

Ionic conductivity and lithium electrode stability in Hydrin: LiBF₄ elastomers

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Three commercial elastomers, Hydrin C, Hydrin H and Hydrin T, which contain ethylene oxide and epichlorohydrin repeat units, have been investigated as polymer electrolytes in contact with lithium electrode. The influence of polyethylene glycol and fine particles of zeolite on ionic conductivity of Hydrin–LiBF₄ electrolytes and the exchange current density of the lithium electrode reaction has been studied by using impedance spectroscopy and cyclic voltammetry. The specific conductivity of the elastomeric electrolyte is about $10^{-5} \text{ S cm}^{-1}$ at room temperature when polyethylene glycol is present. But the mechanical stability of the film is less. The addition of zeolite particles to the elastomers also improves the specific conductivity. When present in low concentrations, the zeolite particles show catalytic effect on the electrochemical reaction at lithium electrode at ambient temperature. The lithium electrode reaction is reversible and the electrolyte possesses good electrochemical stability.

1. Introduction

Studies on polymer-based solid electrolytes have been of increasing interest in view of their applications in high energy density batteries [1]. Although poly(ethylene oxide) (PEO) has been extensively studied as the polymer medium following the investigations of Wright [2,3] and Armand [4], the chances for employing the PEO electrolyte in solid state batteries are rather remote, since it possesses specific conductivity (σ) of about or less than $10^{-8} \text{ S cm}^{-1}$ at ambient temperature, which is very low. Thus, for employing the polymer electrolytes in solid state batteries, the primary problem to be solved is their inadequate ionic conductivity.

In a polymer medium, several factors including the proportion of amorphous phase of the polymer salt complex [5] and segmental motion of the polymer chains [6] influence the ionic conductivity. Attempts have been made to enhance the conductivity by controlling one of these factors individually. For example, syntheses of amorphous polymeric electrolytes are reported and reviewed [7–11]. It is also reported [12–16] that the σ of PEO complexes increases due to fine particles of inert ceramic material when dispersed in the polymer film. The σ increased, also by the addition of plasticizers such as polyethylene glycol to PEO, as a result of facilitating segmental motion of the polymer chains [17,18]. Studies

concerning the combined effects of increased amorphous phase and plasticizers or ceramic particles on specific conductivity appear to be not reported. The present work describes such a study.

Three commercial elastomers, which contain ether oxygen in their structures, were studied as polymer media. As these polymers, possessing solvating properties with Li⁺, exist entirely in the amorphous state, it was anticipated that the composite electrolytes blended with poly(ethylene glycol) and fine particles of zeolite could have high conductivity. Furthermore, their soft and elastomeric nature could provide improved interfacial contact with the electrode. The influence of zeolite on the lithium electrode reaction in these electrolytes was also examined. The results obtained on ionic conductivity, exchange current density, and time dependent stability of symmetrical cells are presented and discussed.

2. Experimental details

The elastomers used in the present work, viz. Hydrin H, Hydrin C and Hydrin T (hereafter referred to as HH, HC, and HT, respectively) were obtained from Zeon Chemical, Inc., Illinois, USA. Reagent grade polyethylene glycol (PEG) of MW 400 (Aldrich), zeolite (Sigma) of average particle size $5 \mu\text{m}$, and acetone (Aldrich) were used as received. LiBF₄ (Aldrich) was dried before use. The lithium metal (Alfa) was in the form of a ribbon of 0.3 mm thickness. It was rinsed with a mixture of hexane and

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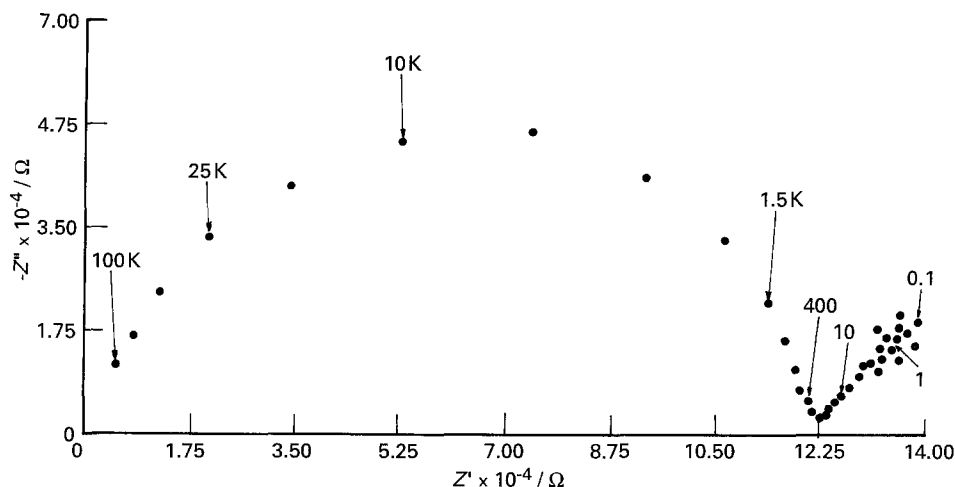


Fig. 1. The Nyquist impedance plot of SS/HH-LiBF₄/SS at 65°C. The frequency range: 0.1 Hz-100 kHz; electrolyte thickness: 130 μm ; area of the electrode: 1.1 cm^2 .

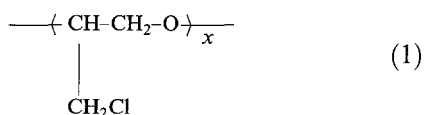
heptane to remove the oil present on its surface before using for the experiments.

Thin films (100-200 μm) of the electrolytes were prepared as follows. Weighed quantities of the elastomer and LiBF₄ at the required ratio were dissolved in acetone. The PEG and zeolite were added to the solution whenever required. The solution was stirred for about 24 h before the film was cast on a Teflon covered glass plate. The solvent was allowed to evaporate for about 24 h at room temperature and the film was dried for 6 h at 60°C in helium atmosphere. The film was transferred into a helium filled dry box for cell fabrication.

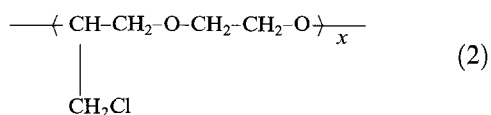
Symmetrical cells of SS/EE/SS and (SS)Li/EE/Li(SS) [SS: stainless steel; EE: elastomeric electrolyte] were constructed in a Teflon holder. The cell was contained in an air-tight glass vessel with electrical connections. The glass vessel was maintained at the required temperature within $\pm 1^\circ\text{C}$ by using a heating tape and a temperature controller. Cyclic voltammetry and impedance spectra (frequency range: 0.1 Hz-100 kHz) were recorded in the temperature range 20-100°C using EG&G electrochemical system (Model 273A) interfaced with an IBM compatible computer. The σ of the electrolyte film obtained from impedance spectra was invariant with the electrode material (Li or SS).

3. Results and discussion

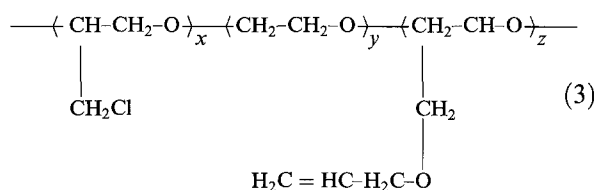
The three polymers studied in the present work have the following chemical composition. Hydrin H is poly(epichlorohydrin).



Hydrin C is a copolymer of epichlorohydrin and ethylene oxide.



Hydrin T is a terpolymer of epichlorohydrin, ethylene oxide, and allyglycidyl ether.



The films made out of the elastomers without the lithium salt were rubbery and had poor mechanical strength. On complexing with LiBF₄, however, the mechanical strength of the films improved in the case of HC and HT, but HH still remained rubbery and free-standing films could not be obtained out of this elastomer. Furthermore, σ of HH is considerably lower than HC and HT (Fig. 2). Therefore, the majority of the experiments were carried out using HC and HT. As a result of preliminary experiments, the desirable weight ratio of the elastomer and LiBF₄ was found to be 4:1. Although the films had poor mechanical strength at lower concentrations of LiBF₄, they became brittle and specific conductivity decreased at higher concentrations. This weight ratio corresponds to oxygen to lithium ratio of 4.1:1, 5.5:1 and 5.7:1 in HH-LiBF₄, HC-LiBF₄ and HT-LiBF₄ electrolytes, respectively.

3.1. Conductivity of HH, HC and HT

The Nyquist plot of SS/HH-LiBF₄/SS cell is shown in Fig. 1. Similar plots are recorded with HC and HT electrolyte films. A fairly well-defined semicircle suggests that the lithium salt added into the elastomeric film undergoes complexation with the oxygen atom of the polymer chain and the behaviour of the complex under potential field is similar to that of PEO-Li complexes. The σ of the electrolytes was calculated by measuring the resistance corresponding to the diameter of the semicircle, and shown in Fig. 2. Results of PEO-LiBF₄ electrolyte from our earlier work [12] are also included for the purpose of

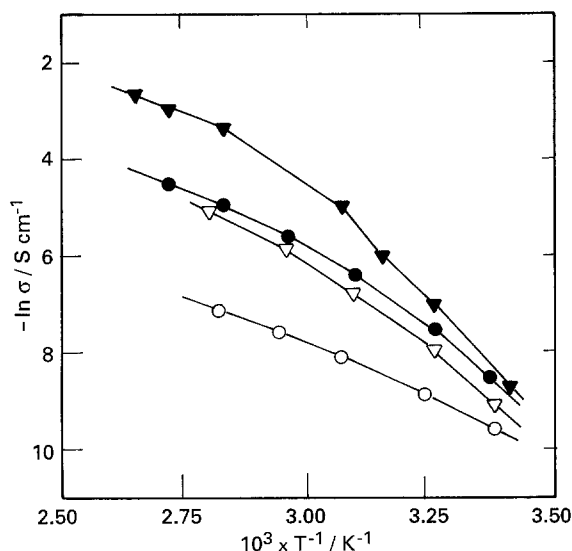


Fig. 2. Dependence of specific conductivity (σ) of Hydrin H (○), Hydrin C (●), Hydrin T (▽) and PEO (▼) electrolytes on temperature. The weight ratio of the polymer and LiBF_4 is 4:1.

comparison. It is interesting to note that the ambient temperature σ of these elastomeric electrolytes is about the same or even less than that of PEO electrolyte, in spite of their amorphous state. However, at higher temperatures, the σ of HH, HC and HT electrolytes is less than that of PEO electrolyte. At 80°C , for example, the σ of HH is less by about four orders of magnitude and the σ of HC and HT is less by two orders of magnitude. The epichlorohydrin in HH (Formula 1) differs from PEO by CH_2Cl substitution of H on the second C atom, resulting in amorphous HH. The expected favourable effect of the amorphous state on σ appears to be offset by chemical and physicochemical factors modified by the substitution of CH_2Cl , which is bulkier and more electronegative than the H atom. Such factors include the degree of dissociation of the salt, the extent of complexation, segmental motion of the

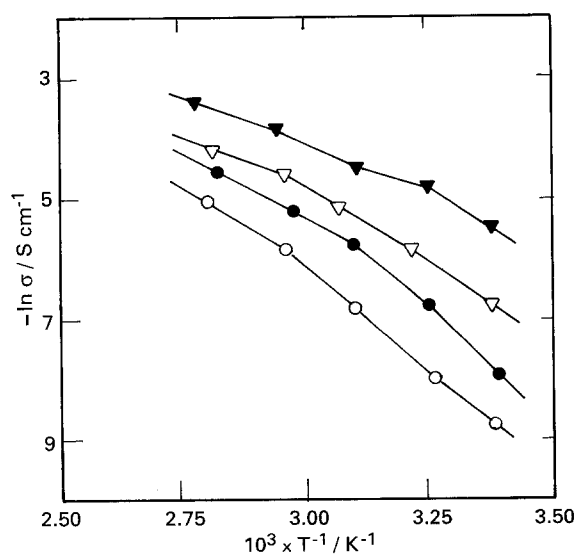


Fig. 3. The specific conductivity (σ) of Hydrin T (HT) containing polyethylene glycol (PEG). The composition of the electrolyte is $(2-x)\text{g HT} + x\text{g PEG} + 0.5\text{g LiBF}_4$. $x = 0$ (○), 0.25 (●), 0.50 (▽) and 0.75 (▼).

polymer chains, the structure of the polymer helix and the distance between the oxygen atoms. Being a copolymer of HH and PEO, HC possesses properties intermediate between those of HH and PEO; and therefore the position of the conductivity curve (Fig. 2) lies in between the curves of HH and PEO. The σ of HT is slightly lower than that of HC. Apparently, the allyl-glycidyl ether repeat units of the terpolymer exhibit negative influence on σ to a small extent.

3.2. HT blended with PEG and zeolite

To enhance the ionic conductivity, composite elastomeric electrolyte films were prepared by mixing with PEG and fine particles of zeolite, and their conductivities were measured. As the HC and HT electrolyte films behave alike throughout the temperature range (Fig. 2), the additives are expected to have similar influence on σ of both the electrolytes. The conclusions made from the results of either HC or HT are likely to be similar for the other.

When blended with PEG, maintaining the weight ratio of the polymer including PEG and LiBF_4 at 4:1, the specific conductivity of HT electrolyte film increased as shown in Fig. 3. The mechanical stability of the film, however, decreased. The increased σ was due to the decreased viscosity of the medium in the presence of PEG, which facilitated segmental motion of the polymer chain and therefore the mobility of the ions. The ambient temperature σ increased from about $10^{-10}\text{ S cm}^{-1}$ (in the absence of PEG) to about 10^{-5} S cm^{-1} when HT and PEG ratio was 1:0.6. Further increase of PEG resulted in the formation of films with poorer mechanical strength.

On increasing the concentration of LiBF_4 , the mechanical strength improved as expected. However, there was a decrease in σ , as shown in

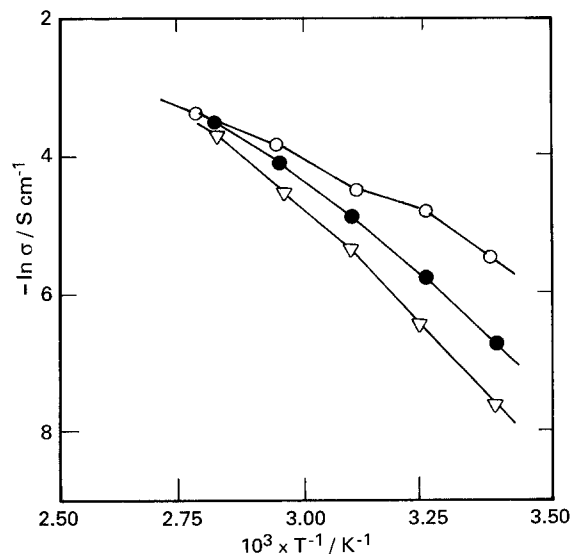


Fig. 4. The influence of the concentration of LiBF_4 in HT blended with PEG on specific conductivity (σ). The composition of the electrolyte is $1.25\text{g HT} + 0.75\text{g PEG} + 0.5\text{g LiBF}_4$ (○); $1.0\text{g HT} + 1.0\text{g PEG} + 1.0\text{g LiBF}_4$ (●); and $1.0\text{g HT} + 1.0\text{g PEG} + 1.5\text{g LiBF}_4$ (▽).

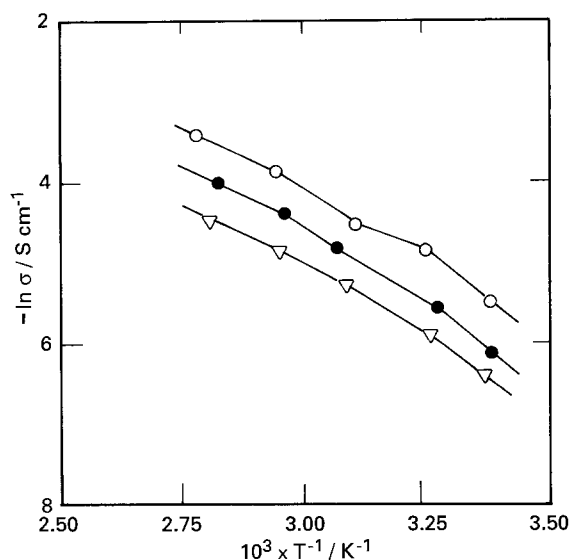


Fig. 5. The influence of zeolite present in HT blended with PEG on specific conductivity (σ). The composition of the electrolyte is 1.0 g HT + 1.0 g PEG + 0.5 g LiBF₄ containing zeolite, nil (○), 14% (●) and 19% (▽).

Fig. 4. This decrease may be due to approaching a saturation limit of the solid solution or shifting of the equilibrium towards ion pair formation. Such effects may be reduced if an inert material such as zeolite is added to the elastomer, instead of increasing the concentration of LiBF₄. However, as shown in Fig. 5, there was a decrease in σ due to the presence of zeolite in the polymer electrolyte containing PEG. The zeolite particles seem to offer resistance to the conduction process by increasing the viscosity of the medium, opposing the influence of PEG on conductivity.

3.3. HC doped with zeolite

The influence of zeolite alone on the σ of the electrolyte and charge-transfer reaction at Li/electrolyte interface was examined. The impedance spectrum of a Li/HC–LiBF₄–zeolite/Li symmetrical cell resulted in two semicircles as shown in Fig. 6. The high-frequency semicircle corresponds to the electrolyte film $R_b C_b$ time constant (where R_b and C_b are resistance and capacitance,

respectively, of the electrolyte film). Although the low frequency semicircle corresponds to interfacial $R_t C_{dl}$ (where R_t and C_{dl} are charge-transfer resistance and double-layer capacitance, respectively) [19], it appears that there is some uncertainty due to the presence of surface films on lithium [20]. However, as it is generally believed that the surface layer on lithium in solid polymer medium is compact and possesses high ionic conductivity [21], the contribution of the surface film resistance to the low frequency semicircle is ignored in the present work, similar to the studies reported previously [22,23].

From the value of R_b obtained from the diameter of the high frequency semicircle, the σ of the electrolyte film was calculated and is shown in Fig. 7 for HC containing different proportions of zeolite. Although σ at high temperature is approximately the same, it increases with the amount of zeolite at ambient temperature. It is interesting to note that the addition of zeolite to the elastomers when blended with PEG results in a decrease of σ from about 10^{-5} S cm⁻¹ at room temperature to about 10^{-6} S cm⁻¹ when doped with 19 wt % of zeolite (Fig. 5). However, in the absence of PEG, the addition of zeolite results in an increase of σ from about 10^{-9} S cm⁻¹ to about 10^{-7} S cm⁻¹ when doped with 26 wt % of zeolite. The addition of zeolite particles to PEO based electrolytes increases the amorphous phase in the electrolyte resulting in an increase of conductivity [12]. As the polymer in the present studies exists entirely in amorphous phase, it is likely that the zeolite particles in the electrolyte influence the interionic forces within the polymer electrolyte facilitating higher conductivity. Or, the ionic transport may be faster in the zeolite particle/polymer interfacial region. Detailed experimental results are required to delineate the mechanism of increased ionic conductivity in the elastomers due to the dispersed fine inert particles.

From the value of the charge-transfer resistance (R_t) obtained from the low frequency semicircle of the Nyquist impedance plot, the exchange current density (i_0) for the reaction $\text{Li}^+ + e^- = \text{Li}$ was calculated using Equation 4, assuming that the lithium

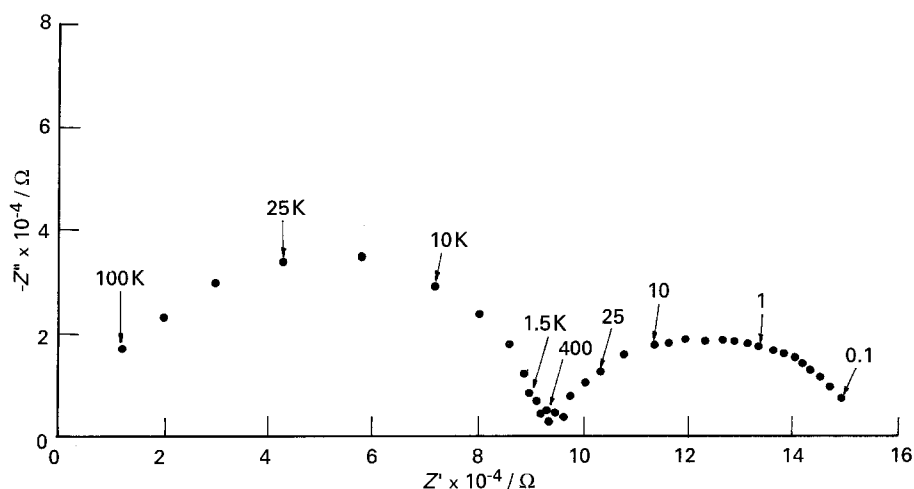


Fig. 6. The Nyquist impedance diagram of Li/HC–LiBF₄–zeolite/Li at 23°C. The frequency range: 0.1 Hz–100 kHz. Concentration of zeolite: 26%; electrolyte thickness: 170 μm ; area of the electrode: 0.65 cm².

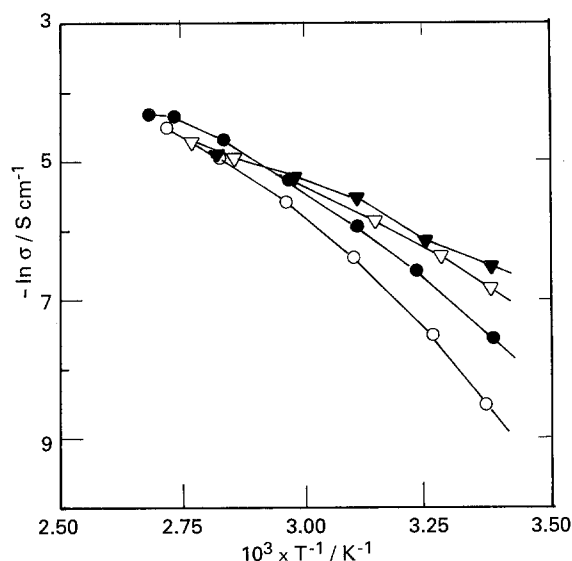


Fig. 7. The influence of zeolite present in HC on specific conductivity (σ). The composition of the electrolyte is 2.0 g HC + 0.5 g LiBF₄ containing zeolite, nil (\circ), 10% (\bullet) and 20% (∇) and 26% (\blacktriangledown).

surface is free from a passive layer.

$$i_0 = \frac{RT}{FR_t A} \quad (4)$$

where R is the gas constant, T the absolute temperature, F the Faraday constant and A the area of the lithium electrode. The dependence of i_0 on the

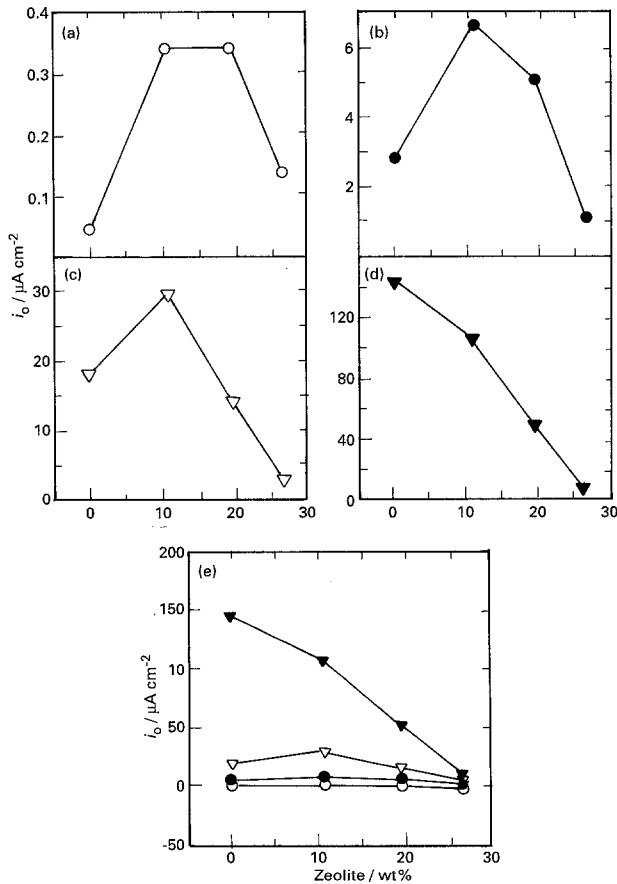


Fig. 8. The influence of zeolite present in 2.0 g HC + 0.5 g LiBF₄ on i_0 , the exchange current density of Li/Li⁺ reaction at (a) 23°C, (b) 45°C, (c) 60°C and (d) 75°C. The plots (a), (b), (c) and (d) together are shown in (e).

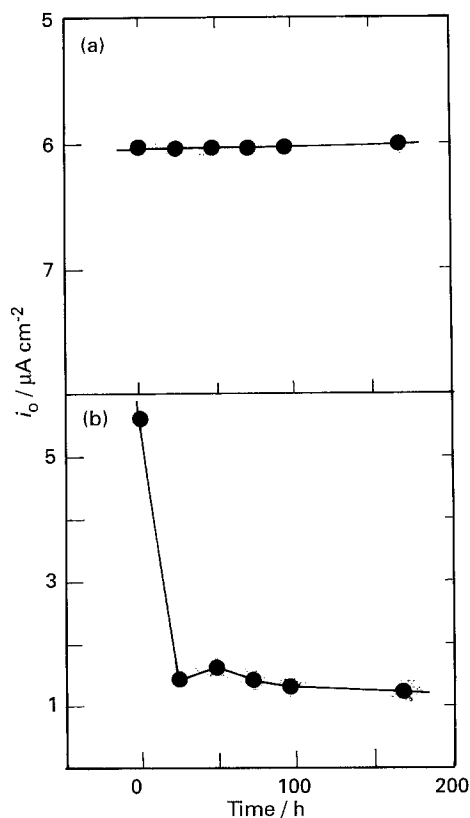


Fig. 9. The time dependence of (a) the specific conductivity, σ and (b) the exchange current density, i_0 in the electrolyte containing 2 g HT + 1.2 g PEG + 0.8 g LiBF₄ + 0.8 g zeolite, at ambient temperature.

concentration of zeolite in HC electrolyte is shown in Fig. 8 at four different temperatures. The i_0 increased for lower concentrations of zeolite in the temperature region 23–60°C, similar to the results reported on the influence of lithium borosulfate particles on i_0 in PEO electrolytes [14]. Further increase in zeolite concentration resulted in a decrease of i_0 . However, at 75°C, the i_0 decreased with zeolite concentration without exhibiting the initial increase. These results can be explained as follows: When present in low concentrations (10% or less), the zeolite particles at the Li/solid electrolyte interface probably act as a catalyst thus enhancing the exchange current density of the reaction. The formation of the three phase boundary viz., the lithium metal/zeolite particle/ polymer electrolyte, appears to be responsible for this. However, if the zeolite concentration is more than 10%, the particles shield the electrode surface, causing a reduction in the active surface area of the electrode. This results in a decreased exchange current density. At 70°C, i_0 is several times higher than the room temperature value in the absence of zeolite due to thermal effects. As a result, the catalytic effect of zeolite at low concentrations is absent. At higher concentrations, the shielding effect dominates over the catalytic effect, resulting in a decreased i_0 . The influence of 26% zeolite in the electrolyte eventually lowers i_0 to such an extent that it is almost the same at all temperatures. This can be clearly seen in Fig. 8(e).

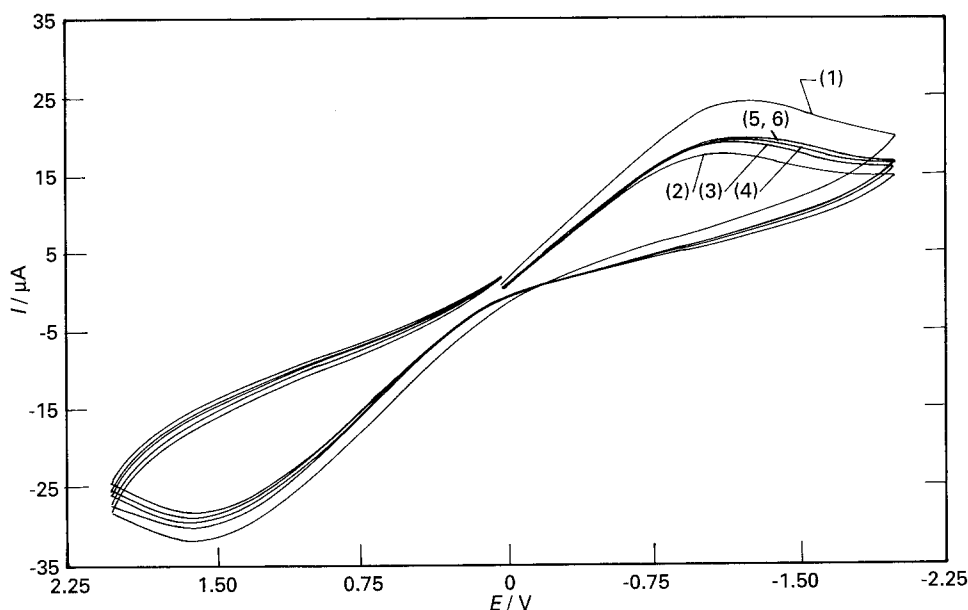


Fig. 10. Cyclic voltammograms of Li/HT + PEG + LiBF₄ + zeolite/Li symmetrical cell at ambient temperature. The traces were recorded at a scan rate of 2 mV/s immediately (1), 24 (2), 48 (3), 72 (4), 96 (5) and 168 h (6) after the cell was assembled. Composition of the electrolyte: same as Fig. 9; electrolyte thickness: 160 μm.

3.4. Stability of lithium electrode

The stability of the Li/HT + PEG + LiBF₄ + zeolite/Li symmetrical cell at ambient temperature was monitored over a period of several hours by periodically recording the impedance spectra and cyclic voltammograms. The cyclic voltammograms were recorded without using a reference electrode for the purpose of examining the electrode reactions qualitatively, similar to the results reported previously [18]. The time dependence on the σ of the electrolyte and i_0 is shown in Fig. 9 and cyclic voltammograms are presented in Fig. 10. The HT electrolyte, containing PEG and zeolite maintains a constant σ (Fig. 9(a)). The value of i_0 is fairly constant following an initial decrease (Fig. 9(b)). The decrease may be attributed to the formation of a stable film on lithium during the initial period of storage or on cycling the symmetrical cell between 2.0 and -2.0 V for the purpose of recording cyclic voltammograms. The cyclic voltammograms also reflect the initial changes that took place at the interphase. There is a decrease in peak currents between the initial curve and the subsequent curve recorded after 24 h of cell assembly (Fig. 10). Following this, the curves are reproducible over a period of 168 h, when these experiments were terminated. The symmetrical shape of the cyclic voltammograms suggests that the electrode reaction is fairly reversible in HT electrolyte containing PEG and zeolite.

4. Conclusions

The solid polymer electrolytes prepared from Hydrin elastomers have low σ (10^{-10} – 10^{-9} S cm⁻¹). However, the σ increases (up to 10^{-6} – 10^{-5} S cm⁻¹) when these electrolyte films contain PEG or zeolite. The presence of zeolite in the electrolyte resulted in an interesting effect on the interfacial reaction. At low temperatures

and low zeolite concentrations, i_0 for Li/Li⁺ reaction increases. On increasing the concentration, i_0 decreases due to the shielding effect of the particles. In view of the present trend of using composite polymer electrolytes with ceramic particles such as alumina, it is important from the present results to note that the influence of such particles exists not only on the bulk properties of the electrolyte but also on the interfacial electrochemical reactions. Higher levels of particle concentration can lead to detrimental effects on the kinetics of the electrochemical reactions, even though there are beneficial effects on the electrolyte properties. From the cyclic voltammograms recorded at room temperature, it is found that there is a good reversibility of the Li/Li⁺ reaction in the elastomeric electrolytes studied in the present work.

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