PCCP



View Article Online

PAPER



Cite this: Phys. Chem. Chem. Phys., 2015, 17, 878

Received 25th September 2014, Accepted 5th November 2014

DOI: 10.1039/c4cp04321a

www.rsc.org/pccp

1. Introduction

Supercapacitors have been regarded as one of the most promising sources for automotive and portable system applications due to high power density, fast charge–discharge rate and long life cycle.¹ A wide range of metal oxides (Ni, Fe, In, Co, Ru, Mn, *etc.*), conducting polymers (polyaniline, polypyrrole, *etc.*) and carbonaceous materials (graphene, single wall carbon nanotubes, multi-wall carbon nanotubes, *etc.*) are used for supercapacitor applications.^{2–6} The enhanced redox capability of conducting polymers and metal oxides makes them more suitable for redox capacitor (or pseudocapacitor) applications while the charge storage capability of carbonaceous materials at the electrode-electrolyte interface makes them suitable candidates for electrochemical double layer capacitor (EDLC) applications. In general, the commercially available EDLCs are made of electrically conductive activated carbon with a specific capacitance in the

Elucidating the effect of copper as a redox additive and dopant on the performance of a PANI based supercapacitor[†]

Kavita Pandey, Pankaj Yadav and Indrajit Mukhopadhyay*

In this article, the effect of copper (Cu) as a redox additive and dopant on the performance of a polyaniline (PANI) based supercapacitor was thoroughly investigated. The electrochemical properties of PANI in H₂SO₄ and in H₂SO₄ + CuSO₄ and Cu doped PANI in H₂SO₄ were studied using cyclic voltammetry (CV) and impedance spectroscopy (IS). The CV result indicates that the capacity of PANI in H₂SO₄ was significantly improved with the introduction of Cu2+ ions into the electrolyte, but it appeared unstable because of underpotential deposition of copper over the PANI surface and the relatively irreversible nature of the redox reaction. However, a stable and improved performance was obtained for Cu doped PANI due to the combined effect of an increase in conductivity and the surface modification of the PANI film. For Cu doped PANI, nearly \sim 2.4 and \sim 1.5 fold improved interfacial capacitance was achieved compared to that of PANI (H_2SO_4) and PANI $(H_2SO_4 + CuSO_4)$ respectively. The obtained Nyquist spectra for all the configurations were analysed using an equivalent circuit to understand the fundamentals of capacitive and resistive response of the supercapacitor. The IS measurements lead to direct determination of parameters like series resistance, rate capability of electrodes, ion diffusion phenomena and interfacial capacitance. The experimental results and their analysis will have significant impact on understanding the effect of dopants and redox additives on the performance of PANI based supercapacitors and also lay the basis for designing a supercapacitor with an appropriate electrode and electrolyte material for numerous industrial and consumer applications.

> range of 80–110 F g^{-1} (40–70 F cm⁻³) for organic electrolytes and 100-160 F g^{-1} (40-70 F cm⁻³) for aqueous electrolytes.⁷ For pseudocapacitor applications, polyaniline (PANI), a conducting polymer, is a material of great interest because of its environmental stability, low cost, easy doping-dedoping, a good reversibility and electro activity.^{8,9} The metal oxides of Ru and Mn are also widely employed for pseudocapacitor applications. Zheng et al.⁵ have employed the hydrous form of ruthenium oxide for electrochemical capacitors. Lee et al.6 have demonstrated a capacitance of 700 F g^{-1} and 200 F g^{-1} for amorphous, hydrated RuO₂ and MnO₂ electrodes respectively. The synthesis of PANI with various carbonaceous materials and metal oxides to develop an economical electrode material with higher capacity is of great interest. Chen et al.10 obtained a remarkable energy density of 84 W h kg⁻¹ for PANI nanotubes grown by utilizing MnO₂ templates. Maser et al.11 demonstrated an order of magnitude increase in the electrical conductivity of the carbon nanotube-PANI composite as compared to pure PANI. Tai et al.¹² fabricated a 3D graphene-PANI composite hydrogel via a self-assembled method which showed a supercapacitive performance of 334 F g^{-1} . Mi et al.13 synthesized a nano fiber structured PANI electrode for supercapacitor application, which showed a specific capacitance of 428 F g⁻¹ in H₂SO₄ electrolyte. Meng et al.¹⁴ demonstrated a

School of Solar Energy, Pandit Deendayal Petroleum University, Gandhinagar - 382007, Gujarat, India. E-mail: indrajit.m@sse.pdpu.ac.in; Fax: +91-79-23275030;

Tel: +91-9586864936

 $[\]dagger$ Electronic supplementary information (ESI) available. See DOI: 10.1039/ c4cp04321a

novel method to prepare paper like CNT–PANI composites which showed a superior electrochemical performance such as higher specific capacitance, lower internal resistivity, and more stability under different current loads.

The capacitive performance of supercapacitors is also being improved by doping the electrode material with different kinds of transition metals or by adding redox active species into the electrolyte. The concept of doping was first introduced for iridium doped PANI by Hu et al.¹⁵ for electrochemical capacitor applications. They have also showed an enhancement in stability, high power performance and electrochemical reversibility of redox reactions by adding platinum nanoparticles in the PANI matrix.16 Khan et al.¹⁷ have proposed that PANI doped with CuO results in nanofiber like morphology with high conductivity. Xu et al.18 have polymerized PANI with Cu2+ ions and used it as an electrode material in supercapacitors which demonstrated a specific capacity of 618 F g⁻¹. Dhibar et al.¹⁹ have polymerized PANI with different doping levels of CuCl₂, which showed a higher specific capacitance and better thermal stability. The use of redox active sources (hydroquinone, KI, CuSO₄ and so on) with conventional electrolytes (H₂SO₄, KOH, KCl, etc.) is directly involved in the electron transfer redox reaction where the capacitance is enhanced due to the surface pseudocapacitive contribution at the electrode-electrolyte interface. Li *et al.*²⁰ have obtained a specific capacity of 223 mA h g^{-1} for redox mediator Fe²⁺ and Cu²⁺ added H₂SO₄ electrolytes. Very recently, Qian et al.²¹ have studied CuS nanotubes in a redox active polyelectrolyte (0.5 M NaOH/0.5 M Na2SO4/0.5 M S powder) and obtained a specific capacitance of 2393 F g^{-1} at 10 mV s^{-1} with an energy density of 592 W h kg⁻¹ at 15 A g⁻¹. Chen *et al.*²² reported a specific capacitance of 553 F g^{-1} and 288 F g^{-1} in hydroquinone added H₂SO₄ and 1 M H₂SO₄ electrolytes, respectively, for the PANI-graphene composite.

Recently, some primary work has been reported on the performance of Cu doped PANI by varying the doping level. However, in the literature there is scarcity of reports concerning the role of transition metals as dopants or redox additives which is essential for designing high power/high energy supercapacitors. In the present work, the electrochemical characteristics and pseudocapacitive effects of Cu²⁺ as a redox additive in electrolytes or a dopant in PANI nanostructure have been investigated. Under the configuration of PANI in 1 M H₂SO₄, PANI in 1 M H₂SO₄ + 0.5 M CuSO₄ and Cu doped PANI in 1 M H_2SO_4 , the present study is mainly focused on (i) elucidating the effect of Cu²⁺ as a redox additive and dopant on the performance of supercapacitors, (ii) studying the influence of redox active electrolytes and doping on the charge transfer phenomenon at the electrode-electrolyte interface and (iii) complex frequency analysis of supercapacitors which is necessary for practical applications. Herein it is observed that CuSO4 as a redox additive offers a higher energy storage with a low power delivering rate while PANI in H₂SO₄ offers a lower capacitance with a high power delivering rate. Interestingly, the Cu doped PANI nanostructure enhances both the energy storage and capacitance retention. Moreover, the obtained result proposes that Cu doped PANI holds promise for devising a high performance electrochemical capacitor.

2. Experimental section

Preparation and characterization of electrodes

The PANI electrodes were prepared from the aniline solution as follows. The monomer solution of aniline purified by double distillation and stored in a nitrogen glove box was prepared in MilliQ water using analytical grade hydrochloric acid (HCl). The electropolymerization was conducted in a one compartment three electrode cell containing a mixture of 2% aniline in 1 M aqueous HCl at room temperature. A fluorine doped glass substrate having a sheet resistance of $\sim 12 \Omega$ \Box^{-1} was used as a working electrode with Ag/AgCl and Pt ring as the reference and counter electrode respectively. The fluorine doped glass substrate was ultrasonically washed with acetone, ethanol and distilled water each for 15 minutes respectively. The cell and counter electrodes were cleaned with freshly prepared $1:1 H_2O_2/$ H₂SO₄ solution followed by ultrasonication in MilliQ water. The same electropolymerization method was employed to deposit copper doped PANI films from the monomer solution containing a mixture of 2% aniline in 1 M HCl and 0.5 M CuSO₄·5H₂O. After each deposition, the remaining electrolyte was soaked from the electrode surface with filter paper and kept for drying.

The surface morphology of all the samples was characterized using a Carl Zeiss scanning electron microscope under ultrahigh vacuum conditions. The samples were placed on circular adhesive carbon films to be affixed to aluminium sample stubs. The FTIR spectra were recorded on a Nikolet 6700. The Raman spectra and XPS were employed to understand the chemical difference between PANI and Cu–PANI.

Electrochemical studies of electrodes

The electrochemical properties of electrode in three different configurations were studied by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) using Ag/AgCl (saturated KCl) and Pt ring as the reference and counter electrode respectively. PANI as a working electrode was examined in 1 M H₂SO₄ and 1 M H₂SO₄ mixed with a 0.5 M CuSO₄ redox active electrolyte which will be further referred to as PANI (H_2SO_4) and PANI $(H_2SO_4 + CuSO_4)$, respectively, in the article. To study the effect of doping on the supercapacitive properties, the Cu doped PANI electrode was examined in 1 M H₂SO₄, referred to as Cu-PANI (H₂SO₄) hereafter. The electrochemical properties of all the configurations were studied through CV within the potential window of 0 to 0.7 V at different scan rates. Moreover, the cycle life of the electrode was tested for 1000 cycles. EIS was carried out at an open circuit potential (OCP) and at different applied potentials by applying a perturbation signal of 10 mV amplitude in the frequency range of 0.1 Hz to 100 kHz. Only after the OCP of the system was stabilized, the electrochemical measurements were carried out at room temperature by using a CH Instrument 660D potentiostat equipped with general purpose electrochemical system software. The interfacial capacitance of the electrodes was calculated by using the equation

$$C = \frac{I\Delta t}{A\Delta V} \tag{1}$$

where I is the discharge current, A is the area of the electrode, Δt is the discharge time and ΔV is the potential range. The real part (C') of the complex capacitance can be extracted from the impedance data according to the equation

$$C'(\omega) = \frac{-Z''(\omega)}{\omega |Z(\omega)|^2}$$
(2)

where $Z''(\omega)$ is the imaginary part of the complex impedance $Z(\omega)$ and ω is the angular frequency. The value of $C'(\omega)$ obtained at low frequency can be used as the static capacitance of the electrode.23

3. Results and discussion

Optical analysis

Fig. 1A depicts the FTIR spectra of PANI and Cu-PANI. The obtained spectra for both the electrodes are essentially the same with some peak shifting indicating the dominance of chain protonation reaction. The common peaks situated at 790, 1130, 1220, 1265 and 1640 cm⁻¹ for both the electrodes are attributed to the following vibrations: out of plane bending vibration of C-H in the π disubstituted benzene ring, C-H bending of the quinoid ring, stretching vibration of the CN^{•+} in the polaron structure of PANI, stretching of C-N secondary aromatic amine and stretching vibration of C=N respectively.²⁴ The red shift of the two absorption peaks from 1568 to 1562 cm^{-1} and 1475 to 1457 cm⁻¹ in Cu-PANI is referred to be a signature of the conversion of quinoid rings to benzenoid rings by a proton induced spin unpairing mechanism.²⁴ This mechanism is considered to be an indication of the increase in the degree of charge delocalization on the PANI backbone due to protonation.²⁵

The Raman spectra of PANI and Cu-PANI at 1064 nm excitation signal are shown in Fig. 1B. For PANI, the peaks observed at 1164, 1210, 1486 and 1586 cm⁻¹ correspond to C-H bending of the quinoid ring, C-H bending of the benzenoid

ring, C=C stretching of the quinoid ring and stretching of the benzenoid ring respectively.²⁴ As compared to the spectra of pure PANI, the C–N^{•+} stretching peak gradually shifts to higher wavenumber from 1341 to 1394 cm⁻¹. Also, the most characteristic Raman band of the radical cation is observed at 1336 cm⁻¹ for Cu-PANI. This typical band is expected when the quinoid rings are converted to benzenoid rings. A similar conclusion for Cu-PANI is drawn from the FTIR analysis. Another change is the 1486 cm^{-1} band assigned to the stretching of the quinoid di-imine units diminishing in Cu-PANI, which indicates the decrease in the amount of quinoid units in the polymer chain due to the doping process.²⁶

PANI and Cu-PANI films were subjected to XPS examination for the confirmation of formation of Cu⁺ within the Cu-PANI matrix. The C 1s core level spectra for PANI and Cu-PANI are given in Fig. S1 of ESI.[†] The Cu 2p core level spectra for Cu-PANI are shown in Fig. 2. The C 1s spectrum for both the electrodes exhibits an asymmetric characteristic indicating the presence of structural defects.²⁷ The four peaks deconvoluted by Gaussian fitting centered at 284.1, 285.08, 285.8 and 286.6 eV belong to C-C or C-H, C-N or C=N, C-N⁺ or C=N⁺ and C=O or C-O respectively for both the films. The C=O/C-O functional groups observed for both the electrodes are attributed to the presence of a BQ and HQ type degradation product. The presence of the Cu $2p_{3/2}$ (Fig. 2) peak centered at 933.6 eV along with the presence of a small satellite peak is assigned to Cu(II). The major Cu 2p_{3/2} peak centered at 932.5 eV is assigned to Cu(1). The observation of the peaks at 933.6 eV and 932.5 eV for Cu-PANI is consistent with the previous reports.¹⁸

Morphological analysis

The surface morphology of PANI and Cu-PANI was studied using SEM as shown in Fig. 3A and B respectively. The electrochemically synthesized PANI has fibrillar like morphology aligned parallel to the plane of the fluorine doped glass



-- 3440 500 2000 2500 3000 3500 1000 1500 Wavenumber (cm⁻¹)

Fig. 1 (A) FTIR and (B) Raman spectra of PANI and Cu-PANI electrodes.



Paper



Fig. 2 Copper 2p XPS spectra of the Cu-PANI film.

substrate while maintaining the random orientation within the plane. The Cu doped PANI (Fig. 3B) also appears to have fibrillar morphology with a smaller diameter of PANI nanorods. The SEM study reveals that the average nanorod diameter of PANI and Cu doped PANI is ~461 nm and ~142 nm respectively. Transition metal salts like Cu were found to be able to interact with PANI chains directly and induce a morphological change in PANI films. The difference in the morphology of PANI and Cu-PANI is most likely to be derived from a change in the coordination geometry of the metal ion, *i.e.* Cu²⁺.²⁸ The Cu²⁺ ion



Fig. 3 SEM images of (A) as-deposited PANI, (B) Cu doped PANI, (C) PANI (H₂SO₄) after cycling for 400 cycles, (D) Cu-PANI (H₂SO₄) after cycling for 400 cycles, (E) PANI (H₂SO₄ + CuSO₄) after cycling for 400 cycles. (F) High magnification image of the squared area

has a coordination number less than or equal to 6 with a tetrahedral coordination geometry. Thus, one Cu²⁺ ion may bind with more than one nitrogen sites of the PANI chain or form an inter-chain linkage among several adjacent PANI chains by coordination. Both intra- and inter-chain connections may lead to a more coil like conformational change or a more twisted aggregation of PANI chains and thus a lower nanorod dimension in Cu-PANI.²⁸ Also, the change of counterion, *i.e.* SO_4^{2-} in CuSO₄, affects the regime of doping and thus the morphology.

To examine the influence of a redox additive and dopant on the reaction mechanism of Cu2+ and PANI, the surface morphology of PANI (H₂SO₄), Cu-PANI (H₂SO₄) and PANI $(H_2SO_4 + CuSO_4)$ after being subjected to 400 cyclic tests was analysed using SEM (Fig. 3C, D and E respectively).

The doping and de-doping of H⁺ ions into or from the PANI and Cu-PANI chain results in the swelling and shrinkage of the nanostructured conducting polymer. The cycling of PANI in 1 M H₂SO₄ + 0.5 M CuSO₄ results in the electrodeposition of Cu fractals on the surface of PANI (Fig. 3E). The deposition and dissolution of Cu on the FTO substrate in CuSO₄ + H₂SO₄ electrolyte has been studied independently and is shown in Fig. S2 of ESI.[†] The high magnification image of the squared area (Fig. 3F) clearly shows that the PANI nanorod undergoes swelling during cycling which may result in a lower effective surface area and interfacial capacitance. To confirm these results, the DC (cyclic voltammetry) and AC (electrochemical impedance spectroscopy) responses of all the configurations were studied as discussed in the following sections.

DC voltage dependent cyclic voltammetry

The electrochemical property of PANI (H₂SO₄), PANI (H₂SO₄ + CuSO₄) and Cu-PANI (H₂SO₄) was examined through cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements. The CV response of Cu doped PANI and PANI films in different electrolytes within an optimized voltage window of 0 to 0.7 V vs. Ag/AgCl reveals an ion-PANI interaction, impact of pore structure and ion size on the adsorption of ions within the PANI matrix, and the transport phenomena. Fig. 4A shows the representative CV behaviour of PANI (1 M H_2SO_4), PANI (1 M $H_2SO_4 + 0.5$ M $CuSO_4$) and Cu-PANI (1 M H_2SO_4) in the three electrode configurations at a sweep rate of 5 mV s⁻¹. The electrochemical response current of all the configurations shows that the positive sweep is nearly asymmetric to their corresponding counter part of the negative sweep with reference to the zero current line. A predominant characteristic peak during the positive and negative sweep is usually the evidence of pseudocapacitive behaviour and corroborates the presence of Faradaic current. A pair of redox peaks at potentials negative to 0.3 V is attributed to the redox transition of PANI between leucoemeraldine (semiconductive state) and polaronic emeraldine form (conductive state). The redox peak at potentials above 0.65 V is attributed to the formation/reduction of bipolaronic pernigraniline and its resonance form, *i.e.* protonated quinonediimine.²⁹⁻³¹ A constant current during the positive and negative sweep in the bias range (~ 0.35 V to 0.7 V) resembles the rectangular shape of nearly



Fig. 4 Electrochemical characterization in a three electrode cell: (A) cyclic voltammetry of different configurations at 5 mV s⁻¹. Effect of the sweep rate on cyclic voltammograms for (B) PANI (H_2SO_4), (C) PANI (H_2SO_4) and (D) Cu–PANI (H_2SO_4).

ideal capacitor with a small internal resistor. The CV response of PANI in all the configurations, at different sweep rates, follows the description of $i = i_r + v_{dc}C_i$, where *i* represents the net current, and i_r , v_{dc} and C_i represent the Faradaic current, the scan rate and the scaled value of interfacial capacitance respectively.³² The voltammetric currents at potentials positive to 0.2 V are linearly proportional to the scan rate of CV (ESI[†]).³⁰ To have an insight into the linear equation $(i = i_r + v_{dc}C_i)$, a scaled version of the obtained data (Fig. 4A) for PANI (H₂SO₄), PANI (H₂SO₄ + CuSO₄) and Cu-PANI (H₂SO₄) is shown in Fig. 4B, C and D respectively. Increasing the sweep rate from 5 to 50 mV s⁻¹ for PANI (H₂SO₄) affects both the regions, *i.e.* the transient region where the current direction is abruptly inversed and the interfacial capacitance region (after the transient period). The change in the transient region with the increase in the sweep rate signifies that a high ionic flux within the porous PANI network is necessitated. However, after this transient period, the interfacial capacitance in the bias range of 0.35 V to 0.62 V was nearly unaffected by increasing the sweep rate (Fig. 4B), suggesting that

the accessibility of PANI pores by electrolyte ions was not obstructed from reaching the inner surface area even at such high sweep rates. Also, the interfacial capacitance in the bias range of 0.15 V to 0.35 V gradually reduces on both sides of the zero current axis with the sweep rate attributed to the presence of inner active sites which cannot precede the redox transition completely. The predominant oxidative and reductive peak shifts negatively and positively (change in ΔE_P) simultaneously with the scan rate. The change in ΔE_P with the scan rate results from kinetic effects and the uncompensated ohmic drop.³³ A change of 0.132 V is observed for the PANI film in H₂SO₄ electrolyte with the change in the scan rate from 5 to 50 mV s⁻¹.

Interestingly, a remarkable change is observed in the CV curves of the PANI film while switching the electrolyte from H_2SO_4 to $H_2SO_4 + CuSO_4$ solution, which can be mainly attributed to the following reasons: first, a higher current is observed for PANI in Cu^{2+} loaded H_2SO_4 electrolyte compared to PANI (H_2SO_4) in all the bias range probed here, which can be considered to be a combination of the following two parts: (a) a higher amount of positive ions (H⁺, Cu⁺) access the pores of PANI and take part in pseudo-Faradaic reaction and (b) the process of progressive occupation of electrode surface sites by underpotential deposited Cu species also contributes to the pseudocapacitance. The explained mechanism becomes more evident when observing the SEM image of PANI in H₂SO₄ + CuSO₄ electrolyte in Fig. 3E, where Cu fractals are grown over the PANI nanorod surface. A similar result is observed for the carbon electrode in H₂SO₄ + CuSO₄ electrolyte by other authors.²⁰ A generally accepted mechanism for electrodeposition and dissolution of Cu in sulphate solution is given by Li *et al.*²⁰ and Senthilkumar *et al.*³⁴ through two consecutive steps as follows:

> $\operatorname{Cu}^{2+}_{(\operatorname{aq.})} + e^{-} \rightleftharpoons \operatorname{Cu}^{+}_{(\operatorname{adsorb})}$ $\operatorname{Cu}^{+}_{(\operatorname{adsorb})} + e^{-} \rightleftharpoons \operatorname{Cu}_{(\operatorname{deposit})}$

Second, a higher rate of change in the transition region with the sweep rate is observed for PANI $(H_2SO_4 + CuSO_4)$ as compared to PANI (H_2SO_4). The higher rate of change suggests that a greater resistance is faced by electrolyte ions travelling within the polymer matrix. The interfacial capacitance of PANI (H₂SO₄ + CuSO₄) decreases at a faster rate compared to PANI (H_2SO_4) at a higher sweep rate. Since the size of H^+ ions in both the solvated and the desolvated state is smaller than that of Cu²⁺ ions, it is expected that ionic accessibility of internal micropores of PANI by H⁺ ions is negligibly affected as compared to Cu²⁺ ions. Also, the electrodeposited Cu fractals on the PANI surface during the electrochemical measurements restrict the ion accessibility of PANI by effectively reducing the total surface area. A similar result for sulphur activated carbon in different aqueous electrolytes, i.e. LiCl and HCl, has been obtained by other researchers.³⁵ The decrease in capacitance at a higher sweep rate also suggests that the electrochemical redox reaction between Cu²⁺ ions in liquid state and deposited copper (solid state) is not fully reversible and the deposited copper is only partly, as opposed to wholly, desorbed and re-oxidised to Cu²⁺ during the positive/negative cycles.^{20,36} A higher peak potential $\Delta E_{\rm P}$ obtained for the H₂SO₄ + CuSO₄ electrolyte compared to H₂SO₄ signifies the higher intrinsic ohmic losses. Moreover the CV plot of PANI ($H_2SO_4 + CuSO_4$) exhibits a higher slope (higher current at higher voltage) compared to that of PANI (H₂SO₄), indicating a significantly higher leakage current for the redox additive electrolyte. From the above discussion it can be inferred that the decrease in capacitance in the transition region and pseudo region at a higher sweep rate for PANI (H₂SO₄ + CuSO₄) is mainly related to the higher resistance faced by the electrolyte ions while traveling within the PANI matrix and a slower pseudocapacitive redox reaction between electrodeposited Cu fractals and electrolyte ions.

In order to assess the effect of Cu doping in the PANI matrix on the electrochemical performance, the CV graphs of Cu–PANI (H_2SO_4), PANI ($H_2SO_4 + CuSO_4$) and Cu–PANI (H_2SO_4) in Fig. 4 were compared. The CV plot of Cu–PANI (H_2SO_4) differed markedly as compared to the other two configurations. First, a higher Faradaic feature is observed for Cu doped PANI than the PANI electrode. The Faradaic current at the electrode–electrolyte interface is mainly influenced by the presence of active sites at the electrode, ion mobility and easy insertion–desertion of electrolyte ions in the polymer matrix. A higher Faradaic feature of Cu doped PANI is apparent from the following morphological and interfacial features: (a) comparatively smaller nanorods with a widely homogeneous distribution in the PANI film offer a higher surface area at the electrode–electrolyte interface which provides a shorter path length for electron and ion transport and (b) during Cu doping through polymerization, Cu²⁺ ions are reduced to Cu⁺ and aniline is oxidised to PANI. The Cu ions act as a redox active catalyst and improve the delocalization of π electrons by enhancing the interactions between Cu ions and the π electron density of the polymer chain.^{18,37}

Second, the existence of Cu²⁺ in the PANI matrix shifts the oxidation-reduction peaks, and also affects its operating voltage range and reversibility. In general, due to the consideration of electronic conductivity, electrochemical reversibility and stability the optimized potential window for PANI based electrodes is between 0.2 and 0.7 V.^{30,38} Due to the narrow potential window between 0.2 and 0.7 V *vs.* Ag/AgCl, the electrochemical energy stored in a supercapacitor is limited as $E = C(\Delta V)^2/4$, where ΔV is the working potential window. In this scenario, the doping of Cu²⁺ in the PANI matrix can effectively improve the energy storage capability of the PANI electrode by improving both *C* and ΔV . In this article, for comparison of different configurations a common mechanistic model in terms of the operating potential window 0 to 0.7 V is used.

Third, the rate of change in the transient region for Cu–PANI (H_2SO_4) and PANI ($H_2SO_4 + CuSO_4$) with the increase in the sweep rate is almost the same. The interfacial capacitance in the bias range (0.35 V to 0.62 V) for Cu–PANI (H_2SO_4) and PANI ($H_2SO_4 + CuSO_4$) is affected by the change in the sweep rate while an independent behaviour of interfacial capacitance with sweep rate is observed for PANI (H_2SO_4). It shall be noted here that such a capacitance is mainly associated with the redox reaction of PANI,²⁹ where the metallic Cu ions in Cu–PANI (H_2SO_4) and PANI ($H_2SO_4 + CuSO_4$) have a favourable pseudocapacitive effect. Also, a similar rate of change in interfacial capacitance in the bias range of 0.15 V to 0.35 V is observed for Cu–PANI (H_2SO_4) and PANI (H_2SO_4).

The Ragone plots (Fig. 5A) obtained from the discharge curves of all the configurations provide information about the available power and the optimum working region of a storage device. A maximum specific energy with a higher specific power is obtained for Cu–PANI (H_2SO_4) as compared to the other configurations. The higher value of specific energy for Cu–PANI (H_2SO_4) is due to the higher specific capacitance and higher working cell voltage. The obtained value of specific energy and power for Cu–PANI is comparable to the previously reported results by other authors.¹⁸ Factors such as discharge current, internal resistance and temperature affect the coulomb and energy efficiency. The coulomb efficiency of PANI (H_2SO_4), PANI ($H_2SO_4 + CuSO_4$) and Cu–PANI (H_2SO_4) at a scan rate of 10 mV s⁻¹ is 86.3%, 84.1% and 78.7% respectively. The energy



Fig. 5 (A) Ragone plot and (B) variation of interfacial capacitance as a function of cycle number for all the configurations

efficiency of PANI (H₂SO₄), PANI (H₂SO₄ + CuSO₄) and Cu-PANI (H_2SO_4) at a scan rate of 10 mV s⁻¹ is 76.8%, 75.3% and 70.8% respectively. Based on the potential window of CV curves (Fig. 4), the electrical energy charged and delivered from the electrode is equal to the area under the charging and discharging curve respectively, where the difference between the charge and discharge energies represents the energy loss in a storage device. The energy losses for PANI (H₂SO₄), PANI (H₂SO₄ + $CuSO_4$) and Cu-PANI (H₂SO₄) are approximately in the range of 7-11%. Such a significant energy loss not only reduces the capacitive performance but also increases the cell temperature to an unacceptable level, especially under repeated operation.³⁹ Fig. 5B shows the interfacial capacitance as a function of cycle number for all the configurations. The Cu-PANI (H₂SO₄) exhibits the highest retention ratio of 54% as compared to 33% and 42% of PANI (H₂SO₄ + CuSO₄) and PANI (H₂SO₄), respectively. The retention ratio for Cu-PANI (H2SO4) is comparable to the previously reported results by other authors for a similar configuration.18

Electrochemical impedance spectroscopy

The analysis of cyclic voltammograms reveals that Cu–PANI (H_2SO_4) exhibits a comparatively higher pseudocapacitance, whereas PANI surface physisorption in the H_2SO_4 + CuSO_4 (redox additive) electrolyte reveals a higher pseudocapacitance with low capacity retention as compared to PANI (H_2SO_4) . The effect of these observed phenomena on the values of resistance and capacitance of supercapacitors can be further explained by electrochemical impedance spectroscopy (EIS). EIS is a frequency domain technique that can reveal the complex phenomena of electron interception and diffusion at the electrode–electrolyte interface.⁴⁰ The principal objective of EIS measurements is to gain an insight into the influence of dopants and redox additive electrolytes on the resistive and capacitive element of supercapacitors.

The EIS spectra obtained for all the configurations as a function of applied potential are shown in ESI.† The left most point of the EIS spectra represents the maximum frequency (100 kHz) while the right most point represents the minimum frequency (0.1 Hz). The obtained Nyquist spectra for all the configurations consist of a linear line in the low frequency region followed by a constant phase element typified by a Warburg element and a semicircle in the high frequency region. From the obtained EIS curve and our previous study,8 a reasonable equivalent circuit (ESI⁺) is proposed to fit the experimental data. The semicircle in the high frequency region is modelled by a parallel combination of Faradaic leakage resistance $(R_{\rm F})$ and the double layer capacitance $(C_{\rm dl})$. The intersection point of the Nyquist spectra at high frequency with the real axis is represented by series resistance $R_{\rm s}$.⁴¹ The Nyquist spectrum in the mid-frequency region pertains to the diffusion of ions into the bulk of the electrode and is represented by Warburg element W_0 . The Warburg element, W_0 , is expressed as $A/(j\omega)^m$, where A is called the Warburg coefficient, ω is the angular frequency and *m* is an exponent. At a very low frequency a straight line parallel to the imaginary axis, inclined at an angle to the real axis, is modelled through a parallel combination of polarizable interfacial capacitance (C_i) and diffusion resistance (R_d) . The expression for the impedance response of CPE is given by

$$Z(\text{CPE}) = \frac{1}{Y_0(j\omega)^n} = \frac{1}{Y_0\omega^n \cos\left(\frac{n\pi}{2}\right) + jY_0\omega^n \sin\left(\frac{n\pi}{2}\right)}$$
(3)

where Y_0 is the CPE coefficient and n = 1 represents the homogeneous electrode surface. To extract the values of electrical components associated with different phenomena, the obtained experimental Nyquist spectra in the frequency range of 100 kHz to 0.1 Hz are fitted through the above discussed circuit by using MATLAB/Simulink. The fitting is optimized through multiple trials to ensure an accurate and reproducible result with a mean error of modulus <5%. In contrast to the previous reports on EIS of PANI where a vertical line is observed in the low frequency region, in the present study, the real part of resistance decreases with decreasing frequency and then again increases with decreasing frequency. The observed trend is consistent with a previous report by Žic *et al.*^{31,42} where the authors have explained this phenomenon is due to the lower value of ionic charge transfer resistance in the PANI layer (R_d). The lower value of R_d in parallel to Q_i facilitates the counter ion flux inside the PANI layer which results in a higher population of quinoidal groups inside PANI.

The dependence of EIS spectra on the applied potential (ESI⁺) for PANI electrodes is well explained by Hu et al. as follows:^{43,44} (i) The high frequency arc, independent of the applied potential at potentials negative to 0.1 V, is attributed to the insulating property of PANI and the double layer charging and discharging process. (ii) The low frequency region, dependent on the applied potential, indicates the Faradaic process of bulk redox transitions of the polymer. This phenomenon is different from the case of metal electrodes and is attributed to the higher conductivity, the charged polymer-electrolyte interface and the more reversible redox characteristics of PANI at more positive potentials. Fig. 6 depicts the Nyquist plot of PANI (H₂SO₄), PANI (H₂SO₄ + CuSO₄) and Cu-PANI (H₂SO₄) at OCP. The value of R_s for all the three configurations is obtained in the order of PANI $(H_2SO_4) > PANI (H_2SO_4 + CuSO_4) > Cu-PANI$ (H_2SO_4) . The series resistance R_s at the electrode-electrolyte interface is ascribed to two major aspects: (i) electronic, which is related to the intrinsic electrical resistance of PANI, intrinsic resistance of the current collector and the contact resistance between the current collector and PANI, and (ii) ionic, which is associated with the resistance of the electrolyte in the interior of the PANI matrix and the resistance of the bulk electrolyte.

The important features of CV in Fig. 2 that influence the supercapacitor performance can also be explained on the basis of EIS fitting parameters. The physisorption of the electrolyte ion on the electrode surface can be well explained based on the values of C_{dl} and R_{F} . At higher frequency, the value of C_{dl} arises from the charge present at the electrode surface that overcome the energy to migrate with the alternating potential.⁴⁵ The fitted values of C_{dl} obtained for PANI (H₂SO₄), PANI (H₂SO₄ + CuSO₄) and Cu-PANI (H₂SO₄) are 7, 6.2, and 22 μ F cm⁻² respectively. The higher value of C_{dl} obtained for Cu-PANI (H₂SO₄) is associated with the doping of Cu into PANI which modifies the PANI surface providing a higher surface area with more accessible sites for the mobile charges near the electrode surface. The lowest value of C_{dl} is obtained for PANI in redox additive electrolyte. This observation is corroborated by PANI morphology studies (Fig. 1E). The growth of Cu fractals on the PANI nanorod restricts the H⁺ ion diffusion in the polymer matrix which results in suppressed Faradaic reaction and charge transfer at the PANI-electrolyte interface. The Faradaic leakage resistance $R_{\rm F}$ represents the resistance of leakage due to overcharge or Faradaic redox reaction caused by impurities or electrode functional groups.⁴⁶ The values of R_F obtained for Cu-PANI (H₂SO₄), PANI (H₂SO₄) and PANI (H₂SO₄ + CuSO₄) are 1.3, 1.7 and 3.1 Ω cm⁻² respectively. A lower value of $R_{\rm F}$ obtained



Fig. 6 Nyquist plot of the different configurations at an open circuit potential. The inset shows the higher frequency details of the impedance spectra.

for Cu-PANI (H₂SO₄) signifies a greater kinetic reversibility of the Faradaic reaction and lower charge accumulation at the electrode-electrolyte interface. The 45° segment, during the transition from the high frequency semicircle to the mid-frequency spike, is known as the Warburg element in the Nyquist plot (Fig. 6). The length of this segment and the exponent (m) indicate the resistance faced by the ions during their transport into the pores and electrode porosity, respectively.⁴⁵ From Fig. 6, it is clear that PANI (H_2SO_4 + CuSO₄) demonstrates the highest resistance faced by the ions during their transport in the polymer matrix, followed by PANI (H_2SO_4) , with Cu-PANI (H_2SO_4) possessing the lowest resistance. The value of the exponent is observed as m = 0.55 for PANI (H_2SO_4) , m = 0.74 for PANI $(H_2SO_4 + CuSO_4)$ and m = 0.49 for Cu-PANI (H_2SO_4). The lower value of the exponent (*m*) signifies that the ion diffusion takes place both at the planar surface and inside the pores whereas a higher value of m for PANI (H₂SO₄ + CuSO₄) indicates that only surface phenomena are associated.

The high retention of capacitance under fast chargedischarge conditions is only possible if the system allows very fast ion diffusion in response to the large perturbation and possesses very low Faradaic leakage resistance R_F. Therefore the high rate retention for Cu-PANI (H₂SO₄) than the other two configurations is the direct consequence of lower $R_{\rm F}$ and lower Warburg length. It is interesting to note from the Nyquist plot of Fig. 6 that the redox additive electrolyte and doping shift the transition frequency (the frequency at which the high frequency circle changes to the mid-frequency spike) which is 1.47, 1 and 1.78 Hz for PANI (H₂SO₄), PANI (H₂SO₄ + CuSO₄) and Cu-PANI (H_2SO_4) respectively. This observation suggests that there is time dependence in the discharge process on the electrode and electrolyte configuration. At a very low frequency the diffusion resistance (R_d) is obtained as 50, 32 and 85 k Ω for PANI (H₂SO₄), PANI (H₂SO₄ + CuSO₄) and Cu-PANI (H₂SO₄) respectively. The lower value of diffusion resistance implies a higher leakage current which causes the supercapacitor to self-discharge

--- PANI (H.SO.)

-PANI (H_SO_+CuSO_)

- Cu-PANI (H SO)

Region II





at a faster rate. A similar conclusion for PANI in $H_2SO_4 + CuSO_4$ electrolyte is drawn from the analysis of CV. The extracted values of interfacial capacitance are 0.238, 0.359 and 0.51 F cm⁻² for PANI (H_2SO_4), PANI ($H_2SO_4 + CuSO_4$) and Cu-PANI (H_2SO_4) respectively. The obtained value of interfacial capacitance is comparable to the value obtained from CVs measured at 5 mV s⁻¹ showing the validity of fitting parameters.

Complex frequency analysis

Complex frequency analysis has emerged as an excellent technique for the investigation of bulk and interfacial electrochemical phenomenon, pseudo and electric double layer capacitance at low frequency.⁴⁷ Fig. 7 shows the relation between the phase angle with the change in frequency. The phase angle changes from 73° to 82° in the order of PANI (H₂SO₄) > PANI (H₂SO₄ + CuSO₄) > Cu–PANI (H₂SO₄).

The lower phase angle signifies the higher resistance and pseudocapacitive behaviour. Thus, it further confirms the outcome of CV and EIS analysis that doping of PANI with Cu offers a comparatively higher intrinsic resistance (*i.e.* diffusion resistance) with a larger pseudocapacitive nature of the electrode during the electrochemical process. Fig. 8 shows the real part of complex capacitance derived from the impedance spectra (Fig. 6) according to eqn (2) for PANI (H_2SO_4), PANI ($H_2SO_4 + CuSO_4$) and Cu–PANI (H_2SO_4) as a function of frequency.

From the plot of C' vs. frequency it is observed that the electrode reaches a full capacitance at low frequency and becomes constant at a higher frequency. The obtained C' vs. frequency plot for all configurations is analysed in two frequency regions, *i.e.* region I (0.1 to 0.9 Hz) and region II (0.9 to 10 Hz). In Region I (*i.e.* low power and high energy), the maximum and minimum capacitance are obtained for Cu–PANI (H₂SO₄) and PANI (H₂SO₄) respectively, whereas in Region II (*i.e.* high power and low energy), the maximum and minimum capacitance are obtained for PANI (H₂SO₄) respectively. A dynamic change in the maximum value of capacitance between Cu–PANI (H₂SO₄) and PANI (H₂SO₄) during the transition from

Regions I to II is further explained by simulating the behaviour of $C' \nu s$, frequency.^{48,49} A detailed derivation and the simulation results are shown in ESI,[†] From the simulation results discussed in ESI,[†] it is concluded that during the electropolymerization process, Cu doped PANI results in a higher polymerization rate which induces a thicker electrode with higher capacitance in the low frequency region. On the other hand, the non-uniform utilization of electrode current at higher frequency causes a decrease in the value of capacitance for the Cu–PANI electrode.

Conclusion

0.10

0.08

0.06

0.04

0.02

Region I

Capacitance (F/cm²)

The effect of copper (Cu) as a redox additive and dopant on the performance of a PANI based supercapacitor was thoroughly investigated. The analysis of CV reveals that Cu-PANI (H₂SO₄) exhibits a comparatively higher pseudocapacitance, whereas physisorption of the PANI surface in H₂SO₄ + CuSO₄ (redox additive) electrolyte reveals a higher pseudocapacitance with low capacity retention as compared to PANI (H₂SO₄). The capacitance of PANI (H₂SO₄ + CuSO₄) appears to be unstable because of underpotential deposition of copper over PANI surface and its relatively irreversible redox reaction. However, a stable and improved performance was obtained for Cu doped PANI due to the combined effect of an increase in conductivity and the surface modification of the PANI film. For Cu doped PANI, nearly \sim 2.4 and \sim 1.5 fold improved interfacial capacitance was achieved when compared to PANI (H₂SO₄) and PANI $(H_2SO_4 + CuSO_4)$ respectively. The high rate retention for Cu-PANI (H_2SO_4) compared to the other two configurations is the direct consequence of lower $R_{\rm F}$ and lower Warburg length. The lower value of diffusion resistance for PANI (H₂SO₄ + CuSO₄) implies a higher leakage current which causes the supercapacitor to self-discharge at a faster rate. From the simulated capacitance vs. frequency plot, it can be inferred that Cu doped PANI results in a higher polymerization rate which induces a thicker electrode with higher capacitance in the low frequency region. On the other hand, the non-uniform

utilization of electrode current at higher frequency causes a decrease in the value of capacitance for the Cu–PANI electrode. The present analysis thus shows the importance of understanding the effect of dopants and redox additives on the performance of PANI based supercapacitors and also lays the basis for designing a supercapacitor with an appropriate electrode and electrolyte material for numerous industrial and consumer applications.

Acknowledgements

The authors gratefully acknowledge DST (Project No. SR/S1/PC-44/ 2011 dated 04/07/2012) for the financial assistance. One of the authors (K.P.) thanks the DST INSPIRE fellowship program for junior research fellowship. Ms Purvi Kikani, FCIPT, IPR, Gandhinagar, and Dr B. P. Singh, CSIR-IMMT, Bhubaneswar, are greatly acknowledged for FTIR, and Raman and XPS measurements respectively. The authors are deeply grateful to anonymous referees for their invaluable suggestions to improve the quality of this article.

References

- 1 L. F. Chen, X. D. Zhang, H. W. Liang, M. Kong, Q. F. Guan, P. Chen, Z. Y. Wu and S. H. Yu, *ACS Nano*, 2012, **6**, 7092.
- 2 S. B. Kulkarni, U. M. Patil, I. Shackery, J. S. Sohn, S. Lee, B. Park and S. Jun, *J. Mater. Chem. A*, 2014, **2**, 4989.
- 3 C. Peng, D. Hu and G. Z. Chen, Chem. Commun., 2011, 47, 4105.
- 4 H. Fan, H. Wang, N. Zhao, X. Zhang and J. Xu, J. Mater. Chem., 2012, 22, 2774.
- 5 J. P. Zheng and T. R. Jow, J. Electrochem. Soc., 1995, 142, L6.
- 6 H. Y. Lee and J. B. Goodenough, *J. Solid State Chem.*, 1999, **148**, 81.
- 7 M. Rose, Y. Korenblit, E. Kockrick, L. Borchardt, M. Oschatz,S. Kaskel and G. Yushin, *Small*, 2011, 7, 1108.
- 8 K. Pandey, P. Yadav and I. Mukhopadhyay, *J. Phys. Chem. B*, 2014, **118**, 3235.
- 9 D. Bhattacharjya and I. Mukhopadhyay, *Langmuir*, 2012, **28**, 5893.
- 10 W. Chen, R. B. Rakhi and H. N. Alshareef, *J. Mater. Chem. A*, 2013, **1**, 3315.
- 11 W. K. Maser, A. M. Benito, M. A. Callejas, T. Seeger, M. T. Martínez, J. Schreiber, J. Muszynski, O. Chauvet, Z. Osváth, A. A. Koós and L. P. Biró, *Mater. Sci. Eng.*, C, 2003, 23, 87.
- 12 Z. Tai, X. Yan and Q. Xue, *J. Electrochem. Soc.*, 2012, 159, A1702.
- 13 H. Mi, X. Zhang, S. Yang, X. Ye and J. Luo, *Mater. Chem. Phys.*, 2008, **112**, 127.
- 14 C. Meng, C. Liu and S. Fan, *Electrochem. Commun.*, 2009, **11**, 186.
- 15 C. C. Hu and C. H. Chu, Mater. Chem. Phys., 2000, 65, 329.
- 16 C. C. Hu, E. Chen and J. Y. Lin, *Electrochim. Acta*, 2002, 47, 2741.
- 17 M. M. Rahman Khan, Y. K. Wee and W. A. Kamil Mahmood, Synth. Met., 2012, 162, 1065.
- 18 H. Xu, J. Zhang, Y. Chen, H. Lu and J. Zhuang, *RSC Adv.*, 2014, 4, 5547.

- 19 S. Dhibar, S. Sahoo, C. K. Das and R. Singh, J. Mater. Sci.: Mater. Electron., 2013, 24, 576.
- 20 Q. Li, K. Li, C. Sun and Y. Li, J. Electroanal. Chem., 2007, 611, 43.
- 21 L. Qian, X. Tian, L. Yang, H. Yuan and D. Xiao, *RSC Adv.*, 2013, **3**, 1703.
- 22 W. Chen, R. B. Rakhi and H. N. Alshareef, *Nanoscale*, 2013, 5, 4134.
- 23 N. Devillers, S. Jemei, M. C. Péra, D. Bienaimé and F. Gustin, J. Power Sources, 2014, 246, 596.
- 24 L. Li, Z. Y. Qin, X. Liang, Q. Q. Fan, Y. Q. Lu, W. H. Wu and M. F. Zhu, *J. Phys. Chem. C*, 2009, **113**, 5502.
- 25 S. Sharma, C. Nirkhe, S. Pethkar and A. A. Athawale, *Sens. Actuators, B*, 2002, **85**, 131.
- 26 C. M. S. Izumi, A. M. D. C. Ferreira, V. R. L. Constantino and M. L. A. Temperini, *Macromolecules*, 2007, 40, 3204.
- 27 W. C. Chen, T. C. Wen and A. Gopalan, Synth. Met., 2002, 128, 179.
- 28 S. Tao, B. Hong and Z. Kerong, Spectrochim. Acta, Part A, 2007, 66, 1364.
- 29 C. C. Hu and J. Y. Lin, Electrochim. Acta, 2002, 47, 4055.
- 30 P. J. Hung, K. H. Chang, Y. F. Lee, C. C. Hu and K. M. Lin, *Electrochim. Acta*, 2010, **55**, 6015.
- 31 M. Žic, J. Electroanal. Chem., 2007, 610, 57.
- 32 J. Zheng, S. S. Moganty, P. C. Goonetilleke, R. E. Baltus and D. Roy, *J. Phys. Chem. C*, 2011, **115**, 7527.
- 33 H. Xie, Y. Zhu, Y. Wu, Z. Wu and E. Liu, *Mater. Res. Bull.*, 2014, 50, 303.
- 34 S. T. Senthilkumar, R. Kalai Selvan and J. S. Melo, *J. Mater. Chem. A*, 2013, 1, 12386.
- 35 W. Gu, M. Sevilla, A. Magasinski, A. B. Fuertes and G. Yushin, *Energy Environ. Sci.*, 2013, **6**, 2465.
- 36 G. Sun, K. Li and C. Sun, *Microporous Mesoporous Mater.*, 2010, **128**, 56.
- 37 C. K. Wu, M. Yin, S. O'Brien and J. T. Koberstein, *Chem. Mater.*, 2006, 18, 6054.
- 38 N. G. Skinner and E. A. H. Hall, Synth. Met., 1994, 63, 133.
- 39 C. C. Hu, J. C. Chen and K. H. Chang, J. Power Sources, 2013, 221, 128.
- 40 K. Pandey, P. Yadav and I. Mukhopadhyay, J. Solid State Electrochem., 2014, 18, 453.
- 41 P. Yadav, B. Tripathi, K. Pandey and M. Kumar, *Phys. Chem. Chem. Phys.*, 2014, **16**, 15469.
- 42 M. Žic, J. Electroanal. Chem., 2009, 635, 29.
- 43 C. C. Hu and C. H. Chu, J. Electroanal. Chem., 2001, 503, 105.
- 44 W. C. Chen, T. C. Wen, C. C. Hu and A. Gopalan, *Electrochim. Acta*, 2002, **47**, 1305.
- 45 C. Masarapu, H. F. Zeng, K. H. Hung and B. Wei, *ACS Nano*, 2009, **3**, 2199.
- 46 M. Kotal, A. K. Thakur and A. K. Bhowmick, ACS Appl. Mater. Interfaces, 2013, 5, 8374.
- 47 C. Yang, M. Zhou and Q. Xu, *Phys. Chem. Chem. Phys.*, 2013, 15, 19730.
- 48 V. Srinivasan and J. W. Weidner, *J. Electrochem. Soc.*, 1999, **146**, 1650.
- 49 S. Motupally, C. C. Streinz and J. W. Weidner, *J. Electrochem. Soc.*, 1995, **142**, 1401.