

**Research Article**

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Hajera Gul

National Centre of Excellence in
Physical Chemistry, University of
Peshawar, Peshawar, 25120,
Pakistan

Anwar-ul-Haq Ali Shah

Institute of Chemical Sciences
University of Peshawar, Peshawar,
25120, Pakistan

Salma Bilal

National Centre of Excellence in
Physical Chemistry, University of
Peshawar, Peshawar, 25120,
Pakistan

Correspondence:**Dr. Salma Bilal**

National Centre of Excellence in
Physical Chemistry, University of
Peshawar, Peshawar, 25120,
Pakistan

Electrochemical behavior of POT in different electrolytes

Hajera Gul, Anwar-ul-Haq Ali Shah, Salma Bilal*

Abstract

Poly(*o*-toluidine), POT salt was synthesized by an emulsion polymerization method. Electrochemical behavior of synthesized salt was investigated by cyclic voltammetry (CV) and galvanostatic charge discharge analysis (GCD). CV was carried out at different scan rate (10 mV/s, 20 mV/s, 30 mV/s, 40 mV/s and 50 mV/s). GCD analysis was carried out at two different current densities (0.5 and 5 A/g). 1 M Sulphuric acid (H₂SO₄), 1 M perchloric acid (HClO₄) and 1 M sodium hydroxide (NaOH) were used as electrolytes. UV-visible spectroscopy was used for investigation of spectral behavior. POT_{0.03} salt showed highest specific capacitance value of 186 F/g in HClO₄ aqueous electrolyte. Synthesized polymer was soluble in a number of organic solvents and thus no binder or additive is required for electrode preparation. These results implied that for supercapacitors POT salt with HClO₄ aqueous electrolyte is a valuable electrode material for supercapacitors.

Keywords: POT, CV, GCD, UV-visible spectroscopy.

INTRODUCTION

Super capacitors (SC), also recognized as “electrochemical capacitors”, corresponds to an exclusive class of energy storage devices that display immense power proficiency^[1, 2], lengthy cycle lifetime and quick rates of charge and discharge, with scope of utilization in memory backup arrangements and handy electronics, to hybrid electric automobiles, energy execution and power on industrial scale. There are two essential types of SC based on energy storage technique^[3]. These are electrical double layer capacitors (EDLC) and the pseudo capacitor (PC)^[4, 5]. Usually, PC display superior specific capacitance than EDLC. PC is utilized to construct super capacitor with enhanced energy and power densities. Auspicious materials for a redox super capacitor are conductive polymers (CP) and transition metal oxides, due to their fast switching among oxidized (doped) and reduced (dedoped) forms when applied potential is altered^[6]. Diffusion of counter-ions into/out of CPs or metal oxide films are involved to maintain its electro neutrality, which is intrinsic property of a redox capacitor. Due to quick switching between redox forms, enhanced conductivity in a doped form, mechanical pliability, minor toxicity and low cost, CP has been comprehensively explored as electrode materials for SC. Among CPs, polyaniline (PANI)^[7], polypyrrole, polythiophene have been enormously studied as an active electrode material for super capacitors because of their low cost when compared to other CPs. PANI is one of the most fascination CP due of its environmental stability^[8, 9], easy synthesis^[10], astonishing optical, electrochemical and electrical properties and due to possibility to be utilized in rechargeable batteries, biosensors, microelectronics devices, electro chromic displays, chemical sensors and SC^[11]. Nonetheless, the basic deprivations of this polymer are its infusibility and insolubility in common organic solvents^[12]. Suitable approaches have been executed to enhance the solubility and processibility of the PANI and its derivatives. It was noted that ring-substituted (alkyl and alkoxy) and N-alkyl-substituted PANI are more soluble than un substituted PANI. Consequently, tremendous considerations have been dedicated to prepare soluble PANI derivatives. For instance, poly(*o*-toluidine), POT, a-CH₃ group substituted PANI derivative, has been reported to show structural properties and redox and electrochromic behavior very similar to that of PANI^[13]. Among all four oxidation states (Scheme 1), emeraldine salt is the only conducting state of POT^[14].

Herein, we prepared POT in its salt form. Its electrochemical properties were investigated in three different electrolytes (H₂SO₄, HClO₄ and NaOH). POT salts shows higher SC value in HClO₄ aqueous electrolyte and can be used as promising electrode material.

No binder was used for preparation of electrode, which not only reduced cost but also ease the procedure [15].

MATERIALS AND METHODS

Materials

Research grade reagents were used throughout the experimental work. o-Toluidine, OT, (Acros) was distilled. While chloroform (Riedel-deltaen), dodecylbenzenesulfonic acid, DBSA, (Acros), sulfuric acid, H₂SO₄, (Riede-de haen), ammonium persulfate, (NH₄)₂S₂O₈, (APS) (Riede-de haen), acetone (Acros), perchloric acid, HClO₄, (Acros), ethanol (Acros), toluene (Acros), 1-propanol (Acros), dimethyl sulfoxide, DMSO, (Acros), tetrahydrofuran, THF, (Acros), m-cresol (Flukachemie AG), N-Methyl-2-pyrrolidone, NMP, and methanol (Riedel-deltaen) were used as received.

Synthesis of Poly(o-toluidine) (POT) Salt

In a typical experiment 50ml of chloroform was taken in a 100 mL round bottom flask. Then 2.3ml of DBSA was added to it under mechanical stirring. To the above solution 1.5ml of OT and 25ml of 0.5M H₂SO₄ were added. 25ml of 0.09 M APS aqueous solution was added to the above mixture. The mixture turned green and polymerization reaction was allowed to proceed for 24 hours. In the end the organic phase containing POT salt was separated and washed four times with 50mL of acetone. After thorough washing, a dark green highly concentrated POT salt was obtained (Figure 1). Then it was dried at room temperature for 24 hours in a Petri dish. On addition of small amount of acetone to the Petri dish the film broke into flakes. Then POT-DBSA salt was separated by filtration and dried in a desiccator. The sample was labeled as POT 0.09. Sample POT0.03 was prepared by same procedure with 0.03 M APS solution.

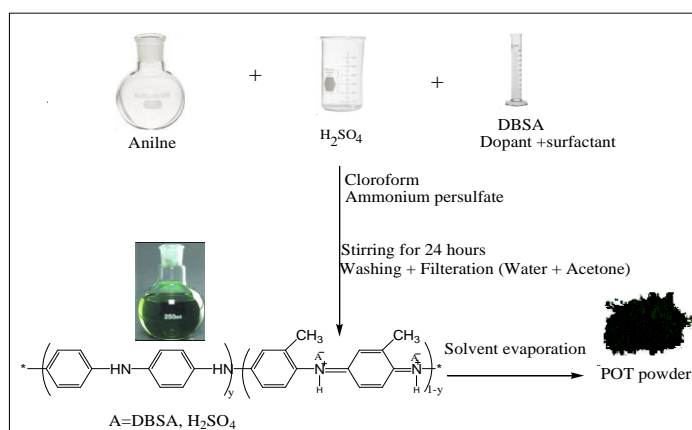


Figure 1: Synthesis of POT salt

Characterization

Cyclic voltammetry (CV) and Galvanostatics charge discharge analysis (GCD) of POT salts was executed in a three electrode electrochemical cell using 3000 ZRA potentiostat/galvanostat Gamry (USA). POT salt was dissolved in 2:1 mixture of toluene and 2-propanol and dip coated on gold working electrode. Whereas, a coiled wire of gold and saturated calomel electrode (SCE) were used as counter electrode and as reference electrode, respectively. Ultraviolet visible (UV-Vis) spectroscopic analysis was carried out in chloroform by using Spectrophotometer (Perkin Elmer, UK,) having cell of quartz of 1 cm path length.

RESULTS AND DISCUSSIONS

Solubility

Synthesized POT salt was soluble in many organic solvents, such as chloroform, DMSO, THF, NMP, ethanol, DMF, methanol, toluene, 2:1 mixture of toluene and 2-propanol.

Cyclic voltammetry

Acidic medium

At five different scan rates, CV of POT were carried out in HClO₄ (Figure 2a) and H₂SO₄ electrolytes (Figure 2b). Both have small radius whose values are rSO₄²⁻ (0.218 nm) and rClO₄⁻ (0.225 nm) individually. There is only slight difference in ionic size of the dopants. Both have regular tetrahedrons molecular structure [16].

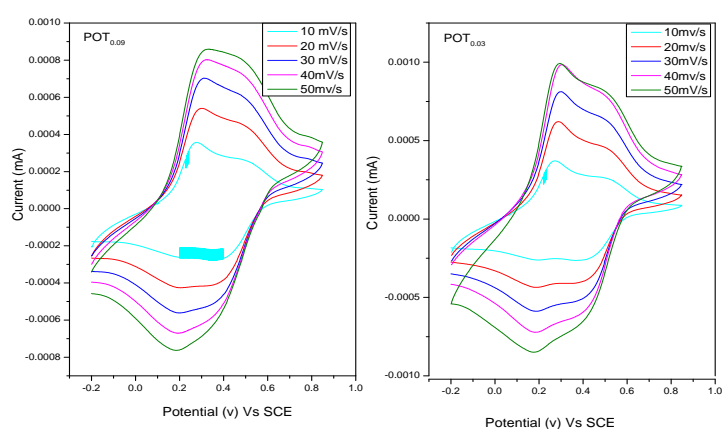


Figure 2a: CV of POT_{0.09} and POT_{0.03} in HClO₄ aqueous electrolyte at different scan rates (10, 20, 30, 40 and 50 mV/s).

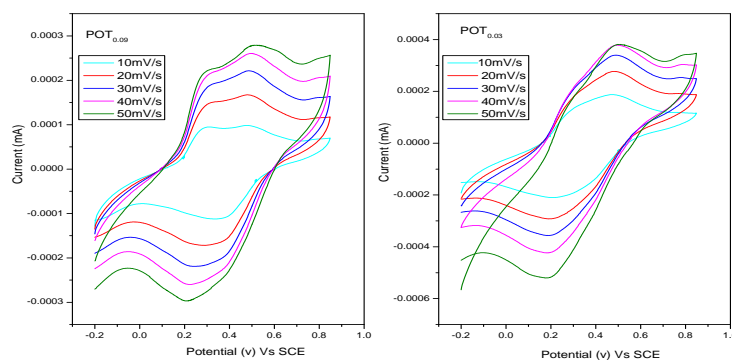


Figure 2b: CV of POT_{0.09} and POT_{0.03} in H₂SO₄ aqueous electrolyte at different scan rates (10, 20, 30, 40 and 50 mV)

CV of POT in H₂SO₄ and HClO₄ electrolyte solutions exhibit two pairs of redox peaks. One is because of switching between semiconducting-state (leucoemeraldine) to the conductive form (emeraldine), the other is due to switching between emeraldine and pernigraniline forms [17, 18]. Absence of intermediate peak between first and second oxidation states shows that no degradation product is formed [17]. It is noted that all the CV curves exhibit identical peak shape, with little variation in the peak potential and evident current enhancement when scan rate is increased. Figure 2a and 2b showed that the anodic peaks moved to further positive potentials with rising scan rate and the cathodic peaks slightly moved in direction of negative potentials. These results suggest that kinetics factor perform significant role in redox process and the anions

cannot participate completely in the process of doping and de-doping at higher scan rates [16, 19].

The correlation among first anodic peak currents and the square root of scan rate are given in Figure 4. In agreement with the principle of anions elective electrode, made up of polymer, the addition and exclusion of anion species occurs which is associated with the POT oxidation–reduction process to sustain the electric neutrality. It reveals that the oxidation–reduction peaks are associated with the transformation between leucoemeraldine and emeraldinestates as well as the doping and de-doping of perchlorate and sulphate anions. The addition and removal of ClO_4^- and SO_4^{2-} could be considered as semi-infinite diffusion control [16].

The specific capacitance (C_{sp}) of the polymer films were calculated using the following formula (1) [20]:

$$C_{sp} = \frac{i}{v \times m} \dots \dots \dots (1)$$

Where I, v and m are the maximum peak current, scan rate and mass of the deposited material, respectively.

It is noticed in the cyclic voltammogram of POT films, in H_2SO_4 and HClO_4 electrolyte solutions (Figure 2a and 2b), the enclosed area by CV in HClO_4 aqueous solution is larger than that in H_2SO_4 aqueous solution, indicating a much higher SC value in HClO_4 aqueous solution than in H_2SO_4 aqueous solution shown in Figure 3. These analysis shows that 1.0 M HClO_4 as electrolyte could greatly enhance the capacitance performance of POT electrode. According to Ma *et al.* [19] the improved capacitance might be due to the following reasons: (1) Properties of CPs are greatly influenced by dopant anions. For the enrichment of electrochemical activities of CPs, the ClO_4^- dopant anions might be more suitable when compared with SO_4^{2-} anions (2) Most importantly the ion transportation in electrolyte and the charge transfer in electrode material are changed when electrolytes are changed and thus results in different specific capacitances. The charge transfer resistance and solution resistance of CPs electrode in 1.0 M HClO_4 are lower than in H_2SO_4 aqueous electrolyte. Consequently, the inner layer of the polymer is accessed more efficiently when the electrolyte ions perforate into the inner electrode material.

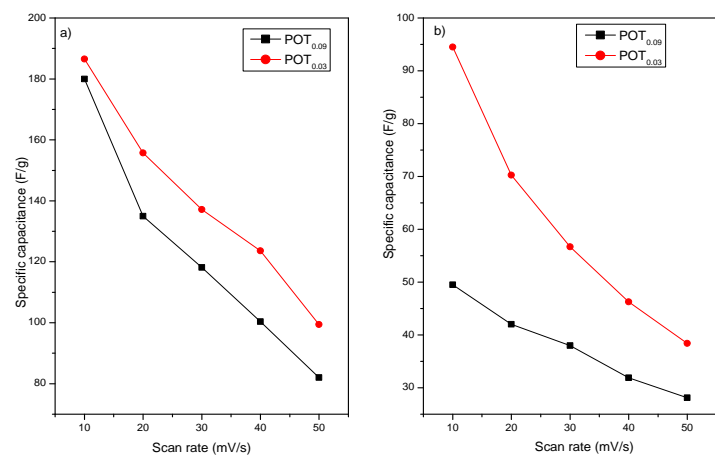


Figure 3: Specific capacitance Vs scan rate a) in HClO_4 and b) H_2SO_4 aqueous electrolytes

The alteration of specific capacitance with scan rate for POT coating is depicted in Figure 3. Maximum SC value of 186 F/g was obtained for the POT_{0.03} electrode at 10 mV/s scan rate in 1M HClO_4 . It is noted that the specific capacitance of the electrodes decline when scan rate is increased. The reason for diminished specific capacitance at higher scan rate is that, the concentration of the ions on the electrode/electrolyte interface raise quickly and the rate of diffusion of electrolyte from electrode/ electrolyte interface to electrode will not be ample to entertain the electrochemical reactions [21]. It is also noted that in same electrolyte and at same scan rate, the SC value of POT_{0.03} is higher than that for POT_{0.09}, this might be due to these reasons (1) over oxidation of POT_{0.09} at high concentration of APS [22]. (2) Higher doping level of POT_{0.03} as compared to POT_{0.09}. A UV-Visible spectrum shows higher doping level of POT_{0.03} than that of POT_{0.09}. Based on previous literature, DBSA play important role in enhancement of SC value of polymer [23]. Thus POT_{0.03} shows higher SC value than POT_{0.09}.

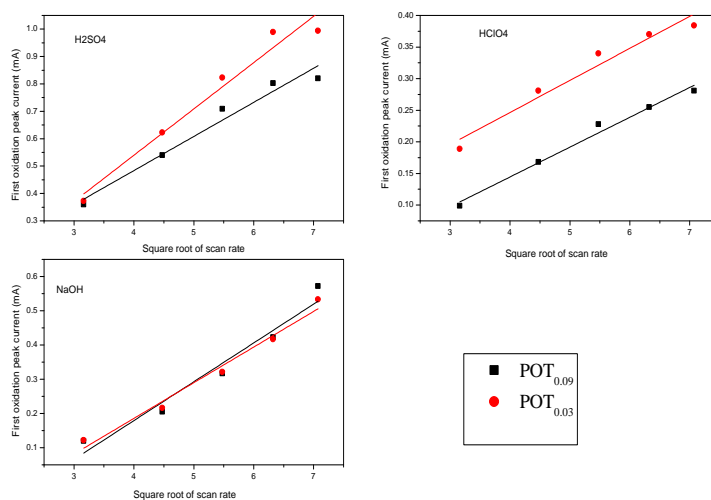


Figure 4: First oxidation peak current Vs square root of scan rate

Basic medium

CV of POT salts in 1 M NaOH is shown in Figure 5. Electrochemical response of POT salts in NaOH is based on attachment/detachment of hydrogen at the start of scans, reversible adsorption of OH^-/OH^- in the middle part of the scans and production of oxide in the last stages of the scans [24]. A pronounced peak marks the cathodic scans may be because of the reduction of the oxide layer [24]. The redox peaks are usually assigned to the redox switching of POT among semiconducting state (leucoemeraldine form) and a conducting state (polaronic emeraldine form) [24]. This produces pseudo capacitance of POT. Further, from Figure 4, it can be noted that with boosting the potential scan rate, the peak potential of oxidation peak shifts to positive potentials. Peak current rises linearly with the square root of scan rate, implying diffusion controlled phenomenon [25].

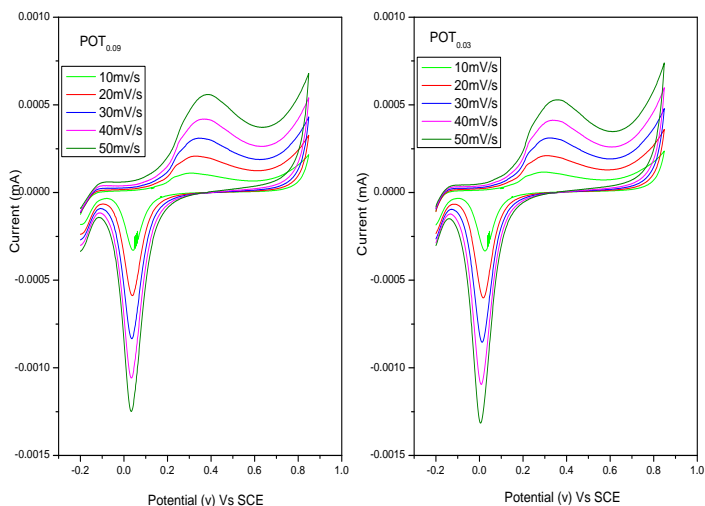


Figure 5: CV of POT_{0.09} and POT_{0.03} in NaOH aqueous electrolyte at different scan rates (10, 20, 30, 40 and 50 mV/s)

Galvanostatics charge–discharge behavior

Figure 6a and 6b shows galvanostatic charge/discharge measurements were carried out at two different current densities, 5 and 0.5 A/g, in potential window of 0-0.9 V. At lower current density, the charging/discharging process acquire longer time [26], which is associated to the sufficient insertion or release of ClO₄⁻ and SO₄²⁻ ions during the charging/discharging process.

The C_{sp} of the electrode can be calculated according to Equation 2 [27].

$$C_{sp} = \frac{I \times \Delta t}{\Delta V \times m} \dots \dots \dots (2)$$

Where I, Δt, ΔV and m are the discharge current (A), discharge time (s), potential window (V) and m mass of the active material, respectively.

Highest SC value of 93F/g was obtained for POT_{0.03} and POT_{0.09} in HClO₄ acid aqueous electrolytes. Which confirmed that POT electrode shows superior performance in HClO₄ acid aqueous electrolytes when compared with that in H₂SO₄ aqueous electrolytes and are in agreement with results obtained from CV. It is noted that for both samples SC value is lower at 5 A/g current density as compared to the value at 0.5 A/g (Figure 7a and 7b). This is because of effective utilization of active material is crucial realization in pseudocapacitance of polymer materials [27].

UV-Visible spectroscopy

Figure 8 illustrates the UV-Vis absorption spectra of POT salts in 2:1 mixture toluene and 2-propanol. Three peculiar absorption peaks at 321-326, 516-524 and 1257-1296 nm are present. The absorption peak at 321-326 nm can be attributed to π-π* transition of the benzenoid rings [28], whereas the peaks at 521-524 and 1257-1296 nm can be assigned to polaron-π* transition and π-polaron transition, respectively [22, 29]. Based on the available literature that the degree of doping can be roughly guessed from the absorption spectra of the polymers, in which the ratio of absorbance at ~800 and ~300 nm manifest the extent doping of polyaniline (A₁₂₅₇₋₁₂₉₆/A₃₂₁₋₃₂₆) [30]. It was noted that for POT salts the relative intensity was higher for POT_{0.03} (1.0144) than that for POT_{0.09} (0.95), indicating higher doping level for POT_{0.03} (Table 1).

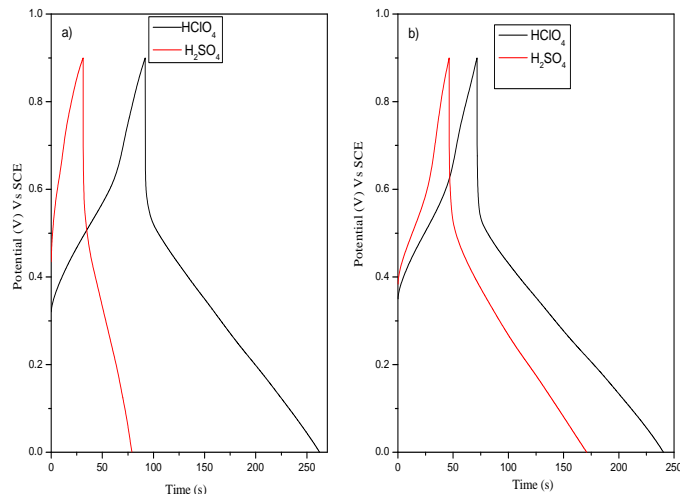


Figure 6a: Galvanostatics charge–discharge curves of a) POT_{0.09} and b) POT_{0.03} at current density of 0.5 A/g.

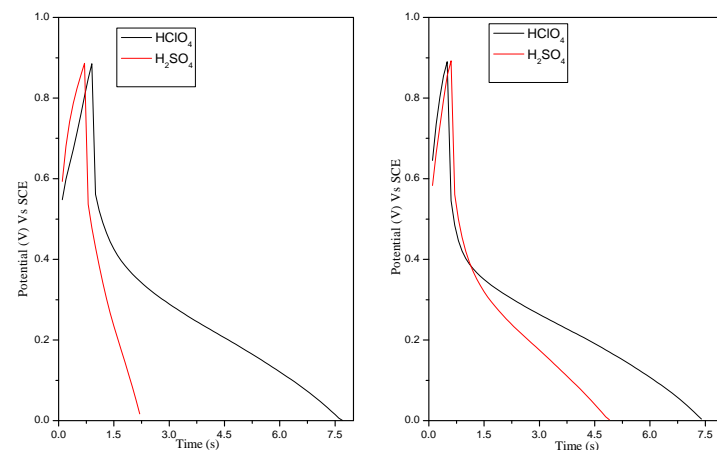


Figure 6b: Galvanostatics charge–discharge curves of a) POT_{0.09} and b) POT_{0.03} at current density of 5 A/g.

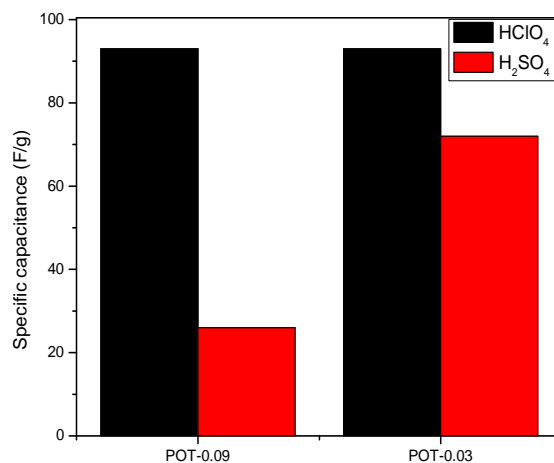


Figure 7a: Specific capacitance at current density of 0.5 A/g.

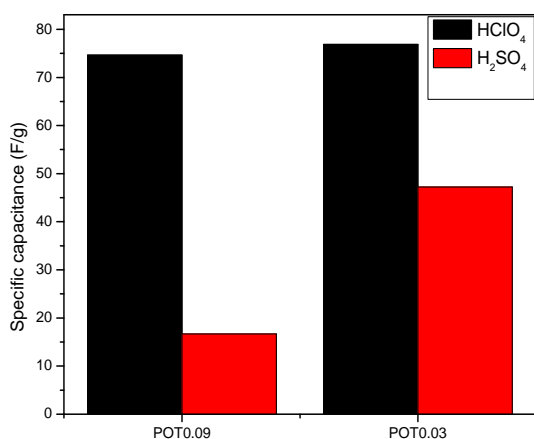


Figure 7b: Specific capacitance at current density of 5 A/g.

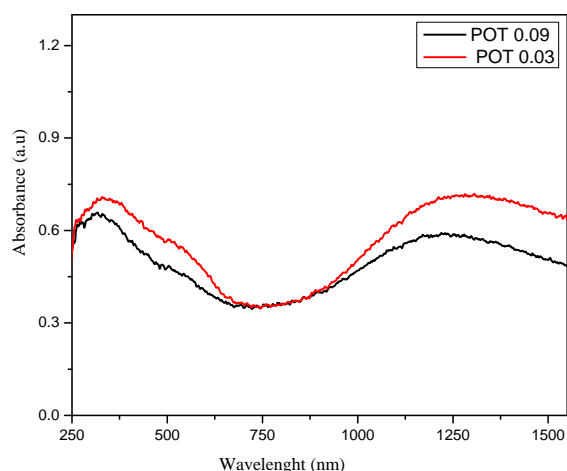


Figure 8: UV-Visible spectra of POT_{0.09} and POT_{0.03}

Table 1: UV-Vis Absorption Peaks of POT Salts

S. No	Sample	Wavelength of absorption peak			Extent of doping ($A_{1257-1296}/A_{321-326}$)
		π - π^* transition (nm)	Polaron- π^* Transition (nm)	π -polaron transition (nm)	
1	POT _{0.09}	321	516	1257	0.95
2	POT _{0.03}	326	524	1296	1.0144

CONCLUSION

POT salt was synthesized by an emulsion polymerization method. Electrochemical behavior of synthesized salt was investigated through CV and GCD for super capacitor application. Synthesized material was soluble in a number of organic solvents and didn't required any binder or additive for electrode preparation. Elimination of binder not only reduced cost but also electrode preparation process was simplified. CV was carried out at different scan rate in 1 M Sulphuric acid (H₂SO₄), 1 M perchloric acid (HClO₄) and 1 M sodium hydroxide (NaOH) electrolytes. The synthesized polymer shows excellent redox behavior in both acidic and basic medium. UV-visible spectroscopy was use for investigation of spectral behavior. POT_{0.03} salt showed improved specific capacitance value as compared to POT_{0.09} salt in HClO₄ aqueous electrolyte. Thus it is concluded that HClO₄ aqueous electrolyte is a valuable electrode material for super capacitors.

No conflict of interest: Nill

Financial assistance: No

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