Performance of phosphoric acid doped polyaniline as electrode material for aqueous redox supercapacitor

S Radhakrishnan, R Muthukannan, U Kamatchi, Chepuri R K Rao*† & M Vijayan
Functional Materials Division, CSIR-Central Electrochemical Research Institute, Karaikudi 630 006, India
Email: ramchepuri@gmail.com

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Phosphoric acid doped polyaniline has been synthesized chemically and electrochemically and tested for its specific capacitance properties by constructing a supercapacitor using stainless steel electrodes. Both the samples are characterized by UV-vis, FTIR, XRD and electrochemical methods. The electrochemically grown samples exhibit higher capacitance values in the range of 244-305 F/g. This is due to the higher purity of the electrochemically prepared polymer due to repeated cycling of the potential. Chemically prepared samples show lower capacitance values due to over-oxidation of the polymer and presence of impurities.

Keywords: Electrochemistry, Conducting polymers, Polymers, Electrode materials, Polyaniline, Specific capacitance, Charge-discharge, Cyclic voltammetry

Conducting polymers (CPs) have a special status in the field of electroactive materials, especially after the noble prize winning work by Shirakawa et al.1. A great deal of progress has been made on these synthetic metals in terms of their synthesis, processability, and device applications.2-4 Particular attention has been given to polyaniline (PAni) due to its environmental stability, thin-film–forming property with tunable conductivity and commercial viability. Polyanilines have been studied extensively due to their applications in practical devices for energy storage, electrochemical sensors, electrochromic devices, electromagnetic interference shielding, and corrosion protection.3-10 Application of the CPs in energy storage devices is also well known11 and recent studies12 in this area have given an impetus to fundamental and applied research on CP-based materials.

There is a growing demand for energy storage systems for portable electronics and electric vehicles which require high power in short duration. This has stirred a great interest in electrochemical capacitors, also known as supercapacitors. An electrochemical capacitor is a kind of charge storage device between traditional electrostatic capacitor and rechargeable battery which can be used for applications ranging from mobile electronic devices to hybrid electric vehicles because of its high power density, excellent reversibility and long cycle life. The electrode materials of electrochemical capacitors can be divided into three categories: (a) High surface area activated carbon (b) Noble/transition metal oxides such as RuO$_2$, MnO$_2$, and (c) Conducting polymers, such as PAni, PPy and PTh. Electrochemical capacitors based on transition metal oxides (TMO) exhibit much higher specific capacitance than conventional carbon materials. To date, amorphous-hydrated ruthenium oxide (RuO$_2$) is the most promising TMO candidate for supercapacitor electrodes owing to its high capacitance of over 700 F/g. However, the high cost of this noble metal oxide severely limits its scale up and commercialization. Due to this, conducting polymers, in particular polyaniline, have attracted a lot of attention.

Majority of the reports on supercapacitor studies on polyaniline are based on electrochemically deposited polyaniline directly on electrodes such as Pt, S.S, graphite and carbon paper. These electrode systems showed high specific capacitance of the order of 700-800 F/g due to their three dimensional nanofiber networks, porosity, thin layer formation and substrate effects. These favorable properties are effectively limited in chemically prepared polyaniline
samples, where the size of the particles is in the range of few micrometers. Moreover, chemically prepared samples are more prone to impurities than electrochemically prepared samples. Not many studies are available in literature reporting high capacitance, high power density and high energy density exhibited by chemically synthesized polyaniline or its composites.\textsuperscript{19-24}

In view of the above, the present investigation aims to study the supercapacitor properties of materials derived from polyaniline doped by phosphoric acid. For this purpose polyaniline doped by phosphoric acid was synthesized chemically and electrochemically. Supercapacitor devices consisting of polyaniline on SS electrodes were fabricated and tested for their electrical properties. The effect of surfactant, CTAB, on the properties of the capacitor was also studied. These results are presented and discussed here.

Materials and Methods

Aniline (CDH, AR), ammonium persulphate (APS) (CDH, AR), ammonia solution (Rankem, GR), cetyltrimethylammonium bromide (CTAB) (Ranbaxy, AR) and phosphoric acid (Rankem, AR) were locally purchased and used as such.

The FT-IR spectra of the polyaniline samples were taken on a Nexus-670 Thermo Nicolet spectrometer as KBr pellet. The UV spectra of the polyaniline samples were taken in the absorption mode on a Varian Carry 500 Scan NIR double beam spectrophotometer. The samples were dissolved in DMSO solvent. Cyclic voltammetry was carried out on Autolab 302 electrochemical system using a three electrode assembly consisting of a platinum foil (2 mm × 2.5 mm) working electrode, a glassy carbon rod (2 mm dia, 8 cm length) as auxiliary electrode and an SCE as reference electrode. Charge-discharge experiments were also conducted on Autolab 302 electrochemical system using a fabricated stainless steel (SS) composite electrode.

The symmetrical capacitor was subjected to charge-discharge tests from 0.0 to 0.75 V in 1 M phosphoric acid and the specific capacitance values were calculated from discharge times. For a symmetrical capacitor total capacitance is:

\[ T_C = \frac{SC}{2}, \text{ where } SC \]

\[ SC = 2 \times I \times t/\Delta E \times m \]

where \(I\) = current (in amperes), \(t\) = discharge time (in seconds), \(m\) = mass of the electroactive material on one electrode and \(\Delta E\) is the potential window scanned.

The electrical resistivity of the polyaniline samples was measured at room temperature on compressed pellet using the conventional four-probe technique. The instruments Keithley-2482 Nanovolmeter and Keithley-2482 Source meter were used for these studies. The polyaniline sample was pressed into pellets of 1 cm diameter at 3-ton pressure.

Synthesis of polyaniline

Two types of synthesis were performed, namely chemical and electrochemical synthesis, in the presence and absence of CTAB. The surfactant was added to control and keep the size of the particles small so that the surface area was higher and diffusion of counter ions is more facile. CTAB is a commonly used surfactant for obtaining small and more uniform sized conducting polymer materials like PAni and PPy. Hence, in the present study we have used this surfactant. Here CTAB is used as both surfactant and soft template as it possesses long chains. Due to its templating property, it restricts the growth of the PAni particles to nano-dimensions. The soft CTAB is easily removed by washing with water.

Chemical synthesis (CS) of polyaniline using phosphoric acid as dopant with CTAB [CS-PAni-PA-CTAB] and without CTAB [CS-PAni-PA]

The chemical polymerization was carried out in a 500 mL beaker containing 4 mL of aniline (43.01 mM) in 100 mL of 2 M phosphoric acid solution. APS solution (9.12 g, 40 mM, in 40 ml of 2 M phosphoric acid) was added dropwise for 30 minutes with effective mechanical stirring. The stirring was continued until complete addition of the oxidizing agent and continued for 5 hours. The green solution was filtered and washed thoroughly with water until the filtrate was colourless.

To improve the doping levels, the precipitate of polyaniline was transferred into a beaker containing 4 mL of aniline (43.01 mM) in 100 mL of 2 M phosphoric acid solution. APS solution (9.12 g, 40 mM, in 40 ml of 2 M phosphoric acid) was added dropwise for 30 minutes with effective mechanical stirring. The stirring was continued until complete addition of the oxidizing agent and continued for 5 hours. The green solution was filtered and washed thoroughly with water until the filtrate was colourless.

A similar procedure was adopted to synthesize PAni-PA-CTAB where 0.1 mM CTAB was added before polymerization commenced. The doping percentage in phosphoric doped polyaniline was about 38-40 %. This was confirmed by converting the
weighed amounts of conducting doped form [PAni.H⁺]H₂PO₄ into the EB form by neutralizing with NH₂OH (pH 9-10). The resultant blue material was dried and weighed. The difference in weights gave the basis for calculation of the doping level.

Electrochemical synthesis (ES) of polyaniline using phosphoric acid as the dopant with and without surfactant [ES-PAni-PA-CTAB] and [ES-PAni-PA]

Cyclic voltammetric method was used to deposit thin films of [ES-PAni-PA] by cycling the potential between -0.2 and 1.2 V at a scan rate of 100 mV/s. To study the effect of a surfactant, i.e., CTAB, polyaniline in presence of CTAB [ES-PAni-PA-CTAB] was also been synthesized in a similar method by adding 0.1 mM of CTAB in the mixture.

For the preparation of supercapacitor electrode, cleaned SS electrode (2 × 2 cm²) was used. PAni-PA and PAni-PA-CTAB film was deposited by cycling the potential between -0.2 to 0.8 V for 125 cycles. The loading of ES-PAni-PA-CTAB on the SS electrode is 3 mg/two electrodes.

Results and Discussion

Synthesis and characterization of polyanilines: Bulk and thin films

Polyaniline, doped by phosphoric acid (PAni-PA) has been synthesized and studied for the use as supercapacitor electrode material. The polymer has been synthesized according to known procedure in presence of 1 M phosphoric acid by oxidative polymerization of aniline monomer by ammonium persulphate as described in the experimental section.

The chemically prepared polymers were characterized by recording FTIR spectra as KBr discs (Fig. 1). The band at 802 cm⁻¹ indicates that there is a head-to-tail coupling in the polymers and is assigned to C-H₆op. The band at 1123 cm⁻¹ shown by the polyaniline samples is due to charge delocalization on the polymer backbone. The intensity of this band is significantly lowered in the dedoped EB (emeraldine base) spectra due to removal of the charges. Bands due to aromatic ring breathing mode are observed in the region 1600-1400 cm⁻¹. Band at 1482.8 cm⁻¹ is the characteristic band assigned to N-B-N and the band at 1571 cm⁻¹ is due to nitrogen quinoid (N=Q=N). The C-N stretching is observed between 1297.5 cm⁻¹. The aromatic C-H stretching is observed at 2923 cm⁻¹.

The chemically synthesized conducting polyanilines were studied by UV-vis spectroscopic technique in DMSO solvent in the 400-1000 nm wavelength region. In general, polyaniline doped with mineral acid such as HCl, shows bands at 326, 423 and 826 nm. The band at 326 nm is assigned to \( \pi \rightarrow \pi^* \) and bands at 423, 826 nm are assigned to polaronic excitations. In the present study, two bands are seen around 350 nm and 650 nm for CS-PAni-PA and CS-PAni-PA-CTAB. The bands at 348 nm and 610 nm are due the formation of polaron after doping reaction by PA. Thus UV-vis spectral studies show that the formed polymers are conducting and, partially doped. The study also shows that presence of CTAB did not influence the wavelength of absorption.

In general, the conductivity of conducting polymers depends on only one variable, viz., the extent of oxidation or reduction of the polymer. However, the conductivity of PAni depends upon two variables: (i) degree of oxidation, and, (ii) degree of protonation. The conductivity of the polyanilines was measured by four probe technique. The conductivity of CS-PAni-PA and CS-PAni-PA-CTAB prepared in the presence of aqueous solutions of 1 M PA and 1 M PA+CTAB respectively showed a conductivity of 16.99 S/cm and 1.69 S/cm respectively. The decrease in conductivity of CS-PAni-PA-CTAB as compared to that of CS-PAni-PA is due to the formation of low molecular weight polymers that would result in decrease in conjugation length in the latter.

The morphology of the PAni-PA and PAni-PA-CTAB has been studied by scanning electron microscope. The surface morphology of PAni-PA polymer at different magnifications has been shown in Fig. 2(a, b). The SEM images show that material is porous and the particles are larger than 10 µm. The observed morphology of CS-PAni-PA-CTAB as seen

![Fig. 1 – FT-IR spectra of the PAni-PA recorded as KBr pellets. [(a) electrochemically; (b) chemically prepared samples].](image-url)
by SEM images in Fig. 2(c, d) is different from that of CS-PAni-PA. The structure of CS-PAni-PA-CTAB consists of round globules of less than 1 µm. This is due to the presence of the surfactant, CTAB, which acts as a soft template to restrict the growth of polymer to nano dimensions. SEM images of the electrochemically grown PAni-PA samples on SS electrode are shown in Fig. 2(e & f). Careful scrutiny shows globular structure of the polymer.

Electrosynthesis of PAni-PA films
The electrochemical polymerization of aniline (5 mM) in 1 M aqueous solution of PA as an electrolyte was performed using cyclic potential sweep method by switching the potential between -0.2 V and +1.0 V at a scan rate of 50 mVs⁻¹ (Fig. 3a). In Fig. 3a the peak appearing at +0.97 V in the first cycle is ascribed to oxidation of aniline into anilinium cation. In the subsequent cycles, new peaks I and III appear at 0.193 V and 0.698 V respectively, which indicate that these radical cations formed at peak I undergo further couplings. The peak current increases continuously with successive potential scans, suggesting a build up of electroactive PAni on the electrode surface. In the forward cycle during growth, three peaks are observed at +0.193, +0.442 and at +0.698 V. Similarly, in the reverse cycle, three reduction peaks are observed at +0.589, +0.364 and

![SEM images](image-url)

Fig. 2 – SEM images of chemically grown samples (a and b) CS-PAni-PA, (c and d) CS-PAni-PA-CTAB, and, electrochemically grown sample (e and f) ES-PAni-PA.
-0.017 V. The CV peaks in both the forward and reverse cycles indicate the electroactive nature of PANi deposited on the electrode surface.

Figure 3b shows the cyclic voltammogram for ES-PAni-PA film on Pt electrode surface obtained by potential sweeping in an aqueous 1 M solution of PA as an electrolytic medium, without monomer at a scan rate of 50-300 mV/s. Three redox peaks (Table 1) at +0.195 V (peak I), +0.476 V (peak II) and +0.723 V (peak III) are observed. The radical cations at peak I, are subsequently oxidized into imines at peak III. The peak II is essentially due to adsorption of quinone/hydroquinone, generated during the growth of the polymer film on degradation of the radical cation which gets strongly adsorbed in the polymer matrix.

ES-PAni-PA-CTAB films synthesized on Pt electrode surface by the above procedure (Fig. 4(c, d)) also showed three redox peaks at +0.154 V (peak I), +0.432 V (peak II) and +0.674 V (peak III) (Table 1).

**Supercapacitor properties**

**Mechanism of doping, charging and discharging in polyaniline supercapacitors**

The doping process of PANi involves protonation of the imine nitrogens available on the quinoid segments, \(-N=Q=N-\), by phosphoric acid. The acid has three \(pK_a\) values of \(pK_{a1} = 2.15\), \(pK_{a2} = 6.85\) and \(pK_{a3} = 12.35\). Dissociation of the first proton is quite facile in the doping process. As the acid concentration is high [1 M], dissociation of the second proton from \(H_3PO_4^-\) does not take place as it is energetically less favorable. Instead, the needed second proton is taken from another \(H_3PO_4\) molecule. Hence, the following reaction takes place:

\[-N=Q=N-]+2H_3PO_4 \rightarrow [-HN^+\cdot=Q\cdot\cdot+\cdot\cdot+\cdot\cdot]\cdot[H_2PO_4^-] \uparrow\]

\[-HN^+\cdot\cdot\cdot+\cdot\cdot\cdot+\cdot\cdot\cdot][H_2PO_4^-] \downarrow\]

This fact is also evidenced in the FTIR spectrum. The band due to \(P=O\) from \(\cdot\cdot\cdot[\cdot\cdot\cdot][H_2PO_4^-] \cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\..
discharged state of a capacitor, PANi of both the positive and negative electrodes is in the ES form, and the capacitor voltage is close to 0 V. Upon charging the capacitor between 0 and 0.75 V, the positive electrode transforms from ES to PE state, whereas the negative electrode transforms from ES to LE state. Therefore, half the N atoms of the PANi allow insertion of H$_2$PO$_4^-$ ions in the positive electrode and a similar number of N atoms allow expulsion of H$_2$PO$_4^-$ ions from the negative electrode at a given time. Thus, the mechanism shown in Scheme 1 should operate in the device during the charging and discharging operations.

**Assembled capacitor**

Two capacitors were assembled by combining two SS electrodes on which either ES-PAni-PA or ES-PAni-PA-CTAB had deposited electrochemically with a fresh cotton cloth in between as separator. The devices were studied for their capacitance properties. The supercapacitor exhibited a specific capacitance of 244, 194, 172, 160 and 133 F/g at current densities of 1, 2, 3, 4 and 5 mA/cm$^2$ respectively. The capacitor was tested for 300 charge-discharge cycles to estimate the changes in the capacitance values and also the stability of the electrode material. Figure 5 shows the charge-discharge curves for the 1$^{st}$ and 300$^{th}$ cycles for the capacitor. The capacitor exhibited a capacitance of 244 F/g and 166 F/g at 1 mA/cm$^2$ (Fig. 6) in the 1$^{st}$ and 300$^{th}$ discharge cycles respectively. These values were reduced to 136 F/g and 122 F/g respectively for 1$^{st}$ and 300$^{th}$ cycles at 2 mA/cm$^2$ current density. The values further fall to 96 F/g at 3 mA/cm$^2$ (Fig. 6). The decrease of capacitance with cycle number is due to increase in the resistance values of the electrode materials after repeated doping-dedoping processes.

A capacitor was fabricated using two ES-PAni-PA-CTAB/SS electrodes and was studied for its electrical properties. Due to the smaller particle size of ES-PAni-PA-CTAB material, as compared to the pure ES-PAni-PA material, the capacitance values obtained in this case are found to be higher. The device exhibited capacitance values between 305 F/g and 248 F/g when current density was varied between 1 mA/cm$^2$ and 5 mA/cm$^2$ (Fig. 5). The stability of the electrode was tested by 300 charge-discharge cycles.
Repeated charge-discharge studies showed that the capacitor exhibited a specific capacitance of 305 F/g in the first cycle which declined to 197 F/g in the 300th cycle at 1 mA/cm² current density (Fig. 6). The capacitor showed a capacitance values of 289 F/g and 165 F/g at 2 mA/cm² and 3 mA/cm² respectively which declined to 160 F/g and 149 F/g respectively in the 300th cycle. Overall, the ES-PAni-PA-CTAB electrodeposited material capacitor showed about 20 % increase in its capacitance at 1 mA/cm². The increase in capacitance at 2 mA/cm² and 3 mA/cm² is 42 % and 52 % respectively. Comparison of performances of the ES-PAni-PA and ES-PAni-PA-CTAB materials in the supercapacitor is shown in Fig. 4.

The chemically prepared samples of CS-PAni-PA and CS-PAni-PA-CTAB were also checked for the charge-discharge properties. These samples showed lower values of SC, i.e., 108, 93, 81, 76 and 67 F/g at discharge current densities of 1, 2, 3, 4 and 5 mA/cm² respectively. The lower values are mainly due to the over-oxidation of polyaniline formed by the use of the strong oxidizing agent, APS. The chemically prepared samples were not purified and used as prepared. In general, the purity of the material, is also questionable in chemically synthesized samples as compared to electrochemically grown samples. Due to repeated cycles involved in electrochemically grown samples, the purity is high and hence showed high capacitance values.

![Fig. 5 – Charge-discharge test for 1st and 300th cycles at 1 mA cm⁻² for PAni-PA.](image)

![Fig. 6 – (a) Plots of specific capacitance versus current density. Plots of specific capacitance versus cyclic number at a current density of (b) 1 mA.cm⁻²; (c) 2 mA.cm⁻²; (d) 3 mA.cm⁻² for PAni-PA and PAni-PA-CTAB.](image)
Electrochemical impedance spectroscopy was employed to obtain equivalent circuit parameters such as the charge transfer resistance and ohmic resistance. Typical Nyquist diagrams for the device at 0.2 and 0.6 V in 1 M phosphoric acid are shown in Fig. 7. The impedance plots show a distorted semi-circle in the high-frequency region due to porosity of electrode and a vertically linear spike in the low-frequency region. The high frequency intercept of the semi-circle on the real axis provides the value of ohmic resistance ($R_{\text{ohm}}$) and the diameter of the semi-circle gives an approximate value of the ($R_{\text{ct}}$) of the PANI/electrolyte interface. The value of $R_{\text{ct}}$ increases with the applied voltage, which is deduced from the diameter of the semi-circle. The impedance data obtained after fitting is collected in Table 2 which is comparable to data available in literature\textsuperscript{15-18}.

**Table 2 – Circuit parameters obtained from curve fitting of the impedance plots**

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Solution resistance (ohm cm$^2$)</th>
<th>CPE, Y0 ($s^{-n}$cm$^2$)</th>
<th>Freq. power $0 &lt; n &lt; 1$</th>
<th>Electrode resistance (ohm cm$^2$)</th>
<th>Warburg ($s^{-\text{cm}^2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAni-PA-BC (0.2 V)</td>
<td>0.211</td>
<td>2.42×10\textsuperscript{-4}</td>
<td>0.99</td>
<td>3.0</td>
<td>0.126</td>
</tr>
<tr>
<td>PAni-PA-BC (0.6 V)</td>
<td>0.209</td>
<td>2.63×10\textsuperscript{-4}</td>
<td>0.89</td>
<td>17.99</td>
<td>0.106</td>
</tr>
<tr>
<td>PAni-PA-AC (0.2 V)</td>
<td>0.182</td>
<td>3.56×10\textsuperscript{-4}</td>
<td>0.89</td>
<td>3.952</td>
<td>0.106</td>
</tr>
<tr>
<td>PAni-PA-AC (0.6 V)</td>
<td>0.199</td>
<td>2.79×10\textsuperscript{-4}</td>
<td>0.89</td>
<td>20.34</td>
<td>0.088</td>
</tr>
</tbody>
</table>

AC = after cycling; BC = before cycling

**Conclusions**

Chemically and electrochemically synthesized polyaniline doped by phosphoric acids materials were studied for their supercapacitance properties by fabricating a device. The present study shows that chemically prepared CS-PAni-PA and CS-PAni-PA-CTAB exhibit lower capacitance values due to over-oxidation of the polymer and presence of impurities. Electrochemically grown samples exhibited higher capacitance values as compared to...
the chemically synthesized samples. This is due to the higher purity of the polymer formed due to repeated cycling of the potential between -0.2 and 1 V. Among the electrochemically fabricated devices, the supercapacitor with CTAB (i.e., with ES-PAni-PA-CTAB electrode material) shows higher capacitance values, as compared to the ES-PAni-PA capacitor, due to smaller particle size in the former. Due to lower size particles, the surface area is higher and porous.

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