Original Research Paper

Volume - 16 | Issue - 07 | July - 2026 | PRINT ISSN No. 2249 - 555X | DOI : 10.36106/ijar

Physics

IRRADIATION EFFECTS ON PHYSICAL AND CHEMICAL PROPERTIES OF POLYMER ELECTROLYTES

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ABSTRACT Solid polymer electrolytes have potential applications in various high energy electrochemical devices like rechargeable batteries, fuel cells, display devices etc One of the most studied systems is polyethylene oxide (PEO), which serves as a model polymer for a variety of applications. PEO has an exceptional property of dissolving high concentrations of wide varieties of salts to form polymeric electrolytes. PEO, like many other polymer electrolytes, has a tendency to crystallize at ambient temperature and hence produces lowering in ionic conductivity. There is a search for additives or processes which may reduce crystallinity and enhance conduction. One such process is irradiation. Irradiation by ion beams, electrons or photons produces changes in polymers, which may be advantageous or harmful.

KEYWORDS : Gamma Irradiation; Polymer Electrolyte; Ion Conductivity

INTRODUCTION

Polymer electrolytes are materials with a potential for extensive use in practical devices and appliances [1, 2], it is useful to study the effect of irradiation on them. The risk of degradation on appliances being exposed to radiation environment in nuclear reactors or outer space has to be considered as well as the possibility of improvement of properties on controlled irradiation [3,4].

So identifying radiation resistant materials as well as radiation sensitive materials is necessary. Studies indicate that there is a variation in various physical and electrical properties of a polymer salt complex by exposure to high energy radiation like ion beam, electron beam, x-ray and γ-ray [5]. When exposed to such radiation, it produces changes is microstructure and molecular weight of the system through cross–linking and scission of the long polymer chains. Both processes may occur simultaneously, but usually one dominates [3, 6]. The irradiation effect is manifested by changes in crystallinity, melting temperature, mechanical properties and affects the dynamical disorder due to segmental motion of polymer chains. These are crucial in determining electrical properties like ion conductivity of the polymer-salt complex [6, 7].

1. Electrical Property

The present topic is concerned with polymer electrolytes suitable for use in solid state batteries where the ion conductivity is an extremely important property. Addition of a salt increases the amorphous region of the system thus increasing conductivity.

Ion Conductivity in Polymer Electrolytes

Polymer electrolytes shows dynamic disorder since the local environments changes substantially with time due to some liquid-like motion. Polymer chains, thus, execute motion in a very small time scale ~ $10^{-9} – 10^{-11}$ sec and such motion is called segmental motion [1-5]. This segmental motion occurs in the amorphous region which contributes to the conductivity. When an ionic salt is dissolved in the polymer, selected sites of the polymer act as coordination sites and form weak bonds with cation part of the salt. As the polymer undergoes segmental motion, the ion gets transferred from one such site to another. This diffusion of ions through the polymer matrix increases the conductivity of the sample. The ionic conductivity of a polymer salt complex depends not only on the nature of host polymer and the salt but also on temperature and salt fraction [6-8].

Measurement of Transference Number:-

Polymer electrolytes must be good ion-conductors and poor electron conductors. So it is important to measure the transference number and check that it is very close to 1.

1.1 Variation of Conductivity with Temperature

The process of ion-conduction is by hopping and is assisted by disorder, unlike electron conduction in metals. So an increase in temperature causes an inverse in ion conductivity. Further with rise in temperature, the crystalline phase dissolves in the amorphous phase of the polymer system favouring more segmental motion. This also causes rise in conductivity with temperature. There are various empirical relations between conductivity (σ) and temperature (T) [6-8].

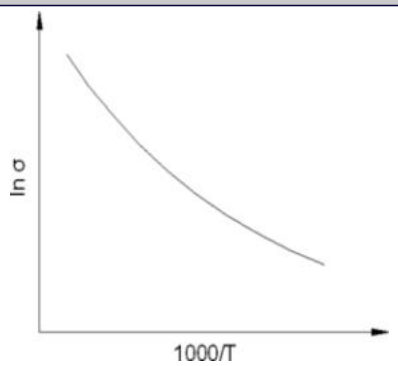

Figure 1: Plot of Log (σ) vs. 1/T (σ-conductivity, T- temperature).

For a partially crystalline polymer, the relation between σ and T can be expressed by Arrhenius form

$$\sigma = \frac{}{T} \exp\left(\frac{}{kT}\right)$$

where A is a pre exponential factor and E_2 is the activation energy for migration. For a fully amorphous polymer Vogel- Tamman – Fulcher (VTF) relation holds good.

$$\sigma = \frac{\sigma_0}{} \exp\left(-\frac{B}{\quad\quad\quad\quad}\right)$$

where σ_0 is a pre-exponential constant, B is a pseudo-activation energy related to the configurationally entropy and T_0 is a parameter generally associated with glass transition temperature, T_g. [9-11].

The third type is a combination of the above two with Arrhenius-type behaviour below a particular temperature (often the melting temperature of crystalline PEO) and VTF-type behaviour for temperatures above this value [12].

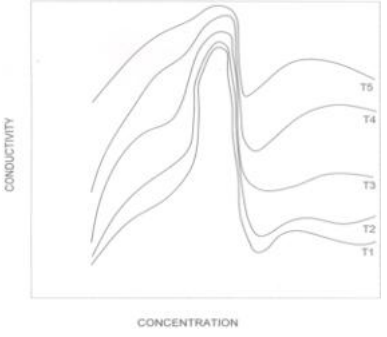

Figure 2: Plot of Conductivity Versus Salt Fraction for Various Temperatures ($T_1 < T_2 < T_3 < T_4 < T_5$).

1.2 Variation with Salt Content

The conductivity of a polymer electrolyte, usually increases with increase in salt content, reaches a maximum and then decreases with

increasing salt fraction. In the first portion of the graph, as salt concentration increases, crystallinity decreases and due to increasing charge carrier concentration, the overall conductivity increase [13,14]. But in the second portion of the graph, as salt fraction increases there appears transient cross linking between the polymer chains which results in the reduction of segmental motion and impedes the movement of the ions through the system leading to decrease in conductivity [15,16]. The conductivity of polymer electrolytes with a certain salt fraction increases as temperature increases and vice versa. The variation in conductivity with salt concentration for different temperatures for a typical polymer electrolyte is shown in fig.7 [9,17,18].

Measurement of Conductivity Impedance Spectroscopy (IS)

Impedance Spectroscopy is used to find the dynamics of bound or mobile charges in the bulk or interfacial regions of materials. In the present study, the conductivity measurements are performed using impedance spectroscopy technique [13, 14, 19]. The dc ionic conductivity is measured using the ac method to eliminate electrode polarization. The dc conductivity is obtained from frequency response curve plotted against complex admittance [20-24]. A small alternating voltage is applied to the sample and amplitude and the phase shift (or the real and imaginary parts) of the resulting current is measured. It E (t) be the excitation signal (potential difference) at time t, then

$$E(t) = E(0)\exp(j\omega t)$$

where E(0) is the amplitude of the signal at time t =0 and ω is the radial frequency. In a linear system, the response signal current I(t) is shifted in phase (φ). If I(0) be the initial current then,

$$I(t) = I(0)\exp[j(\omega t-\varphi)]$$

The impedance is thus represented as a complex number

$$Z=E/I = Z(0)\exp(j\varphi)$$

where Z(0) is the amplitude part and φ is the phase shift.

Plotting Impedance

The real part (Re) of Z is plotted on the X axis and the imaginary part (Im) is plotted on Y axis. This plot is called Cole-Cole plot or a Nyquist plot. From this plot the resistance of the sample is obtained as the intercept of the curve on the real Z axis at ω=0. A plot of the real part of impedance/ admittance vs. frequency is called a Bode plot.

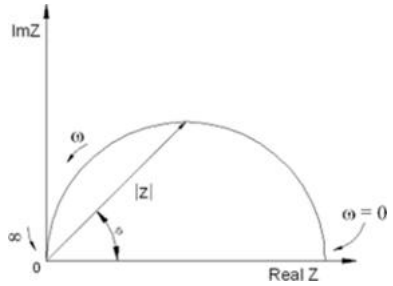

Figure 3: A Typical Cole-cole Plot.

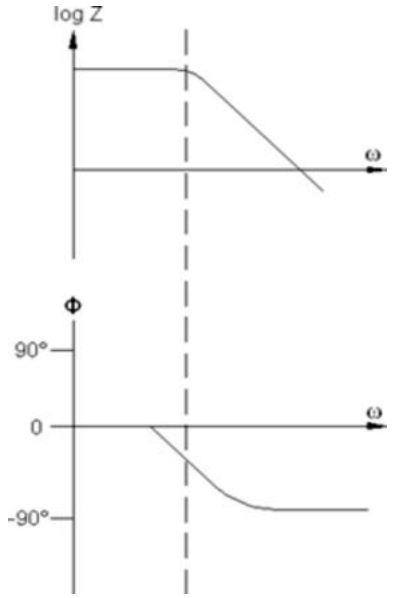

Figure 4: A Typical Bode Plot ofLog(Z) vs. ω and φ vs. ω.

Equivalent Circuit

The use of IS as a tool for investigating properties of materials and systems gives the direct connection between the behaviour of real systems and idealised model circuits consisting of discrete electrical components. The passive circuit elements can be combined in series and parallel to build equivalent circuits which can be used to model various phenomena going on at the interface. However, the equivalent circuit is not unique; an equivalent circuit consisting of three or more circuit elements may be rearranged in various ways to get exactly the same impedance [25]. The simplest equivalent circuit is a parallel circuit of resistance R and capacitance C (figure 5).

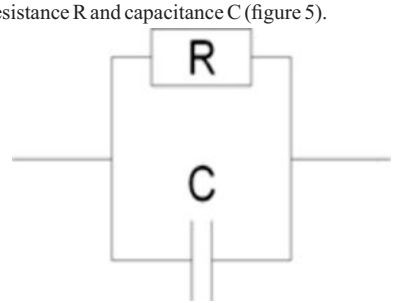

Figure 5: The Parallel Circuit of Resistance R and Capacitance C

The complex impedance diagram will give a semicircle centred on the real axis. The diameter of the semicircle will give R. The capacitance C may be determined from the frequency of the semicircle maximum. This is shown in fig. 3. The plot of admittance of this circuit is a straight line (fig. 6) with Re (Y) giving the real part of the admittance and Im (Y) gives the imaginary part of admittance. The arrow indicates the direction of the increasing frequency.

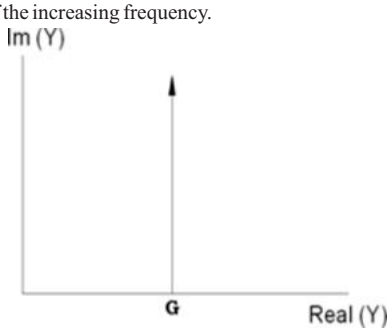

Figure 6: Complex Admittance Plot for the Simple Parallel R – C Circuit with Bulk Resistance $R=G^{-1}$

For a relatively complicated circuit consisting of circuit components C_1, C_2, R1 and R_2 (fig.7) the admittance plot will be a combination of semi-circle and a straight line shown in fig.8 and the impedance plot is a pair of semicircles (fig.9).

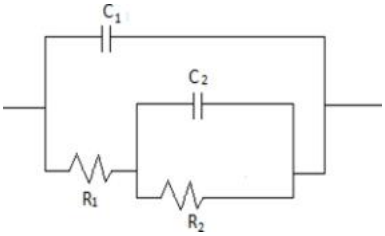

Figure 7: Equivalent circuit with circuit components C_1, C_2, R_1 and R_2.

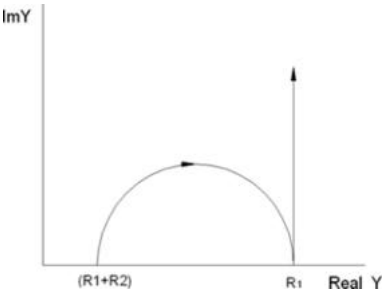

Figure 8: Complex Admittance Plot for Equivalent Circuit in Fig. 7

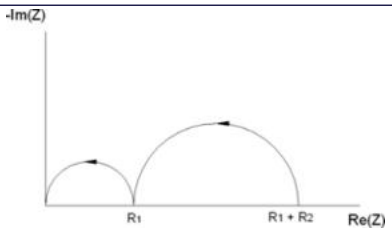

Figure 9: Complex Impedance Plot for the Equivalent Circuit in Fig.7.

In general, in an electrochemical cell, there are two electrodes separated by the electrolyte. The interface of electrode and electrolyte behaves as a capacitor arising out of electron-ion interactions. So the equivalent circuit corresponding to this cell usually consists of a solution resistance, a double layer capacitor, a charge transfer (or polarization) resistance. Besides these, diffusion of ions through the electrolyte is associated with impedance called Warburg impedance which is effective in low frequency regions. The double layer capacitance is in parallel with the charge transfer resistance and Warburg impedance. The following figure is an effective circuit diagram corresponding to an electrochemical cell [26].

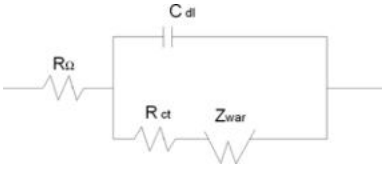

Figure 10: Equivalent Circuit Modelling Mixed Kinetic and Diffusion Control.

This circuit models a cell where polarization is due to a combination of kinetic and diffusion processes. The Nyquist plot for this circuit is shown in figure 11.

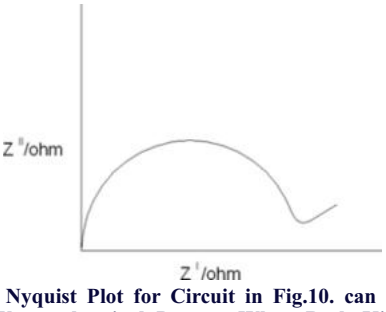

Figure 11: Nyquist Plot for Circuit in Fig.10. can be used to Describe Electrochemical Process When Both Kinetics and Diffusion are Important.

Effects of Irradiating a Polymer Sample

Ionizing radiation produces changes in various properties of polymers and is a useful technique to modify polymers. It is a very important way to generate new properties or improve existing properties in polymers. The combined action of ionizing radiation and oxygen on polymers may rapidly lead to a severe deterioration of the polymer properties. The resulting effects are strongly dependent on the chemical structure of the polymer. The radiationdamage and oxidative degradation cause chemical changes in the polymer structure with build up of a variety of new functional groups as carbonyls, carboxyls, esters, hydroxyls etc. [27].

One characteristic property of polymer electrolytes is that at ambient temperatures the polymer has a tendency to crystallize and thus lower the ionic conductivity. There are various ways to suppress crystallization and enhance conductivity ─ addition of plasticizers, addition of insulating nanoparticles acting as fillers. Conductivity in solid polymer electrolytes can also be enhanced effectively by using ionizing radiation. The property of the polymer alters significantly [28, 29] depending on the type of radiation used, nature of polymer and on dose. Studies have been made on the effect of various radiations like ion beam, electron beam, neutron beam, X- ray, gamma ray on polymer electrolyte systems [30].

Gamma Irradiation of Polymers

Application of gamma radiation on polymer electrolytes can effectively enhance conductivity. Gamma irradiation causes chain scission or degradation and crosslinking. Although both these processes occur simultaneously, usually, one dominates over the other, depending on the condition of irradiation and the shape, size and chemical nature of the polymer etc. Application of gamma radiation leads to variation in various morphological, physical and electrical properties of the polymer electrolyte. This has wide applications in analyzing the changes in the behaviour of polymers in radiation environments encountered in nuclear reactors, space crafts, particle accelerators etc. [31].

CONCLUSIONS

The conductivity improvement is not monotonic since at higher radiation dose, crosslinking leads to lowering in flexibility of the chains resulting in lowering in conductivity [28, 29]. Such competition between scission and crosslinking for different gamma doses, resulting in non-monotonic variation of properties is not surprising and has been reported for other polymer systems [26, 27].

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