



Short Communication

The electrochemical performance of electrodeposited chitosan bio-nanopolymer in non-aqueous electrolyte: a new anodic material for supercapacitor

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Abstract

The polymeric film electrodes of chitosan are deposited by electrochemical deposition method on the stainless steel substrates. The prepared film electrodes are characterized by X-ray diffraction, scanning electron microscopy, Fourier transform infrared spectroscopy, contact angle techniques and evaluated for the supercapacitor application by studying electrochemical properties through cyclic voltammetry. The XRD study depicts nanocrystalline nature of deposited chitosan with 36 nm crystallite size. The uniform, compact and spongy chitosan thin film covers the utmost substrate surface and has hydrophilic nature with mean water contact angle 57.9°. The chitosan electrode exhibits 13 kW kg⁻¹ power density from the galvanostatic charge discharge study. The chitosan electrode shows the maximum electrochemical capacitance of 36 F g⁻¹ in non-aqueous KCl electrolyte, which presents a new anodic material for supercapacitor application.

Keywords Chitosan · Electrodeposition · Polymer · Supercapacitor · Thin film

1 Introduction

A capacitor is a device which stores the charges and the capacity is expressed in terms of C g⁻¹ and the capacitance in terms of F g⁻¹. The capacitor which stores the charges in very huge amount is called as supercapacitor. The capacitance of capacitor depends upon area of material exploited as well as the mass of the active material [1–3]. Therefore the capacitance can be expressed in terms of interfacial and specific capacitance.

Many more strategies were explored to achieve maximum capacitance as well as the stability of the electrode material. The idea of supercapacitor started with the use of carbon nano tube (CNT) which is from the utilization of double layer capacitance [4]. In next stage, it was achieved with transition metal oxides and ferrites [4–8]. These transition metals were again consumed with different sulphides and phosphates to attain extreme capacitance [9–11].

Also the metal oxide based metal organic framework was employed as a new material in supercapacitor application [12]. In the middle, conducting polymers like polyaniline, polypyrrole etc. also played an important role in achieving better capacitance [13–15].

From the earlier reports, it is inferred that there was a use of metal based material or artificially synthesized polymer for supercapacitor application. Now keeping in the mind the eco-friendly approach and taking into account of the view of elemental abundance in future, it is a time to find other electrode materials for supercapacitor. In this aspect, chitosan was applied to achieve expected results. The work has been processed by using metal oxide and carbon based material incorporating chitosan. Graphene based porous carbon aerogels on nickel foil displayed a high capacitance of 197 F g⁻¹ [16]. Chitosan with activated carbon has high capacitance of 264 F g⁻¹ on titanium foil [17]. The chitosan based ternary composite like

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chitosan-graphene oxide-polyaniline on graphite electrode and graphene oxide-chitosan-copper on PET film possess capacitance of 609 F g^{-1} and 356 F g^{-1} , respectively [18, 19]. The electrodeposited MnO_2 -chitosan on nickel foam exhibited 424 F g^{-1} capacitance [20]. Also, the efforts have been made to chitosan based membrane cum binder to improve the capacitance [21].

The literature depicts that chitosan can be a suitable candidate for the supercapacitor and would have highest value of capacitance when incorporated with carbon based materials and metal oxides using the substrates like graphite, nickel foil, nickel foam etc. [16–20]. To the best of our knowledge chitosan has not been yet used as single source as electrode material for the supercapacitor. Chitosan is a linear polysaccharide consists of glucosamine repeating unit with hydroxyl and amine functional groups as shown in Fig. 1 [16, 22]. This is derived from partial N-deacetylation of chitin which is a biopolymer widely distributed in nature and available in insects, crab shell and shrimp shell etc. The animal based polymer-chitosan is versatile biomaterial which has significant application in water purification, cosmetics, and textiles as well as in biomedical field [23–27]. In the present work, chitosan is deposited on low cost stainless steel substrates by electrodeposition. The deposited material is characterized for the structural and morphological information and electrochemical experiments are carried out to find its application in the supercapacitor.

2 Experimental

In the present investigation, chitosan films were electrodeposited by using electrochemical analyzer (Model CHI 66E) on stainless steel substrates. Prior to the deposition, stainless steel substrates were polished by zero grade polish paper. After that the substrates were cleaned ultrasonically for 30 min. The deposition of chitosan film was carried out by using chitosan flakes (from shrimp shells 75% deacetylied) purchased from Loba Chemie Pvt. Ltd.

A chitosan solution was prepared by dissolving chitosan flakes in 1% acetic acid with 100 mg/ml weight to volume ratio. It was found that chitosan flakes were initially dispersed in the solvent and dissolved slowly which formed clear and transparent solution. The deposition of chitosan films were carried out from this transparent solution. For the deposition, conventional three electrodes assembly was used in which, graphite electrode was a counter and stainless steel electrode acted as a working electrode, while saturated calomel electrode (SCE) was used as a reference electrode to measure the reaction potentials.

The cathodic deposition was carried out at -1.5 V/SCE on the stainless steel electrode. The films obtained were first cleaned in the doubled distilled water to remove unbounded chitosan and then well dried in the air. The film was thin and transparent, and weighted about $0.00030 \text{ g cm}^{-1}$.

The chitosan films were characterized to get the structural and morphological information. The XRD was carried out to recognize the structure and crystallite size of material deposit with the help of Bruker AX5 D8 advance model. The FTIR analysis was conducted by using Alpha T Bruker spectrograph to know the functional groups and hence to confirm the deposited material. The morphology of the material was studied by scanning electron microscope model JEOL JSM-6360. The contact angle of deposited material was obtained using Rame-hart Model A-100. The electrochemical study for supercapacitor was carried out by using ZTV MP1 multichannel electrochemical workstation in the non-aqueous KCl electrolyte for various scan rates. The stability of electrode was tested to find the reliability of the material in the supercapacitor application.

3 Results and discussion

3.1 Deposition mechanism of chitosan film

The chitosan films were deposited from chitosan solution on to stainless steel which acted as a working electrode.

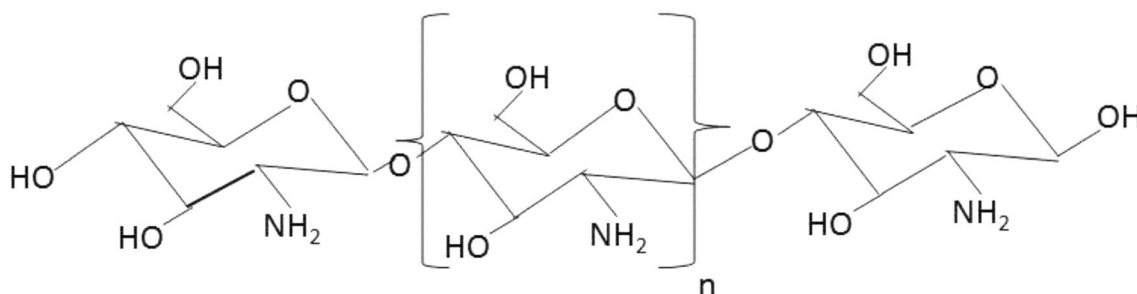


Fig. 1 Chemical structure of chitosan

The deposition was carried out for 600 s at -1.5 V/SCE applied potential. In case of chitosan, amine group is protonated < 6.3 pH and becomes a cationic polyelectrolyte [28]. After the application of electric potential, the positively charged molecules of chitosan polymer is attracted towards negatively charged cathode. At that moment chitosan loses its charge and diffuse as chitosan thin film on the substrate as shown in Fig. 2 [16]. The chitosan film observed on the substrate is insoluble due to increase in local pH due to deprotonating of amine group [29]. In brief, a polymeric film of biopolymer has been synthesized by means of one step potentiostatic deposition on low cost stainless steel.

3.2 XRD study

In order to know the structure of the deposited material, the X-ray diffraction study is necessary. The X-ray diffraction (XRD) was carried out by using the CuK_α of copper target which produces the diffraction after interaction with the matter on the substrate. Figure 3 provides the structural information of the deposited material. From the figure, the peak at angle 20.3° indicates the formation of orthorhombic structure of chitosan on the substrate [30]. Similar observation also evidenced for chitosan nanocomposite used for bio-medical application [31]. From the XRD information the crystalline size of the material was calculated using the Sherrer's formula [32]. The calculated value inferred that the synthesized material is nanocrystalline with crystallite size 36 nm.

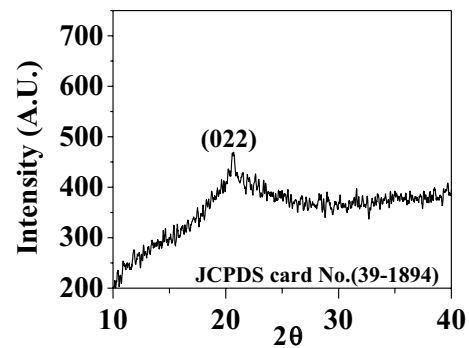


Fig. 3 The XRD of electrodeposited chitosan thin film

3.3 FTIR study

The Fourier-transform infrared spectroscopy (FTIR) also supports the formation of the chitosan on the substrate by means of stretching and bending frequencies of functional respective functional group. The FTIR spectrum of chitosan film is shown in Fig. 4. The peaks of different frequencies appeared because of transmitted rays from chitosan in IR region. The figure shows the vibration spectra within the frequencies 750 to 3750 cm^{-1} corresponding to N–H and O–H stretching in contribution with intra-molecular hydrogen bonds. The absorption band at around 3364 cm^{-1} can be attributed to OH stretching. Further, the presence of C=O due to stretching of amide group is confirmed around the signal at 1646 cm^{-1} . Also the spectrum at around 1255 cm^{-1} is because of the bending vibrations of hydroxyl group

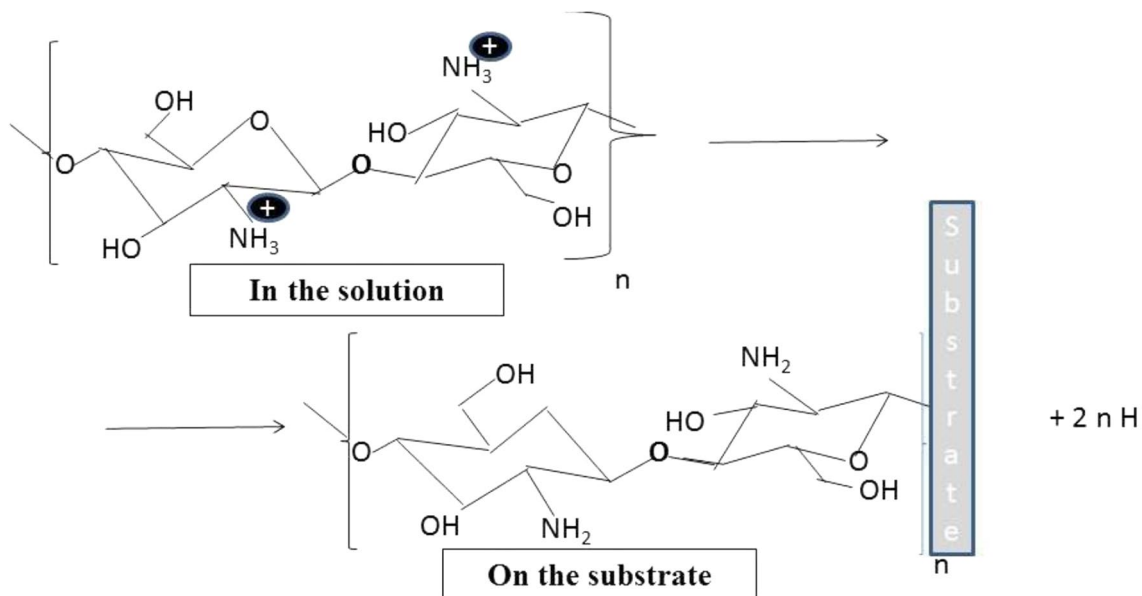


Fig. 2 The deposition mechanism of chitosan on the substrate

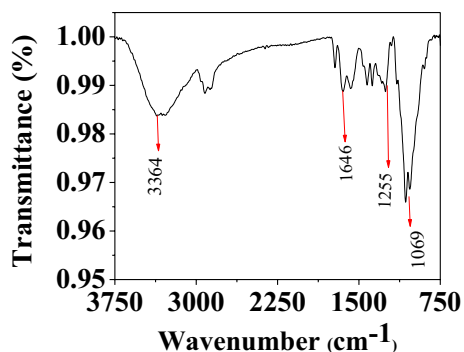


Fig. 4 The FTIR spectrum of as deposited chitosan film

present in the chitosan. The absorption band arrived at 1069 cm^{-1} corresponds to C–O band stretching of chitosan sample. The spectrum obtained in present work has close resemblance with the spectra of chitosan samples described by others in literature [33, 34].

3.4 Scanning electron microscopy

The chitosan thin film material is delicate one and found to be burned at high electron energy. To overcome this situation the scanning electron microscopic study was carried out at 10 kV applied potential. Figure 5 shows the scanning electron microscopy of the chitosan thin film carried out to study the morphology of the material. The figure shows uniform and compact like morphology of chitosan film spreads over the entire substrate at $205\times$ and $500\times$ magnifications (in the inset). Sincerely looking insight to the morphology, sponge like appearance with large number of pores is observed which are beneficial for the rapid conduction of ions inside the active material to improve the supercapacitance.

3.5 Contact angle and electrochemical study

The water contact plays an important role in achieving capacitance by means of electron transfer through the

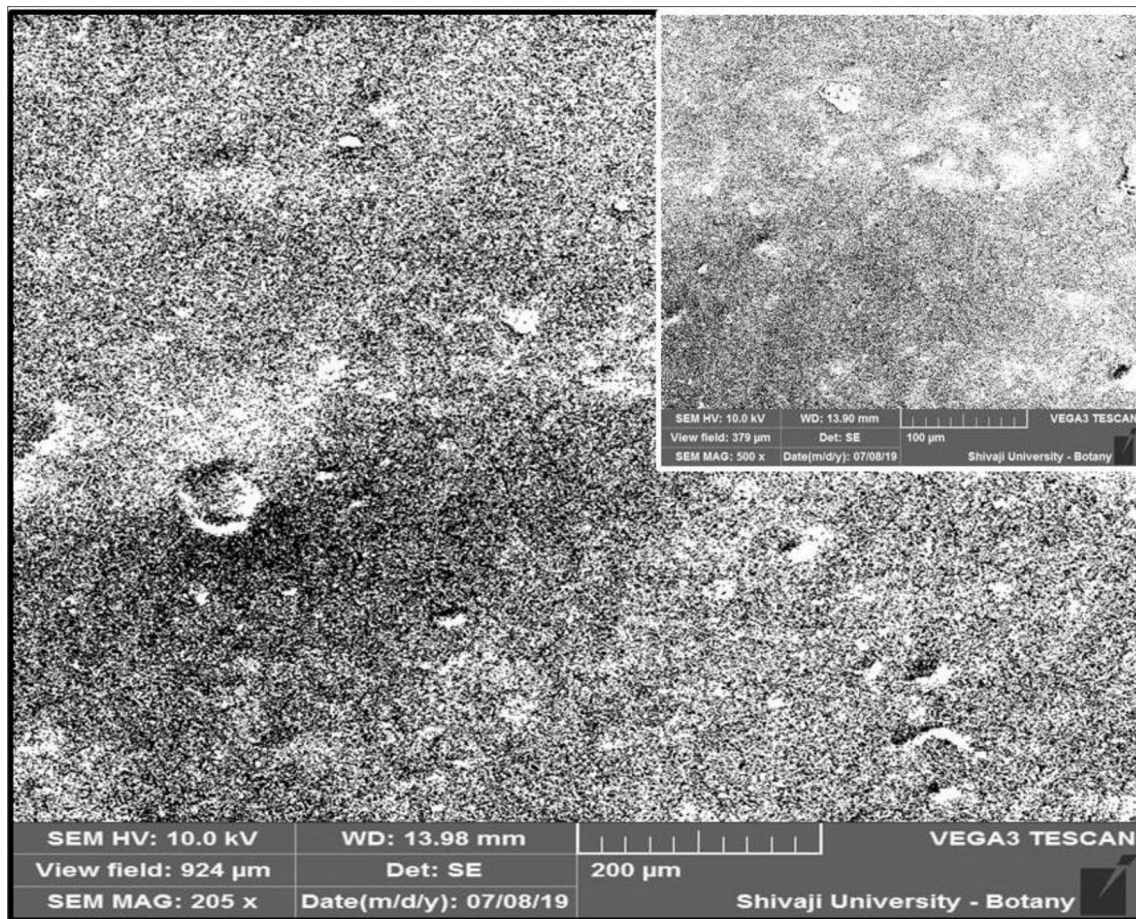


Fig. 5 The scanning electron micrographs (SEM) of chitosan film at $205\times$ magnification and $500\times$ (in the inset)

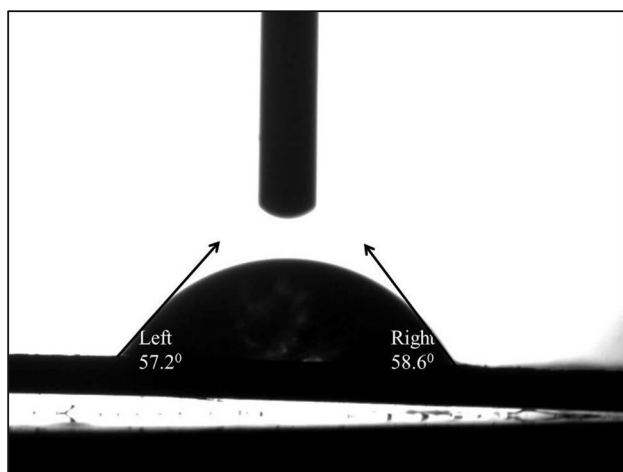


Fig. 6 The contact angle of chitosan film

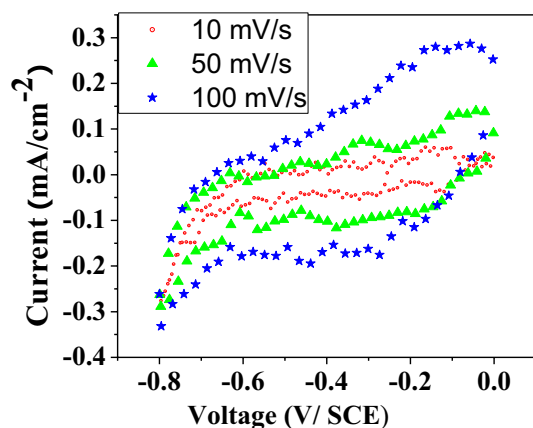
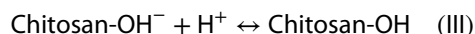
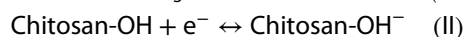
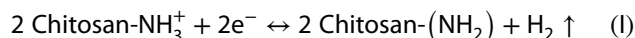


Fig. 7 Cyclic voltammetry (CV) study of chitosan electrode (Film thickness $0.00030 \text{ g cm}^{-1}$)

electrolyte. Figure 6 shows the contact angle of 57.9° depicting hydrophilic nature of the film.

To study the electrochemical performance of chitosan electrode, the cyclic voltammetry (CV) study was carried out in traditional three electrode system. In the system chitosan electrode, platinum mesh and SCE acted as working, counter and reference electrodes, respectively. The CV plots studied at different scan rates from 5 to 100 mV s^{-1} are shown in Fig. 7. Figure shows that there is an increase in the current with an increase in the scan rate with redox peaks. The redox peaks are due the intercalation and deintercalation of the charges into the active sites. In the chitosan, hydroxyl ($-\text{OH}$) and amino ($-\text{NH}_2$) are reactive functional groups. These groups might be responsible for the capacitive behavior of chitosan electrode by protonation and de-protonation. The chitosan electrode carries excess positive charge which acts as cationic natural polymer due to NH_3^+ group [35]. The transfer of species

for the conduction of current can be shown from following reactions (I-III) which are responsible for the production of pseudocapacitance. In the proposed reaction, the first reaction shows the hyperpositive chitosan reacts with electron which turns in the formation of amine with H_2 evolution. This type of reduction reaction occurred in potential range of -0.6 to -0.3 V/SCE . The reduction peaks is due to the electron transfer and hydrogen evolution. In next reactions, OH group consumes electron and becomes negative charged with a reduction peak in between -0.3 and -0.1 V/SCE . These reactions are reversible and show the oxidation peaks in the reverse scan. As the scan rate increases multiple redox peaks disappear and can be seen integrated within the said potential range.



The capacitance or interfacial capacitance (C) from the CV plots are calculated by using the formula,

$$C = \frac{\int I}{V \times \left(\frac{dv}{dt}\right)} \quad (1)$$

where $\int I$ —current, V —potential window and $\left(\frac{dv}{dt}\right)$ —scan rate.

The unit of specific capacitance (C_s) is F g^{-1} which is obtained by using the weight of the electrode material (W) given by,

$$C_s = \frac{C}{W} \quad (2)$$

The different values for the supercapacitor study have been calculated for the chitosan electrode using above formula are shown in Table 1.

The stability of electrode was tested at 5 mV s^{-1} scan rate to find the potential application in supercapacitor for 5000 cycles as shown in Fig. 8. The cyclic voltammetric study shows that curves are symmetric. After 5000 cycles the percentage retention observed is 85% which may be because of loss of active sites during the cycling.

The galvanostatic charge–discharge (GCD) curves of the supercapacitor recorded in the potential range of $0-0.8 \text{ V}$ and at a current densities of $0.3, 0.5, 0.6, 0.8, 0.9$ and 1 mA cm^{-2} are shown in Fig. 9. It is observed that the discharging time decreases with increase in current density which results in increased power density as shown in Table 2. From the GCD curves, the power density is calculated by using the formula (3) [36, 37],

Table 1 Supercapacitance study of chitosan electrode from cyclic voltammetry

Sr. no	Scan rate (mV s ⁻¹)	Specific capacitance (F g ⁻¹)
1	5	36
2	10	17
3	20	9
4	50	6
5	100	5

Table 2 Power density of chitosan electrode from galvanostatic charge–discharge

Sr. no	Current density (mA cm ⁻²)	Discharging time (s)	Power density (kW kg ⁻¹)
1	0.3	5.55	4
2	0.5	0.65	6
3	0.6	0.61	8
4	0.8	0.18	10
5	0.9	0.08	12
6	1.0	0.07	13

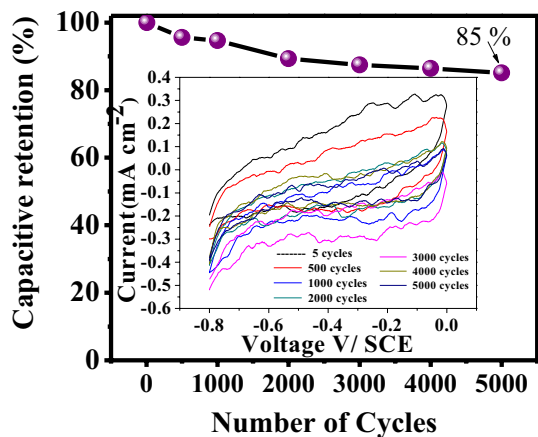


Fig. 8 Cyclic stability and capacitive retention of chitosan electrode for 5000 cycles

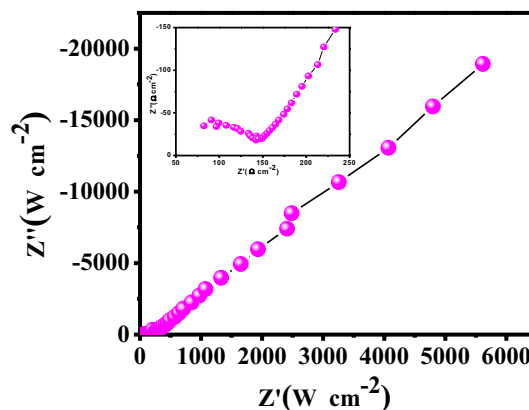


Fig. 10 Electrochemical impedance (EIS) spectra of chitosan electrode. Inset shows the semicircle

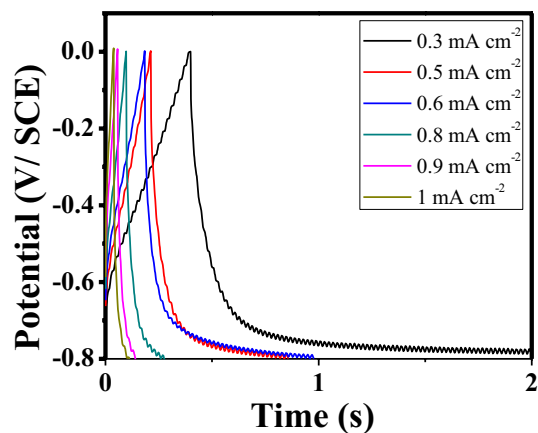


Fig. 9 Galvanostatic charge–discharge (GCD) study of chitosan electrode

$$P = \frac{E \times 3600}{T_d} \tag{3}$$

where, T_d is discharging time, $E = \frac{0.5 \times C_s \times (V^2_{max} - V^2_{min})}{3.6}$, V_{max} and V_{min} are the maximum and minimum potential

during the discharge, and $C_s = \frac{I \times \Delta t}{\Delta V}$ where, I —current density, Δt —time of discharge, ΔV —potential range

The maximum power density is attained to be 13 kW kg⁻¹ at 1 mA cm⁻² current density. The variation of power density with applied current with the discharging time is shown in Table 2.

The electrochemical impedance spectroscopy data for the chitosan electrode is expressed as Nyquist plot over the frequency range of 0.1 to 10³ Hz as shown in Fig. 10. This figure shows the small semicircle (inset of Fig. 10) in the first segment, followed by a vertical line. In the high frequency region, the relatively small semicircle represents the dominant resistive nature of the supercapacitor system consisting of electrode–electrolyte and current-collector. At the starting point of the semicircle, line represents the resistance (R_s) of the electrolyte in contact with the current collector and electrode called as series resistance.

In electrochemical reaction, electrons transferred in the electrode possess some resistance called as charge transfer resistance as R_{ct} . The minimum R_{ct} is required for the best electrochemical behavior [38]. In the present case more R_{ct} may result into low capacitance of the material.

The specific capacitance and power density of the material can be increased by increasing the material deposit and obtaining the proper composite with other anodic materials on the low resistance substrates [16–20]. After the electrochemical study, it can be concluded that the chitosan thin film electrode is an anodic material which has potential application in supercapacitor.

4 Conclusions

A new polymeric material, chitosan from biological source has been electrodeposited on the low cost stainless steel substrate. The material has orthorhombic structure and uniform and compact as well as spongy morphology. The chitosan has water contact angle of 57.9° depicting hydrophilic nature. It has potential application in supercapacitor as examined from electrochemical studies. The electrode shows maximum capacitance of 36 F g⁻¹ and power density 13 kW kg⁻¹ in non-aqueous methanol electrolyte.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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