Electrical and solid-state battery performance of a new PVC/PEO+KBr blend-based polymer electrolyte system

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Abstract Solid polymer blend electrolyte based on polyvinyl chloride (PVC) and polyethylene oxide (PEO) complexed with potassium bromide (KBr) for different weight percent ratios were prepared using solution cast technique. Various experimental techniques such as X-ray diffraction (XRD), AC conductivity, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and transference number measurements were employed to characterize these polymer blend electrolyte system. The conductivity analysis shows that the 15 wt% of potassium bromide-doped polymer blend electrolyte exhibits high ionic conductivity, and it has been found to $2.56 \times 10^{-5}\,\mathrm{S\ cm^{-1}}$ at room temperature. The temperature dependence of ionic conductivity and transference number data indicated the dominance of ion-type charge transport in these specimens. The electrochemical cells have been fabricated using PVC+PEO+KBr electrolyte for which the open-circuit voltage and short-circuit current are 3.2 V and 1380 μA, respectively.

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Introduction

Recently, the development of portable electronic devices, especially mobile phones and laptops, has been remarkable, leading to a strong need of high-energy batteries. Indeed, the replacement of common liquid electrolytes by an ionic polymer membrane is an important technological development for lithium ion technology, as it provides the prospect of a favorable combination of high energy and long life [1], but there is higher risk of fire explosion. In order to overcome this problem, the development of solid-state batteries using a solid electrolyte may be one solution. A solid polymer is a thin film consisting of ionic salts dissolved in an appropriate polymer which enables ionic conduction at ambient temperature in solid state [2]. The electrical and ionic conductivities can be modified by copolymerization, plasticization, blending, addition of ceramic fillers, and addition of ionic salts.

Polyethylene oxide (PEO) is one of the most popular polymers used, due to its high solvating power with metal ions, good process ability, and outstanding mechanical properties [3, 4]. Although the ionic conductivity of PEO polymer electrolytes at 100 °C is about 10^{-4}–10^{-3} S cm^{-1}, at room temperature it is usually less than 10^{-6} S cm^{-1}. It can solvate a wide variety of salts even at very high salt concentrations. The solvation of salts occurs through association of metallic cations with oxygen atoms in the backbone. However, the multiphase nature of PEO is most often regarded as a major problem in real working systems, since the ionic conduction has been shown to take place mainly in the amorphous phase. The suppression of crystallinity of polymer chains improves the polymer chain mobility, which, in turn, leads to better ionic conduction. Later, many efforts have been focused on the bulk properties of polymer electrolytes based on the complexation of PEO with various metal salts [5, 6] and on the characteristics of electrochemical processes at the electrode polymer electrolyte interface.

Polyvinyl chloride (PVC) is a commercially available inexpensive polymer and is compatible with a large number of plasticizers, such as ethylene carbonate (EC), propylene carbonate (PC), dibutyl phthalate (DBP), and dioctyl adipate (DOA). Many researchers have reported plasticized polymer electrolytes with enhanced ionic conductivity in PVC-based polymer electrolytes [7–11]. Polymer blends have gained commercial and technological importance over homopolymers and copolymers in the last decade and have become a part of the macromolecular science. Blending involves physical mixing of two or more polymers, which is a simple process compared to the laborious chemical process involved in the synthesis of new long-chain molecules. The production cost is much less compared to that in the development of a new material. The main advantages of blend-based polymer electrolytes are simplicity in preparation and easy control of physical properties by compositional change. Polymer blending is one of the most effective methods in reducing the crystallinity and enhancing the amorphous nature. Polymer blends often exhibit properties that are superior to the individual component polymers [12–15].

Less effort has been made on solid polymer blend electrolytes and batteries based on potassium complex system. Apart from scientific interest, the use of potassium has several advantages over lithium counterparts. Potassium is much more abundant and less expensive than lithium [16, 17]. The softness of this metal makes it easier to achieve and maintain a good contact with other components in the battery. Further, potassium is more moisture-resistant than lithium. Keeping these aspects in view, this study reports a new K$^+$ ion conducting polymer blend electrolyte system based on PEO and PVC complexed with potassium bromide (KBr).

Experimental description

Films of (thickness≈50–100 μm) pure PVC+PEO (50:50) (Aldrich, MW 6×10^4 and 6×10^5) and complexed with KBr for various compositions 47.5:47.5:05, 45:45:10, and 42.5:42.5:15 by weight percent were prepared using solution-cast technique. Tetrahydrofuran (THF) was used as a solvent. The mixture of polymers and salt solutions were stirred for 12 h to get homogeneous solution and cast onto polypropylene dishes. The dish solutions were kept at room temperature for one week and vacuum dried thoroughly at 10 mbar to remove any solvent traces. Thus the polymer blend films were obtained and stored in desiccators.

The X-ray diffraction studies were performed by means of SEIFERT X-ray diffractometer with Cu Kα radiation (λ=1.54178 Å operated at 40 kV and 30 mA), in the 2θ range 10–70° at room temperature. The conductivity of these solid polymer blend films was investigated with a

conductivity cell consisting of two blocking stainless steel electrodes. Impedance measurements were carried out in the temperature range of 303–363 K using 3532-50 LCR HiTester over a frequency range of 100–1 MHz. The instrument was interfaced to a computer for data collection. The transference number measurements were made using Wagner's polarization technique.

Electrochemical cells were fabricated with configuration of K(anode)/polymer blend electrolyte/(I$_2$+C+electrolyte) (cathode). The discharge characteristics like as-open-circuit voltage (OCV), short-circuit current (SCC), power density, etc. were monitored under a constant load of 100 kΩ. Differential scanning calorimetry (DSC) measurements were carried out using NETZSCH DSC 204 in the range of 320–345 K, and all the measurements were taken at a heating rate of 5 °C min^{-1} under nitrogen atmosphere.

Results and discussion

X-ray diffraction analysis

The X-ray diffraction patterns of pure PVC+PEO, KBr, and various compositions of PVC+PEO+KBr systems are shown in Fig. 1. The XRD profile of KBr shows well-defined sharp peaks (Fig. 1(a), which indicates the crystal nature of salt. There are no such well-defined peaks observed for pure PVC+PEO; instead, a broad peak (Fig. 1(b)) was observed at 2θ region 11–16° which can be associated with the amorphous nature of PVC in the pure PVC+PEO film [18]. The relative intensity of this broad peak decreases with increase of KBr salt concentration. Pure PVC+PEO blend film exhibits two distinct crystalline peaks (Fig. 1(b)) of PEO, a maximum intensity peak at 19.7° and next maximum peak at 23.9° [19]. It indicates that the amorphous nature of host polymer blend
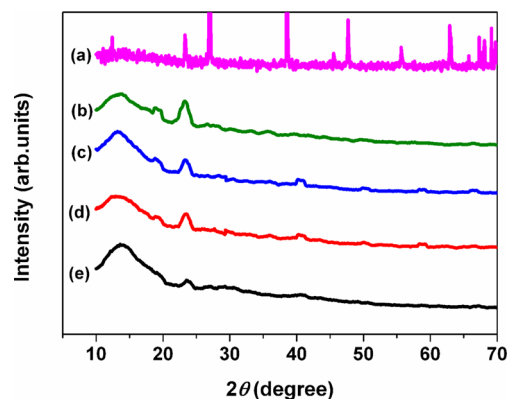
Fig. 1 XRD patterns of (*a*) KBr salt, (*b*) pure PVC+PEO, (*c*) PVC+PEO+KBr (47.5:47.5:5), (*d*) PVC+PEO+KBr (45:45:10), and (*e*) PVC+PEO+KBr (42.5:42.5:15)

increases with increasing KBr concentration (Fig. 1(c–e)). The diffraction peaks of KBr dispersed in complexed films are less intense compared to the pure PVC+PEO film. This result was interpreted by Hodge et al. [20], in terms of a correlation between the intensity of peak and the degree of crystallinity. They reported that the intensity of XRD pattern decreases as the amorphous nature increases with addition of dopant. This kind of amorphous nature results in greater ionic diffusivity and high ionic conductivity, which can be observed in amorphous polymers having a flexible backbone [21, 22]. The new peaks were observed at $2\theta=40°$ and $58°$; this may be due to KBr salt effect. No sharp peaks were observed corresponding to KBr salt in complexed polymer blend electrolyte films which indicated the complete dissolution of salt in the polymer matrix.

Impedance analysis

The ionic conductivity of solid polymer blend electrolyte (PVC+PEO+KBr) system was determined from the complex impedance plots. The Nyquist plots of PVC+PEO+KBr polymer blend electrolyte samples for various compositions at 303 K are shown in Fig. 2. The complex impedance diagram shows two well-defined regions. The high-frequency region in semicircle, which is due to a bulk effect of electrolyte, and the linear region in low-frequency range are attributed to the effect of blocking electrodes. In the ideal case at the low-frequency region, the complexed impedance plots show the straight line parallel to the imaginary axis, but the double layer at the blocking electrodes causes the curvature [23]. The ion migration and bulk polarization are physically parallel, and therefore, the semicircle at high frequency can be observed in all the samples. The bulk resistance was measured from a high-frequency intercept on the real axis. The ionic conductivity of electrolytes was calculated using the following equation:

$$\sigma = t \big/ R_{\mathrm{b}} \times A \qquad (1)$$

where t is the thickness of the polymer blend electrolyte (cm); A, the area of the blocking electrode (cm^2); and R_{b}, the bulk resistance of polymer blend electrolyte. The bulk resistance decreases in the polymer electrolyte system due to enhancement of ionic mobility and the number of charge carrier ions along with concentration of dopant [24–26].

Compositional dependence of conductivity studies

The variation of AC conductivity (σ) as a function of concentration of KBr in the pure PVC+PEO for various temperatures is shown in Fig. 3. The conductivity data of these samples at
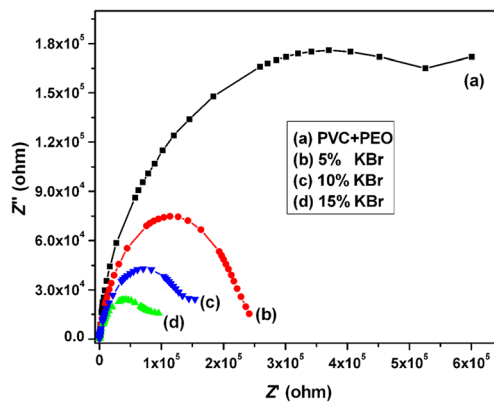

Fig. 2 Nyquist plot for PVC+PEO polymer blend electrolyte doped with different weight percent of KBr at 303 K

room temperature is given in Table 1. From the figure, it is observed that the conductivity of pure PVC+PEO is about 10^{-6} S cm^{-1} at room temperature, and its value increased to 10^{-5} S cm^{-1} on complexing with 15 wt% of KBr. The ionic conductivity measurements were carried out with an aim to observe the effect of KBr (K$^+$) on electrical properties of the electrolyte system. The ionic conductivity was increased gradually as the wt% of KBr was increased which is due to increased K$^+$ charge carriers in the system. The conductivity is increased with the addition of salt which is attributed to a reduction of crystallinity of the polymer blend electrolyte and also increase in the number of mobile charge carriers. The coordination interactions of either ether oxygen atoms of PEO or the chlorine atoms of PVC or both with K$^+$ cations of PVC+PEO system are responsible for the increase of ionic conductivity. The maximum conductivity is obtained due to the effective interaction between oxygen atoms and K$^+$ cations in the electrolyte [27].

A reduction of crystallinity in PVC+PEO electrolytes can also be seen from the XRD analysis that shows a decrement in the intensity of sharp crystalline peaks with the addition of KBr salt, which results in a dominant amorphous phase in the
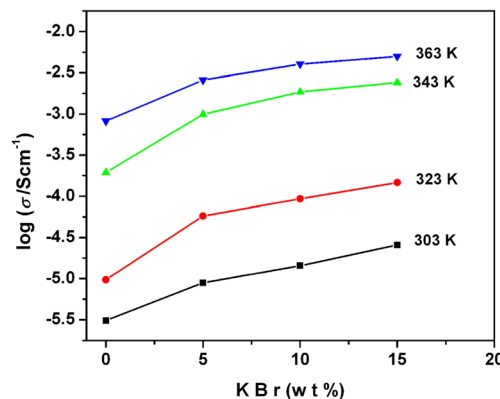

Fig. 3 Composition vs. conductivity plots of PVC+PEO+KBr polymer blend electrolyte system at different temperatures
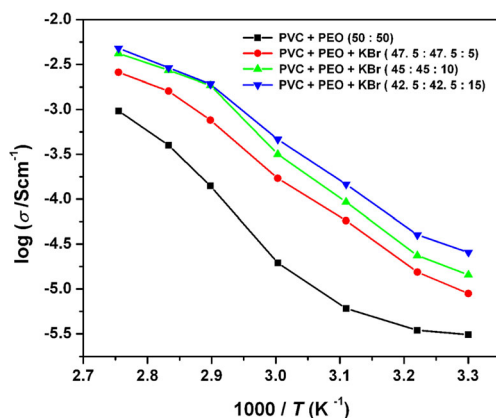
Table 1 Conductivity and transport number data of PVC+PEO+KBr electrolyte system

Polymer blend electrolyte system (wt%)	Conductivity at RT (303 K) S cm^{-1}	Activation energies (eV)	Transport numbers	
			t_{ion}	t_{ele}
PVC+PEO (50:50)	3.09×10^{-6}	0.46	–	–
PVC+PEO+KBr (47.5:47.5:5)	8.88×10^{-6}	0.33	0.93	0.07
PVC+PEO+KBr (45:45:10)	1.44×10^{-5}	0.25	0.96	0.04
PVC+PEO+KBr (42.5:42.5:15)	2.56×10^{-5}	0.20	0.97	0.03

electrolytes. The polymer chain in the amorphous phase is more flexible to the segmental motion of the polymer, which facilitates high ionic mobility [28, 29]. Salt dissociation is an additional factor to the enhancement of ionic conductivity. The dissociation of salt will promote more free K$^+$ ions to transfer into the electrolyte. The conductivity increases with salt concentration due to the rise of the number of charge carriers.

Temperature-dependent conductivity studies

The variation of conductivity as a function of temperature for pure PVC+PEO and different compositions of the PVC+PEO+KBr polymer blend electrolyte system over the temperature range of 303–363 K is shown in Fig. 4. The conductivity increases with temperature in pure PVC+PEO and in all the compositions of the PVC+PEO+KBr polymer blend electrolyte system. The bulk resistance has been calculated from the impedance plot, and logarithms of conductivity were plotted against the inverse temperature dependence of the conductivity. At ambient temperature, the highest ionic conductivity value was found to be 2.56×10^{-5} S cm^{-1} for PVC+PEO+KBr (42.5:42.5:15) polymer blend electrolyte. The conductivity of pure PVC+PEO was 3.09×10^{-6} S cm^{-1} at room temperature, and its value increased on complexing with

KBr, as the rise of conductivity is significant with the increased concentration of KBr. From Fig. 4, it is observed that as the temperature increases, the conductivity nature is also found to increase, and this behavior is in agreement with the theory [30]. It indicated that ion transport in polymer blend electrolytes was correlated with polymer segmental motion. The variation of electrical conductivity (σ) as a function of temperature (T) in the entire temperature range can be fitted to the relation

$$\sigma = \sigma_o \exp(-E_a/kT) \qquad (2)$$

where σ_o is a constant; k, the Boltzmann constant; E_a, the activation energy; and T, the absolute temperature. The magnitude of ionic conductivity was found to increase with increasing temperature in all the compositions of polymer blend electrolyte system including pure PVC+PEO film. It may be explained on the basis of an increase of either ionic mobility or the concentration of carrier ions [31]. The Arrhenius behavior observed for log (σ) vs. 1,000/T plots is in agreement with the theory established by Tareev [32]. This is rationalized by considering the free volume model [11]. The enhancement of ionic mobility can be interpreted by ionic transport mechanism involving coordinating sites, local structural relaxations, and segmental motion of the polymer chain in free volume model. When the temperature increases, the vibration energy of a segment of polymer blend chain becomes sufficient to push

Fig. 4 Ionic conductivity of PVC+PEO+KBr polymer blend electrolyte films at different weight percent ratios
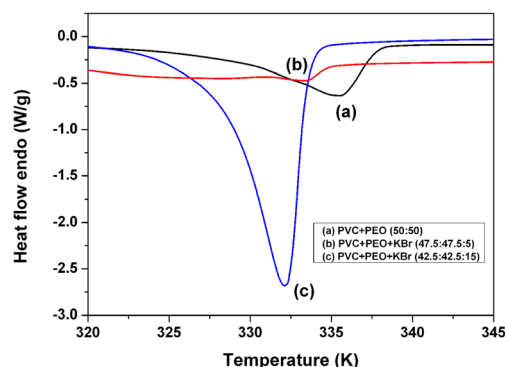
Fig. 5 DSC thermographs of (*a*) pure PVC+PEO, (*b*) PVC+PEO+KBr (47.5:47.5:5), and (*c*) PVC+PEO+KBr (42.5:42.5:15)
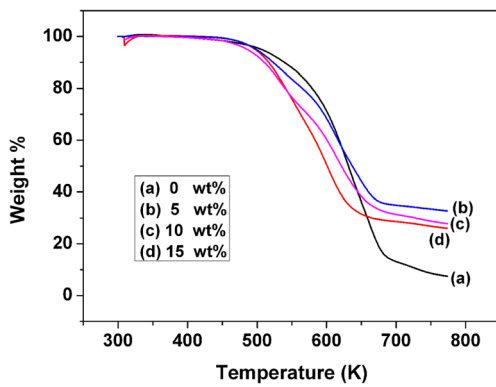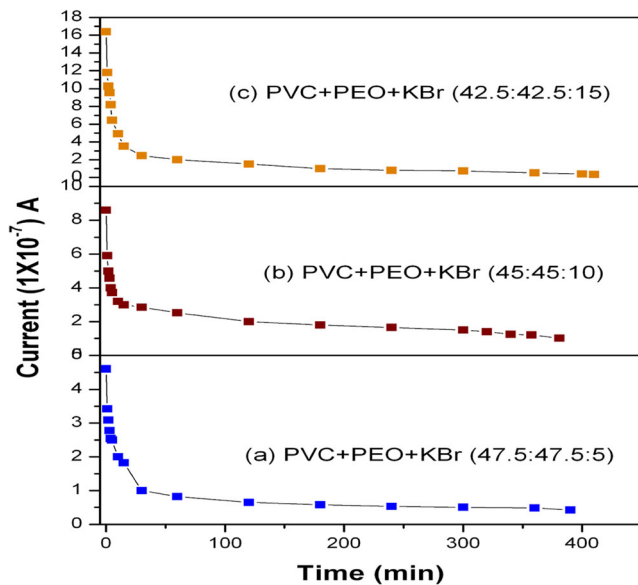
Fig. 6 TGA plots of (*a*) pure PVC+PEO, (*b*) PVC+PEO+KBr (47.5:47.5:5), (*c*) PVC+PEO+KBr (45:45:10), and (*d*) PVC+PEO+KBr (42.5:42.5:15)

Fig. 8 Discharge characteristics of PVC+PEO+KBr electrochemical cell at constant load of 100 KΩ
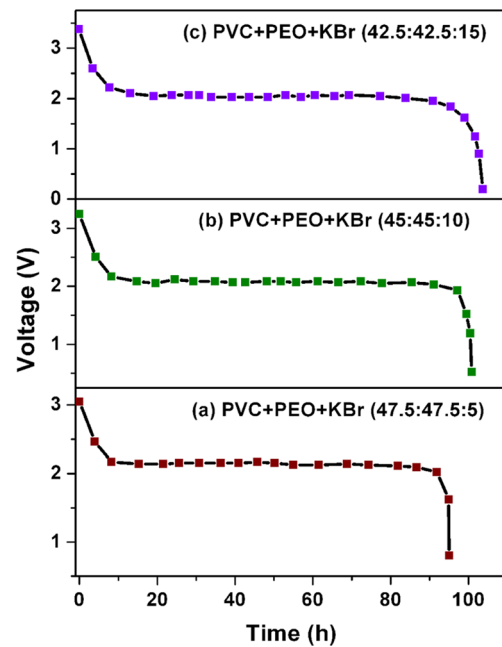
against the hydrostatic pressure imposed by its neighboring atoms and create a small amount of space surrounding its own volume in which the vibrational motion can occur [33]. Therefore, the free volume around the polymer chain causes the conductivity to increase. The amorphous nature also provides a bigger free volume in the polymer blend electrolyte system with increasing temperature [34, 35].

Activation energies

The activation energy values of different polymer blend electrolytes were calculated from the slopes of linear fit of the Arrhenius plots of different polymer blend electrolytes, and these are listed in Table 1. The activation energy is a combination of energy of charge carrier creation (defect formation) and the energy of ion migration that can be

evaluated by linear fitting to the log (σ) vs. 1,000/T plots [36, 37]. Therefore, it can be suggested that the value of E_a is due to energy that is required to provide a conductive condition for migration of ions. The conductivity does not show any abrupt change with temperature (Fig. 3), indicating that the electrolyte exhibits an amorphous nature. The activation energy is found to decrease gradually with increasing KBr salt concentration.

Thermal properties

DSC–TGA analysis

The DSC thermographs of PVC+PEO+KBr polymer blend electrolytes for two different composition ratios are shown in Fig. 5. The melting temperature (T_m) of PVC+PEO+KBr polymer blend electrolyte was found to around 330–340 K, with an increase in KBr content corresponding to lower T_m. The T_m of pure PVC+PEO film shifted to lower temperatures when the salt was added to the polymer system. The lower T_m upon salt addition is quite common [38] and has been related to the decrease in spherulite sizes [39] and their surface free energy. When the salt concentration further increases in the host polymer matrix, then T_m is decreased due to the suppression of crystallites, increasing the amorphous nature. As a result, more flexible amorphous environments are getting trapped or adjacent to the crystalline matrix, and the suppressed crystalline portion of the PVC+PEO blend complexes melts probably at lower temperatures.

Fig. 7 Transference traces of PVC+PEO+KBr polymer electrolytes at different concentrations of KBr salt

The TGA thermographs of the PVC+PEO+KBr polymer blend electrolyte system for various composition ratios are shown in Fig. 6. The thermal decomposition temperature is determined from the differential curve, and it is about 686 K for pure PVC+PEO (Fig. 6(a)). The absence of weight losses prior to polymer melting indicates no impurity such as solvent, water, etc. is present and confirms that drying under vacuum and nitrogen gas is efficient. The degradation temperature decreases continuously with increasing KBr in PVC+PEO, and this result directly indicated an increase of amorphous fraction of the electrolyte. The thermal stability of the polymer blend is reduced with an addition of ionic salts due to the growth of amorphous fraction, which is a typical characteristic of polymers. The source of incomplete decomposition at high salt content is not clear, but is believed to be associated with the Cl^- anion-containing backbone [40, 41].

Transference numbers

To verify the dominant conducting species in the present electrolyte system, transference number measurements were carried out using the well-known Wagner's polarization technique [42]. In this method, the sample is sandwiched between two electrodes (among which one is a blocking electrode) and is polarized under dc constant voltage. Appearance of initial current on application of a potential was proportional to the applied field, and afterwards, the polarization current starts decreasing with time. It is polarized by an applied electric field due to migration of ions [5].

In this method, the dc current was monitored as a function of time on application of fixed dc voltage of 1.5 V across the cell K/PVC+PEO+KBr/C. The plots of current versus time for PVC+PEO+KBr are shown in Fig. 7. The initial current (I_i) is the total current which is due to contribution of ions (i_{ion}) as well as electrons (i_{ele}). As the polarization builds up because of the applied voltage, the ions were blocked at the blocking electrode,

thereby blocking the ionic current (i_{ion}), and the final current (I_f) comprises only the electronic current (i_{ion}). The transference numbers (t_{ion} and t_{ele}) have been evaluated using the following formula:

$$t_{ion} = I_i - I_f \big/ I_i \tag{3}$$

$$t_{ele} = I_f \big/ I_i \tag{4}$$

where I_i and I_f are the initial and final currents, respectively. The values of ionic transference number for the PVC+PEO+KBr electrolyte system are in the range of 0.93–0.97 (Table 1) and close to unity; these polymer blend electrolytes are very much suitable for solid-state electrochemical cells [43].

Discharge characteristics

Solid-state batteries were fabricated at ambient temperature using the polymer blend electrolyte films based on PVC+PEO complexed with potassium bromide salt. Polymer batteries were fabricated with the configuration of anode/polymer blend electrolyte/cathode. The choice of choosing anode in a solid-state battery depends on the mobile species in the electrolyte [44]. In the present investigations, potassium metal was used as the anode material in these polymer blend electrochemical cells. The iodine+graphite+electrolyte (I_2+C+electrolyte) (5/5/1 ratio) were made in the form of a pellet at the pressure of ~5 ton/cm² after a proper mixing of constituents for using the cathode material. Here, iodine acts as "active cathode"; addition of graphite powder to the cathode material enhances its electronic conductivity, and hence, cathode can also act as a current collector. Addition of polymer electrolyte to the cathode mixture provides more interfacial contact area between the cathode and electrolyte; this then reduces the interfacial resistance and gives better battery performance [45].

Table 2 Cell parameters of K/(PVC+PEO+KBr)/(I₂+C+electrolyte) polymer blend electrolytes

Cell parameters	PVC+PEO+KBr (47.5:47.5:5)	PVC+PEO+KBr (45:45:10)	PVC+PEO+KBr (42.5:42.5:15)
Open-circuit voltage (V)	3.02	3.25	3.37
Short-circuit current (μA)	1,220	1,310	1,380
Effective area of the cell (cm²)	1.39	1.39	1.39
Weight of the cell (g)	1.82	1.78	1.85
Discharge time for plateau region (h)	95	110	122
Power density (W/kg)	2.02	2.39	2.51
Energy density (Wh/kg)	191.9	262.9	306.2
Current density (μA/cm²)	808	940	990
Discharge capacity (μA/h)	12.8	11.9	11.3

The discharge characteristics of the cell K/PVC+PEO+ KBr/(I$_2$+C+electrolyte) at an ambient temperature for a constant load of 100 kΩ is shown in Fig. 8. The initial sharp decrease in the voltage and current for these cells may be due to polarization and/or the formation of a thin layer of potassium salt at the electrode–electrolyte interface. The SCC was obtained by introducing a constant load of 100 kΩ in the circuit. The cell parameters, e.g., OCV, SCC, current density, and power density, were evaluated for all the batteries and are given in Table 2. The current density was calculated using a short-circuit value and the area of the cell. The power density values were obtained by taking the weight of the cell into consideration. The energy density values were calculated by evaluating the time taken for the plateau region from Fig. 8. From Table 2, it is clear that the cell with the composition PVC+PEO+KBr (42.5:42.5:15) exhibits better performance and stability than that with the other compositions. These results are well in comparison with existing reports and are even with better performance [46–50]. Hence, these cells are interesting alternatives for solid-state batteries at room temperature.

Conclusions

Polymer blend electrolytes based on PVC+PEO and complexed with KBr for various compositions were prepared using solution-cast technique. The structural and complexation behavior have been studied by XRD. DSC measurements revealed the decrease of melting temperature (T_m) with increase in salt content because of charge neutral contact ion pairs. From the impedance spectroscopy, the conductivity was found to increase with increasing temperature as well as dopant concentration. The activation energy is found to decrease with the addition of 5–15 wt% of KBr content which indicates the free pathways produced for the K$^+$ ion migration. The solid-state electrochemical cells were fabricated using PVC+PEO+KBr electrolyte films, and their discharge characteristics were examined by a constant load of 100 kΩ.

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