with time curve; (b) cyclicvoltammogram (response's rectangular component, eliding redox peaks);

As an electrode material for batteries or supercapacitors, polyaniline has received substantial research [11]. In Fig.4, the polyaniline structure is shown. With its high electroactivity, high doping level, high stability, and large specific capacitance (400–500 Fg⁻¹ in an acidic medium), polyaniline possesses several ideal qualities for usage in a supercapacitor device. In Addition, it is simple to produce, has excellent environmental stability, and has electrical conductivity that can be adjusted. According to reports, polyaniline has a capacitance range of 44 to 270 mAhg⁻¹. Of all conducting polymers, polyaniline possesses the most varying specific capacitance; electrodeposited polyaniline can achieve higher specific capacitance than chemically produced polyaniline. According to a study [24], polyaniline had a cycle life of more than 5000 cycles for a positive electrode doped with lithium, during which time the specific capacitance decreased from 100 to 70 F g⁻¹. A test with a constant current charge-discharge (0.5mAcm²) results in 380 F g, 18Whkg of specific energy, and 1.25kWkg of specific power (at 20mAcm²). A cycle-life of 4200 cycles was found using cyclic voltammetry. The gadget charges at



1.25 to 1.5 volts and discharges at 1.4 to 1.0 volts. Poly(*n*-methyl aniline) (Figure. 3e) is a modification that can be made to polyaniline to make it more stable [11]. The methyl groups of this polymer block the proton exchange sites, preventing the polymer from degrading chemically and increasing its redox activity. This conducting polymer can have a capacity of 52mAhg^{-1} when combined with such a lithium negative electrode.

3.1) Specific capacitances and equivalent circuit system

The existence of solution Warburg impedance (W), resistance (R_s), double layer capacitance (C_{dl}), charge transfer resistance (R_{ct}), and in relation to constant phase elements is a characteristic of the majority of the circuits (CPE). The Faradaic capacitance (CF), geometric capacitance (C_g), limiting capacitance (CL), and contact capacitance (CC) are all denoted by the capacitances. The Randles circuit [240], which is depicted in Fig.5, is an equivalent circuit made up of solution double layer capacitance (C_{dl}), resistance (R_s), Warburg impedance (W) and charge transfer resistance (R_{ct}). It is essential to emphasize this equivalent circuit before going into the analysis. In conjunction with other components, the Warburg impedance, which incorporates the diffusional properties of the electroactive species, has also been widely used in the domain of supercapacitors.

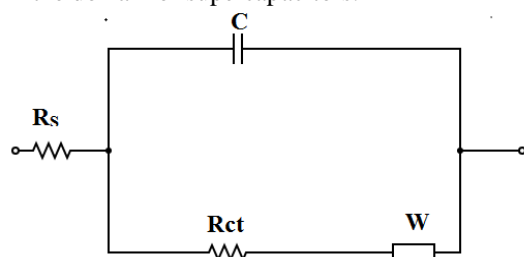


Figure. 5. Electrochemical systems equivalent circuit.

We see that the configuration of the electrode also affects the time constant; for microelectrodes, a τ increases with the radius. It has constants are preferred when designing supercapacitors to ensure quick charge-discharge characteristics. For just about any electrochemical system, there are two distinct methods for creating equivalent circuits: (i) fitting impedance data using the software that comes with the electrochemical workstation, and (ii) trying to formulate the actual and imaginary components of the impedance and performing non-linear regression analysis to use any computer programming language. The fit of the Nyquist data using the built-in program developed by that of the electrochemical workstation is shown in Fig. 13 as an illustration. However, if the fit is done using the right computer programme, there are several options accessible. The impedance equations created for a particular analogous

circuit provide us a better understanding of the role that each circuit parameter plays in understanding its influence

4). Conclusion

In conclusion, direct coating of CPs PANi was accomplished by employing an in situ polymerization technique when ethanol was present. This procedure offers a quick and effective way to create nanocomposites based on CPs. The conducting-polymer composites performed more capacitively well, according to the electrochemical characteristics. For instance, with a current density of 0.3 A/g , the specific capacitance of sample AC-PANi was found to be as high as 361 F/g . After 1000 cycles, the capacitive retention was 82%, which is significantly higher than that of pure PANi. The contributions of both EDL capacitance and pseudocapacitance, along with the composites' excellent electrical conductivity, are credited with the high capacitive performance of the AC conducting-polymer composites. This article reviews the development of PANi based electrochemical supercapacitors during the last ten years. Different procedures for electrochemical and chemical synthesis have been suggested. The emphasis is on the electrochemical characterisation of the polymers and their composites. There is a compilation of the precise capacitances calculated using various methods. It is highlighted how effective impedance studies are at determining system parameters from the fitting of comparable circuit data. It is suggested to model supercapacitors from the standpoint of electrical double layer theories.

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