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Influence of gamma irradiation on the electrical properties of $LiClO_4$-gelatin solid polymer electrolytes: Modelling anomalous diffusion through generalized calculus

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HIGHLIGHTS

- Impedance spectroscopy analysis of the gelatin based solid polymer electrolytes.
- Electrolytes exhibits both normal diffusion and anomalous diffusion.
- XRD, SEM, CV and FTIR analysis are done for different experimental aspects.
- The effect of gamma irradiation on the samples with and without salt is analyzed.
- Generalized calculus helps to explain the anomalous behaviour of the motion of ions.

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ABSTRACT

Solid polymer electrolytes with gelatin as host polymer are subjected to gamma irradiation with dose varying from 0 to 100 kGy. Two sets of samples are studied, one with and one without addition of lithium perchlorate as ionic salt. The effect of varying plasticizer content, salt fraction and radiation dose on the impedance is measured. The dc (direct current) ion-conductivity is determined from impedance spectroscopy results. It is shown that relative to the unirradiated sample, the room temperature dc ion-conductivity decreases in general on irradiation, by an order of magnitude. However on comparing results for the irradiated samples, a dose of 60 kGy is seen to produce the highest ion-conductivity. Considering the variation of all parameters, the highest dc-conductivity of 6.06×10^{-2} S/m is obtained for the un-irradiated sample at room temperature, with 12.5 wt% $LiClO_4$ and 35.71 wt% of glycerol as plasticizer. The samples are characterized in addition by XRD, SEM and FTIR respectively. Cyclic voltametry is performed for the confirmation of the electrolytic performance for pristine and gamma irradiated samples. To understand the experimental results, a model incorporating normal, as well as anomalous diffusion has been applied. Generalized calculus is used to model the anomalous diffusion. It is shown that this model successfully reproduces the experimental frequency dependence of the complex impedance for samples subjected to varying gamma dose. The physical interpretation of the model parameters and their variation with sample composition and irradiation dose is discussed.

1. Introduction

This article is concerned with the effect of gamma-irradiation on a bio-polymer which is a potential candidate for use in electrochemical devices. Solid polymer electrolytes (SPE) have been in use for several decades (Vincent, 1987; Gray, 1991; Armand, 1994). In the bio-polymer class (Vaghari et al., 2013; Khanmirzaei and Ramesh, 2014; Kamal et al., 2014; Babu et al., 2013; Basu et al., 2012, 2013; Basu and Tarafdar, 2014; Armand, 1997; Ghaz-Jahanian et al., 2015), carbohydrate polymers (Tiwari et al., 2011a, 2011b; Mattos et al., 2010; Sultana et al., 2010; Ramesh et al., 2011; Kumar et al., 2012) have been extensively studied in recent years. They have been used in electrochemical devices (Hassan et al., 2014; Reddy et al., 2015, 2006a) such as super-capacitors, fuel cells, and solar cells due to their easy availability, cost effectiveness and biodegradability. Proteins have not been studied so extensively. Here we explore the possibility of using gelatin – a polymer of animal origin, which has been studied in some earlier works (Basu et al., 2012, 2013; Basu and Tarafdar, 2014; Mattos et al., 2008, 2006). Gelatin, a natural polymer, is soluble in luke-warm water. It can be obtained by selective hydrolysis of collagen, which is a

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fibrous material found in skin, bones and connective tissues of animals. This is a heterogeneous mixture of three extended polypeptide chains, super-coiled together to form a right-handed triple helix. The triple-helix structure is stabilized by the formation of inter-chain hydrogen bonds between C=O and N–OH groups (Rokhade et al., 2006; Kaur et al., 1994; Rajbaidya et al., 2006). We add $LiClO_4$, which is the most popular salt for supplying charge carriers to the polymer host (Vincent, 1987; Gray, 1991, Macdonald 2005).

Our focus in this paper is on the effect of gamma irradiation on electrical properties of gelatin based solid polymer electrolytes (SPE) with and without $LiClO_4$ as a source of charge carriers. All the values of dc conductivity measured at room temperature for salt free and salt added systems, both pristine and gamma-irradiated samples are depicted in Tables 2 and 3.

It has been shown that gamma-irradiation has a significant effect on polymers, causing changes in molecular weight distribution and macromolecular architecture. The details depend on the particular polymer and may be beneficial or detrimental for a definite application. For example PEO based polymer films with ammonium perchlorate show enhanced ion-conductivity on irradiation (Nanda et al., 2010; Tarafdar et al., 2010; Sinha et al., 2008; Ghosal et al., 2014; Saha et al., 2015). This shows that controlled gamma irradiation may be used to treat such films, improving their performance as solid electrolytes. There is another side to the problem, since polymer electrolytes are materials with potential for extensive use in practical devices and appliances, one must also consider the risk of degradation (Gumel et al., 2013; Cheneler and Bowenb, 2013; Lotfy and Fawzy, 2014) on appliances being exposed to a high radiation environment in nuclear reactors or outer space.

Bio-based systems are much more complex than synthesized materials and it is difficult to work out an exact analytical theory describing their properties. Diffusion and ion-conduction in such a complex environment may involve several processes including anomalous diffusion, as observed in convoluted or fractal spaces (Basu et al., 2012, 2013; Lenzi et al., 2009; Macdonald et al., 2011; Santoro et al., 2011; Lenzi et al., 2011; Basu et al., 2015). Anomalous diffusion has been tackled by setting up equivalent circuits with distributed elements. However, recent developments in generalized calculus (Basu et al., 2012, 2013; Macdonald et al., 2011; Basu et al., 2015; Das, 2011) show that a more elegant way to model conduction in complex systems is to represent anomalous diffusion by incorporating derivatives of non-integer order in the equations describing the system. In the present work we use this formalism and find good agreement between experiments and theory for pristine as well as irradiated samples. The parameters used in the model are physically meaningful quantities and their variation with irradiation dose and sample composition provides interesting insight about the system. In our earlier work (Basu et al., 2015) we observe the anomalous behaviour in irradiated samples without salt using another model called PNP (Poisson-NernstPlanck) proposed by Lenzi et. al which is further modified for our systems. In our present report results of two sets of experiments – (i) with gelatin and varying wt% of glycerol as plasticizer, but no salt, exposed to gamma radiation of doses varying from 0 to 100 kGy. In the present paper we show that the result for glycerol content of 35.71 wt% as it gives the highest ion-conductivity for pristine systems. We denote this sample as **SG**(σ_{max}) in Table 2, (ii) in the second set 35.71 wt% glycerol is added to prepare gelatin films with different wt% $LiClO_4$ and varying gamma dose in Table 3. This sample is designated **SL**(σ_{max}). It was shown earlier that 12.51 wt% of $LiClO_4$ gives the highest ion-conductivity for un-irradiated systems (Basu et al., 2012), whereas in case of irradiated samples, the maximum dc conductivity is observed for 7.89 wt% of salt. Both the systems (i) and (ii) give maximum dc conductivity at 60 kGy (designated by **SG**(σ_{max}) and **SL**(σ_{max})) dose, when gamma dose is varied. However, the magnitude of the conductivity is decreased from the pristine samples by about one order of magnitude after irradiation.

2. Materials and sample preparation

Gelatin (purified) has been procured from Merck. Lithium perchlorate ($LiClO_4$) is from Loba Chemie Pvt. Ltd. Glycerol (Merck specialities private Ltd.) is added as plasticizer and formaldehyde (Merck specialities private Ltd.) as an anti fungal cross-linking agent. We use deionized Water (Ellora Enterprise (HYDROLAB)). It was not possible to prepare films without plasticizer as they become brittle on drying and break . Without including formaldehyde the samples develop fungal growth.

2.1. Sample preparation

We prepare two types of Gelatin films as detailed below. Here the weight fraction of a constituent is defined as (mass of salt or plasticizer)/(sum of mass of all the constituents).

- The first set of samples (i) has the following constituents – Gelatin with (w_g) wt% glycerol as plasticizer and 0.25 g formaldehyde. Weight percentage of glycerol is varied between w_g=0 to 40. Mass of glycerol taken for different samples was 0.25 g, 0.50 g, 0.75 g, 1.00 g, 1.25 g, 1.35 g, 1.50 g, corresponding to w_g=10, 18.18, 25, 30.77, 35.71, 37.5 and 40 respectively.
- The second set (ii) has w_g=35.71% and the salt $LiClO_4$ is added with weight percent – (w_s) salt and 0.25 g formaldehyde. Mass of $LiClO_4$ taken for different samples was 0.1 g, 0.2 g, 0.3 g, 0.4 g, 0.5 g, corresponding to w_g=2.7, 5.41, 7.89, 10.26 and 12.5 respectively.

Transparent films with the above composition were prepared by solution casting (Basu and Tarafdar, 2014; Mattos et al., 2008). 2 g of commercial gelatin (Merck) was dispersed in 15 ml of distilled water and heated to 50 °C for twenty five minutes under magnetic stirring for complete dissolution. After that the solution was cooled down to room temperature (30 °C) and the requisite amounts of glycerol and lithium perchlorate with 0.25 g of formaldehyde were added to the mixture and the stirring continued for a few minutes. This solution was then poured onto a petri dish and allowed to dry for several days. After drying the dish was placed under vacuum at room temperature (30 °C). The dried films had a thickness in the range of 280 to 540 μm.

2.2. Gamma irradiation

The samples were exposed to gamma irradiation at UGC-DAE gamma chamber, Kolkata. Co^{60} was used as the gamma source. Doses of 10, 20, 40, 60, 80 and 100 kGy at the rate of 3.4 kGy/h under normal atmosphere were applied to different films.

3. Characterization techniques

3.1. XRD analysis

XRD was done on Bruker D8 advance (Germany) at Physics Department, Jadavpur University. We observe the pattern for salt free and salt added system for different dose rate. XRD analysis is done for the structural analysis both for the pristine and gamma irradiated samples.

3.2. Scanning electron microscopy

SEM imaging was done at the Metallurgy Department and