

Conductivity and discharge characteristics of (PVC + NaClO₄) polymer electrolyte systems

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Abstract

A sodium ion conducting polymer electrolyte based on polyvinyl chloride (PVC) complexed with NaClO₄ was prepared using a solution-cast technique. Investigations were conducted using XRD, FTIR and SEM. Frequency dependent conductivity (σ_{ac}) values were obtained from complex impedance plots (Cole–Cole plots). Activation energy values were determined from the conductivity data are decreased with increasing ionic conductivity. The transference number measurement was performed to characterize the polymer electrolyte for battery applications. Transference number values show that the charge transport in this electrolyte is predominantly due to the ions ($t_{ion} = 0.98$). Using the electrolyte, cells with a configuration Na/(PVC + NaClO₄)/(I₂ + C + electrolyte) were fabricated and their discharge profiles studied.

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1. Introduction

Complex impedance spectroscopy (CIS) is a powerful technique for investigating the electrochemical properties of materials used in solid-state batteries. It was first applied by Bauerle in 1969 to analyse the response of solid electrolyte cells to sinusoidal perturbations. Since then this technique has been used to characterize a wide range of materials, which includes polymers, oxides, glasses, halides and ceramics and it has been instrumental in the development of both electrode and electrolyte mate-

rials for solid state electrochemical devices, such as batteries, sensors, fuel cells, super capacitors and electrochromics. Several theories were proposed to describe the complex impedance spectroscopy [1–4]. By using complex impedance spectroscopy, Cole–Cole plots [5] were constructed and bulk resistance R_b of the polymer was determined. Using the bulk resistance, frequency dependent conductivity was evaluated to characterize the polymer [6].

Extensive research has been carried out on Li salts complexed polymer electrolytes. However, only a few attempts have been made on electrolytes based sodium complexed films. Use of sodium in the polyelectrolytes have several advantages over their lithium counterparts. Sodium is available in abundance at a cheaper cost than lithium. It is feasible

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to obtain solid electrolytes of sufficiently high conductivity because sodium does not form any alloy with the electrode materials, such as aluminum and nickel. Furthermore, the softness of these materials makes it easier to achieve and maintain contact with other components in the battery. Investigations have also been made [7–9] on sodium ion-conducting polymer electrolyte based on PEO, polypropylene oxide (PPO), and polybismethoxy ethoxy phosphazene (MEEP) complexed with NaI, NaClO₄, NaSCN, and NACF₃SO₃.

We have directed our attention to poly vinyl chloride (PVC) as a host polymer of polymer electrolytes. 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). Several researchers have reported plasticized polymer electrolytes with enhanced ionic conductivity in PVC based polymer electrolytes [10–16]. In the present paper, the authors report new thin film ion conducting polymer electrolytes based on PVC complexed with NaClO₄ salt. Various experimental techniques, such as X-ray diffraction (XRD), infra-red (IR), frequency dependent conductivity and transport number measurements were carried out to characterize these electrolytes. Based on these electrolytes, electrochemical cells were fabricated and their discharge characteristics studied. These studies have revealed that the conduction in these polymer electrolytes is predominantly ionic. Various cell parameters were evaluated and are reported in this paper.

2. Experimental details

Thin films (thickness 100–200 μm) of pure PVC and various compositions of complexed films of PVC with a salt of NaClO₄ were prepared with the following weight percent ratios (90:10), (80:20) and (70:30) by the solution-cast technique using tetrahydrofuran (THF) as a solvent. The solutions were stirred for 12–15 h. The stirred solution was cast onto polypropylene dishes and evaporated slowly at room temperature. The films were dried rigorously in a high vacuum (10⁻³ Torr) to eliminate all traces of tetrahydrofuran.

The XRD patterns of the films were made with a HZG4/B-PC X-ray diffractometer with Co K α radiation and graphite monochromator. The IR spectra were recorded using a 60-SXB FTIR spectrophotometer in the range 400–4000 cm⁻¹. The

morphology of the samples was characterized by an JSM-5610LV scanning electron microscope (SEM). The frequency dependent conductivity was measured using an Agilent 4294A precision impedance analyzer in the range 40 Hz–100 kHz and temperature range 298–373 K. The total ionic transference numbers were measured using Wagner's polarization technique [18]. Electrochemical cells were fabricated with a configuration Na/(PVC + NaClO₄)/(I₂ + C + electrolyte). The details about the fabrication of the electrochemical cells have been given elsewhere [17]. The discharge characteristics of these cells were monitored for a constant load of 100 k Ω .

3. Results and discussion

3.1. Evidence of complex formation

The XRD patterns of pure PVC, NaClO₄ and complexed PVC are presented in Fig. 1. The patterns of pure PVC and complexed PVC indicate low crystallinity. By contrast, NaClO₄ is found to be crystalline. No peaks corresponding to NaClO₄ is observed in complexed PVC, which indicates the absence of excess salt (uncomplexed) in the material.

The IR spectra were recorded in the range 400–4000 cm⁻¹ in the transmittance mode. The spectra for pure PVC, pure NaClO₄ and (PVC + NaClO₄) complexes are shown in Fig. 2. The following changes in spectral feature have been observed after comparing the spectrum of complexed PVC with

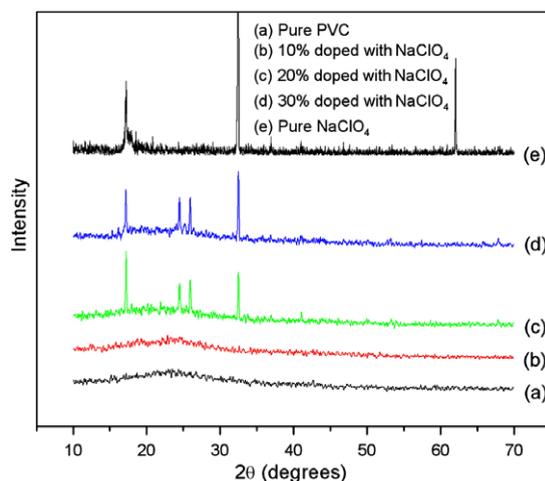


Fig. 1. XRD patterns of NaClO₄ complexed PVC.

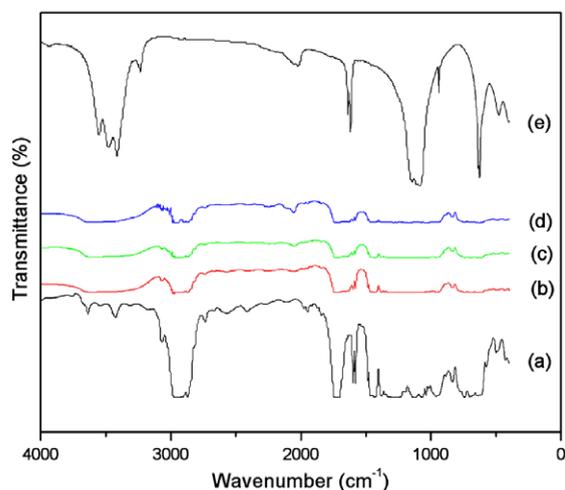


Fig. 2. IR spectra of NaClO_4 complexed PVC: (a) Pure PVC; (b) (PVC + NaClO_4) (90:10); (c) (PVC + NaClO_4) (80:20); (d) (PVC + NaClO_4) (70:30); (e) Pure NaClO_4 .

that of the pure PVC and NaClO_4 . The peak at 1075 cm^{-1} is assigned to the CH-rocking vibration

in the pure PVC, which is shifted 1101 cm^{-1} in the complex. This suggests that the Na^+ ion may be located on the vinyl chloride of the polymer chain- $[\text{CH}_2-\text{CH}_2\text{Cl}]_n$. The peak at 839 cm^{-1} in pure PVC shifted to 833 cm^{-1} in the polymer complex.

The disappearance of pure PVC bands at 1017, 1039, 1075, 1125, 1271, 2116, 2282, 3178, 3429, 3548 and 3640 cm^{-1} in the complexes suggest the co-ordination or complexation of Na^+ ions to the chlorine of PVC. The disappearance of some of the peaks observed for pure NaClO_4 (3552, 3481, 3415, 3237, 2025, 1617, 1144 cm^{-1} , etc.) in polymer complexes may be due to the fact that the ClO_4^- ion is in different surroundings in polymer complexes compared with those in the pure NaClO_4 salt. In summary, these observations confirm the complexation of NaClO_4 with PVC.

SEM graphs of the breaking surface of pure PVC and the complex samples with different NaClO_4 contents are shown in Fig. 3(a)–(d), respectively.

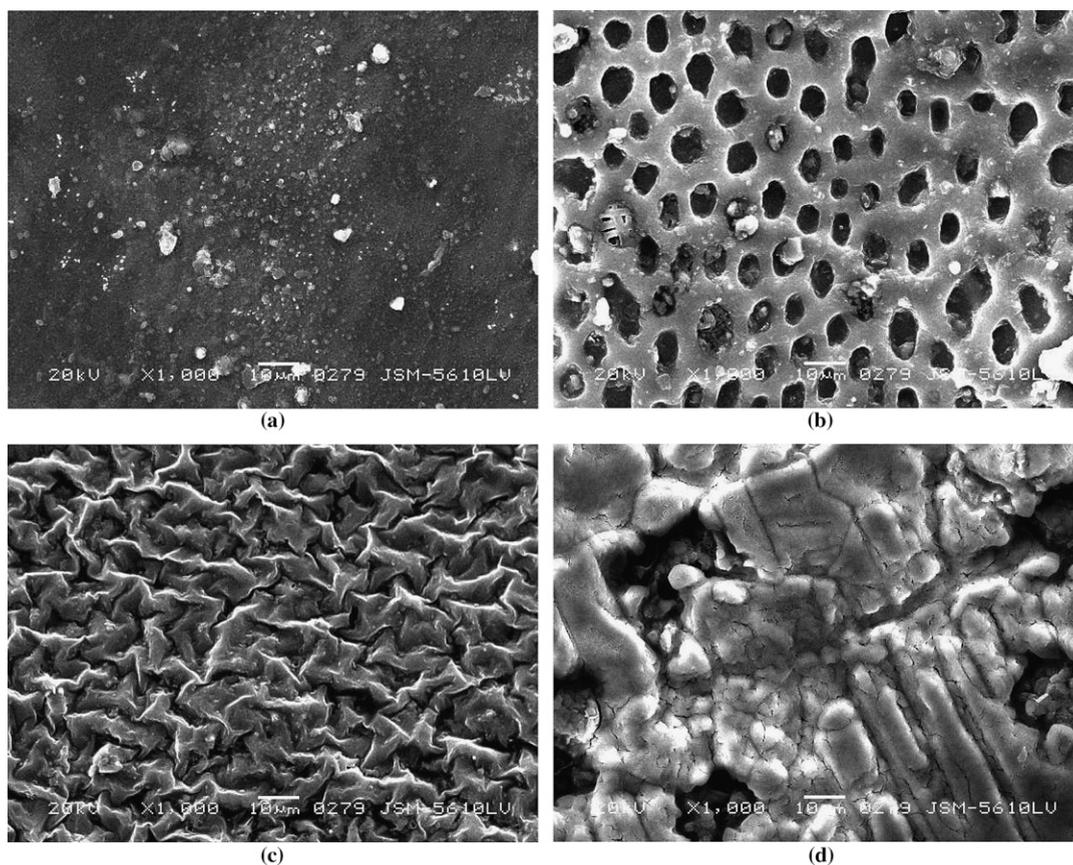


Fig. 3. SEM photographs of samples: (a) Pure PVC; (b) (PVC + NaClO_4) (90:10); (c) (PVC + NaClO_4) (80:20); (d) (PVC + NaClO_4) (70:30).

Several holes shown in Fig. 3(b), which have formed on the surface, are due to the rapid penetration of the Na^+ ions in to the polymer matrix or due to the rapid evaporation of THF used in the preparation of the film. The fractured surface of the composite sample with 20wt% NaClO_4 has morphology like interpenetrating net works (Fig. 3(c)). It shows that an extensive plastic-shearing deformation of the PVC matrix occurred, and the better toughness of the material is exhibited. There are many big holes with different sizes and polymer strings on the breaking surface for the complexed sample with 30 wt% NaClO_4 , as shown in Fig. 3(d). An extensive plastic deformation of the PVC matrix is evidenced by the appearance of numerous stings, craters, cavitation or the voids formed by debonding of some particles from the PVC matrix [18–20]. Hence, the morphological features of the fractured surface for the composite samples correspond to the impact-resistant toughness of the materials. In contrast to

the composite samples, the several holes surface of 10wt% NaClO_4 shown in Fig. 3(b) is more flexible due to the penetration of the salt ions into the polymer matrix and because of this, the conductivity and discharge capacity are also increased.

3.2. AC-impedance studies

Complex impedance is given by

$$Z = Z' - jZ''$$

$$Z = \frac{D}{\omega C} - \frac{j}{\omega C}$$

where Z' = real part of impedance; Z'' = imaginary part of impedance; D = loss tangent; ω = angular frequency; C = capacitance of the film. Fig. 4(a)–(d) shows that the typical real (Z') and imaginary (Z'') parts of the impedance data plotted in complex impedance plane for (PVC + NaClO_4) (90:10) polymer electrolyte at different temperatures. The plots

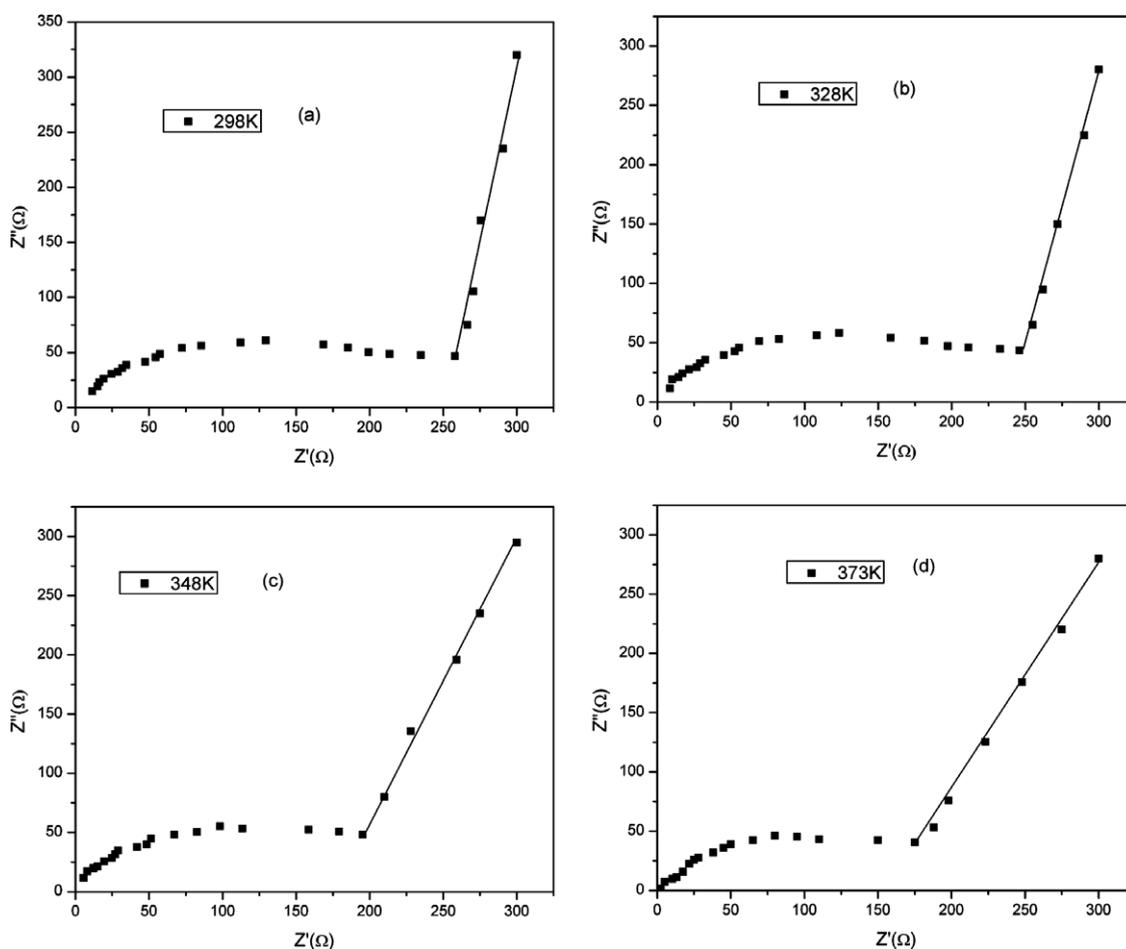


Fig. 4. Impedance plots (Cole–Cole plots) of (PVC + NaClO_4) (90:10) polymer electrolyte at different temperatures.

clearly show that there is an inclined straight line at the lower frequency region, followed by a semicircular arc at the higher frequency region. These results suggest that the migration of ions may occur through the free volume of matrix polymer, which can be represented by a resistor. The immobile polymer chains, on the other hand, become polarized in the alternating field, and can therefore be represented by a capacitor. The ionic migration and bulk polarization are physically in parallel, and therefore, the portion of the semicircle can be observed at high frequencies.

3.3. Ion conduction mechanism

Fig. 5 depicts the AC conductivity versus inverse temperature for sample pure PVC and all compositions of (PVC + NaClO₄). Observing Fig. 5, the conductivity values do not show any abrupt jump with temperature, indicating that these electrolytes exhibit a completely amorphous structure [21]. The increase in conductivity with temperature can be linked to the decrease in viscosity and hence, increased chain flexibility [22].

The activation energy (E_a), which is a combination of the energy of defect formation and the energy of defect migration, can be calculated from the plots. The activation energy for sample pure PVC and (PVC + NaClO₄) (90:10); (80:20); (70:30) are 0.45, 0.12, 0.18 and 0.24 eV, respectively. The low activation energy for the sodium ion transport is due to the completely amorphous nature of the polymer electrolytes that facilitates the fast Na⁺ ion motion in

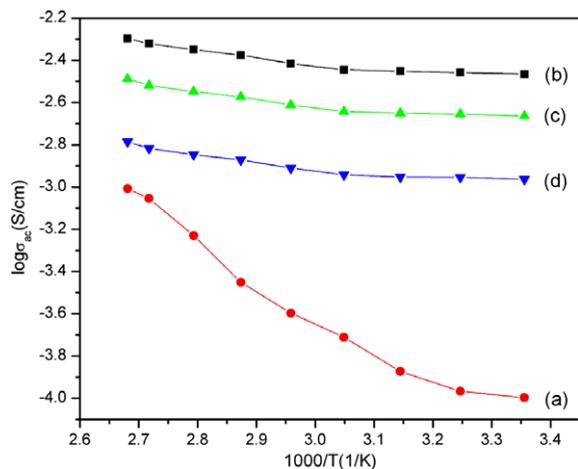


Fig. 5. Plots of log of AC conductivity vs. $1000/T$ for: (a) Pure PVC; (b) (PVC + NaClO₄) (90:10); (c) (PVC + NaClO₄) (80:20); (d) (PVC + NaClO₄) (70:30).

the polymer network. The completely amorphous nature also provides a bigger free volume in the polymer electrolyte system upon increasing the temperature [21]. Thus, the systems with the low values of activation energies are desirable [23]. It can be observed that sample (PVC + NaClO₄) (90:10) has

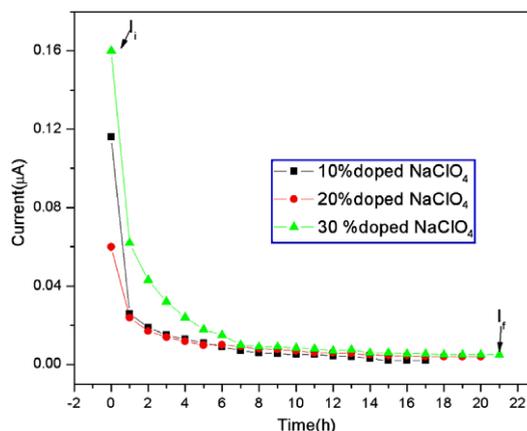


Fig. 6. Plots of current vs. time for (PVC + NaClO₄) polymer electrolytes.

Table 1
Transference numbers of (PVC + NaClO₄) polymer electrolyte system

Polymer electrolyte (wt)%	Transference numbers	
	t_{ion}	t_{cle}
(PVC + NaClO ₄) (90:10)	0.98	0.02
(PVC + NaClO ₄) (80:20)	0.93	0.07
(PVC + NaClO ₄) (70:30)	0.97	0.03

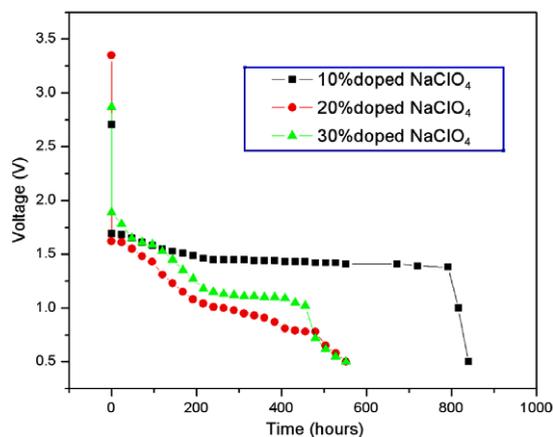


Fig. 7. Discharge characteristics of solid-state electrochemical cell in the configuration Na/(PVC + NaClO₄)/(I₂ + C + electrolyte).

Table 2
Various cell parameters for (PVC + NaClO₄) polymer electrolyte cells

Cell parameters	(PVC + NaClO ₄) (90:10)	(PVC + NaClO ₄) (80:20)	(PVC + NaClO ₄) (70:30)
Effective area of the electrolyte (cm ²)	1.54	1.54	1.54
Cell weight (g)	2.30	1.27	1.32
Open circuit voltage (OCV) (V)	2.71	3.25	2.87
Short circuit current (SCC) (μA)	270	240	220
Load (kΩ)	100	100	100
Current density (μA cm ⁻²)	175.32	155.84	142.85
Discharge time for plateau region (h)	792	480	456
Power density (mW kg ⁻¹)	10.35	12.26	17.39
Energy density (mW h kg ⁻¹)	8197	5885	7931
Discharge capacity (μA h ⁻¹)	2.38	1.33	1.77

a higher ionic conductivity and lower activation energy compare to the other three samples.

3.4. Transference numbers

The transference number measurements have been done in the (PVC + NaClO₄) polymer electrolyte systems using Wagner's polarization technique. In this technique, the dc current is monitored as a function of time on the application of fixed dc voltage (1.5 V) across a Na/(PVC + NaClO₄)/C cell. The plots of (PVC + NaClO₄) polymer electrolyte systems are given in Fig. 6. The values of ionic and electronic transference numbers (t_{ion} and t_{ele}) obtained in these electrolytes are given in Table 1. For the compositions of the (PVC + NaClO₄) polymer electrolyte system, the value of ionic transference numbers (t_{ion}) is in the range 0.93–0.98. This suggests that the charge transport in these polymer electrolytes is predominantly ionic.

3.5. Discharge characteristics

Using (PVC + NaClO₄) polymer electrolyte systems, solid-state electrochemical cells were fabricated with the configuration Na (anode)/(PVC + NaClO₄)/(I₂ + C+electrolyte) (cathode). Sodium metal was used as the negative electrode, and mix of iodine (I₂), graphite(C) and electrolyte in the ratio 5:5:1 as the positive electrode.

The discharge characteristics of the cells (anode)/(PVC + NaClO₄)(90:10)/(cathode), (anode)/(PVC + NaClO₄)(80:20)/(cathode) and (anode)/(PVC + NaClO₄)(70:30)/(cathode) at ambient temperature for a constant load of 100 kΩ are presented in Fig. 7. The initial sharp decrease in voltage of these cells may be due to polarization and/or formation of a thin layer of sodium salt at the electrode/electrolyte interface. The open-circuit voltage (OCV),

short-circuit current (SCC) and other cell parameters for these cells are given in Table 2.

From Table 2, it is clear that the SCC and the discharge time for the plateau region are found to be greater in (PVC + NaClO₄) (90:10) cell compared to the other two complexed cells. This has been explained in terms of high ionic conductivity and more amorphosity are observed in (PVC + NaClO₄) (90:10) electrolyte system compared to the other two complexed systems.

4. Conclusions

From the Cole–Cole plots, AC conductivity was evaluated at the different temperatures. The activation energy value obtained from conductivity data decreases with increasing ionic conductivity and vice versa. Using (PVC + NaClO₄) polymer electrolyte systems, electrochemical cells were fabricated and discharge characteristics of these cells were studied. The transference number data indicate that conduction in these electrolytes is predominantly ionic. (PVC + NaClO₄) (90:10) Cell was found to be more stable than the other two complexed system cells.

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