Tunable electrochemical activity of polyaniline salt by doping anion exchange

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Abstract: The exchange of mobile anion of chemically synthesized polyaniline with counter anions of electrolyte solutions is studied by using cyclic voltammetry (CV). The synthesized polyaniline (PANI) doped with sulfuric acid (H₂SO₄) and dodecyl benzenesulfonic acid (DBSA) is soluble in a wide range of organic solvents which makes it appealing for further processability. The exchange of dopant anions (of H₂SO₄ and DBSA) with a variety of counter anion has been inspected by electrochemical cycling in aqueous sodium sulfate (Na₂SO₄), sodium perchlorate (NaClO₄), and sodium hydroxide (NaOH) solution. The CV measurements have revealed that PANI remains redox active at higher scan rate and there is exchange of dopant anion with SO₄²⁻ and ClO₄⁻ of electrolytes. In NaOH solution, the emeraldine salt form of PANI is transformed into emeraldine base due to deintercalation of the anion form polymer matrix. The results indicate a significant change in electrochemical conductance and behavior of PANI in each electrolyte. Furthermore, the polymer film displayed a high specific capacitance value of 588 F/g in 1.0 M NaClO₄ solution in the optimized potential window of -0.2 V to 0.9 V at 20 mV/s.

Keywords: conducting polymer; polyaniline; dopant anions, electrochemical behavior; cyclic voltammetry: neutral and alkaline electrolytes.

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1. Introduction

Conducting polymers presents polyaniline (PANI) as the most extensively explored member of the group. PANI serves as a workhorse due to its easy synthesis, cost effectiveness, significant stability, and high conductivity in doped state highlighting its applications in diverse technologies including sensors, catalysis, corrosion inhibition, supercapacitors, electronics, and gas separation membranes [1-5]. For this, it is required to synthesize PANI with desirable features like morphology, solubility, electrochemical and mechanical stability, charge holding capacity, conductivity, permeability, and adhesion to metal electrode and other

materials. The dopant anion present in the polymer matrix greatly influences these features of PANI. Hence, a variety of dopant anions should be employed to prepare PANI [2-6]. Therefore, it is of immense importance to incorporate specific ions of interest into polymer matrix for the control release and selective interaction of dopant anions during corrosion protection of metals, cyclic redox process of supercapacitors, drug delivery, and other analytical applications [4, 7]. In this regard, the choice of dopant anion for intercalation in PANI during the polymerization as well as exchange with the counter

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anion of the electrolyte during electrochemical redox process profoundly matters [3-4, 8].

PANI synthesis as a conductive emeraldine salt is being practiced either by chemical or electrochemical oxidation method using low pH solution. The low pH is obtained by using a surfactant or an acid assisted polymerization as shown in Figure 1, where A^- is the dopant anion incorporated into PANI. Literature reported that incorporation of sulfonated aromatics (*p*-toluene sulfonic acid, benzene sulfonic acid, diphenyl phosphate, camphor sulfonic acid, dodecylbenzenesulfonic acid, dinonylnaphthalene sulfonic acid etc.) as dopant anions in PANI turned it into more conductive, easily processable, soluble, and thermally stable emeraldine salt [1, 4-5, 9-11].

Figure 1. Polymerization of aniline

The post-processed coating of PANI is investigated by various electrochemical techniques for numerous analytical applications using a variety of electrolytes. These electrolytes include hydrochloric acid (HCl), perchloric acid (HClO_4), sodium chloride (NaCl), oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$), sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), lithium chloride (LiCl), etc. [1, 12-15]. During electrochemical redox process, PANI undergoes elimination or addition of electrons accompanied by subsequent inclusion or exclusion of dopant anion as presented in Figure 2. The type, dimension, size, and mobility of the anion are of great significance. Small and mobile anions intercalated in PANI can easily leave and enter the polymer matrix allowing reversible electrochemical oxidation-reduction process. This is anionic doping of polymer which is accomplished by replacement of electrolyte anion resulting in structural

2. Materials and Methods

Analytical grade chemicals are used for all experiments. Vacuum distilled aniline (Reidel-de Häen) was used for polymerization. Ammonium persulfate (APS), and sulfuric acid (H_2SO_4) was obtained from Reidel-de Häen, whereas, 2-propanol was procured from EMPLURA. The surfactant, dodecylbenzenesulfonic acid (DBSA) and phosphoric acid (H_3PO_4) were purchased from Sigma Aldrich and DAEJUNG, respectively. Chloroform (CHCl_3), perchloric acid (HClO_4), Na_2SO_4 , NaClO_4 , and toluene

modification in the polymer matrix [4, 5, 16]. On the other hand, introduction of large sized anions into PANI matrix are sterically confined due to which anionic exchange during electrochemical redox process is replaced by rapid proton exchange process [8].

Figure 2. Reversible doping/dedoping of PANI

Earlier, we reported the chemical synthesis of PANI and its electrochemical activity in aqueous acidic electrolytes (HClO_4 , H_2SO_4 , and H_3PO_4) by using Cyclic Voltammetry (CV) [1]. The electrochemical stability and charge transfer resistance of PANI was also studied by Galvanostatic Charge–Discharge (GCD) as well as Electrochemical Impedance Spectroscopy (EIS). PANI exhibited tremendous supercapacitor behavior in acidic electrolytes. In extension of our previous work, this article studies, the exchange of doped anions with the anions of neutral and alkaline electrolytes by using CV. The anion replacement test of PANI by CV was carried out as a function of potential sweep rate, potential upper limit, type, and concentration of supporting electrolyte. It is being studied in order to obtain the optimum conditions for better electrochemical properties of this new pseudocapacitive electrode materials that can retain its electrochemical properties in neutral and basic solutions. The results are displayed and discussed below.

were provided by Scharlau. Millipore water was used throughout the work.

The synthesis of PANI salt was implemented by chemical oxidation pathway, similar to our previous report [1]. 7.47 mmol DBSA was introduced in 50 mL chloroform. It was stirred to prepare homogeneous solution. Afterwards, 12.5 mmol H_2SO_4 (25 mL) and then 16.42 mmol aniline was added dropwise. At last, 0.75 mmol APS was poured into the reaction mixture to start the reaction. After 24 hours of stirring at room temperature, the reaction mixture was taken in a

separating flask and deionized water was added to it. It was then allowed to stay for few hours. The lower organic layer was separated and then washed repeatedly with deionized water and acetone. Finally, the obtained precipitates were then filtered, and again washed with acetone. A green color PANI salt was dried in oven at 60°C and stored in an air tight glass vial.

Three electrode single compartment cell was used for the electrochemical investigations. The electrode was prepared by coating the polymer film of 0.20 mg on gold sheet substrate as a current collector. For this, PANI was dispersed in a 2:1 mixture of toluene and 2-propanol and air dried before measurement. Gold sheet and silver/silver chloride (Ag/AgCl) was used as counter and reference electrode, respectively. The electrochemical properties were studied by CV with Reference 3000 ZRA potentiostat/galvanostat at room temperature. Cyclic Voltammograms (CVs) for PANI were recorded in Na₂SO₄, NaClO₄, and NaOH aqueous solutions at various potential ranges. The potential was scanned from -0.2 V to different upper

potential limits like 0.9, 1.0, 1.1, and 1.2 V at 100 mV/s sweep rate. The effect of electrode potential on the electrochemical stability of PANI was investigated by cycling the potential for particular time in each electrolyte. The influence of counter-ion (ClO₄⁻, SO₄²⁻, and OH⁻), concentration, and scan rate on electrochemical stability and charge storage is also evaluated from this study.

The most suitable method applied to choose an appropriate electrolyte and check stability of electrode material for supercapacitors is CV [17]. The integrated area of CV was used to calculate specific capacitance 'C' (F/g) employing the following formula [18].

$$C = \frac{\int_{E_1}^{E_2} i(E)d(E)}{2vm(E_2 - E_1)} \quad (1)$$

where $\int_{E_1}^{E_2} i(E)d(E)$ represents charge, m is weight (g) of polymer sample, ' v ' is the potential sweep rate (mV/s), and $E_2 - E_1$ is the potential range.

3. Results and Discussion

3.1. Influence of Potential Window on Electrochemical Stability in Neutral Electrolytes

In order to investigate the electrochemical performance of PANI electrode, two neutral electrolytes that is Na₂SO₄ and NaClO₄ were selected. The electrochemical stability of PANI was studied in 0.5 M of Na₂SO₄ and NaClO₄ solutions, separately. Figure 3 shows CV curves of PANI coated on Au sheet in the potential window of -0.2-0.9 V keeping potential sweep rate at 100 mV/s. The film shows two pair of redox couples. These are not very sharp but can be clearly seen in the CVs. Usually, first redox couple (Ipa/Ipa1) is referred to leucoemeraldine/emeraldine transition whereas the second redox couple (Ipb/Ipb1) is related to emeraldine/pernigraniline transformations. The first redox transition is observed below 0.23 V while the second is obtained above 0.4 V. The first redox peak is broader in Na₂SO₄ as compared to that in NaClO₄, while, the reduction peaks are also broad in both solutions. Such broadness in the peaks represents difficult charge transfer in the CV process. These type of CVs are also observed in the weak acid solution like in H₃PO₄ [19-21]. The CV curves exhibit that the prepared PANI retained a reversible and electroactive nature in neutral media. This might be caused by the incorporation of dopants i.e. H₂SO₄ and DBSA in the polymer chain.

Figure 3. CVs of PANI on Au in 0.5 M Na₂SO₄ and NaClO₄.

The effect of upper potential on electrochemical stability of PANI in 0.5 M of neutral electrolytes was investigated using various higher potentials like 0.9, 1.0, 1.1, and 1.2 V, respectively. As the potential of working electrode was varied at 100 mV/s for multi-cycles, the intensity of anodic and cathodic peaks decreased. The peaks became broader and their positions shifted towards the center [18]. The PANI was found to be electrochemically active up to 52 cycles in potential window of -0.2 to 0.9 V in 0.5 M Na₂SO₄ and around 80 cycles in 0.5 M NaClO₄ as presented in Figure 4 and 5. The electrochemical activity of PANI reduced with the increase in upper potential up to 1.2 V. With the continuous potential cycling, the electrode material lost its electrochemical activity with the gradual removal of

DBSA or HSO_4^- anions from polymer chain and deprotonation in neutral electrolytes. Thus, deprotonation of material occurred without undergoing degradation [22]. Owing to higher electrochemical stability of polymer, the potential window of -0.2 V to 0.9 V was assumed to be an appropriate potential range for the prepared polymer. This potential window was selected for further study. These results are in agreement with that of acidic electrolytes.

Figure 4. Electrochemical activity of PANI at various upper potential limits a) 0.9 V, b) 1.0 V, c) 1.1 V, and d) 1.2 V in 0.5 M Na_2SO_4 .

Figure 5. Electrochemical activity of PANI at various upper potential limits a) 0.9 V, b) 1.0 V, c) 1.1 V, and d) 1.2 V in 0.5 M NaClO_4 .

3.2. Influence of Voltage Window on Electrochemical Stability in Alkaline Electrolyte

To investigate the electrochemical activity in alkaline medium, NaOH electrolyte was selected. For this, the potential of the working electrode coated with

PANI was swept between -0.2 to 0.8 V at 100 mV/s. The concentration of the electrolyte was 0.5 M. The CVs exhibited a couple of broad and sharp peak. The broad peak was observed in the anodic half around 0.55 V and a sharp peak around 0.03 V in cathodic half of the CV (Figure 6). Moreover, the polymer film changed its color from green to bluish with the first potential scan. The color change might be caused by transformation of PANI emeraldine salt form in to emeraldine base due to deprotonation [22]. Thus, the original state of the synthesized PANI changed in alkaline medium, therefore, the influence of potential window on electrochemical activity was not studied. However, the PANI remained electrochemically active in deprotonated form in NaOH solution for more than 500 cycles as shown in Figure 7. Due to the transformation of the required emeraldine salt in alkaline medium, further studies were carried only in neutral electrolytes.

Figure 6. CV of PANI on Au in 0.5 M of alkaline medium at 100 mV/s.

Figure 7. Electrochemical activity of PANI emeraldine base in 0.5 M of NaOH.

3.3. Effect of Type of Electrolyte on Electrochemical Stability

The counter-ion and electrolyte effect was evaluated from the above experiment conducted at a potential range of -0.2 to 0.9 V in 0.5 M of respective neutral electrolytes at 100 mV/s. The PANI salt is electrochemically active up to 80 cycles in NaClO₄ and 52 cycles in Na₂SO₄ solution. It can be concluded from the results that the electrochemical stability of PANI is higher in NaClO₄ than Na₂SO₄ that could be as of counter-ion effect of the respective electrolyte. These results follow Hofmeister series of anions which is as given as [23]; ClO₄¹⁻ > SCN¹⁻ > I¹⁻ > NO₃¹⁻ > Br¹⁻ > Cl¹⁻ >> HCO₃⁻ -OAc⁻ -SO₄²⁻ -HPO₄²⁻. This suggests that ClO₄¹⁻ anions of NaClO₄ show more hydrophobicity than SO₄²⁻ anions and hence, shields the bipolaron from the nucleophilic attack by OH¹⁻ anions [24].

3.4. Effect of Electrolyte Concentration on Electrochemical Stability

After the optimization of potential window and type of electrolyte, the effect of electrolyte concentration on the electrochemical stability was examined to obtain the most suitable electrolyte for the prepared of PANI. Figure 9 shows CV curves of PANI in various concentrations of NaClO₄ and Na₂SO₄ at 100 mV/s. The concentration range was from 0.01 to 1.0 M. The CV plots revealed that the magnitude of current increases with the increase in concentration of electrolytes. In higher concentration (i.e., 1.0 M) of both the electrolytes, the peaks are more clear and sharp, whereas, with the decrease in concentration peaks became broad. Besides, the peak current values decreased and peak position shifted with decrease in concentration. All these changes are ascribed to the Internal Resistance (IR) drop caused by the increased and decreased conductivity of PANI electrode [25-26]. As shown in the Figure 8, the peaks are not well resolved in 0.01 M of the electrolyte, therefore, no conclusion can be drawn for the shift in peak position and peak current reduction. Hence, the electrochemical activity of PANI cannot be evaluated below 0.05 M concentration.

Figure 8. CVs of PANI in various concentrations of (a) Na₂SO₄ and (b) NaClO₄.

Figure 9. Electrochemical activity of PANI in various concentrations of Na₂SO₄.

Figure 10. Electrochemical activity of PANI in various concentrations of NaClO₄.

The concentration effect on electrochemical stability of PANI is depicted in Figures 9 and 10. The result for cycling stability of PANI depicts that the electrochemical activity of the polymer is high in 0.05 M solution. As the concentration is increased to 1.0 M, the electrochemical activity is decreased shown by decrease in the number of cycles. Hence, 1.0 M concentration was selected for the specific capacitance measurement.

3.5. Effect of Scan Rate on Electrochemical Stability

Figures 11a and 11c illustrate CVs of the PANI as a function of potential scan rate in 1.0 M NaClO₄ and Na₂SO₄. Various potential sweep rates (20-100 mV/s) were applied to the electrode in the optimized potential window (-0.2 to 0.9 V). The CV plots show that the anodic peak intensity (current) increases with the increase in scan rate, retaining its position (potential).

Figures 11. CVs of PANI at various potential scan rates in 1.0 M (a) Na₂SO₄ and (c) NaClO₄; Dependence of first anodic peak current on square root of scan rate in 1.0 M (b) Na₂SO₄ and (d) NaClO₄.

The shape of all CVs displays a good electrochemical behavior of the prepared PANI electrode. The electrode processes are assumed to be controlled kinetically or by diffusion. The first anodic peak current is plotted as a function square root of the scan rate shows linear relation as displayed in Figures 11b and 11d for both the electrolytes. This suggests that

4. Conclusions

PANI was prepared by chemical oxidative polymerization pathway using sulfuric acid and dodecylbenzene sulfonic acid as dopants. It was the

the electrode processes of PANI coated electrode are diffusion controlled [1, 27].

3.6. Specific Capacitance of PANI

The energy storage property of PANI electrode was monitored as a function of scan rate, as depicted in Figure 12. For this, the optimized potential window (-0.2 to 0.9 V) and concentration (1.0 M) of both neutral electrolytes were used. The specific capacitance was calculated from equation 1 as mentioned above. A higher specific capacitance of 588 F/g was obtained for PANI in 1.0 M NaClO₄ than Na₂SO₄ (454 F/g). This can be due to the conductivity, mobility, and charge on anions of electrolyte [28]. Lower peak current is observed in electrolyte having SO₄²⁻ as compared to ClO₄¹⁻. The reason is a high anion charge and large size of SO₄²⁻ as compared to ClO₄¹⁻ which caused a high conductivity [29]. These results are in accordance with the trend observed for acidic electrolytes. With the increase in scan rate, the specific capacitance decreased from 454 to 132 F/g in case of Na₂SO₄ and from 588 to 159 F/g in NaClO₄. It can be attributed to the internal resistance or diffusion limitation of electrolyte ions which leads to insufficient redox reactions [30-31]. Thus, it might become difficult for the electric charges to occupy the available sites at the electrode/electrolyte interface [30].

Figure 12. Specific capacitance of PANI at different potential scan rates in 1.0 M (a) Na₂SO₄ and (c) NaClO₄.

applied as electrode material for supercapacitor using aqueous neutral and alkaline electrolytes.

The electrochemical properties of PANI were comparatively investigated in alkaline NaOH, and in neutral (Na₂SO₄ and NaClO₄) electrolytes in detail by using CV. Various experimental variables like potential range, scan rate, concentration, and type of electrolytes were optimized in order to obtain the best set of conditions for the prepared PANI salt.

The optimized values for potential range, scan rate, and concentration of electrolyte was found to be -

0.2 to 0.9 V, 100 mV/s, and 1.0 M NaClO₄, respectively. The high specific capacitance of 588 F/g and better electrochemical stability of the system makes PANI as a promising electrode material and NaClO₄ as an ideal candidate of a neutral electrolyte to produce cost-effective and environment friendly aqueous supercapacitor.

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Conflicts of Interest

The authors declare no conflict of interest.

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