



Electrical impedance response of gamma irradiated gelatin based solid polymer electrolytes analyzed using a generalized calculus formalism



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ABSTRACT

The electrical impedance response of gelatin based solid polymer electrolyte to gamma irradiation is investigated by impedance spectroscopy. An analysis based on Poisson–Nernst–Planck model, incorporating fractional time derivatives is carried out. A detailed derivation for anomalous impedance function is given. The model involves boundary conditions with convolution of the fractional time derivative of ion density and adsorption desorption relaxation kinetics. A fractional diffusion–drift equation is used to solve the bulk behavior of the mobile charges in the electrolyte. The complex adsorption–desorption process at the electrode–electrolyte interface produces an anomalous effect in the system. The model gives a good fit for the observed impedance data for this biopolymer based solid electrolyte in a wide range of frequencies. We have compared different parameters based upon this model for both irradiated and unirradiated samples.

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1. Introduction

Impedance spectroscopy provides a detailed picture of how charge carriers behave in a conducting system, when analyzed through a realistic model. Analysis of the results for the complex impedance is usually carried out, through devising equivalent circuits consisting of lumped elements like capacitors and resistors [1] and often constant phase elements (CPE). However, as the behavior of the system gets more and more complex, it may involve maybe rough electrodes, porous electrolytes and/or materials with fractal microstructure [2–9]. In this case an equivalent circuit with a finite number of elements is found to be inadequate. The ‘elements’ used in the circuit are moreover fictitious objects and not readily understood in terms of the physical or electrochemical properties of the real system. In such a situation it is more satisfying to look for a model involving properties such as the diffusion coefficient of charge carriers and dielectric constant of the electrolyte material and investigate their interactions through the basic equations involved, i.e. Poisson equation, equation of continuity and so on with appropriate boundary conditions. The scale invariant characteristics of the system like electrode roughness and fractal microstructure (like in electrochemical double layers capacities EDLC formed in Carbon–Aerogel based rough electrodes of super-capacitors) still show up in the results,

these can be taken care of in an elegant manner by introducing generalized calculus with non-integer derivatives in the basic equations [2,5–11]. This is an alternative to using equivalent circuits with a very large number of lumped circuit elements and hence parameters. While the latter approach may give a very good fit to experimental results, the former with a smaller number of physically meaningful parameters gives a better understanding of the situation, maybe at the expense of a more precise fit to experimental curves. This is our approach in the present paper.

In this work we report results on a solid polymer electrolyte with gelatin as the main constituent. The process of conduction may be divided into three (i), (ii) and (iii) basic phenomena described in the following paragraphs.

- (i) The first one is the diffusion–drift phenomenon, which can be a Fickian process or non Fickian process governed by an integer order time derivative or fractional order time derivative in the diffusion equation respectively. The non-integer order derivatives (fractional derivatives) in the rate of diffusing species imply that the process is non-Markovian, and with a memory [3]. The non-Fickian nature of diffusion starting from Cattaneo’s diffusion (1948) is described in detail in [3]. The impedance spectroscopy data as obtained in these experiments may be related to anomalous diffusion in the bulk material due to spatial disorder in the solid electrolyte matrix. The spatial disorder leads to non-Debye relaxation which manifests itself as temporal fractional

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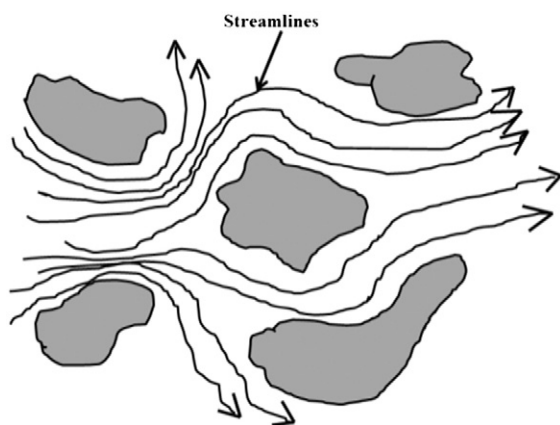


Fig. 1. The disorder in diffusing path which manifests as fractional time derivative in the diffusion expression.

derivatives [3,4,12,13]. Fig. 1 describes pictorially, the heterogeneity in the bulk electrolyte.

The structure is heterogeneous on micro-scales but appears homogeneous on scales much larger than the heterogeneities. This is one of the plausible reasons of ions in the bulk electrolyte (in this case solid polymer) obeying fractional diffusion equation at the small time scales and normal integer order diffusion equation at larger time scale. The process of transport may be mixed as well, i.e. governed by anomalous and normal diffusion taking place simultaneously.

- (ii) The second process is that of local charge separation giving rise to a potential obtained from Poisson's equation. We use it to get the potential profile in the bulk electrolyte and thus the electric field function. We then apply Gauss's law at the boundary electrodes to get the surface charge density and thereby the total charges at the surface; from there we derive the rate of change of the total charge, giving the current function. The potential at the electrode and the current at the electrodes give the impedance function (in frequency domain).
- (iii) The third phenomenon which is very important is at the surfaces (i.e. at the two electrodes), this is the kinetics of adsorption-desorption which gives the current density at the boundary – related to convolution of 'memory kernel' – the adsorption-desorption kinetics with (fractional) rate of change of ion density. With the memory kernel as zero we get the blocking electrode case – i.e. the classical case where the current at the boundary is zero.

The behavior of an ideal system revealing scale-invariant or fractal microstructure above a certain frequency ω_c (i.e. at short time scales) is expected to be as follows: for frequencies below ω_c , the real part of the impedance is constant giving the DC limit response. Anomalous response is seen at high frequencies, where it is observed that the real part of the impedance increases with decrease in frequency. This can be explained by adding fractional order impedance in the calculations [13–16]. By taking the 'electrode (brass)–electrolyte' impedance as follows, like a fractional order capacitor

$$Z_i(\omega) = C_q(i\omega)^{-q} \quad C_q > 0, \quad 0 < q < 1.$$

We can explain the growth of impedance as frequency decreases. This interfacial impedance contributes to the total resistance of the cell the term, which is as follows

$$\text{Re}\{Z_i\} = \text{Re}\{C_q(i\omega)^{-q}\} = C_q\omega^{-q} \cos(q\pi/2)$$

which is frequency dependent and particularly as $\omega \rightarrow 0$ it diverges, that is one way to explain the anomalous impedance observed. But in the interface impedance the manifestation of fractional order q comes through the roughness of the electrode surface (as observed in supercapacitors) [6–11,13]; whereas in our case the brass electrodes are smooth, without noticeable roughness—at the macro-scale at least. The other way to explain this anomalous behavior is to have different mobility for anions and cations and therefore different diffusion constants [17],

$$D_+ = 10D_-.$$

But we are dealing with ions having same mobility and the diffusion constants. The ions in this case are principally H_3O^+ and OH^- . With normal integer order Fickian diffusion has a strong adsorption condition at the electrodes [18], to explain the anomalous impedance we introduce the fractional order diffusion in the bulk as well as at the boundary condition for interface of the electrodes.

It is to be noted that in real experiments, the external part of the measurement set-up, outside the electrode–electrolyte system also shows up in impedance measurements. This usually produces a rise in impedance below the frequency ω_c [30]. Since we are not interested in this part, the results for very low frequencies need not be taken into account while comparing theory and experiment.

2. Materials and method of measurement

Gelatin films with formaldehyde as cross linking antifungal agent and different wt.% of glycerol as plasticizer are prepared by solution cast method [19,20]. The masses of glycerol used for the different samples were 0.25, 0.50, 0.75, 1.00, 1.25, 1.35 and 1.50×10^{-3} kg (corresponding to weight percent of plasticizer 10.00, 18.18, 25.00, 30.77, 35.71, 37.50 and 40.00% respectively). The transparent films (thickness $\sim 500 \mu\text{m}$) are then exposed to gamma chamber ($^{60}\text{Co}_{\gamma\text{rays}}$) at the Department of Food Technology, Jadavpur University and UGC-DAE CSR, Kolkata center with doses (20 kGy, 40 kGy, 60 kGy, 80 kGy, 100 kGy) at the rate of 6.4 kGy/h and 3.4 kGy/h respectively. An Agilent LCR meter (E4980A precision meter) was used to measure the complex impedance Z at room temperature (30 °C) in the frequency range from 20 Hz to 2 MHz.

3. Experimental results

The ion-conductivity σ (dc) obtained from the Cole–Cole plots is shown in Fig. 2 as function of the plasticizer fraction without irradiation (A) and with irradiation (B) and (C). The dc conductivity σ (dc) increased by four orders of magnitude with the addition of 10 wt.% glycerol, σ (dc) is maximum for 35.71 wt.% glycerol $\sim 9.14 \times 10^{-3}$ S/m at room temperature (30 °C) without irradiation (Fig. 2(A)). After irradiation the conductivity of the sample containing 35.71 wt.% glycerol is seen to decrease by one order of magnitude and we obtained the maximum conductivity at 60 kGy dose $\sim 9.63 \times 10^{-4}$ S/m at room temperature (30 °C) (Fig. 2(C)). For higher doses the dc conductivity falls off the same as earlier works [5,19,20]. In the absence of added salt, the charge carriers were assumed to be primarily Hydronium ions (H_3O^+) [19–21]. There may have been a small percentage of impurity ions, such as P, S, Ca, Cl and N coming from the gelatin (Merck, 99.9% pure). Energy-dispersive X-ray spectroscopy results before irradiation [19,20] and after irradiation which are not displayed in this work indicated the presence of slight amounts of C, O, N, P, S, Ca and Cl in the polymer matrix. We will assume that the major phenomena is due to univalent hydronium (positive ion) and hydroxide (OH^- negative ion); and their mobility is same, and so is their diffusion coefficient D . We neglect the effect of trace impurity ions.

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