

## Ion-Conductivity Study and Anomalous Diffusion Analysis of Plasticized Gelatin Films

Tania Basu, T. R. Midya, Sujata Tarafdar

Condensed Matter Physics Research Centre, Physics Department, Jadavpur University, Kolkata 700032, India

Correspondence to: T. Basu (E-mail: tania16basu@gmail.com)

**ABSTRACT:** In this article, we report a study on ion conduction in gelatin films with different concentrations of glycerol as a plasticizer; these films might be a candidate for electrolyte materials in solid polymer batteries. The ion conductivity was appreciable, showing a maximum of about  $9.14 \times 10^{-3}$  S/m at room temperature without the addition of any ionic salt. Analysis of the impedance measurements was done with a model based on material properties instead of the usual equivalent circuit formalism, where circuit elements are difficult to interpret. Generalized calculus was used to model the anomalous diffusion in the system. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

**KEYWORDS:** biopolymers & renewable polymers; electrochemistry; morphology; plasticizer

Received 7 February 2013; accepted 17 April 2013; Published online

DOI: 10.1002/app.39431

### INTRODUCTION

The study of solid polymer electrolytes (SPEs) has been of great interest for the last few decades.<sup>1–3</sup> Usually, an ionic salt is added to an insulating host polymer [e.g., poly(ethylene oxide) or poly(methyl methacrylate)] to supply charge carriers for conduction. Recently, it has been suggested that biopolymers may be used as the host polymer because of their easy availability, low cost, and principal biodegradation properties. Examples of such environmentally friendly biopolymers include starch, chitosan, and gelatin.<sup>4–9</sup> Lithium perchlorate, in addition to a plasticizer and a crosslinking agent, was usually added as the supplier of charge carriers in earlier studies. However, natural polymers may show an appreciable ion conductivity ( $\sigma$ ) simply on the addition of the optimum concentration of plasticizer and crosslinking agent<sup>10</sup> even without the addition of salt. The strong effect of glycerol as a plasticizer to improve the conductivity of biopolymers has been demonstrated for cassava starch<sup>11</sup> and gelatin.<sup>12</sup> In this article, we report work on transparent films of gelatin with glycerol as a plasticizer and formaldehyde as an antifungal crosslinking agent but no added salt. We varied the fraction of glycerol and studied  $\sigma$  by impedance spectroscopy. We studied the range between 0 and 40 wt % plasticizer. The direct-current conductivity [ $\sigma(\text{dc})$ ] increased sharply with the initial increase of plasticizer content, reached a maximum value at 35.71 wt % with some fluctuations, and then showed a decreasing trend similar to that of Kahlout et al.<sup>12</sup>

A detailed analysis of the conduction behavior on the basis of a fractional calculus approach to treat anomalous diffusion gave

quite satisfactory agreement between the theoretical and experimental results.

In this study, we analyzed the results on the basis of a model proposed by Lenzi et al.,<sup>13</sup> this model incorporates anomalous diffusion through a fractional order diffusion equation. This model was applied successfully to a gelatin-based polymer electrolyte.<sup>9</sup> The usual procedure of analyzing impedance spectroscopy results is to construct an equivalent circuit that reproduces the impedance data best. However, such an equivalent circuit with lumped circuit elements is often inadequate to explain the behavior of complex materials, and distributed elements are introduced in the form of constant-phase elements. The resulting equivalent circuit often has a considerable number of free parameters, and it is difficult to interpret the physical significance of the elements. It has been shown that the introduction of a fractional diffusion equation is equivalent to the use of a constant-phase element<sup>14</sup> and that anomalous diffusion can be modeled by fractional differential equations.<sup>15</sup> We used the technique suggested by Lenzi et al.,<sup>13</sup> where the impedance of a material is calculated from a physical model describing the drift and diffusion of charge carriers through a material in an electric field. We calculated the real and imaginary parts of the impedance at various frequencies ( $f$ 's) for different weight fractions ( $x$ 's) of plasticizer and compared them with our experimental results. The agreement was good, and the few quantities that were used as fitting parameters were physically meaningful quantities related to the material properties. A modified version of this formalism was developed more recently,<sup>10</sup> where adsorption/desorption at the

electrode–electrolyte interface was taken into account. For these samples and setup, however, we assumed the brass electrodes to have perfectly blocking, and we stuck to the earlier theory.<sup>13</sup>

## EXPERIMENTAL

### Sample Preparation

Gelatin films with glycerol as a plasticizer and formaldehyde as an antifungal crosslinking agent were prepared with various  $x$  values of glycerol, where  $x$  is defined as follows:

$$x = \frac{\text{Mass of glycerol}}{\text{Sum of mass of all the constituents}} \quad (1)$$

Transparent films of gelatin [thickness ( $d$ ) = 280–540  $\mu\text{m}$ ] were prepared by a solution casting technique with different weight percentages of glycerol instead of any salt. 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 g (corresponding to weight percent of plasticizer 10.00, 18.18, 25.00, 30.77, 35.71, 37.50, and 40.00%, respectively). Gelatin (2 g, Merck) was dispersed in 15 mL of distilled water and stirred continuously while the solution was heated for 15 min up to 50°C to completely dissolve the host polymer. After that, the solution was cooled to room temperature while stirring continued. Glycerol of a required weight and formaldehyde (0.25 g) were added to the solution after a few minutes. The resulting transparent homogeneous solution was then poured into a Petri dish with a diameter of 10 cm and dried *in vacuo*. Optical images of the transparent film are shown in Figure 1.

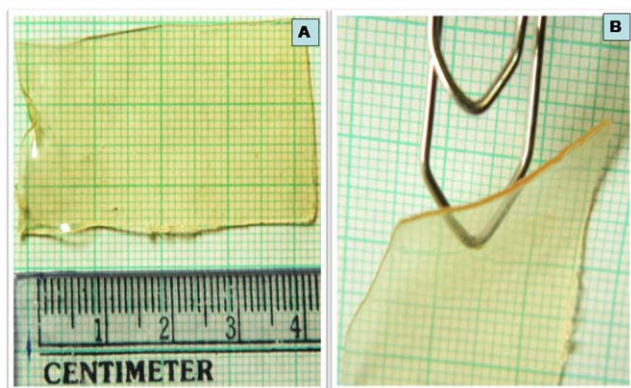
### X-Ray Diffraction (XRD) Analysis

XRD was done on a Bruker D8 Advance (Germany) at the Physics Department, Jadavpur University, Kolkata.

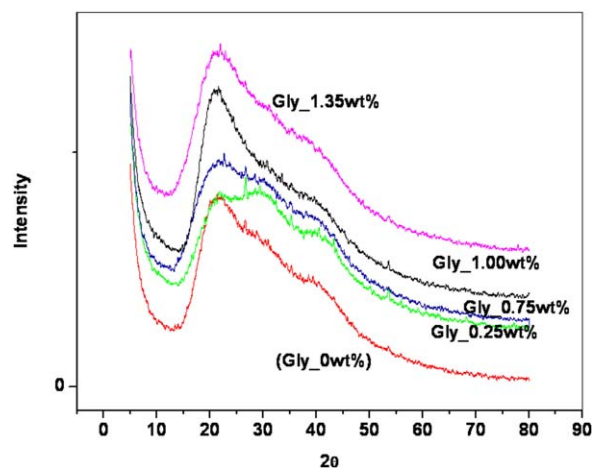
The samples with different concentrations of plasticizer did not show well-resolved peaks; this indicated an amorphous nature, as shown in Figure 2. The low crystallinity was due to the application of heat during the formation of the gelatin films.<sup>10</sup>

### Scanning Electron Microscopy (SEM)

SEM imaging done at Central Glass and Ceramic Research Institute (CGCRI), Kolkata, with an LEO S 430I (United Kingdom) showed an image of pure gelatin with no additive [Figure



**Figure 1.** Gelatin films with glycerol 35.71 wt %: (A) top view and (B) side view. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 2.** XRD for different weight percentages of the glycerol (Gly) plasticizer. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

3(A)]. The scale bar is 200  $\mu\text{m}$ . Here, some strands of a network structure were seen, but it was not possible to get a higher magnification as the sample was overheated and burned. Figure 3(B), for a sample containing 18.18 wt % glycerol, showed a smooth and homogeneous transparent film; this was in good agreement with the XRD result. The scale bar here is 50  $\mu\text{m}$ . Energy-dispersive X-ray spectroscopy results indicated the presence of slight amounts of C, O, N, P, S, Ca, and Cl in the polymer matrix.

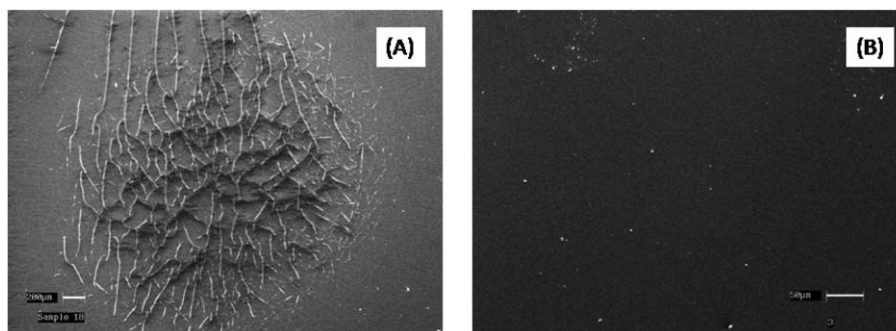
Samples with a higher glycerol content showed a distinctive network structure (Figure 4). Interestingly, Figure 4(A), which shows the sample with 25 wt % glycerol, shows a taut and compact network, whereas the network was loose and more sparse in Figure 4(B,C)], which shows a sample with a higher percentage of glycerol. We show later that the tighter network was correlated with a lower conductivity, as was observed in the study in ref. 9.

### Direct Current (dc) as a Function of Time: Transference Number

A dc voltage was applied to the sample, and the current was measured as a function of time on a 2400 source meter (Keithley). The fall in current was monitored by a video camera. The transference number was determined to be 0.97; this indicated predominantly ionic conduction in the samples.

### Cyclic Voltammetry

Cyclic voltammetry was done to study oxidation–reduction processes in the electrolyte. The study was carried out at Indian Association for Cultivation of Science (IACS), Kolkata, on a gelatin solution contain 35.71 wt % glycerol and 0.25 g of formaldehyde (1) without salt and (2) with a trace of lithium perchlorate. Glassy carbon was used as the working electrode and platinum was used as the counter electrode within a voltage range of  $\pm 2$  V. The sample without salt did not give satisfactory results, but the addition of a trace amount of salt showed a good voltammogram. The results for the first and second samples for a scan rate of 100 mV/s for three cycles are shown in Figure 5. The anodic peak was obtained at 0.5 V, and the cathodic peak was obtained at  $-0.664$  V. The electrolyte showed



**Figure 3.** SEM images of (A) pure gelatin and (B) gelatin with 18.18 wt % glycerol and 0.25 g of formaldehyde.

an electrochemical window of  $\sim 1.2$  V. The first few cycles showed that the features of the voltammograms remained quite stable. Only the peak currents increased with the cycles, and the peaks shifted to the negative and positive sides. The results were qualitatively similar to earlier reports.<sup>16–20</sup>

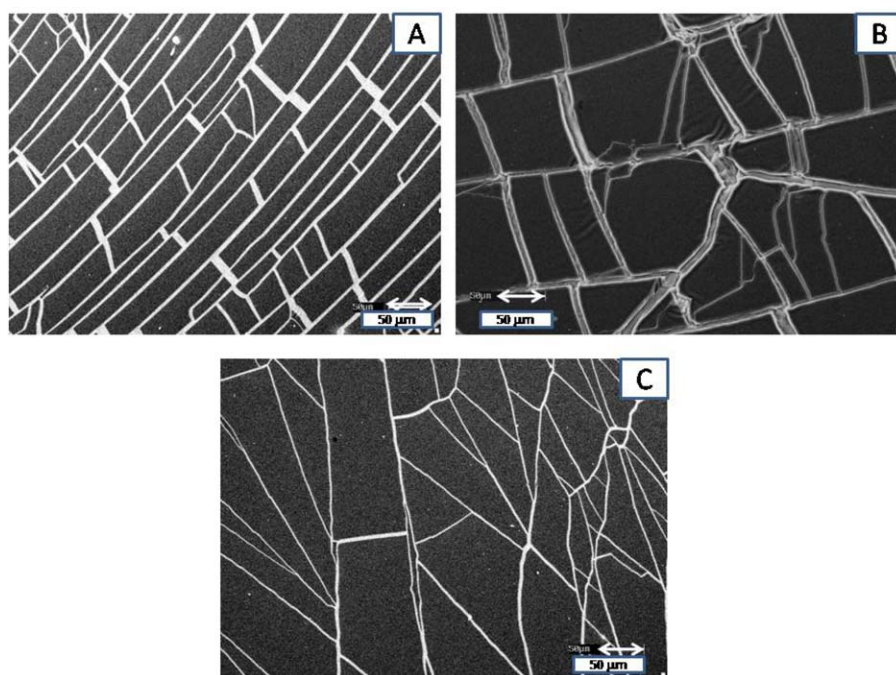
### Impedance Spectroscopy

An Agilent LCR meter (E4980A precision meter) was used to measure the complex impedance ( $Z$ ) at room temperature ( $30^\circ\text{C}$ ) in the  $\omega$  range from 20 Hz to 2 MHz.  $\sigma(\text{dc})$  obtained from the Cole–Cole plots is shown in Figure 6 as function of the plasticizer fraction.  $\sigma(\text{dc})$  increased by four orders of magnitude with the addition of 10 wt % glycerol. The conductivity continued to increase at a slower rate with some fluctuations up to 35.71 wt % and then shows a decreasing trend. The variation of the real and imaginary parts of the impedance as functions of  $\omega$  for different plasticizer fractions are shown in Figures 7 and 8 and are compared with the theory in a later section.

### THEORY

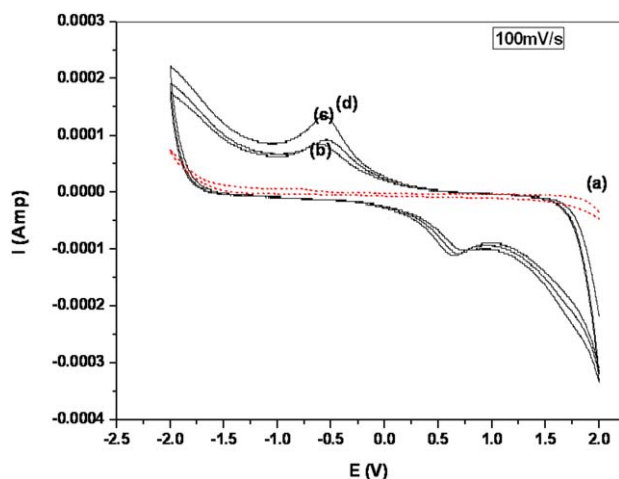
We applied the theory developed by Lenzi et al.<sup>13</sup> for a liquid electrolyte, assuming that it was applicable for a solid electrolyte as well. The ion-conduction mechanism in noncrystalline solid electrolytes is very similar to that in liquids, in particular for polymer samples above the glass transition where dynamic disorder is present. Such materials, although apparently solid, are characterized by segmental motion, with parts of the macromolecular chain in incessant motion on very small spatial and temporal scales;<sup>21</sup> this leaves the center of mass of the molecule stationary.

We give the final expression obtained from the theory; the details were given elsewhere.<sup>9,13</sup> The material is considered to be a slab of area  $A$  and  $d$  between two parallel-plane rectangular electrodes. The origin is fixed at the center of the system, and the  $z$  axis is taken normal to the electrodes. The material consists of a uniform solvent with dimensionless, equally charged



**Figure 4.** SEM image of gelatin with 25, 35.71, and 37.5 wt % glycerol.





**Figure 5.** Cyclic voltammograms [Current ( $I$ ) as a function of Voltage ( $E$ )] of the gelatin sample at scan rate of 100 mV/S. The solid lines (black, b,c) show the results for the sample with a trace of  $\text{LiClO}_4$ . The broken line (red, a) shows the results without salt. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

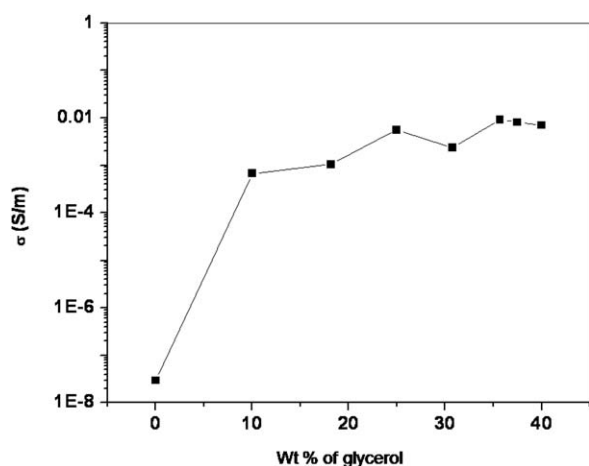
positive and negative ions moving with certain mobility. The external field causes a local bulk density of positive (negative) ions represented by  $\delta_{n\pm}$ . The three basic equations for the system are the equation of continuity, current density, and the Poisson equation. Solving these three equations, one finally arrives at the following expression for  $Z$  as a function of  $\omega$ .<sup>13</sup> Anomalous diffusion is introduced by the incorporation of a time derivative of order  $\gamma$ :

$$Z = \frac{2}{i\omega\epsilon S(\beta)^2} \left[ \frac{1}{\lambda_D^2 \beta'} \tanh\left(\frac{\beta' d}{2}\right) + \frac{(i\omega)^r}{2D_\gamma} d \right] \quad (2)$$

where

$$i = (-1)^{1/2}, \beta' = \pm \sqrt{\frac{1}{\lambda_D^2} + \frac{(i\omega)^\gamma}{D_\gamma}}$$

where  $\epsilon$  is the dielectric permittivity of the continuum hosting the mobile charge carriers,  $\lambda_D$  is the Debye length ( $\lambda_D = \sqrt{\frac{k_B \epsilon T}{2Nq^2}}$ )



**Figure 6.** Variation in  $\sigma(\text{dc})$  with the plasticizer concentration at room temperature.

and  $\epsilon = \epsilon_0 \epsilon_r$ , where  $k_B$  is Boltzmann's constant,  $N$  is the concentration of charge carriers,  $\epsilon_0$  is the permittivity of free space,  $\epsilon_r$  is the relative permittivity or dielectric constant,  $\gamma$  is the fractional order of the time derivative,  $S$  is the surface area,  $D_\gamma$  is the anomalous diffusion coefficient,  $T$  is the absolute temperature, and  $q$  is the charge of the mobile carriers.

$\gamma = 1$  gives back the normal result. This expression for impedance, which involves only anomalous diffusion, characterized by the fractional order  $\gamma$ , does not, however, give a realistic dispersion with  $\omega$ . Lenzi et al.<sup>13</sup> showed that changing the mode of diffusion from normal to very slightly anomalous causes a drastic change in the impedance behavior. Even setting  $\gamma$  to 0.99 instead of 1 changes the  $Z(\omega)$  variation completely; however, a combination of two additive contributions, one from normal and one from anomalous diffusion, can produce a result similar to the experimental data obtained in many situations. Assuming a normal diffusion regime to be present in addition to the fractional diffusion, we introduce a contribution of  $h$  fractions of anomalous diffusion and  $1 - h$  fractions of normal diffusion in the equation. So the final expression for  $Z$  is as follows:

$$Z = \frac{2}{i\omega\epsilon S\beta^2} \left[ \frac{1}{\lambda_D^2 \beta} \tanh\left(\frac{\beta d}{2}\right) + h \frac{(i\omega)^\gamma}{2D_\gamma} d + (1-h) \frac{i\omega}{2D} d \right] \quad (3)$$

where

$$\pm \beta = \pm \sqrt{\frac{1}{\lambda_D^2} + h \frac{(i\omega)^r}{D_r} + (1-h) \frac{i\omega}{D}}$$

where  $h$  is the fractional contribution of anomalous diffusion,  $(1 - h)$  is the fractional contribution of normal diffusion, and  $D$  is the normal diffusion coefficient.

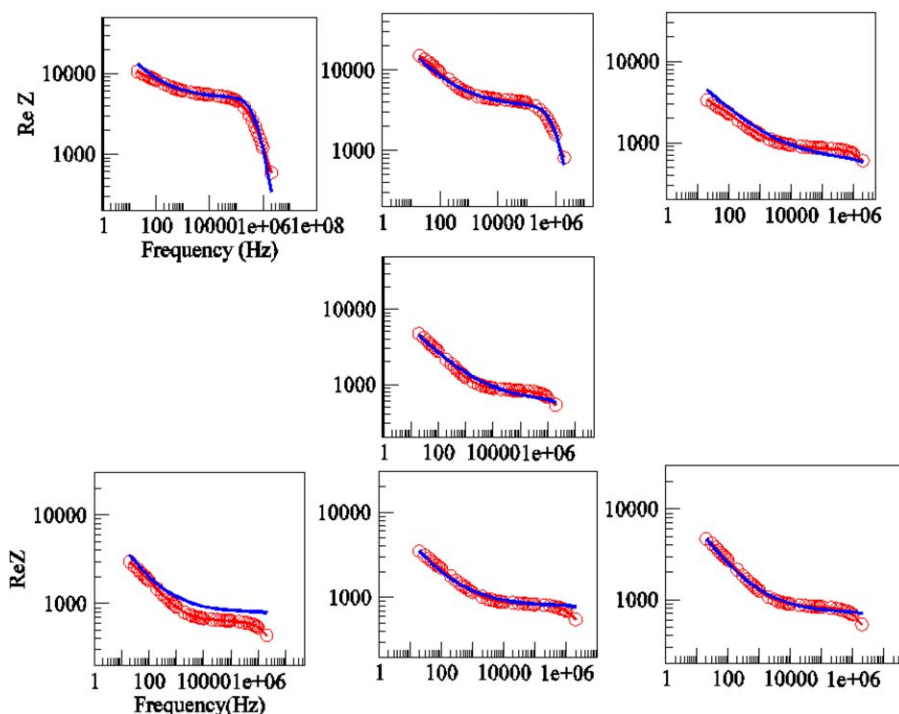
We used this formalism to interpret our experimental results for  $Z$  as function of  $\omega$  for different plasticizer fractions.

## COMPARING THEORY AND EXPERIMENT

### $Z(\omega)$ in the $\omega$ Domain

We calculated  $Z(\omega)$  from eq. (3) with Mathcad to handle the complex algebra. The real and imaginary parts of  $Z$  were evaluated, and the parameters were adjusted manually to reproduce the experimentally obtained values for the real and imaginary parts of  $Z$  as function of  $\omega$ . Because the parameters represent physically meaningful quantities in this formalism, we tried to ensure that they took realistic values.

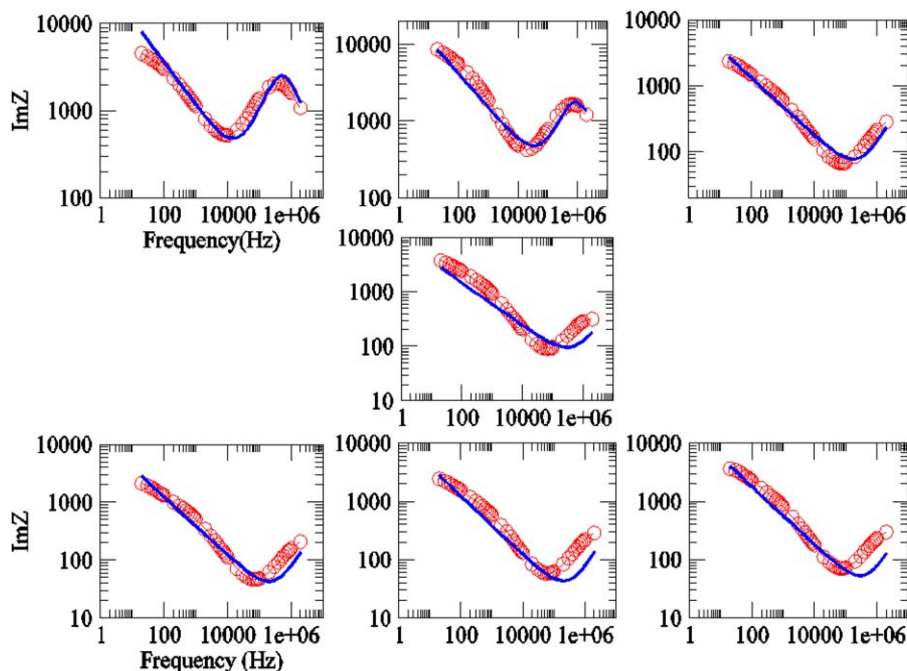
Table I gives the plasticizer percentage and the film  $d$  as input, the calculated  $\lambda_D$ , and the parameters in the expression for  $Z$  that were found to give the best fit to the experimental data. The parameters were different for different  $x$ 's. The values of the real and imaginary parts of  $Z$  were very sensitive to small variations in the parameters. The physical significance of the parameters was as follows:  $\epsilon$  is the dielectric permittivity of the continuum hosting the mobile charge carriers. In this case,  $\epsilon$  was the effective dielectric permittivity of gelatin with different weight percentages of glycerol and formaldehyde, which varied for samples with different  $x$  values. The mechanism of ion conduction was described by the fractional diffusion equation with an order of derivative  $\gamma$  lying between 0 and 1. As already



**Figure 7.** Real part of  $Z$  ( $ReZ$ ) versus frequency ( $f$ ) (solid blue line for theoretical value and red circles for experimental values). With increasing weight percentage of plasticizer from 0 to 40,  $x$  increased from left to right (upper row) and then from left to right (lower row). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

explained, there were two different diffusion processes at work; their relative magnitudes were given by  $h$ , which is the fractional component of anomalous diffusion, where  $1 - h$  is the normal diffusion fraction. These could vary with plasticizer

fraction as the charge distribution within the material changed. The diffusion coefficients corresponding to normal and anomalous diffusion  $D$  and  $D_\gamma$  were also free parameters in this formalism. All parameters were adjusted to give a best fit to the



**Figure 8.** Imaginary part of  $Z$  ( $ImZ$ ) versus frequency ( $f$ ) (solid blue line for theoretical value and red circles for experimental values). With increasing weight percentage of plasticizer from 0 to 40,  $x$  increased from left to right (upper row) and then from left to right (lower row). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

**Table I.** Experimental Input Parameters and Best Fit Model Parameters for Samples with Various  $x$  Values

Plasticizer concentrated $x$ (%)	$d$ ( $\mu\text{m}$ )	$\lambda_D$ ( $\mu\text{m}$ )	$\epsilon_r$	$h$	$\gamma$	$D_\gamma 10^{-8}\text{m}^2/\text{s}$	$D 10^{-8}\text{m}^2/\text{s}$	$N (10^{20} \text{m}^{-3})$
10.00	288	4.000	48	0.320	0.552	0.58	1.95	2.147
18.18	348	4.079	52	0.370	0.550	0.50	2.55	2.236
25.00	386	4.123	56	0.529	0.570	3.50	10.00	2.357
30.77	378	4.153	58	0.3900	0.650	3.30	6.50	2.407
35.71	463	4.483	69	0.661	0.595	5.90	12.00	2.457
37.50	540	4.552	72	0.628	0.569	5.00	11.20	2.487
40.00	460	4.597	74	0.627	0.589	4.00	9.80	2.506

experimental curves for  $Z(\text{real})$  and  $Z(\text{imaginary})$  as function of  $\omega$ .

The calculation of  $\lambda_D$  for different  $x$  values was a problem here because the charge carriers were not precisely identified. We assumed that water retained in the gel primarily provided the charge carriers; the impurity ions may also have had a role. The effective number of carriers depended on the nature of the host material. A stiffer host could trap the mobile ions. The mobile ions may also have formed aggregates, so we kept  $N$  as an adjustable parameter here. The best fit values of the order  $10^{20} \text{m}^{-3}$  were, however, very realistic and agreed with previous reports.<sup>9</sup> Figures 7 and 8 show the theoretically calculated curves compared with the experimental values. The agreement was good for all  $x$  values. The number of adjustable parameters was not very large relative to the total number of data points that had to be fit.

## DISCUSSION

We studied the morphology and impedance behavior of a gelatin-based solid polymer electrolyte and observed a considerable increase in  $\sigma(\text{dc})$  with the plasticizer concentration. Usually, an ionic salt is added to the polymer host to enhance conduction, but our results show that the gel itself exhibited a significant  $\sigma$  with the addition of an adequate amount of plasticizer. This was reported for other studies as well.<sup>11,12,21</sup> Compared with an earlier study,<sup>9</sup> where  $\text{LiClO}_4$  was added to gelatin, we found that the maximum  $\sigma(\text{dc})$  obtained in this study (with  $x = 35.71\%$ ) had an order of magnitude of  $10^{-3} \text{S/m}$  higher than the corresponding sample in ref. 9, which had no salt. This was due to a slight difference in the preparation technique used in the two cases. In the earlier study, the sample was not stirred during cooling, and this allowed the formation of the dense network structures shown in the SEM images. It was observed in the earlier study<sup>9</sup> that samples with denser networks had lower  $\sigma$ s, possibly because of a higher rigidity induced by the network. In this sample, the SEM image at  $x = 37.5 \text{wt } \%$  showed a less dense morphology. This was probably due to the continuous stirring of the sample during cooling, which inhibited network formation.<sup>22–24</sup> We observed, therefore, that the characteristics of these systems depended very strongly on the preparation details, which determined the morphology.

In the absence of added salt, the charge carriers were assumed to be primarily hydronium ions ( $\text{H}_3\text{O}^+$ ).<sup>25</sup> There may have

been a small percentage of impurity ions, such as P, S, Ca, Cl, and N, coming from gelatin (Merck, 99.9% pure). The mobility and effective number of mobile ions were strongly dependent on the plasticizer component, which made the system soft and pliable. Too much of the plasticizer, of course, caused the sample to lose rigidity altogether. It became jelly-like and unsuitable for application in devices. Interestingly, there was a weak double peak in the variation of  $\sigma(\text{dc})$  with  $x$ , which was similar to earlier results.<sup>9,26,27</sup>

The parameters in Table I reveal some characteristic trends. We saw that  $\lambda_D$  and  $\epsilon_r$  increased monotonically with the plasticizer concentration. The parameters associated with anomalous diffusion were  $\gamma$ ,  $D_\gamma$ , and  $h$ . The parameter  $\gamma$ , which was the order of the fractional derivative involved, took values of 0.55–0.66 for the different  $x$  values studied. This was quite different from the value  $\gamma = 1$  corresponding to normal diffusion.  $h$ , compared to normal diffusion, was the least for the 10 wt % sample. It increased irregularly with a maximum at 35.71 wt %, where  $\sigma$  was highest. Contributions from the normal and anomalous diffusion processes were shown to be equally important from the values of  $h$  from 0.32 to 0.66.  $D_\gamma$  varied over a wide range and spanning an order of magnitude; it took a maximum value at 35.71 wt %. The normal diffusivity ( $D$ ) was also maximum here. The effective  $N$  varied very little, not more than 20% over the whole composition range. We, therefore, concluded that change in the mobility of the carriers was responsible for the variation in  $\sigma$ , rather than their number.

Comparing the results with those of a sample containing lithium salt,<sup>9</sup> we noted the following differences. Both diffusion coefficients were always smaller than those in Basu et al.<sup>9</sup>  $\epsilon$  and  $\lambda_D$  were also smaller by an order of magnitude compared to their values in ref. 9; this was consistent with the overall lower conductivity observed in this case. The values of  $h$  in both cases were of similar magnitude, but in Basu et al.,<sup>9</sup>  $\gamma$  was 0.8, much closer to 1, so we observed that the degree of anomaly of the anomalous diffusion component was much more pronounced in the highly plasticized samples compared to the samples containing salt.

To conclude, biopolymers are a promising class of materials for providing cost-effective and environmentally friendly technology. This study suggested that with proper processing, materials such as gelatin may be suitable for use as proton-conducting electrolytes in electrochemical devices, even without the use of

toxic and expensive Li salts. Furthermore, the formalism of analyzing such materials with this model<sup>9,13</sup> and on the basis of a physically realistic picture with fractional calculus to represent anomalous diffusion was quite successful.

#### ACKNOWLEDGMENTS

The authors sincerely thank Partha Pratim Roy, Animesh Layek, and Somnath Midya, Jadavpur University, for their help with the experiments and Shantanu Das for stimulating discussion on fractional calculus. Abhisek Dey and Sohini Mukherjee, Indian Association for the Cultivation of Science (IACS), are gratefully acknowledged for conducting cyclic voltammetry. One of the authors (T.B) thanks Department of Science and Technology (DST), Government of India, for the award of an Inspire research fellowship.

#### REFERENCES

1. Vincent, C. A. *Prog. Solid State Chem.* **1987**, *17*, 145.
2. Gray, F. M. *Solid Polymer Electrolytes*; VCH: New York, **1991**.
3. Armand, M. *Solid State Ionics* **1994**, *69*, 309.
4. Tiwari, T.; Srivastava, N.; Srivastava, P. C. *Ionics* **2011**, *17*, 353.
5. Tiwari, T.; Pandey, K.; Srivastava, N.; Srivastava, P. C. *J. Appl. Polym. Sci.* **2011**, *121*, 1.
6. Mattos, R. I.; Pawlicka, A.; Tombelli, C. E.; Donoso, J. P. *Mol. Cryst. Liq. Cryst.* **2008**, *483*, 120.
7. Mattos, R. I.; Pawlicka, A.; Lima, J. F.; Tombelli, C. E.; Magon, C. J.; Donoso, J. P. *Electrochim. Acta* **2010**, *55*, 1396.
8. Pawlika, A.; Firmino, A.; Vieira D, Sentanin, F.; Grote, J. G.; Kajzar, F. *Proc. SPIE* **2009**, *7487*, 74870J-1.
9. Basu, T.; Maitra, M. G.; Midya, T. R. M.; Tarafdar, S. *J. Phys. Chem. B* **2012**, *116*, 11362.
10. Ramasamy, P. *Ionics* **2012**, *18*, 413.
11. Ayala, G.; Agudelo, A.; Vargas, R. *Dyna* **2012**, *171*, 138.
12. Kahlout, A. A.; Vieira, D.; Avellaneda, C. O.; Leite, E. R.; Aegerter, M. A.; Pawlika, A. *Ionics* **2010**, *16*, 13.
13. Lenzi, E. K.; Evangelista, L. R.; Barbero, G. *J. Phys. Chem. B* **2009**, *113*, 11371.
14. Das, S. *Functional Fractional Calculus*, 2nd ed.; Springer: Berlin **2011**.
15. Ribibeiro, H. V.; Rosato, R.; Tateishi, A. A.; Lenzi, E. K.; Mendes, R. S. *Acta Acientiarum Tech.* **2012**, *34*, 201.
16. Avellaneda, C. O.; Vieira, D. F.; Al-Kahlout, A.; Leite, E. R.; Pawlicka, A.; Aegerter, M. A. *Electrochim. Acta* **2007**, *53*, 1648.
17. Avellaneda, C. O.; Vieira, D. F.; Al-Kahlout, A.; Heusing, S.; Leite, E. R.; Pawlicka, A.; Aegerter, M. A. *Solar Energy Mater. Solar Cells* **2008**, *92*, 228.
18. Leones, R.; Sentanin, F.; Rodrigues, L. C.; Ferreira, R. A. S.; Marrucho, I. M.; Esperanca, J. M. S. S.; Pawlicka, A.; Carlos, L. D.; Silva, M. M. *Opt. Mater.* **2012**, *35*, 187.
19. Yan, R.; Zhao, F.; Li, J.; Xiao, F.; Fan, S.; Zeng, B. *Electrochim. Acta* **2007**, *52*, 7425.
20. Yao, H.; Nan, L.; Xu, J. Z.; Zhu, J. *J. Tanlanta* **2007**, *71*, 550.
21. Ratner, M. A.; Nitzan, A. *Solid State Ionics* **1988**, *28–30*, 3.
22. Pradhan, D. K.; Samantaray, B. K.; Choudhury, R. N. P.; Thakur, A. K. *J. Power Sources* **2005**, *139*, 384.
23. Ioannis, S. *Chronakis, Food Res. Int.* **1996**, *29*, 123.
24. Ding, P.; Pacek, A. W.; Frith, W. J.; Norton, I. T.; Wolf, B. *Food Hydrocolloids* **2005**, *19*, 567.
25. Martucci, F. J.; Ruseckaite, R. A. *J. Food Eng.* **2010**, *99*, 377.
26. Sugimoto, H.; Miki, T.; Kanayama, K.; Norimoto, M. *J. Non Cryst. Solids* **2008**, *354*, 3220.
27. Polu, A. R.; Kumar, R. *E-J. Chem.* **2012**, *9*, 869.