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## **Chemical routes to materials**



# Environmental friendly solid blend polymer electrolytes based on PVA:starch:ceric ammonium nitrate for electric double layer capacitor (EDLC) applications

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## ABSTRACT

The solid blend polymer electrolytes based on polyvinyl alcohol/cassava starch are prepared by solution casting technique. The amorphous nature of the polymer electrolytes is analyzed by X-ray diffraction pattern. Fourier transform infrared spectra affirms the complexation between salt and blend polymers. The thermal behavior of solid polymer electrolyte was carried out by thermogravimetric analysis at 30-500 °C at nitrogen atmosphere. The surface morphology and EDAX spectrum of prepared high conducting electrolyte are observed in the SEM image. The impedance spectroscopy technique is used to measure the ionic conductivity values in frequency range of 42 Hz-1 MHz at room temperature. The maximum ionic conductivity of  $1.53 \times 10^{-5}$  S/cm is observed for 2% of salt doped system. Through electrochemical studies of electric double layer capacitor device, the non-faradaic behavior is observed. From linear sweep voltammetry analysis, the potential window of the higher conducting sample is obtained as -2 to +2 V. By analyzing cyclic voltammetry graph, the specific capacitance values are obtained and it denotes that increasing scan rate decreases the specific capacitance value. At low scan rate of 25 mV s, the specific capacitance value is 16 F/g, and for 100 mV s, it is 4.5 F/g. Charge–discharge studies of device appear linear slope and energy density, and power density values are observed from the number of cycles.



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## **GRAPHICAL ABSTRACT**



## Introduction

In recent years, the solid polymer electrolytes have flexibility, strength, and high conductivity compared to liquid state electrolytes and used for electrochemical applications. Solid polymer electrolytes play an important role in battery, supercapacitor, and solar cells and act as separator. Many researchers investigated to improve the performance of polymer electrolytes through polymer-salt complexes, blending polymers, cross-linking, and additives such as fillers and plasticizer, and these are the various methods to enhance the strength and conductivity of the polymer electrolyte membranes [1, 2]. Blending of two polymers is one of the methods to develop the electrical and mechanically stable electrolyte with the help of molecular interactions like hydrogen bonding, dipole-dipole forces, and charge transfer complex of polymer mixture [3]. In recent research, nonbiodegradability of materials and toxicity cause great damage to the environment and these can be overcome by using easily degradable, eco-friendly materials like naturally available polymers. Blending with biopolymer improves the biodegradable properties of the electrolytes and provides better environment

[4, 5]. PVA is a semicrystalline and biocompatible polymer with high dielectric strength, dopant-dependent electrical properties, and better charge storage capacity. It has carbon chain backbone with hydroxyl groups which can act as electron donor to support the blending system [6, 7]. In this present work, PVA having excellent film forming ability, good mechanical strength, electrochemical stability, and biodegradable property is selected for preparation of solid polymer electrolytes [2, 8]. Few works are reported on the blending system of PVA with other synthetic polymers and natural polymers such as PVA-PVP-NH<sub>4</sub>SCN [9], PVA-PAN [10], PVA-MC [8], and PVA-CS [11], and polu et.al reported that PVA blend with synthetic polymer has maximum ionic conductivity of  $3.78 \times 10^{-5}$  S/cm at room temperature [12]. Increasing interest toward blending with biopolymers shows better electrode/electrolyte contact, mechanically adhesive. So that cassava starch has been chosen as suitable biopolymer here [1].

Generally, starch can be derived from corn, potato, rice, maize, and Manihot esculenta plants as granules. It is a polysaccharide material which consists of the mixture of linear amylose and branched amylopectin with weight percentage of 20% and balance for amylopectin granules [13]. For the current work, cassava starch from Manihot esculenta is selected as a biopolymer. It has own natural value of electro-conductivity, environment friendly, low cost, and easily degradable material [14]. Starch has some deficiencies such as low tensile strength, low thermal stability, and low permeability due to hydrophobicity which can be overcome by blending or adding salt system, and the semicrystalline nature of starch can be reduced [15, 16]. Zahid et.al reported gel electrolyte using cassava starch for zinc-air battery [17], and solid polymer electrolyte was prepared using cassava starch by arrieta et.al with good electrochemical performance [18]. The addition of salt plays an important role in polymer electrolyte because charge carriers are created by some metal ions to improve the conductivity and also lattice energy of salt should be low. The ionic bond can be broken easily with small amount of energy to release the ions [8]. Ammonium salts have great attention recently due to their compatibility and high conductivity, and the H<sup>+</sup> ions play better performance in conduction and form bonding with atom easily [19]. Ammonium-based works are showing better conductivity and thermal stability as shamsuri et.al reported blend polymer doped with ammonium thiocyanate with maximum conductivity of  $1.45 \times 10^{-4}$  S/cm [8] and aziz et.al reported maximum conductivity of  $2.08 \times 10^{-5}$  S/cm for ammonium iodide [4]. In the present paper, it is focused to prepare solid polymer electrolytes on PVA: cassava starch with various concentration of ceric ammonium nitrate salt as a dopant. EDLC is fabricated with high ionic conductivity solid polymer electrolyte which provides the safety, less fabrication cost, long life cycle with better potential window and eco-friendly [4].

## **Experimental procedure**

### Materials

PVA (Polyvinyl alcohol) with molecular weight,  $M_w = 125000 \text{ g/mol}$  (S D fine Chem Ltd, India.); cassava starch from Manihot esculenta and ammonium cerium nitrate (Sigma-Aldrich) are used as a raw material. All the polymer electrolytes are prepared using deionized water as solvent throughout the work.

#### **Preparation method**

Solid polymer electrolytes are prepared using PVAcassava starch with a different weight percentage of cerium ammonium nitrate (CAN) by solution casting technique. The suitable weight ratio of PVA—starch has been taken with 15 ml of water in a beaker separately and various concentration of ammonium cerium nitrate (1, 2, 3, 4, 5 wt%) dissolved in water. The solution was mixed together and stirred continuously until we obtain homogeneous viscous solution. Further, the viscous liquid is poured in a polypropylene dish and allowed to dry at room temperature for 3 days to confirm the removal of solvent evaporation. Then, the polymer electrolytes are peeled out from the petri dishes for further studies.

#### Fabrication and characterization of EDLC

## Preparation of electrodes

The electrodes are prepared by certain composition of materials like activated carbon, carbon black and a binder with mixing solvent in the concentration of (85:5:10) weight percentage. Before coating this mixture, impurities of copper foil are removed by etching process. In this work, (rGO) reduced Graphene oxide is used as an activated material, carbon black, and PVDF as binder mixing with 15% NMP solvent to get the slurry. The prepared materials were coated on copper foil with electrode active area of 2 cm<sup>2</sup>. Then, the coated electrodes were dried for 24 h at 80°.

EDLC was fabricated by using polymer electrolyte sandwiched between the two electrodes in threeelectrode system. Components of EDLC cell using polymer electrolyte are shown in Fig. 1. The electrochemical performance of cyclic voltammetry of the cell was analyzed by the CH instrument Model 6008e. EDLC cell was evaluated at different scan rates, and specific capacitance ( $C_{sp}$ ) is determined by the equation

$$C_{\rm sp} = i/sm\,({\rm F/g})$$

where *i* represents the anodic–cathodic current (A), *s* is the potential scan rate (V/s), and *m* is the average mass of the active material.





#### Characterization techniques

The solid polymer electrolytes are investigated by some instrumental techniques to analyze their structural, vibrational, thermal, morphology, electrical, and electrochemical performance. The phase identification like crystalline or amorphous nature of blend polymer electrolytes is investigated by Bruker-made X-ray diffractometer having Cu-K $\alpha$  radiation with scan rate of  $2\theta = 10^{\circ}$ - $60^{\circ}$ . FTIR spectra for blend polymer electrolytes has been recorded with Shimadzu-IR Affinity-1 spectrometer in the wave number range of 400–4000 cm<sup>-1</sup>, and it is used to collect

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the vibrational information of complex polymer systems. The thermal stability of solid polymer electrolyte was determined by thermo-gravimetric analysis. The sample are heated at the range of 30–500 °C at nitrogen atmosphere. The electrical properties of polymer electrolytes are recorded using impedance analyzer of HIOKI-3532 LCR meter by sandwiching the electrolyte between two silver electrodes. The frequency range of impedance spectroscopy is 42 Hz–1 MHz at ambient temperature. The prepared electric double layer capacitor (EDLC) is tested for electrochemical performance through cyclic voltammetry and linear sweep voltammetry (LSV) studies using CH instrument model 6008e to analyze the capacitor behavior and potential window of the EDLC.

## **Results and discussion**

## **XRD** analysis

The XRD pattern for PVA:CS:CAN blend electrolytes is shown in Fig. 2. In all samples, diffraction peak of  $2\theta = 19.3^{\circ}$  indicates the presence of PVA and its semicrystalline nature. The crystalline peak of polymer electrolyte has distinct change because of the addition of salt that can change into amorphous phase [2]. The addition of various percentage of ammonium ceric nitrate salt decreases the peak intensity of the crystalline peaks [6]. The broad peaks, centered around the  $2\theta = 30.5^{\circ}$  and  $2\theta = 40^{\circ}$ , are assigned to the amorphous phase of cassava starch [20]. The amorphous phase within the polymer blend increases the dissociation of salt, and it enhances the overall ionic conductivity value [21]. In 1% of salt doped system, it shows the sharp peak due to semicrystalline nature of polymer but PVA:CS:-CAN(94:4:2) system shows more amorphous nature and less peak intensity that denotes good dissociation of salt or strong interaction between the blend polymers with salt. This system shows more amorphous nature than the other prepared systems [22]. This amorphous phase accelerates segmental motion of ion in polymer complex, and it results in increased ionic conductivity [11].

#### **FTIR** analysis

The FTIR spectral analysis is used to identify the molecular structure and chemical interaction between blend polymer electrolytes on the addition of salt. In this present work, FTIR spectra is used to collect the information about interaction between ions and blend polymer electrolyte in terms of peak intensity and wavenumber shifting [23]. The FTIR spectrum of PVA/cassava starch blend electrolytes with various concentration of CAN has shown in Fig. 3. The molecular interaction between PVA/CS with ceric ammonium nitrate shows several functional groups such as hydroxyl, carboxyl, and amine which depends on the wavenumber between 400 and 4000 cm<sup>-1</sup>.



Figure 2 XRD pattern of PVA/CS doped with different concentrations of CAN (a) 1%, (b) 2%, (c) 3%, (d) 4%, (e) 5%.



Figure 3 FTIR spectra of PVA/CS doped with different concentrations of CAN (a) 1%, (b) 2%, (c) 3%, (d) 4%, (e) 5%.

The hydroxyl group (O–H) of pure PVA appearing at 3425 cm<sup>-1</sup> is shifted to 3305–3325 cm<sup>-1</sup> due to the addition of salt [8]. The C–H stretching from alkyl group of the spectrum of PVA has shifted to the wavenumber of 2927 cm<sup>-1</sup> due to blending with salt [24]. The carboxylic group of C=O vibrational spectrum of PVA is observed to shift at 1710 cm<sup>-1</sup> because of the addition of salt, reported by shamsuri et al. [8]. In the report of burdaiah et.al and shamsuri et.al, the band at C=C vibrational modes of



carboxamide group appears the peak at 1649 cm<sup>-1</sup> which describes the PVA interaction with higher intensity. The PVA interaction was clearly observed by the bands of C–H bending [3] at 1436  $\text{cm}^{-1}$  and C– H rocking of PVA at 844 cm<sup>-1</sup> which indicates the presence and strong interaction of PVA polymer [25]. The presence of cassava starch peaks was observed to shift to 1085 cm<sup>-1</sup> at C–O vibration of C–OH group [26], C–O vibration of C–O–C at 1029  $\text{cm}^{-1}$ , and C–O vibration of C–O–H groups band at 921 cm<sup>-1</sup> which indicates the strong bonding interaction between the PVA and cassava starch [19]. Further, ceric ammonium nitrate salt plays an important role in blend electrolytes that modifies the peak intensity, shape, and position in complex formation of blend polymer and salt. Generally, CAN supplies free ammonium ions and an oxidant for functional groups [27] that indicates the amine group in C-N stretching which can reveal the strong interaction of the salt with blend polymer at various concentrations [28]. The 2% of CAN shows the higher ionic conductivity that is in agreement with the XRD pattern.

### Thermal studies

## TGA/DTG

The thermal analysis is carried out for high conducting polymer PVA/CS/CAN electrolyte by thermo-gravimetric analysis to examine the decomposition temperature, weight loss percentage, and phase transition of the electrolyte [24]. Figure 4 shows the TGA curves of high conducting PVA/CS/ CAN electrolyte. After device fabrication, heat is generated through the cell so the polymer electrolyte degrades. So TGA is very safe to analyze the thermal stability of electrolyte before device formation to avoid the short circuit issues [29]. The TGA curves show two-stage degradation of the high conducting polymer electrolyte. In this work, initially weight loss occurs due to evaporation of water or moisture absorbed in electrolyte by the environment [10]. The content of ammonium ceric nitrate decomposes at the earlier stage, and the reaction occurs between 155 and 190 °C in the sample [30]. Generally, PVA thermally decomposes at 260 °C. In this present work, PVA blended with cassava starch started decomposition at 238 °C which revealed the interaction of starch in the film [24]. The cassava starch thermal degradation begins at 270 °C reported by pawlicka et al., and



Figure 4 The TGA curves of high conducting PVA/CS/CAN electrolyte.

when it was blended with PVA, it decomposes at 292 °C [16]. Finally, the prepared electrolytes were fully decomposed at 300–500 °C through gradual weight loss as shown in the graph.

## FESEM morphology

SEM morphology of PVA/CS/ACN electrolyte was shown in Fig. 5a. The surface structure of the SPE samples can be seen from the captured images which can be used to analyze and study the behavior of the prepared samples. It shows homogeneous surfaces with cracks and good structural integrity. The miscibility of the polymers is clearly observed in the morphology images [4]. This is attributed to the improvement due to better dispersion of ions which in turn enhances the ionic conductivity [31]. The addition of salt to PVA:starch polymer blend film creates the porous nature which is used to enhance the disorderness. It enhances the ionic conductivity of the prepared SPEs [32].

The Energy Dispersive Analysis of X-rays (EDAX) of prepared SPE is shown in Fig. 5b. The presence of C and O is extreme, and it reflects the presence of maximum PVA polymer in prepared SPE [33]. The presence of Ce is due to the addition of salt (ACN). The membrane surface was covered by the salt sedimentation, and the surface pores were filled because of the ceric sedimentation which is observed from EDAX analysis [34].



Figure 5 a, b SEM morphology and Energy dispersive analysis (EDAX) for high conducting PVA/CS/ CAN electrolyte (scale: 1 µm).

## **AC** impedance studies

## Nyquist plot

The Nyquist plot of solid polymer electrolyte has been investigated using AC impedance spectroscopy. The Nyquist plot of PVA/CS/CAN blend polymer electrolyte doped with various salt ratios at room temperature has been shown in Fig. 6a. Generally, the plot consists of two regions that the semicircle appearing on the higher frequency region and the spectra of spikes can be appearing at the low frequency region [9]. The impedance spectra of semicircle appears due to ionic conduction in bulk of the

0.87K 0.58K

0.29K

0.00K

0.0

electrolyte, and the spikes appear due to effect of blocking electrodes or electrolyte interface [7]. The bulk resistance value of solid polymer electrolyte can be extracted by using Z-view software from the plot at spike appearing area that is indicated as Z'-axis. Thus, the  $R_{\rm b}$  values are used to calculate the ionic conductivity value by using this equation,

Ce Lß2

6.5

Ce Lß

<sup>Ce Lα</sup> Ce Lβ6

5.2

Ca K<sub>β1</sub>

Ca Ka

3.9

$$\sigma = t/R_{\rm b}A$$

**S Kβ1** 

2.6

**S** Kα

Mg Kα

Mα Al Kα

1.3

where *t* is the thickness of the electrolyte,  $R_b$  is the bulk resistance of the film, *A* is the area of the electrolyte, and  $\sigma$  is the conductivity of the electrolyte [35]. The highest conductivity of the sample is  $1.54 \times 10^{-5}$  S/cm for (94:4:2) blend electrolyte, and





**Figure 6 a** Nyquist plot of PVA/CS/ CAN polymer blend electrolytes at room temperature. **b** Conductance spectra of PVA/CS/CAN blend polymer electrolytes at room temperature.

the ionic conductivity values for all electrolytes at room temperature were tabulated in Table 1. The PVA/cassava starch electrolyte with 2% salt ratio shows less bulk resistance value with maximum conductivity but after increasing salt concentration it shows high bulk resistance due to aggregation of salt in the polymer matrix, reducing conductivity [36]. Comparison of ionic conductivity values of PVA/ CS/CAN with other electrolytes is given in Table 2. Finally, the plot results that decreasing the crystalline nature and increasing the amorphous phase in the addition of salt can dissociate the ions to improve the conductivity value are apparently agreement with XRD results.

 Table 1 Conductivity values of polymer blend electrolytes at room temperature

PVA:STARCH:CAN	Conductivity (S/cm)
94.5:4.5:1	$1.39 \times 10^{-6}$
94.0:4.0:2	$1.53 \times 10^{-5}$
93.5:3.5:3	$1.88 \times 10^{-6}$
93.0:3.0:4	$1.10 \times 10^{-6}$
92.5:2.5:5	$3.86 \times 10^{-6}$

#### **Conductance** spectra

The conductance spectra shows the plot between logarithm of conductivity and logarithm of frequency for all blend electrolytes. Depending on the frequency, graph reveals three distinct regions (lower frequency region, plateau region on mid-frequency and a dispersive region at higher frequencies) [37].

The low frequency dispersion region occurs due to the space charge polarization effect between electrode-electrolyte interface and so more charge accumulation occurs in this region. The plateau region is connected with the DC conductivity of blend electrolyte, and when it is extrapolated to zero frequency, we can obtain dc conductivity of the electrolytes [35, 38]. The high frequency region increases the conductivity due to high mobility of charge carrier according to Jonscher's powers law relation. The charge carrier increases because of the addition of salt concentration up to 5% that means there is a better interaction occurs between the blend polymer and ions [35, 39]. Thus, the graph shows higher conductivity for 2% of salt doped system in agreement with the Cole-Cole plot. The conductance spectra of PVA/ CS/CAN blend electrolytes doped with various concentrations of salt at room temperature is shown in Fig. 6b.

#### **Dielectric spectra**

Dielectric spectra is one of the studies for further enhancement of ionic conductivity pattern which is used to study the polarization effect between electrode and electrolyte interface. It is used to calculate the electrical charge stored in a material ( $\varepsilon'$ ) while the amount of energy losses in electric field reverse direction ( $\varepsilon''$ ) [40]. The dielectric constant and dielectric losses are calculated by the following equation

$$\varepsilon^* = \varepsilon' - i\varepsilon'$$

Table 2Comparison of ionicconductivity values of PVA/CS/CAN with otherelectrolytes

SPE materials	Ionic conductivity	Device	Reference
PVA/CS/NH <sub>4</sub> I	$9.71 \times 10^{-7}$	EDLC	[21]
PVA/MAA:EA/KCl	$1.85 \times 10^{-7}$	_	[36]
PVA/CS/NH <sub>4</sub> I	$9.10 \times 10^{-7}$	EDLC	[11]
CS/PVA/NH <sub>4</sub> I	$1.77 \times 10^{-6}$	_	[7]
PVA/DEXTRAN/NH4I	$2.08 \times 10^{-5}$	EDLC	[4]
PVA/CS/CAN	$1.54 \times 10^{-5}$	EDLC	Present work

Bold font denotes this article work comparing with other works



**Figure 7 a** Variation of dielectric constant with frequency for PVA/CS/CAN blend polymer electrolytes. **b** Variation of dielectric loss with frequency for PVA/CS/CAN blend polymer electrolytes.

where  $\varepsilon^*$  is the dielectric permittivity,  $\varepsilon'$  is the real part of dielectric constant, and  $\varepsilon''$  is the imaginary part of the dielectric loss of polymer blend electrolyte system. The dielectric permittivity of polymer electrolyte increases in lower frequencies with space comparing with other works charge polarization at electrodes resulting which attributes the non-Debye nature of the polymer blend electrolyte [10]. In higher frequencies, the polarization effect decreases charge accumulation due to high periodic reversal of the electric field and thus it

decreases the value of dielectric constant. There is no excess of ion diffusion in the direction of field [41, 42]. Figure 7a shows the variation of dielectric constant with frequency for PVA/CS/CAN blend polymer electrolytes doped with various concentrations of salt.

In this diagram, sharp rise was recorded for the (94.0:4.0:2) blend electrolyte because of maximum conductivity and high number of ions in this system. The addition of salt plays a vital role that up to 2% of salt, it increases the dielectric constant but in other higher concentration ratio, it decreases  $\varepsilon'$  and conductivity values due to aggregation of ions [22]. Figure 7b shows the variation of dielectric loss with frequency for blend polymer electrolytes doped with various concentrations of salt. Above the 2% of salt doped system shows more dielectric loss in agreement with dielectric spectra.

#### Tangent loss spectra

Tangent loss spectra describes the energy dissipation in dielectric to analyze the electrical properties of the blend electrolyte. The dielectric loss (tan  $\delta$ ) depends on the frequency which can be represented by relaxation peak [43]. It can be calculated by the equation which indicates the amount of energy lost to the amount of energy stored in a material.

 $\tan \delta = \varepsilon' / \varepsilon'$ 

The tangent spectra  $\tan \delta$  with frequency for PVA/ CS/CAN blend electrolyte doped with various concentration of salt was shown in Fig. 8 [44]. The relaxation peak  $\tan \delta$  increases with increase in frequency and reaches maximum value and then it





Figure 8 Tangent spectra with frequency for PVA/CS/CAN blend polymer electrolytes.

decreases with increasing frequency due to increasing concentration of salt [45]. PVA/CS/CAN electrolyte reveals that the peak shows decrease with increasing frequency due to salt concentration and peak shifts toward right side for 2% of ceric ammonium nitrate system that means charge carrier supports for ionic conductivity. The highest conductivity of the electrolyte shows the relaxation peak at higher frequency side with low relaxation time due to amorphous nature of the electrolyte [46]. The tangent spectra results also agree with the other analysis like XRD, impedance plot, and conductance spectra which confirm that 2% of salt doped electrolyte provides the better performance.

## **Electrochemical stability of EDLC**

### Cyclic voltammetry

The electrochemical behavior of the fabricated EDLC is analyzed with the assistance of cyclic voltammetry studies. This study provides the potential window between the reaction products and reversibility of a reaction [47]. The conductivity measurements show that the composition 94:4:2 (PVA:STARCH:CAN) poses higher conductivity, and its cyclic voltammetry (CV) results are presented in Fig. 9. The electrolyte placed between two activated carbon electrode and the stability is observed by changing scan rate ranges from -2 to +2 V at room temperature [19]. Due to the absence of electron transfer within electrolytes



Figure 9 Cyclic Voltammetry graph of EDLC prepared with high conducting PVA/CS/CAN polymer electrolyte.

 Table 3
 Specific capacitance values for EDLC prepared with high conducting PVA:STARCH:CAN polymer blend electrolyte

Scan rate mV s	Specific capacitance (F/g)	
25	16	
50	8.4	
75	6.4	
100	4.5	

due to the capacitance behavior, there is no significant oxidization and reduction peaks [48, 49]. The charge double layer at the surface of the carbon electrodes is significant; there is non-Faradaic reaction between the electrolyte and electrodes [50]. Due to the charge storage and capacitance effect between the electrodes and electrolytes, the specific capacitance decreases with increasing scan rate which is listed in Table 3 [51]. The specific capacitance values for the prepared EDLC are given in Table 3.

#### Linear sweep voltammetry (LSV)

The electrochemical stability of the EDLC device constructed using higher conductive polymer electrolyte was obtained with the help of linear sweep voltammetry by varying the scan rate from (25–100 mV/s) with the step size of 25 mV/s. Increasing current density mainly depends on the voltage between electrolyte and electrode interface [52]. As mentioned earlier, due to non-faradic behavior of electrolyte system the electrochemical stability window of film is stable up to 1 V which is



Figure 10 LSV graph of EDLC prepared with high conducting PVA/CS/CAN polymer electrolyte.

shown in Fig. 10 [44, 53]. In general, the decomposition voltage electrolyte was observed to be more than 2 V. This result indicates best electrochemical performance of the prepared high conducting polymer electrolyte for the electrochemical application.

## Charge-discharge studies

Galvanostatic charge–discharge studies are used to examine the cyclic stability of the fabricated EDLC at constant current of 1 mA. Figure 11 shows the GCD stability curve of the device [50]. The charge–discharge curve of 5 cycles was shown in graph, and almost linear discharge slope reveals the capacitive behavior of the EDLC device [5]. The specific capacitance was calculated by the following formula,

$$C_{\rm sp} = I/m({\rm d}v/{\rm d}t)$$

where  $C_{sp}$  is the specific discharge capacitance value, *I* is the current, m is the mass of the electrode material, and dv/dt is observed from the discharging slope; here, dv is the potential change during discharging and dt is the time interval [53]. The specific capacitance of first cycle is 29.45 F/g is slightly higher than specific capacitance of CV curve during higher cycles. The capacitance values of 100th cycle are slightly less at 28.2 F/g, and the 1000 cycles ions are unstable; because of desorption process, they decrease specific capacitance value at 24.5 F/g [40]. In charge–discharge study, Coulombic efficiency, energy density, and power density are important tools to examine the performance, rate of energy, and



Figure 11 The Galvanostatic charge–discharge stability curve of the device.

power per unit volume in EDLC device [21]. The  $E_d$  energy density value from 1st cycle to 1000 cycles is 1.6–1.3 Wh/kg for prepared device, and power density value exhibits a drop from 99 to 95 W/kg. Aziz et al. reported energy density and power density value at the range up to 0.55 Wh/kg and 64–58 W/kg for EDLC device [4]. The coulombic efficiency was calculated by the following parameters  $\eta = t_d/t_c$ - × 100, where  $t_d$  and  $t_c$  represent the discharge and charge times [5]. In this work, 1st cycle has 72% and it increases up to 90% of efficiency up to last cycle.

## Conclusion

PVA/CS/ceric ammonium nitrate solid polymer electrolytes are successfully prepared by solution casting technique. The XRD studies confirm the amorphous nature of the prepared electrolytes. The complexation of PVA/cassava starch and salt is observed by the shifting of wavenumber in FTIR spectra. Thermal decomposition of polymer electrolyte of PVA/starch was completely decomposed at 30-500 °C. The surface morphology of PVA/CS/ CAN electrolyte was examined by SEM images. The ionic conductivity values are obtained by impedance spectroscopy, and it shows maximum conductivity of  $1.53 \times 10^{-5}$  S/cm at room temperature. The electrochemical stability of EDLC device prepared with high conductive polymer electrolyte was analyzed by cyclic voltammetry studies. The linear sweep voltammetry studies confirm the decomposition



voltage of the electrolytes. The electrochemical performance and stability by charge–discharge study are important tools for EDLC device to give better results in number of long cycles. Thus, it is suggested that the polymer electrolyte with high ionic conductivity is suitable for electrochemical devices.

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## Data availability

The data relevant to my research work is available.

## Declarations

**Conflict of interest** The authors have no conflict of interest.

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