

Preparation and Structural Characterization of PVP-CH₃COONa Based Polymer Films

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Abstract

PVP based polymer electrolyte films were prepared by dissolving sodium acetate with different wt.% compositional ratios by solution cast technique. XRD revealed the crystalline phase of the prepared samples. XRD pattern demonstrated a wide peak at 24.5° attributed to the host polymer indicating orthorhombic cross section showing semicrystalline phase. FTIR and Raman studies affirmed to identify the functional group of the materials, bond formation between the dopant salt and the host polymer. The dispersion of salt particles in the polymer film impacts the segmental movement of the particles in the polymer matrix. With the arranged NCPEs, a rechargeable cell was prepared and its electrochemical investigations were studied.

Keywords: Solid polymer electrolyte films, solution cast technique, XRD, FTIR, Raman and cyclic voltammetry studies

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INTRODUCTION

In the present scenario, an attractive attention has been made towards solid polymer electrolytes due to their vast advantages and also their low production cost, and excellent structural, thermal and electrochemical properties. Solid polymer films have taken a revolutionary development in the fields of batteries, fuel cells and humidity sensors [1]. Solid polymer films are prepared by doping inorganic salt in the host polymer. The mechanism of solid polymer electrolytes and their advantages were reported by Wright and Armand in 1970s. Based on the advantages of solid polymer electrolytes, they have taken a new development role in the applications of energy storage devices. The physical and electrochemical studies of polymer electrolytes bring a new revolution in the fields of energy storage applications [2]. The solid polymer electrolytes must possess uniform surfaces with less brittle nature. The work on these polymer electrolytes, has received great attention which lead a new way to the researches for the development of energy storage devices [3, 4].

Polyvinyl pyrrolidone (PVP) was chosen because of its wide properties besides it possessing a high electrochemical stability [5, 6]. Most of the researchers have focused on PVP based solid polymer electrolytes because

it shows good electrochemical performance of the cell such that it can be used in many potential applications [7]. It is also used as an electrochromic display material in microelectronics as well as in pharmaceuticals as a binary agent [8, 9]. Inorganic salt like potassium acetate is used as dopant material to the host polymer in order to enhance the ionic conductivity. In the present investigation, solid polymer films were prepared with different wt.% composition ratios of PVP-CH₃COONa in order to improve the ionic conductivity of the composite films.

EXPERIMENTAL WORK

All the chemicals such as PVP polymer with an average molecular weight (M.W: 36,000), sodium acetate (CH₃COONa) 98% were used in the preparation of solid polymer films. All the chemicals used in the present investigation were purchased from Sigma Aldrich, India. Double distilled water was used as a common solvent in this process. All the chemicals were dried under vacuum oven at 40°C for 1 h. Later, the precursor materials of PVP polymer and sodium acetate were weighed properly in different wt.% concentrations, PVP: x wt.% LiI (where x=5, 10, 15 and 20). This homogeneous mixture was added to 20 ml double distilled

water and kept continuous stirring for 24 h. Later it was poured in to polypropylene dishes, and allowed to evaporate the solution slowly in a hot air oven to remove the moisture and solvent solution. Finally, the obtained samples were placed in vacuum desiccators.

RESULTS AND DISCUSSION

XRD Analysis

XRD is used to study the phase transformations of the samples. XRD sample of PVP blended CH₃COONa with mentioned wt.% proportions are shown in Figure 1. In XRD spectra, a wide peak at 24.5° credited to pure PVP which relates to orthorhombic cross section showing the semi-crystalline nature [10]. The characteristic peak somewhat moved upon expanding the salt concentration in the PVP polymer [11]. As increasing the salt wt.% ratios, the peak intensity is diminished which is shown in Figure 1. Among all the wt.% compositions, XRD peaks with less intensity have been observed for 80% PVP polymer blended with 20% CH₃COONa. This might be due to amorphous nature, which increases the delicate quality in the polymer chains where the sub-atomic chains are sporadic and trapped in indistinct areas as opposed to crystalline region [12, 13].

FTIR Studies

Fourier transform infrared (FTIR) is an intense method to recognize the chemical complexation, band structures and functional groups of the materials between the dopant and the host polymer. The prepared samples were recorded in the wavenumber ranging 450– 4000 cm⁻¹ as depicted in Figure 2. A wide spectrum appeared at 3100 to 3700 cm⁻¹ which relates to O-H group. Rest of the peaks observed at 944.5, 1105.6 and 1569.2 cm⁻¹ related to C-O bending, C-O stretching and C=O vibrations separately.

Upon adding the salt wt.% ratio to the PVP matrix, the characteristic absorption peak has been moved and peak intensities are diminished, widened to 1127.2, 1277.83, 768.8, 1264.22, 665.1, 1216.48 and 749.9 cm⁻¹. This might be because of the interlayer distance in polymer chains. The dispersion of salt particles in the polymer film impacts the segmental movement of the particles in the polymer matrix [14, 15].

Raman Studies

Figure 3 demonstrates the Raman spectra of CH₃COONa with different wt.% proportions doped with PVP polymer. Figure shows the three principle groups for all the wt.% proportions.

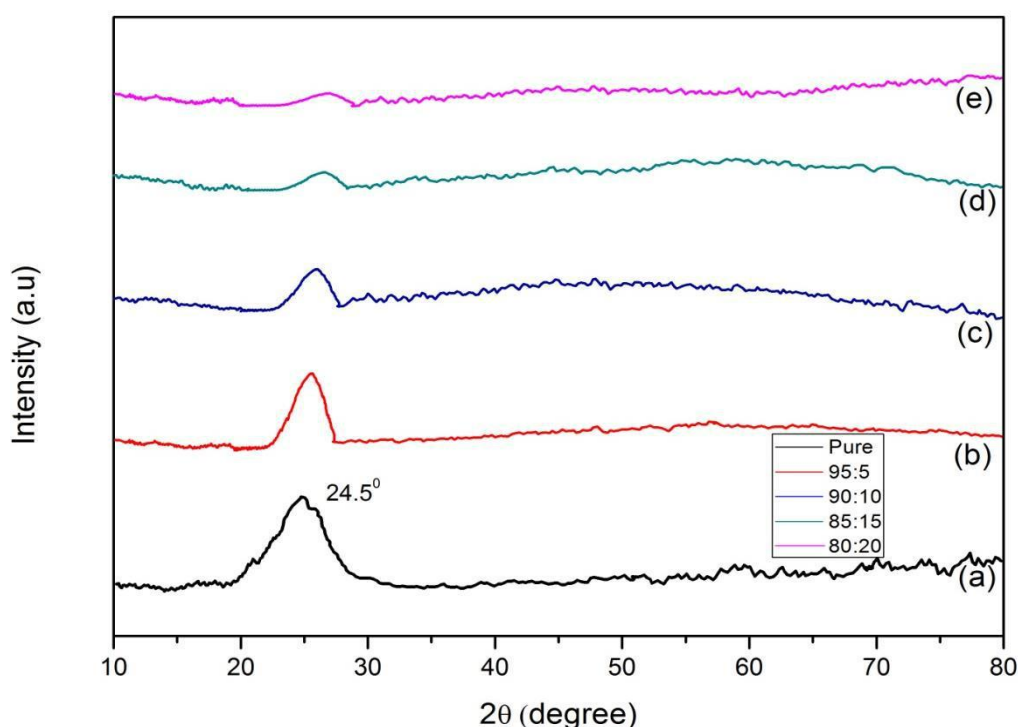


Fig. 1: XRD Pattern of PVP-CH₃COONa Solid Polymer Electrolyte Films for Different wt.% Ratios.

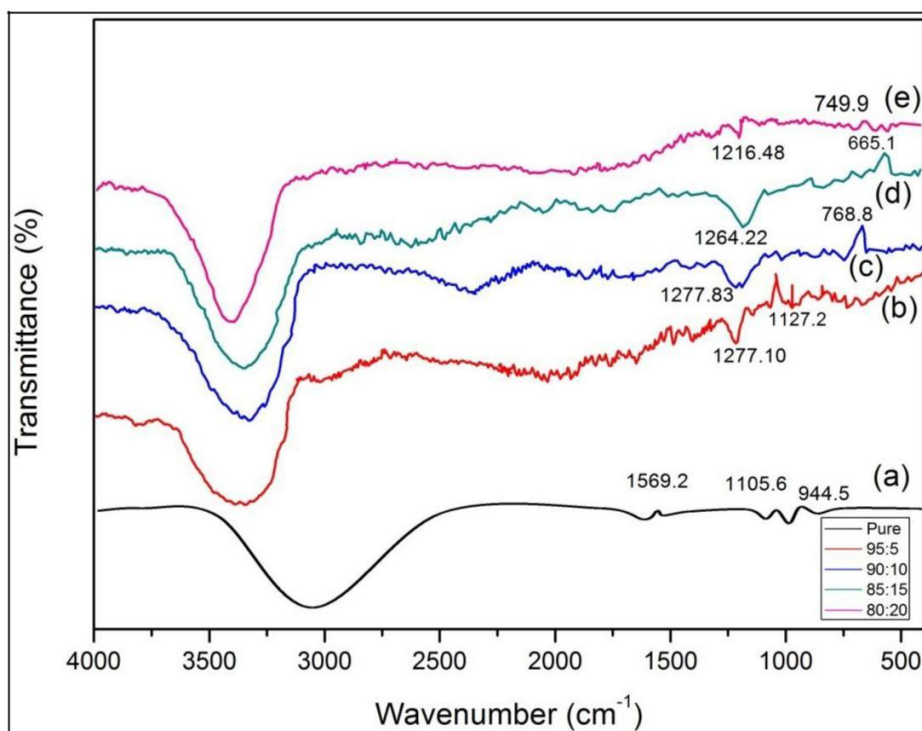


Fig. 2: FTIR Spectra of PVP-CH₃COONa Solid Polymer Electrolyte Films for Different wt.% Ratios.

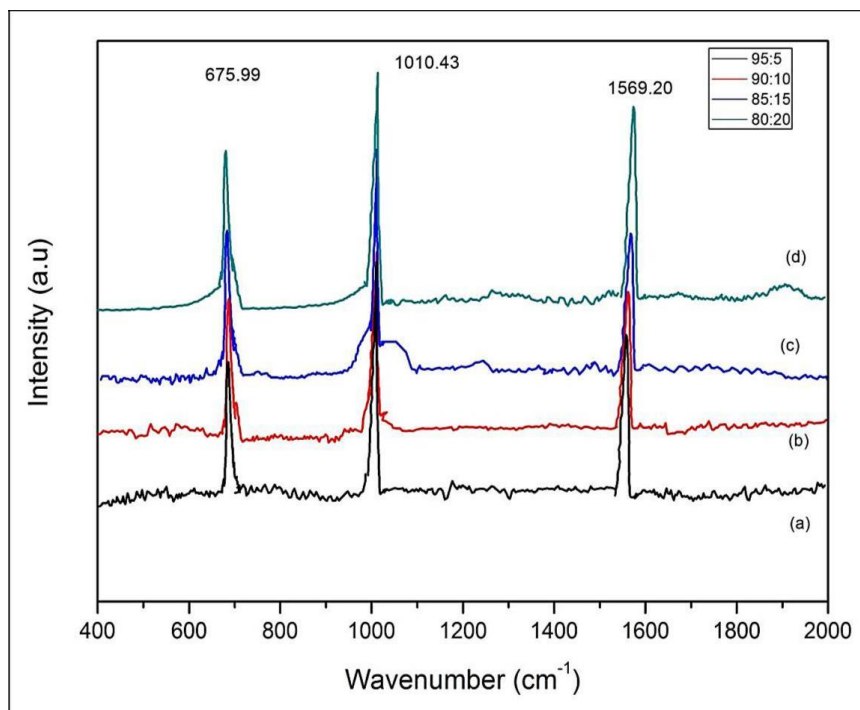


Fig. 3: Raman Spectra of PVP-CH₃COONa Polymer Electrolyte Films for Different wt.% Ratios.

The groups at 675.99, 1010.43 and 1569.20 cm⁻¹ relate to dynamic modes ascribed to C-O twisting, C-O extending and C=O vibrations separately. Besides these groups, some exaggeration peaks are additionally seen at 1310 and 1885 cm⁻¹ because of the nearness of PVP. For higher wt.% composition (80:20), the

band at 1010.43 cm⁻¹ is diminished. This might be because of C-O extending and additionally rocking methods of CH₂ vibrations of PVP polymer framework. This demonstrates that disintegration has been occurred between sodium salt and the polymer matrix [16].

Cyclic Voltammetry Studies

Cyclic voltammetry (CV) studies have been carried out for the prepared polymer films with different wt.% proportions between the potential ranging from 0.0010 to 0.0020 V at the rate 20 mV.s⁻¹ is shown in Figure 4. From the figure, oxidation and isolated redox peaks have been observed for the samples by expanding the dopant fixation in the host polymer. This might be due to the result of the unit of the samples from the terminal surface. The CV bend showed the oxidation peak at 0.0017 V and reduction peak at 0.0007 V. The oxidation peak is credited to the change of sodium acetate derivation into sodium. The diminishment of iodine and carbon is due to solvent in sodium. The oxidation and reduction peaks are vanished after 5 h with persistently repeated cycling.

Polarization Studies

Solid state battery has been synthesized for the most extreme ionic conductivity acquired polymer electrolyte film with the sample 80 PVP:20 CH₃COONa. The galvanostatic charge/release execution was done from 2.6 to 4.6 V for the setup configuration Na⁺/(PVP-CH₃COONa)/(I₂+C+electrolyte) as depicted in Figure 5.

The anode thickness of the cell has been manufactured with the molar proportion of 5:5:1. The applied potential is stable up to ~4.6 V for the readied polymer film. In the

prepared cell, sodium metal is used as an anode. The mixture of iodine and carbon powder pieces of the samples is utilized as cathode for improvement of electronic conductivity [17]. The manufactured battery was permitted to equilibrate for 30 min and the OCV was estimated at 2.51 V. The battery was cycled galvanostatically at 15 μA which is depicted in Figure 6 and the discharge capacity of the cell with respect to cycle number is shown in Figure 7.

During the completion of cycles, a vast limit misfortune happens after broadened cycling. The limit diminishes consistently at a rate of 0.04% for each cycle. It is observed that the discharge capacity is vanished after 7th cycle with continuous repeated cycling [18]. This might be because of salt dopant in the polymer network which is credited to the high surface territory esteem and adjustment of the structure. Consequently the charge exchange response and ohmic polarization of the films increases [19].

Electrochemical Studies

Cell parameters have been assessed for PVP-CH₃COONa (80:20) wt.% proportion and depicted in Figure 8. Initially, the decay in the voltage appeared at 0.75 V. This decrement might be because of larger part of particles; conduction happens in the prepared films instead of the electrons and polarization takes

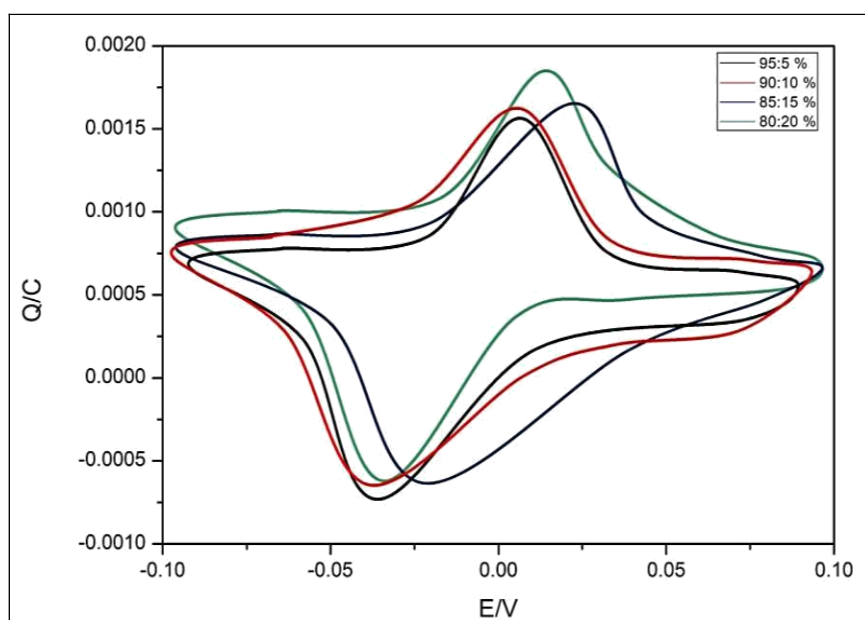


Fig. 4: Cyclic Voltammetry of PVP-CH₃COONa Solid Polymer Electrolyte Films.

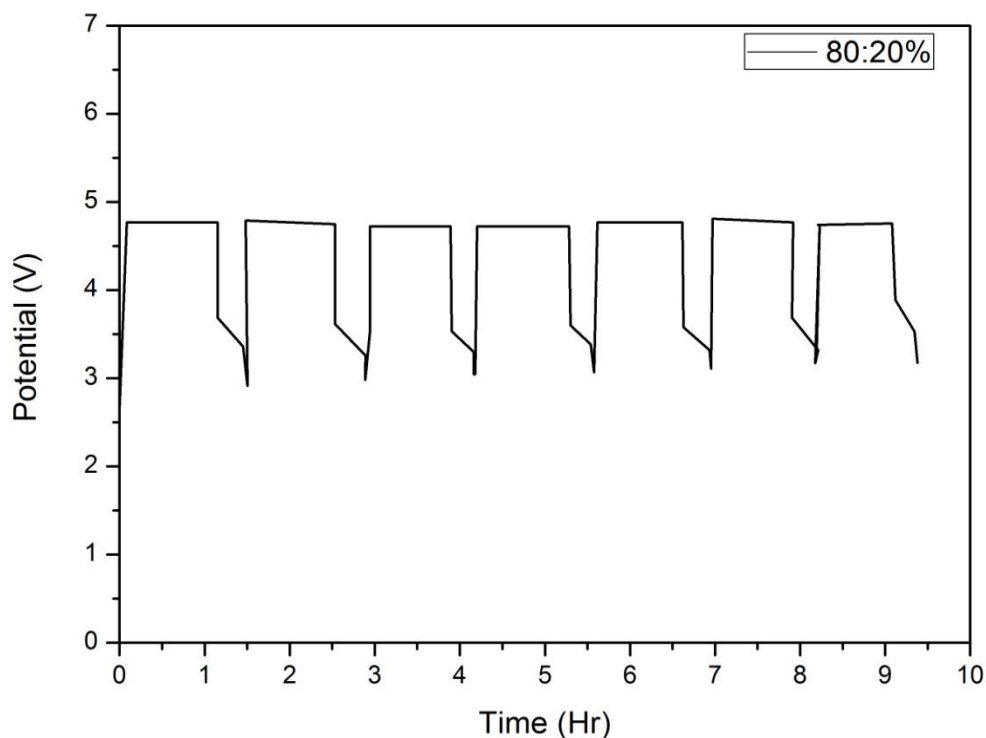


Fig. 5: Variation of Time vs. Potential of PVP-CH₃COONa Composite Polymer Electrolyte Films for (80:20) wt.% Ratio.

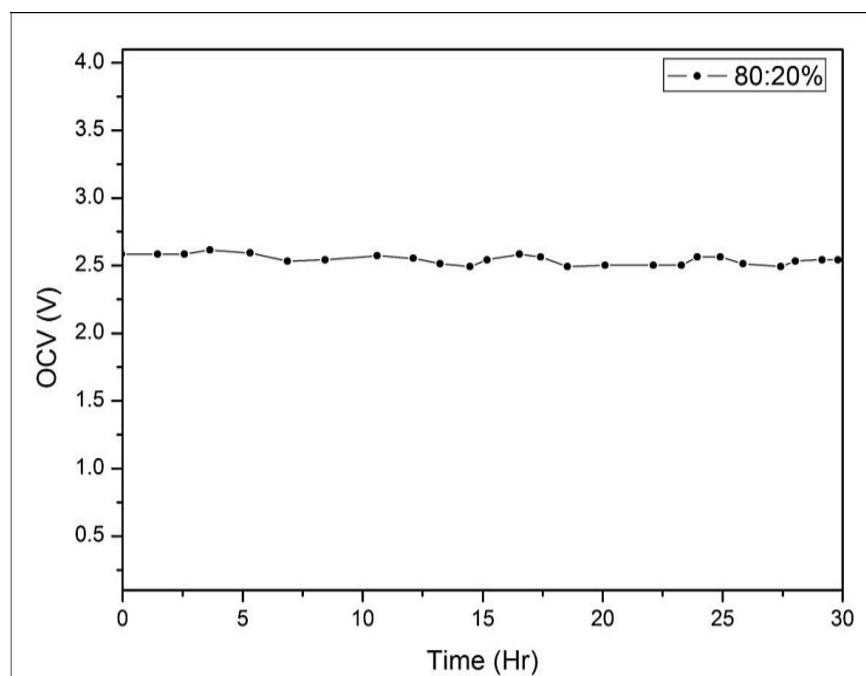


Fig. 6: OCV of Solid Polymer Electrolyte Film for (80:20) wt.% Ratio.

places at the electrolyte interfaces [20, 21]. It was observed that the manufactured cell demonstrated the OCV at 2.6 V at around 24 h when the test was ended. As the current is applied to the cell, the power density ascends to a specific level because of the doping of salt particles that have brought down the molecular

size and improves the electrochemical proficiency through the intercalation and de-intercalation procedures of the Na⁺ particles. The polymer electrolyte for the composition of Na⁺/(PVP-CH₃COONa)/(I₂+C+electrolyte) showed better execution because of the attribution of particles which diminish in tiny

thickness of the film and achieves high ionic conductivity. This could build the execution of the cell.

CONCLUSION

PVP based polymer electrolyte films are setup by dissolving sodium acetate with different wt.% ratios utilizing solution cast technique. XRD covers the crystalline nature of the polymer electrolyte films. XRD design demonstrated a wide peak at 24.5°, which

attributed to host polymer which was compared to orthorhombic cross section showing semicrystalline phase. FTIR and Raman studies affirmed to identify the functional group of the materials, bond formation between the dopant salt and the host polymer. The CV bend showed the oxidation peak at 0.0017 V and reduction peak at 0.0007 V. The polymer electrolyte for the composition of Na⁺/(PVP-CH₃COONa)/(I₂+C+electrolyte) showed better execution.

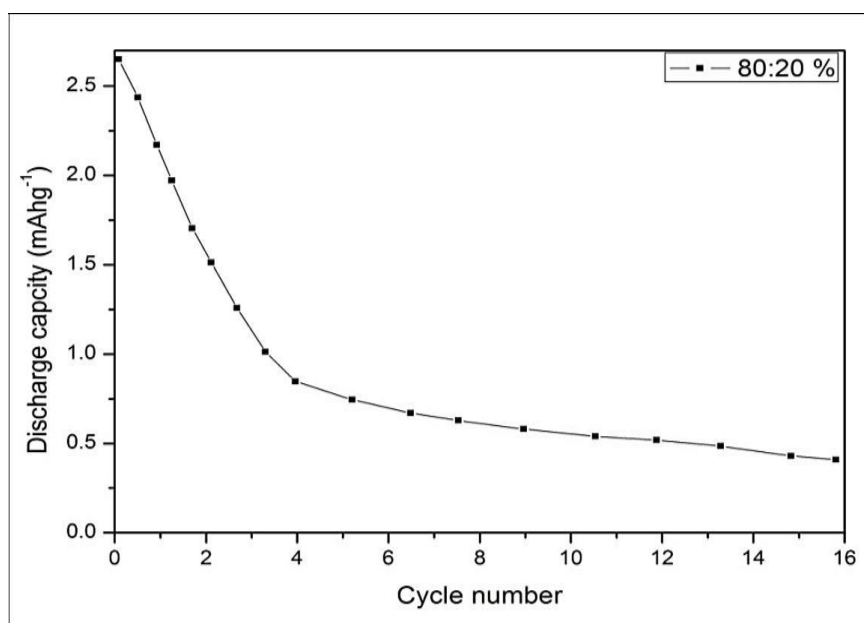


Fig. 7: Variation of Cycle Number vs. Discharge Capacity of Solid Polymer Electrolyte Film for (80:20) wt.% Ratio.

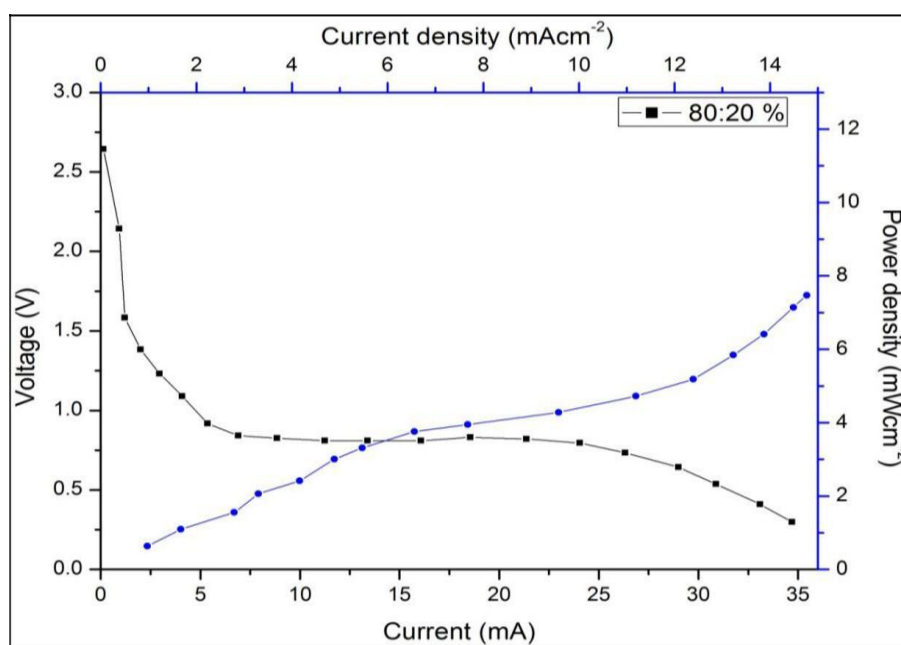


Fig. 8: Cell Parameters of Solid Polymer Electrolyte Film for (80:20) wt.% Ratio.

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Cite this Article

M. Seshu Kumar, M.C. Rao. Preparation and Structural Characterization of PVP-CH₃COONa Based Polymer Films. *Research & Reviews: Journal of Physics*. 2018; 7(2): 25–31p.