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Bayesian Neural Networks Model for Ionic Conductivity of Nanocomposite Solid Polymer Electrolyte System (PEO - $LiCF_3SO_3$ – DBP - ZrO_2)

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In this study, the ionic conductivity of a nanocomposite polymer electrolyte system (PEO-$LiCF_3SO_3$-DBP-ZrO_2), which has been produced using solution cast technique, is obtained using artificial neural networks approach. Several results have been recorded from experiments in preparation for the training and testing of the network. In the experiments, polyethylene oxide (PEO), lithium triflate ($LiCF_3SO_3$), dibuthyl phatalate (DBP) and zirconia oxide (ZrO_2) are mixed at various ratios to obtain the highest ionic conductivity. The effects of chemical composition on the ionic conductivity of the polymer electrolyte system are investigated. Electrical tests reveal that the ionic conductivity of the polymer electrolyte system varies with different chemical compositions. In neural networks training, different chemical compositions are used as inputs and the ionic conductivities of the resultant polymer electrolytes are used as outputs. The experimental data is used to check the system's accuracy following the training process. The neural network is found to be successful for the prediction of ionic conductivity of nanocomposite polymer electrolyte system.

Keywords: Composites; film and sheet; chemical reactions

1. INTRODUCTION

Polymer electrolytes have gained importance due to their vast number of potential applications such as solid state batteries or fuel cells, photochemical solar cells, supercapacitors, sensors and electrochemical display devices [1]. Much interest is devoted to solid polymer electrolytes (SPE) compared with conventional systems containing liquid electrolyte. Other advantages of SPE include their ability to form thin films, they are light weight, they posses good electrode-electrolyte contact due to their flexibility, they posses high ionic conductivity [2].

Most studies are centered primarily on using polyethylene oxide (PEO) as a polymer host because of its ability to solvate ionic salts to form solid electrolytes. The complexes of PEO with a number of alkali salts have been recorded such as $LiBF_4$, $LiB(C_6H_5)$, NaSCN and KYF_4 [3], $AgNO_3$ and $NaNO_3$ [4]. However, the main drawback is the high degree of crystallization of PEO which causes low cation mobility. One of the approaches to overcome this drawback is to use plasticizer. The plasticizer enhances the power of salt-salvation and increases ion mobility of the polymer electrolyte [5]. Alternatively, inorganic fillers are used to improve the electrochemical and mechanical properties [6]. The fillers affect the PEO dipole orientation by their ability to align dipole moments, while the thermal history determines the flexibility of the polymer chains for ion migration. They generally improve the transport properties, the resistance to crystallization and the stability of the electrode/electrolyte interface.

The successful employment of polymer electrolytes in engineering applications relies on the ability of the polymer electrolytes to meet design and service requirements, which are determined by the physical properties of the polymer electrolytes. These properties can be precisely obtained with relevant tests and experiments as stated in the standard. Also, other mathematical functions can be employed for modeling of these materials behavior. However, it may be possible that all the materials' behavior may not be modeled properly with mathematical functions due to the complexity of the composition dependence.

Recently, with the developments in artificial intelligence, researchers focused a great deal of attention to the solution of non-linear problems in materials science [7-8]. In this study, Bayesian neural-networks [9-10] are employed to predict the ionic conductivity of nanocomposite polymer electrolyte system (PEO - $LiCF_3SO_3$ – DBP - ZrO_2).

2. MATERIALS AND EXPERIMENTAL PROCEDURES

Films of PEO were used as host polymer electrolytes, and were prepared by standard solution-casting techniques. The materials used in this work were PEO (MW = 600,000, Acros), lithium triflate ($LiCF_3SO_3$) (Aldrich), dibutyl phatalate (DBP) (Alfa Aesar, 99% purity) and zirconia oxide (ZrO_2). Prior to use, the PEO was dried at 50 ^oC for 48 hours. All components were added and dissolved in acetonnitrile. The solutions were stirred for 24 hours at room temperature until homogenous solutions were obtained. The solutions were cast onto glass petri dishes and were left to evaporate slowly to form films. All samples were prepared at room temperature and stored under dry conditions. The ionic conductivities of the samples were measured at temperatures ranging from 298 to 373 K using HIOKI 3531 LCR Hi-Tester with a frequency range of 50 Hz to 5 M Hz.

3. BAYESIAN NEURAL NETWORK

Neural networks are parallel-distributed information processing systems used for empirical regression and classification modeling. Their flexibility enables the discovery of complex relationships

in data compared with traditional linear statistical models. Neural networks consist of a number of highly interconnected processing elements operated into layers, which the geometry and functionality similar to that of the human brain is shown in Fig. 1.

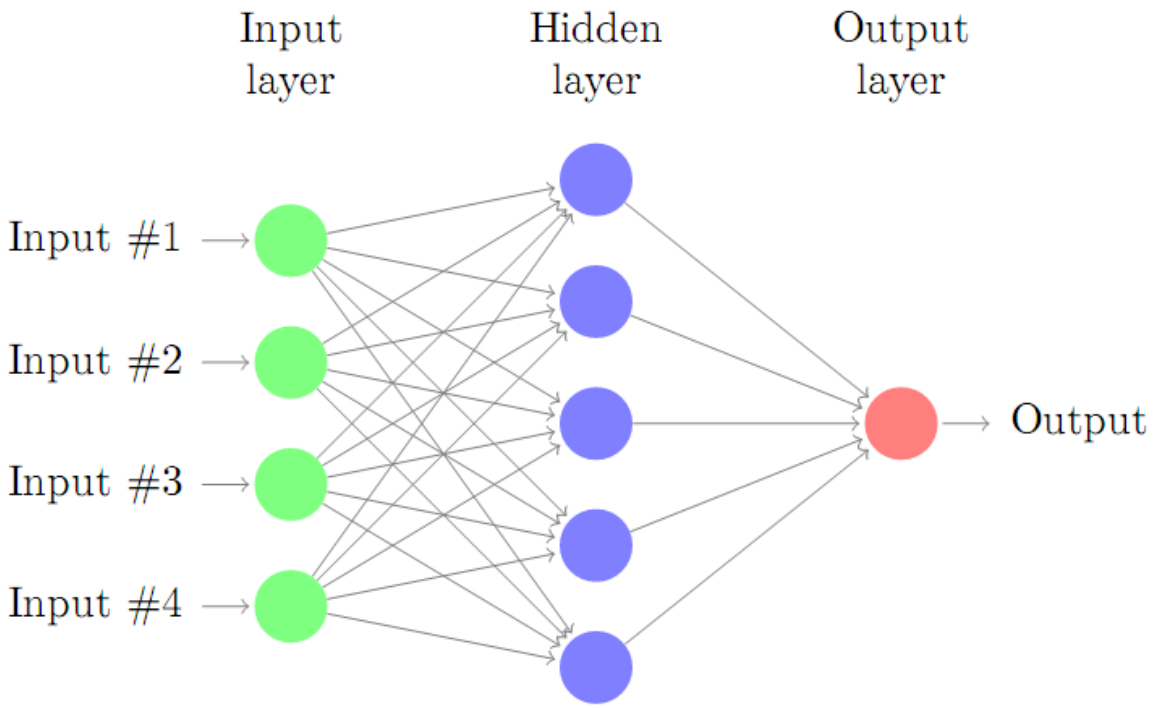

Figure 1. The structure of three-layered neural network used in the present study.

A neural network is trained on a set of examples of input and output data. The outcome of this training is a set of coefficients (called weights) and a specification of the functions, which in combination with the weights; relate the input to the output.

The training process involves a search for the optimum non-linear relationship between the inputs and the outputs. Once the network is trained, the estimation of the outputs for any given inputs is very rapid. The neural network used has been developed in a statistical framework, as it is able to infer the appropriate complexity of the model automatically [11- 13].

This helps to prevent the problems of over-fitting the very flexible equations used in neural network models.

The output variable is expressed a linear summation of activation functions h_i with weights w_i and the bias θ:

$$y = \sum_i w_i h_i + \theta \qquad (1)$$

The activation functions for a neuron i in the hidden layer given by:

$$h_i = \tanh\left(\sum_j w_{ij} x_j + \theta_i\right) \quad (2)$$

with weights w_{ij} and biases θ_i. The weighting is simplified by normalizing the data within the range of ± 0.5 using the normalization function:

$$x_j = \frac{x - x_{\min}}{x_{\max} - x_{\min}} - 0.5 \quad (3)$$

where x is the value of the input and x_j is the normalized value. In the Bayesian neural network, [9 - 11], training is achieved by altering the parameters by back-propagation to optimize an objective function which combines an error term to assess how good the fitting is and regularization term to penalize large weights:

$$M(w) = \beta\left(\frac{1}{2}\sum_i \left(t^{(i)} - y^{(i)}\right)^2 + \alpha\left(\frac{1}{2}\sum_i w_i^2\right)\right) \quad (4)$$

where β and α are complexity parameters which greatly influence the complexity of the model, $t(i)$ and $y(i)$ are the target and corresponding output values for one example input from the training data $x(i)$.

The Bayesian framework for neural networks has two further advantages. Firstly, the significance of the input variables is quantified automatically. Consequently, the significance perceived by the model of each input variable can be compared against existing theory. Secondly, the network's predictions are accompanied by error bars which depend on the specific position in input space. These advantages quantify the model's certainty about its predictions.

4. RESULTS AND DISCUSSION

The database compiled from the experimental data consists of 5 inputs, which include the chemical compositions and temperature, as shown in Table 1.

Table 1. Conductivity values of different composition polymer electrolyte samples at elevated temperature

PEO (wt%)	Litriflate (wt%)	DBP (wt%)	ZrO_2 (wt%)	Temp (K^{-1})	Ln Conductivity (Scm^{-1})
100	0	0	0	3.354016	-19.2717
100	0	0	0	3.298697	-18.063
100	0	0	0	3.245173	-17.674

100	0	0	0	3.193358	-17.1852
100	0	0	0	3.143171	-15.9783
100	0	0	0	3.094538	-14.2205
100	0	0	0	3.047387	-14.4928
100	0	0	0	3.001651	-14.3082
100	0	0	0	2.957267	-14.1637
100	0	0	0	2.914177	-14.0225
100	0	0	0	2.872325	-13.8795
100	0	0	0	2.831658	-13.7202
100	0	0	0	2.792126	-13.508
100	0	0	0	2.753683	-13.2849
100	0	0	0	2.716284	-13.1124
100	0	0	0	2.679887	-12.9568
100	12	0	0	3.354016	-11.5653
100	12	0	0	3.298697	-9.86043
100	12	0	0	3.245173	-9.01149
100	12	0	0	3.193358	-8.36447
100	12	0	0	3.143171	-7.96044
100	12	0	0	3.094538	-7.8341
100	12	0	0	3.047387	-7.71295
100	12	0	0	3.001651	-7.50196
100	12	0	0	2.957267	-7.44732
100	12	0	0	2.914177	-7.38902
100	12	0	0	2.872325	-7.31272
100	12	0	0	2.831658	-7.24743
100	12	0	0	2.792126	-7.22658
100	12	0	0	2.753683	-7.19811
100	12	0	0	2.716284	-7.17433
100	12	0	0	2.679887	-7.11601
100	12	28	0	3.354016	-9.95058
100	12	28	0	3.298697	-8.85547
100	12	28	0	3.245173	-7.78723
100	12	28	0	3.193358	-7.28902
100	12	28	0	3.143171	-7.14601
100	12	28	0	3.094538	-7.01056
100	12	28	0	3.047387	-6.91076
100	12	28	0	3.001651	-6.81245
100	12	28	0	2.957267	-6.76799
100	12	28	0	2.914177	-6.70074
100	12	28	0	2.872325	-6.64539
100	12	28	0	2.831658	-6.60027
100	12	28	0	2.792126	-6.5571
100	12	28	0	2.753683	-6.53619
100	12	28	0	2.716284	-6.52932
100	12	28	0	2.679887	-6.47597
100	12	28	2	3.354016	-8.32245
100	12	28	2	3.298697	-7.69962
100	12	28	2	3.245173	-7.57134
100	12	28	2	3.193358	-7.48046
100	12	28	2	3.143171	-7.39226
100	12	28	2	3.094538	-7.32935

100	12	28	2	3.047387	-7.26443
100	12	28	2	3.001651	-7.23904
100	12	28	2	2.957267	-7.217
100	12	28	2	2.914177	-7.19945
100	12	28	2	2.872325	-7.17563
100	12	28	2	2.831658	-7.15622
100	12	28	2	2.792126	-7.14474
100	12	28	2	2.753683	-7.1309
100	12	28	2	2.716284	-7.12467
100	12	28	2	2.679887	-7.11478

Figs. 2 – 3 show the behavior of the training and test data. It can be seen that both graph exhibit a similar degree of scatter, indicating that the complexity of this particular model is optimum. The error bars in Figs. 2 – 3 include the error bars of the underlying function and the inferred noise level in the dataset. When making predictions, MacKay [11 – 13] recommended the use of multiple good models instead of just one best model.

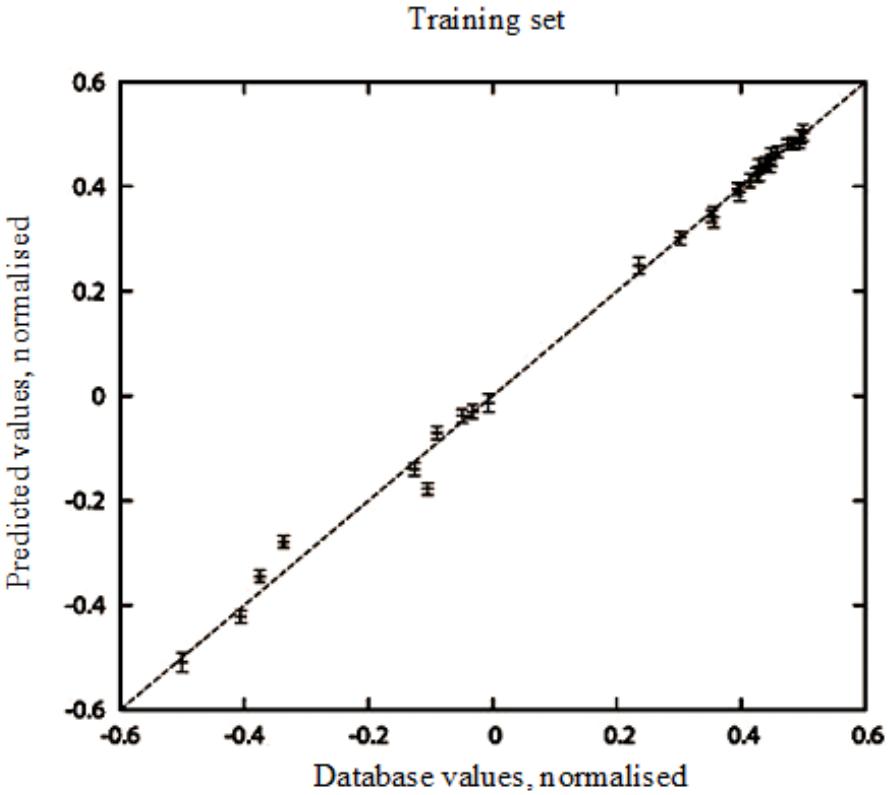

Figure 2. Typical performance of the trained model on training data.

This is called 'forming a committee'. The committee prediction $\bar{y}$ is obtained using the expression:

$$\bar{y} = \frac{1}{L}\sum_i y_i \qquad (5)$$

where L is the size of the committee and y_i is the estimate of a particular model i. The optimum size of the committee is determined from the validation error of the committee's predictions using the test dataset. In the present analysis, a committee of models was used to make more reliable predictions.

The models were ranked according to their log predictive error. Committees were then formed by combining the predictions of best M models, where M gives the number of members in a given committee model. The test errors for the first 120 committees are shown in Fig. 4. A committee of the best four models gives the minimum error. Each constituent model of the committee was therefore retrained on the entire dataset, beginning with the weights previously determined. Fig. 5 shows the results from the new training on the entire dataset. Consistent with the reduction in test error illustrated in Fig. 3, it is evident that the committee model outperforms the single best model. The retrained committee was used for all further work.

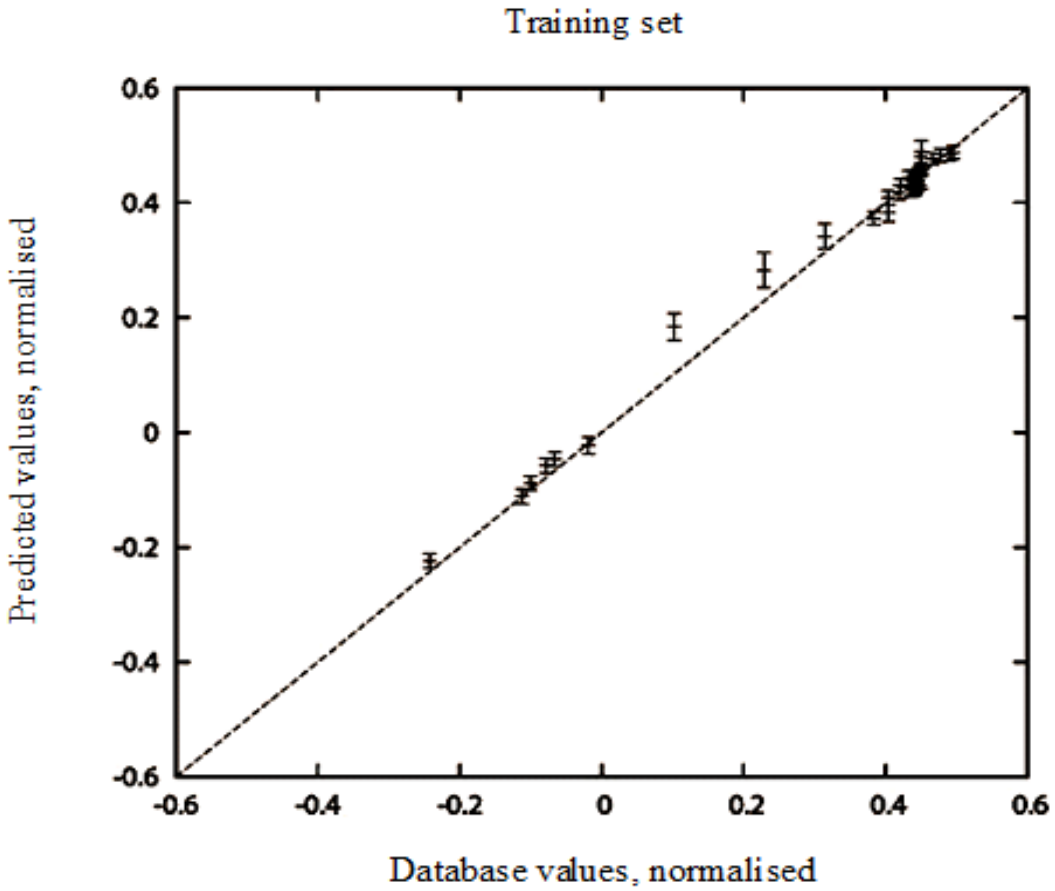

Figure 3. Typical performance of the trained model on test data.

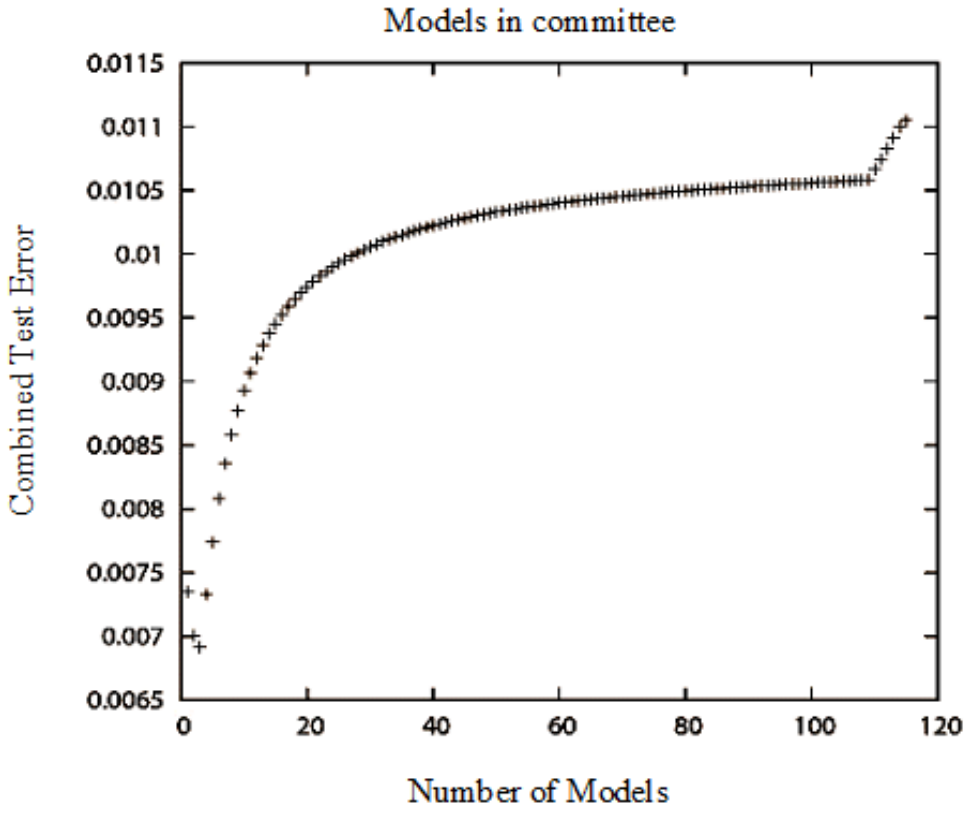

Figure 4. Test error as function of number of members in committee

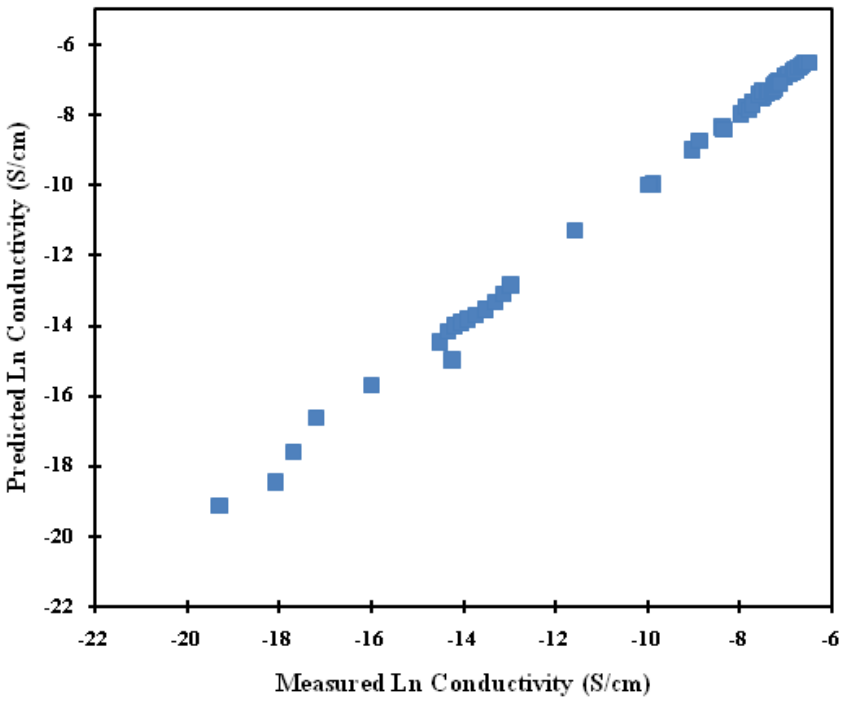

Figure 5. Training data for best committee model (training was done on whole dataset).

Figs. 6 – 11 show the measured and predicted temperature dependence conductivity of the polymer electrolytes. As can be seen from these plots, there exist two temperature ranges above melting temperature for which the variation of conductivity differs. These are the typical of semicrystalline to amorphous phase transitions in the conductive polymeric films. The presence of the two distinct and well defined regions in the plots also suggests that the transport properties of Li^+ are fundamentally controlled by two different mechanisms.

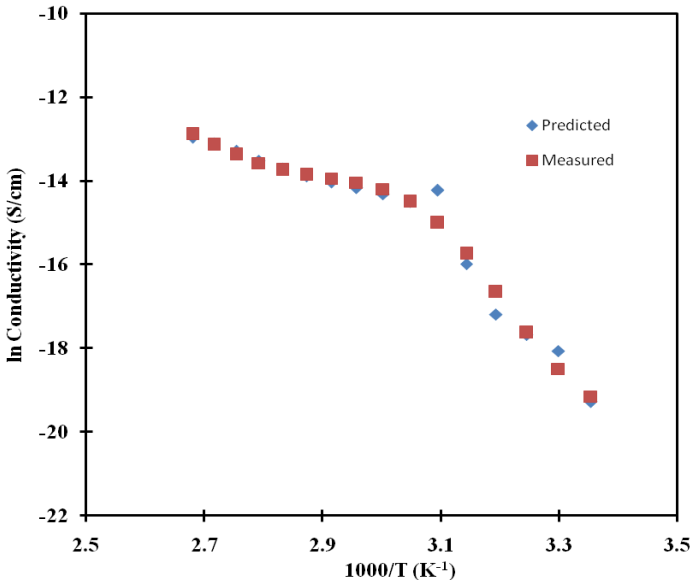

Figure 6. Experimental and neural network curves of pure PEO conductivity as function of temperature.

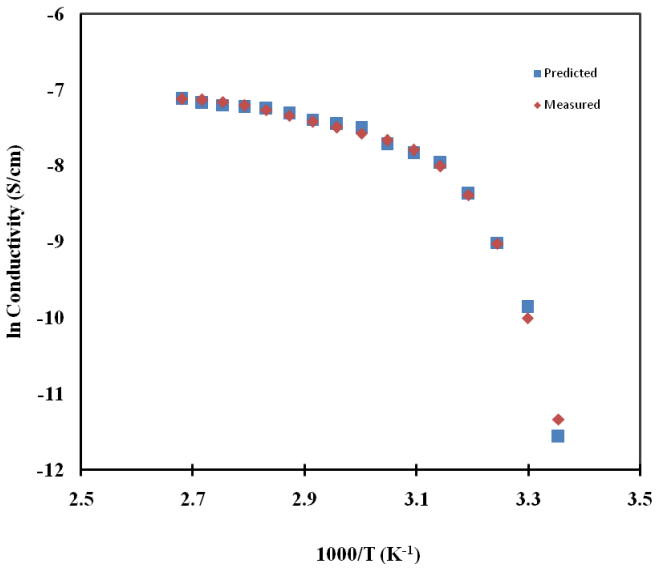

Figure 7. Experimental and neural network curves of pure PEO - Salt conductivity as function of temperature.

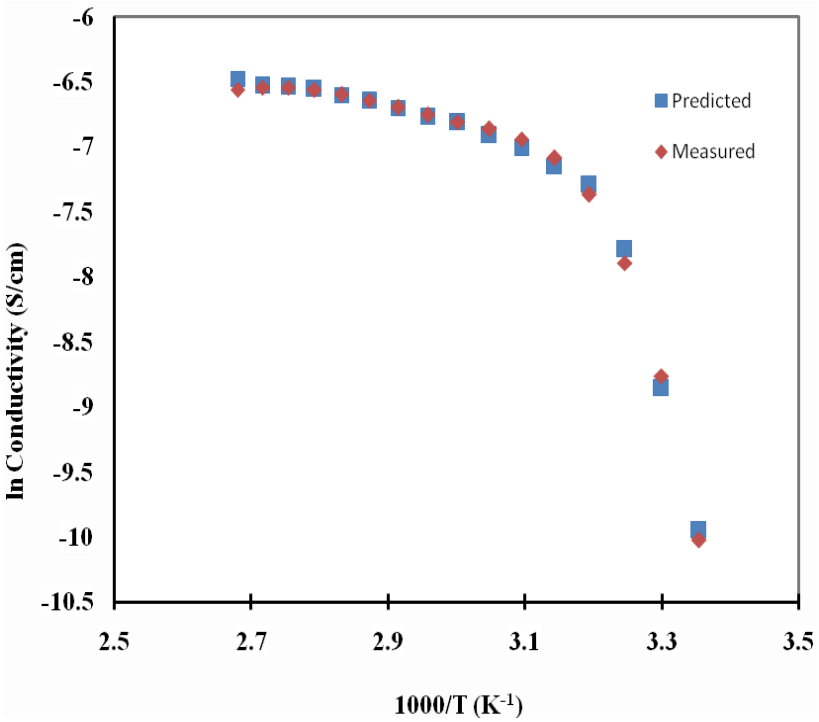

Figure 8. Experimental and neural network curves of PEO-Salt-DBP conductivity as function of temperature.

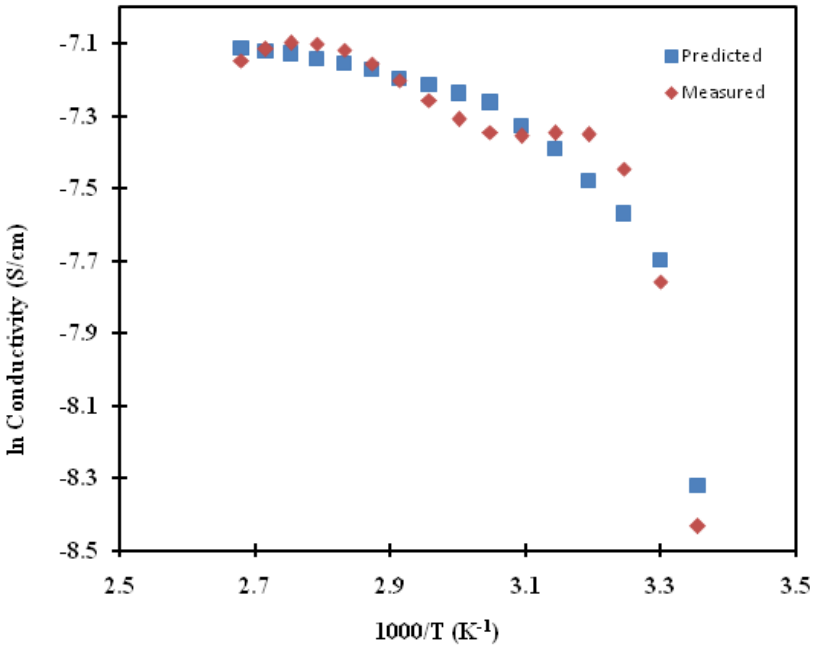

Figure 9. Experimental and neural network results of PEO–Salt–DBP-Filler conductivity as function of temperature.

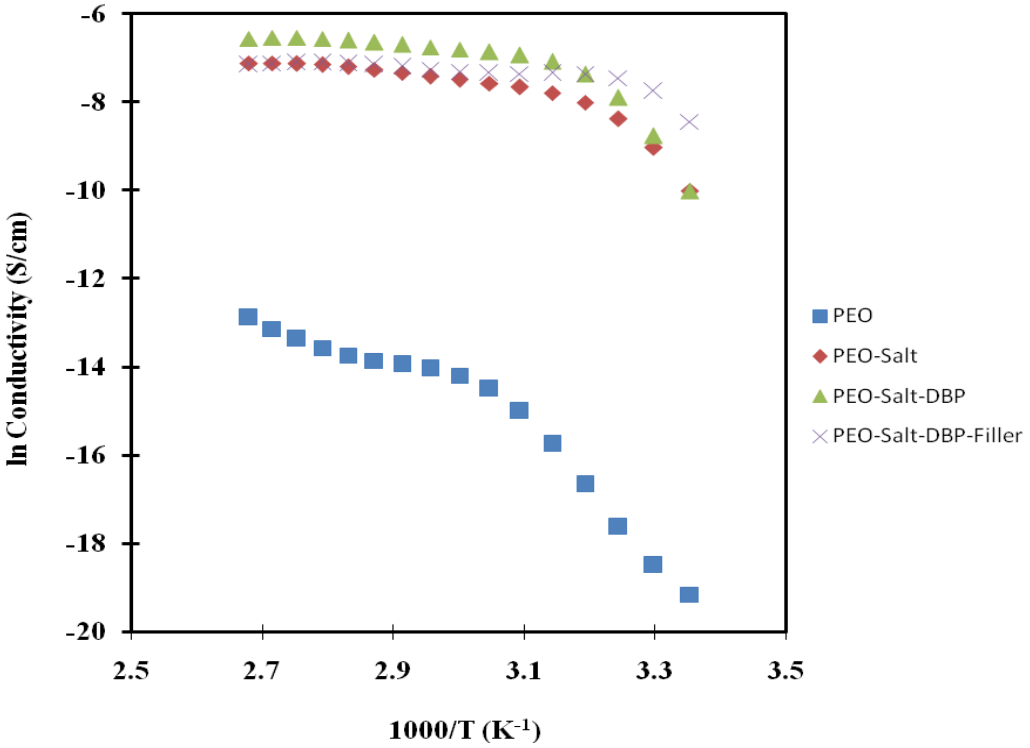

Figure 10. Temperature dependent conductivity of polymer electrolyte system obtained from experimental data.

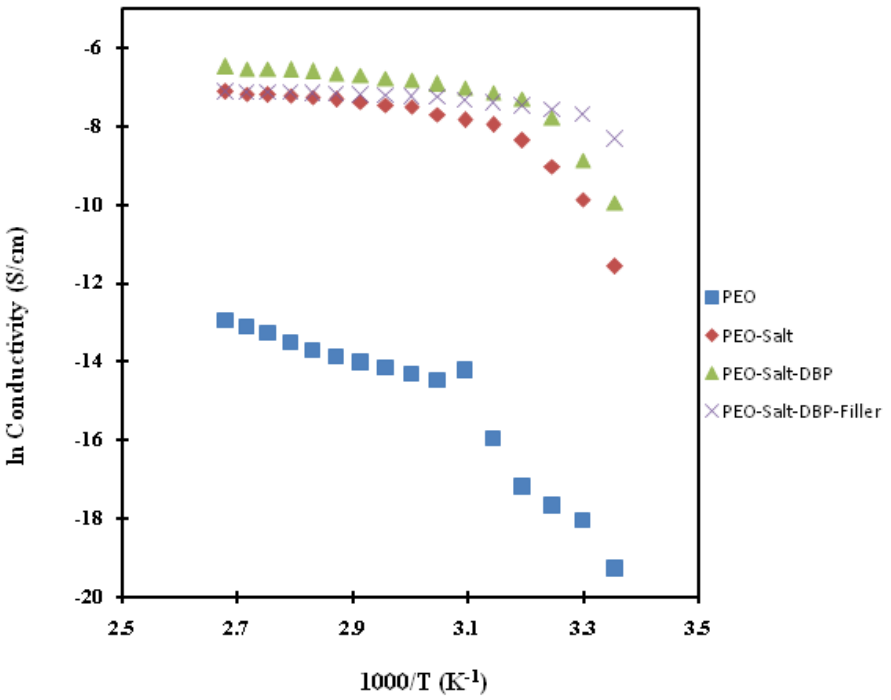

Figure 11. Temperature dependent conductivity of polymer electrolyte system obtained from neural network prediction

The temperature dependence of the conductivity follows the Arrhenius form at low temperature region and Vogel-Tammann-Fulcher (VTF) at the high temperature regions.

In these cases, it can be seen that the measured values lie completely within the predicted values. The model is found to be able to generalize sufficiently to reproduce the general trends in the data, and is capable of making useful predictions of unseen composition and temperature.

5. CONCLUSION

A model has been developed which can predict the ionic conductivity of nanocomposite polymer electrolyte system (PEO - $LiCF_3SO_3$ – DBP - ZrO_2). The generalization ability of the neural network is the basic consideration of this paper. It is concluded observed that Bayesian neural networks are successful in the prediction of experimental results rather than of time-consuming studies.

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