

Impact of ethylene carbonate on electrical properties of PVA/(NH₄)₂SO₄/H₂SO₄ proton-conductive membrane

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Abstract A new proton-conductive membrane (PCM) based on poly (vinyl alcohol) and ammonium sulfate (NH₄)₂SO₄ complexed with sulfuric acid and plasticized with ethylene carbonate (EC) at different weight percent were prepared by casting technique. The structural properties of these electrolyte films were examined by XRD studies. The XRD patterns of all the prepared polymer electrolytes reveal the amorphous nature of the films. ac conductivity and dielectric spectra of the electrolyte were studied with changing EC content from weight 0.00 to 0.75 g. A maximum conductivity of $7.3 \times 10^{-5} \text{ S cm}^{-1}$ has been achieved at ambient temperature for PCM containing 0.25 g of ethylene carbonate. The electrical conductivity σ , dielectric constant ϵ' and dielectric loss ϵ'' of PCM in frequency range (100 Hz to 100 KHz), and temperature range (300–400 K) were carried out. Measurement of transference number was carried out to investigate the nature of charge transport in these polymer electrolyte films using Wagner's polarization technique. Transport number data showed that the charge transport in these polymer electrolyte systems was predominantly due to ions. The electrolyte with the highest electrical conductivity was used in the fabrication of a solid-state electrochemical cell with the configuration (Mg/PCM/PbO₂). Various cell parameters

density, and current density were determined. The fabricated cells gave capacity of 650 μAh and have an internal resistance of 11.6 k Ω .

Keywords Membrane · Polymers · Electrical properties · Electrochemical cell

Introduction

In recent years, proton-conducting polymer electrolytes have been intensively studied as a perspective material for various electrochemical devices such as fuel cells, sensors, electro chromic displays, and electro chromic windows [1]. Proton-conducting membranes such as Nafion have been reported as a very successful host polymer but its applications are limited due to its high cost. Many researchers have studied the behavior of acid-based polymer electrolyte complexes as proton conductors and their applications in solid-state devices, at room temperature, have been demonstrated [2].

Solid acids polymer electrolytes are a fascinating class of materials built upon hydrogen-bonded oxyanion groups. In contrast to polymeric proton conductors, these compounds conduct protons without the assistance of mobile water molecules, opening new technological possibilities and scientific avenues.

In order to enhance electrical conductivity of the polymer electrolytes at ambient temperature without affecting their stability properties to an undesirable level, various approaches are currently in vogue such as copolymerization and plasticization. The essence of plasticization is to enhance the conductivity of the polymer electrolytes by means of additives of low molecular weight and high dielectric constant such as propylene carbonate, ethylene

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carbonate (EC), and poly ethylene glycol [3–5]. EC is used as a plasticizer due to its low viscosity and high dielectric constant (89.6 at 40 °C) [6]. Plasticizers provide more mobile charge carriers and reduce the viscosity of the polymer matrix. Literature studies reveal that the ammonium salts are excellent proton donors to the polymer matrix and ammonium salts doped with poly (vinyl alcohol) (PVA) are rare. Several ammonium salts such as NH_4I [7], $\text{NH}_4\text{SO}_3\text{CF}_3$ [8], and $(\text{NH}_4)\text{SCN}$ [9] were used as doping salts.

Sulfuric acid, H_2SO_4 , is a strong mineral acid that has a high electrical conductivity due to an intra-molecular proton-switch mechanism; its incorporation in a polymer system is expected to enhance its electrical performance [10]. Therefore, in the light of all this, present work has been driven by a desire to develop a radically new, alternative ionic-conducting electrolyte (or membrane) that is based on compounds whose chemistry and properties are intermediate between those of a normal acid, such as H_2SO_4 , and a normal salt, such as $(\text{NH}_4)_2\text{SO}_4$, and not a hydrated polymer. Thus, composite membranes will be developed, in which a solid acid is embedded in an inert polymer matrix, with the polymer providing mechanical support and enhancing chemical stability. In this article, we report the preparation and characterization of a new proton-conducting membrane based on PVA, $(\text{NH}_4)_2\text{SO}_4$, and H_2SO_4 (proton-conductive membrane, PCM). The impact of ethylene carbonate on ion transport characteristics was studied to yield optimum conductivity and then to use them to produce magnesium battery. The prepared polymer electrolytes have been characterized by X-ray diffraction (XRD) and ac impedance spectroscopic techniques.

Experimental

Preparation of PCM

PVA with degree of polymerization $\sim 1,700$ – $1,800$ was obtained from QualiKems chemical company (India). The PVA-based membranes were prepared by dissolving 0.95 g of PVA in distilled water, to get a 10 wt.% solution. The solution was left to stir for 24 h at 90 °C in water bath in order to obtain a transparent low-viscous liquid. After cooling, 0.05 g of $(\text{NH}_4)_2\text{SO}_4$ (domestic source) was added to the solution. The solution was left to stir for 2 h. Then 1 cm³ of 2 M H_2SO_4 (GPR-ADWIC) was gradually added to the beaker. The solution was left to stir for 24 h to prepare the host matrix. After that, ethylene carbonate plasticizer was added gradually in weight 0, 0.125, 0.25, 0.375, 0.50, 0.625, and 0.75 g. The solution was stirred for another 6 h to obtain homogenous solution. The solution was then cast on a glass petri dish for 2 weeks. The final product was vacuum dried thoroughly.

Characterization

In order to investigate the crystalline nature of these polymer electrolyte films, X-ray diffraction studies were carried out using Bruker X-ray diffractometer. The diffraction system based with Cu tube anode of wave length $K_{\alpha 1} = 1.5460 \text{ \AA}$ and $K_{\alpha 2} = 1.54439 \text{ \AA}$. The start angle (2θ) was 4° and the end angle was 60°.

Samples of diameter 0.5 cm were sandwiched between the two similar brass electrodes of a spring-loaded sample holder. The whole assembly was placed in a furnace monitored by a temperature controller. The rate of heating was adjusted to be 2 K/min. Electrical measurements were performed on PM 6304 programmable automatic RCL (Philips) meter in the frequency ranging from 100 Hz to 100 KHz at different temperatures between 293 and 363 K.

Mg/PCM/PbO₂ cell

Solid acid polymer electrolyte exhibiting the highest ambient electrical conductivity was used to fabricate the cell. The cathode pellet was synthesized using 0.25 g PbO_2 powder (Nice chemicals) as the active material, 0.05 g of graphite (QualiKems) powder to enhance electronic conductivity of the cathode, and 10% optimum electrolyte solution as binder to enhance ionic conductivity of the cathode, while 0.2 g magnesium powder (QualiKems) was used to form the anode pellet. A hydraulic press (2 tons cm⁻²) was used to compress the pellets. The diameter of the pellet equals 13 mm. The cells were then assembled by sandwiching the PCM between the two electrodes. The open-circuit voltage (OCV) was measured for the batteries stored at an open-circuit condition for 24 h (Fig. 1). The discharge characteristics of the cell were monitored under a constant load of 100 k Ω . Current drains ranging from 0 to 60 μA were used to plot the current–voltage (I – V) and current density–power density (J – P)

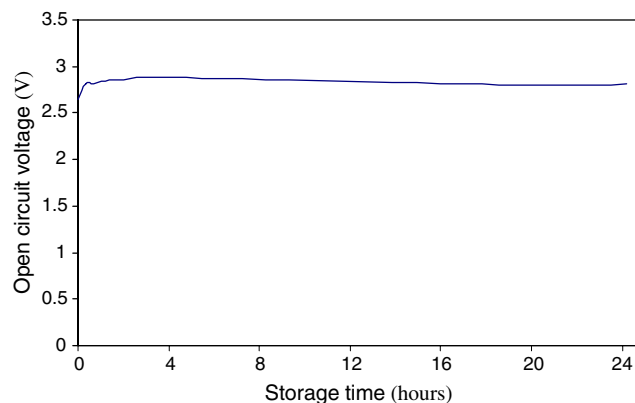
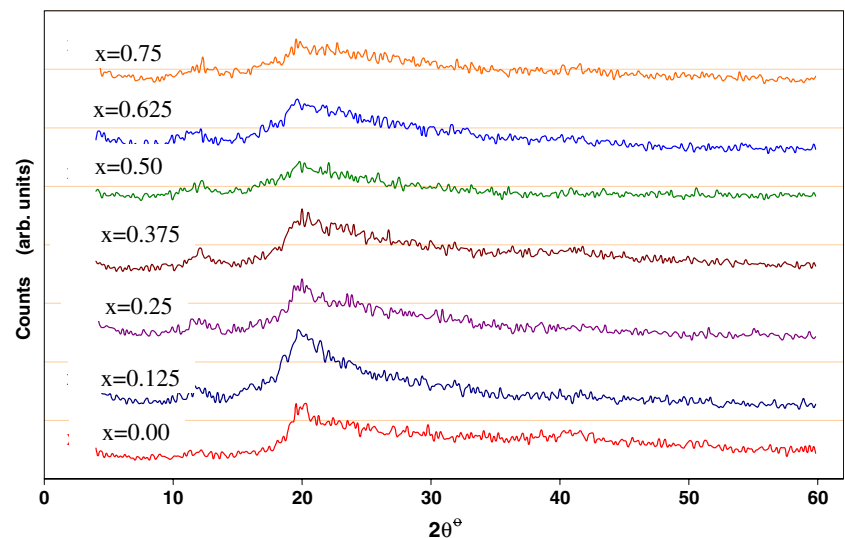


Fig. 1 Open-circuit voltage (OCV) for Mg/PCM/PbO₂ cell during 24 h of storage

Fig. 2 X-ray diffraction patterns for all films at different contents of ethylene carbonate



curves. The average of each battery's voltage was monitored for each current drain after 10 s of operation. The internal resistance of the cell was then calculated by using equation:

$$V = E - Ir$$

where V is the voltage, E is the electromotive force, I is the current, and r is the internal resistance.

Results and discussion

XRD analysis

Figure 2 shows X-ray diffraction patterns of PVA/(NH₄)₂SO₄/H₂SO₄ complexed with different contents of EC. The pure PVA/(NH₄)₂SO₄/H₂SO₄ shows a characteristic peak located at 20°. The high-intensity peak of the PVA/(NH₄)₂SO₄/H₂SO₄ polymer electrolyte decreased as the amount of EC was increased with an incremental broadening of the peak. This can be attributed to the reduction in intermolecular interaction between PVA chains on incorporating EC. As a result of this reduced interaction, the crystallinity of the polymer electrolyte decreases leading to a reduction in the intensity of the XRD peaks [11]. Plasticizers are usually not intended to affect the properties of the final product after it hardens. The plasticizers for polymer soften the final product increasing its fluidity and flexibility [12].

Conductivity studies

Impedance spectroscopy is employed to establish the conduction mechanism, studying the participation of the polymeric chain, mobility, and carrier generation processes. Figure 3 shows the impedance spectra (or Cole–Cole plot)

for PCM doped with different concentration of ethylene carbonate. The plot shows a semicircle arc.

The diameter of semicircle varies with the concentration of plasticizer, where $x=0.25$ g EC shows lowest diameter. The semicircle can be ascribed basically to the bulk properties of the PCM films. The intercept of this semicircle with the real axis (Z') gives an estimate of the bulk resistance (R_b) of the materials to be used subsequently for evaluation of electrical conductivity. The ionic conductivities were calculated using the relation $\sigma_b=(1/R_b \times L/A)$, where A is the known area of the electrolyte film and L is the thickness.

The effect of addition of EC in the membrane on the ionic conductivity is presented in Fig. 4. It can be observed that the highest conductivity is observed for the membrane containing 0.25 g EC at 7.3×10^{-5} S cm⁻¹. Beyond 0.25 g EC, the conductivity decreased. EC does not supply ions to the electrolyte system. It is a plasticizer that is able to

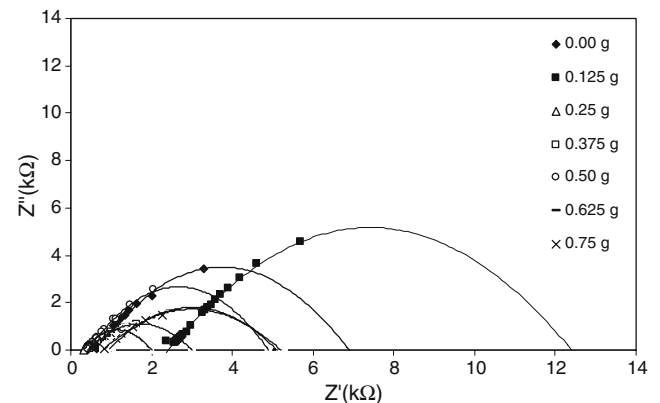


Fig. 3 The impedance spectra for different concentration of ethylene carbonate doped (PCM)

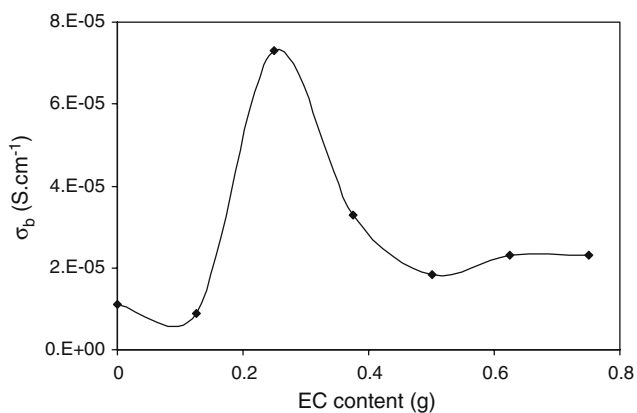


Fig. 4 The effect of addition of EC on the ionic conductivity of membrane at room temperature

dissociate more salt into ions and has a low viscosity that can increase ionic mobility. The ionic conductivity in a polymer is generally linked to the number of ions and the mobility of conducting species in the polymer complexes. The Rice and Roth model [13] expresses the conductivity, σ , as

$$\sigma = 2/3 \left[(Ze)^2 / kTm \right] \eta E_A \tau \exp[-E_A/kT] \quad (1)$$

Where, η is the number density of mobile ions and Z , E_A , and m is the valency, activation energy, and mass of the conducting ion, respectively. T is the absolute temperature, k is the Boltzmann constant, and e is the electron charge. τ is the time of travel between sites. In Eq. (1), the conductivity is expected to increase when η increases. The initial increase in conductivity is presumably due to an increase in the number of charge carriers in the matrix. For a higher concentration of EC, above 0.25 g EC, the build-up of charge carriers is offset by the retarding effect of ion aggregates such as ion pairs and ion triplet formation, which cause constraints in ionic and polymer segmental mobility. Hence, the conductivity reaches the maximum

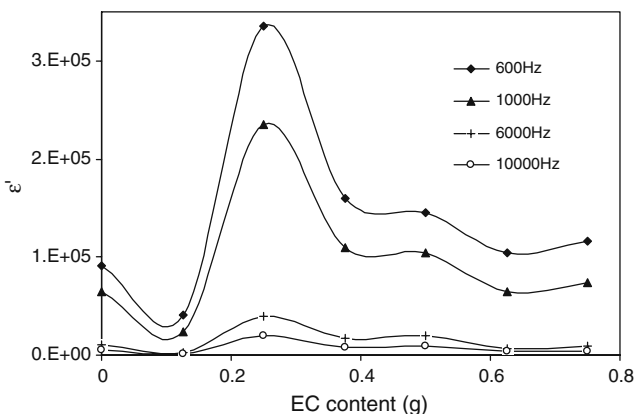


Fig. 5 EC content dependence of dielectric constant ϵ' at selected frequencies

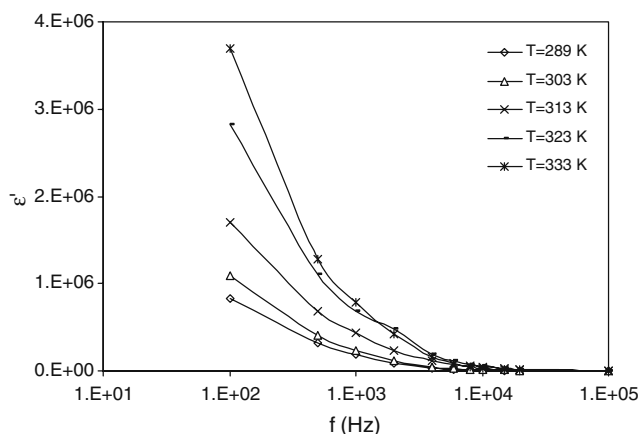


Fig. 6 The variation of dielectric constant ϵ' with frequency for membrane doped with 0.25 g EC at different temperatures

value when a balance between these two opposing forces occurs: increasing the number of charge-carrier ions and decreasing ionic mobility.

The type of conducting species responsible for the ionic conductivity in polymer–ammonium salt systems is H^+ ion [14–17]. For the present polymer–salt system, the NH_4^+ ions of $(NH_4)_2SO_4$ will be coordinated to the OH groups in PVA.

The NH_4^+ cations have ideal tetrahedral structure. One of the four hydrogen atoms in NH_4^+ ions is most weakly bound and can dissociate easily under the influence of an electric field. This H^+ ion can hop from one site to another leaving a vacancy which will be filled by another H^+ ion from a neighboring site. Thus, the charge transport is carried out by structure diffusion or better known as Grotthuss mechanism, i.e., the conduction occurs through proton exchange between PVA/ $(NH_4)_2SO_4/H_2SO_4$ complexed sites. Proton conduction by the Grotthuss mechanism involves intermolecular proton jump creating a vacant site followed by reorientation to occupy the vacant site. Thus, the charge transport is carried out by structure diffusion or better known as Grotthuss mechanism [12], i.e., the conduction occurs due

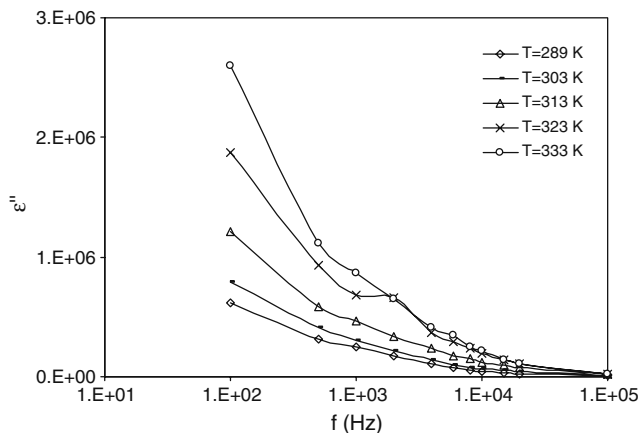


Fig. 7 The variation of dielectric loss ϵ'' with frequency for 0.25 g EC membrane at different temperatures

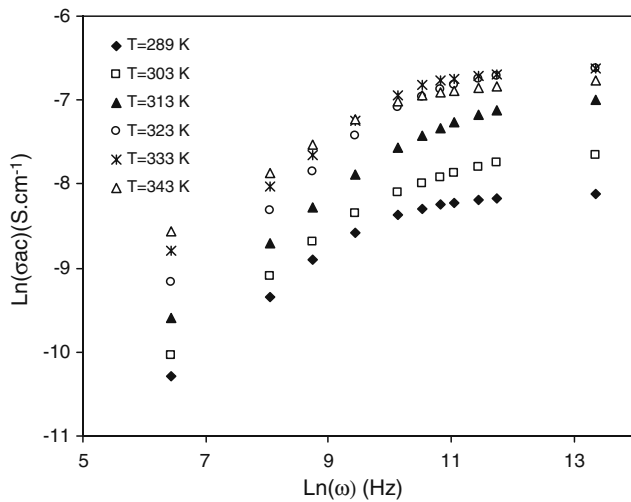


Fig. 8 The frequency dependence of ac conductivity (σ_{ac}) at selected temperatures for sample doped with 0.25 g EC

to a dynamical effect of the anion HSO_4^- reorientation that reinforces the proton transfer in the complex.

Dielectric studies

EC content dependence of dielectric constant (ϵ') at selected frequencies is shown in Fig. 5. From the graphs, ϵ' increases with increasing EC content for every frequency until after 0.25 g EC when the value of ϵ' drops. This implies that, as the EC content increases, the number of stored charges in the sample also increases, which means that the number of mobile ions has increased. Also, due to high dielectric constant of EC which is able to dissociate more salt to cations and anions resulting in an increase in a number of mobile ions. Decrement in dielectric constant at 0.375 g EC is due to decrement in density of charge carriers which is attributed to the reassociation of ions.

The variation of dielectric constant ϵ' and dielectric loss ϵ'' with frequency for membrane with 0.25 g EC at different temperatures is shown in Figs. 6 and 7. From the plots, it is

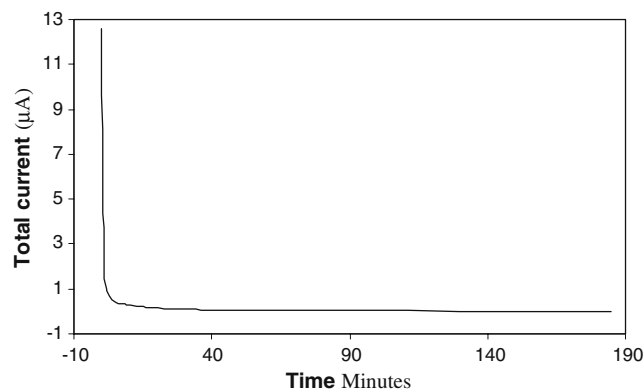


Fig. 9 Variation of polarization current as a function of time for PCM with 0.25 g EC

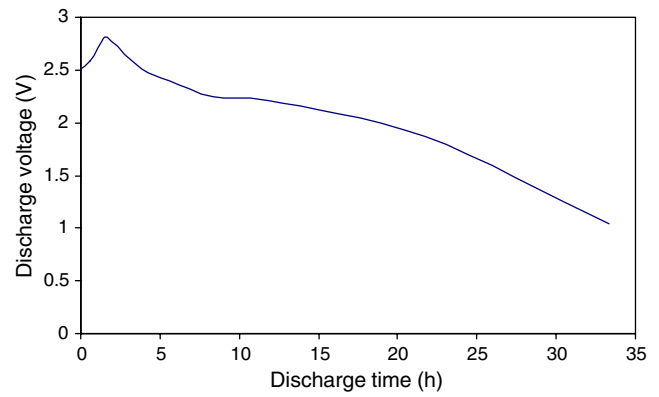


Fig. 10 Discharge plot for Mg/PCM/PbO₂ cell at constant load of 100 kΩ

clear that both the dielectric constant ϵ' and dielectric loss ϵ'' decreases monotonically with increasing frequency and attains a constant value at higher frequencies. Similar behavior was observed in other materials [18, 19].

ac conductivity

The ac conductivity can be obtained from dielectric constant, ϵ' to loss tangent, $\tan \delta$, at every frequency according to:

$$\sigma_{ac} = \epsilon_o \epsilon' \omega \tan \delta \tag{2}$$

or

$$\sigma_{ac} = \epsilon_o \epsilon'' \omega \tag{3}$$

where ϵ'' is dielectric loss, and $\tan \delta = \epsilon''/\epsilon'$. The phenomenon of ac conductivity can be analyzed using Jonscher’s universal power law [20, 21].

$$\sigma(\omega) = \sigma_{dc} + A\omega^s \tag{4}$$

$$\sigma_{ac} = A\omega^s \tag{5}$$

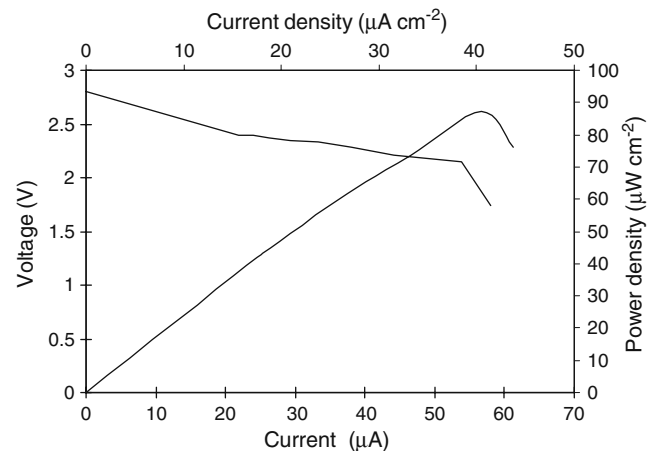


Fig. 11 I - V and J - P curves for Mg/PCM/PbO₂ cell

Here $\sigma(\omega)$ is the total dc and ac conductivity. The dc conductivity, σ_{dc} is the frequency independent component, A is a parameter dependent on temperature, and (S) is the power law exponent with value in the range between 0 and 1.

Figure 8 depicts the frequency dependence of ac conductivity (σ_{ac}) at selected temperatures for sample with 0.25 g EC. The ac conductivity (σ_{ac}) increases with increasing temperature for a particular frequency and it increases with the increase in frequency at a specified temperature. As temperature increases, the number of mobile ions increases due to dissociation of the salt leading to the enhancement in conductivity.

Transference number measurement

Figure 9 shows the variation of polarization current as a function of time. The ionic transference number of the mobile species in the polymer electrolyte was determined by Wagner's dc polarization method [22]. This dc polarization measurement has been used to analyze the mobile species in the electrolyte, which are either ions or electrons. The polarization current has been monitored as a function of time on application of dc potential (1.5 V) across the cell Cu/electrolyte/Cu. The total ionic transference number was calculated from the plot using the standard equation,

$$t_{ion} = \frac{I_i - I_f}{I_i} \quad (6)$$

where I_i is the initial current and I_f is the final residual current. The total ionic transference number has been found 0.996 for 0.25 g EC. This shows that the charge transport in this polymer electrolyte is mainly due to ions.

Discharge characteristics

The OCV curve of Mg/PCM/PbO₂ battery at room temperature is shown in Fig. 1. The voltage was observed raised in the first 2 h and later stabilized at 2.8 V. The OCV remained constant at 2.8 V at the rest time of storage. This confirms low self-discharge of the fabricated battery. Figure 10 shows the discharge curves of the battery at a constant load $R=100$ kOhms. The discharge capacity C of the limited electrode (PbO₂) was evaluated from the equation [23]:

$$C = \frac{1}{R} \int_0^t V(t) dt$$

by integrating the area under curve of Fig. 10. The first discharge curve has discharge capacity of 650 μ Ah and potential plateau, at 2.23. It only represents the surface capacity of the limited electrode. Figure 11 shows the $I-V$ and $J-P$ characteristics for the Mg/PCM/PbO₂ battery at

room temperature. The $I-V$ curve had a simple linear form which indicates that the polarization on the electrode was primarily dominated by ohmic contributions. The plot of the operating $J-P$ suggests that the contact between electrolyte/electrodes was good. The voltage of the battery dropped to a short circuit current density of 40 μ Acm⁻², and the maximum power density was determined to be 90 μ Wcm⁻². The internal resistance of the battery was obtained from the gradient of the $I-V$ graph, which was 11.6 k Ω .

Conclusion

We have successfully developed proton-conductive membrane based on PVA, (NH₄)₂SO₄, and H₂SO₄. It is evident from the investigation that incorporation of ethylene carbonate as the plasticizer increases the amorphous phase and enhances the conductivity. The PVA/(NH₄)₂SO₄/H₂SO₄ system with 0.25 g of ethylene carbonate exhibits a maximum conductivity of (7.3×10^{-5} S cm⁻¹), with a negligible electronic transport number. Therefore, this material establishes a new polymer electrolyte system.

Solid-state Mg/PCM/PbO₂ cell has been assembled, and their electrochemical performance was studied. The high open-circuit voltage of 2.8 V of the fabricated cell qualifies that cell for promising technology in the field of electrochemical devices. However, the plasticized PVA/(NH₄)₂SO₄/H₂SO₄ polymer electrolyte system with an enhanced amorphous phase and conductivity requires further investigation for device applications.

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