Conductivity, Thermal and Neural Network Model Nanocomposite Solid Polymer Electrolyte System (PEO – LiPF₆ – EC – CNT)

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In this study, the ionic conductivity of a nanocomposite polymer electrolyte system (PEO-LiPF₆-EC-CNT), 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 hexafluorophosphate (LiPF₆), ethylene carbonate (EC) and carbon nanotubes (CNT) are mixed at various ratios to obtain the highest ionic conductivity. The effects of chemical composition and temperature 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 and temperatures 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: Polymer Nanocomposite Electrolytes; Carbon Nanotubes; Neural Networks, Differential Scanning Calorimetry

1. INTRODUCTION

Polymer electrolytes are of technological interest due to their possible applications in various electrochemical devices such as energy conversion units (batteries or fuel cells), electrochromic display devices, photochemical solar cells, supercapacitors and sensors [1-3]. Among the various applications, the use of polymer electrolytes in lithium batteries has been most widely studied. It shall be noted that much initial work on polymer electrolytes were focused on the complexes of

poly(ethyleneoxide)(PEO)withinorganicsalts[4–5].Poly (ethylene) oxide (PEO) has been a popular choice of polymer matrix for lithium-ion conductors[6]. Studies have proved that in PEO based polymer electrolytes systems, conductivity will increase asthe salts concentrations increases [7-11].

 LiPF_6 is the most common lithium salt employed in lithium-ion batteries because it offers good electrolyte conductivities and film forming. Unfortunately, high lithium ionic conductivity cannot be attained at ambient temperature with the pristine PEO matrix. Thus, considerable efforts have been devoted to improve the ionic conductivity of polymer electrolytes. A common approach is to add low molecular weight plasticizers to the polymer electrolyte system [12]. The plasticizers impart saltsolvating power and high ion mobility to the polymer electrolytes. However, plasticizers tend to decrease the mechanical strength of the electrolytes, particularly at a high degree of plasticization [13, 14]. Alternatively, inorganic fillers are used to improve the electrochemical and mechanical properties [15]. 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 conductivity enhancement depends on the filler type and size. In 1999, the addition of carbon to improve the conductivity and stability of polymer electrolytes was proposed by Appetecchi and Passerini [16]. However, the room temperature conductivities for various weight percent of carbon are within the range of 10^{-6} S cm⁻¹. 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 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 modelling of these materials behaviour. But all materials behaviour may not be modelled properly with mathematical functions due to the complexity of the composition dependence. The neural network model has been developed and it was successful to predict the role of salt, plasticizer and filler for the ionic conductivity enhancement in the nanocomposites polymer electrolyte system [17, 18].

Recently, with the developments in artificial intelligence, researchers focused a great deal of attention to the solution of non-linear problems in materials science [19, 20]. In this study, Bayesian neural-networks [21 - 23] are employed to predict the ionic conductivity of nanocomposite polymer electrolyte system (PEO - $LiPF_6$ - EC - CNT).

2. EXPERIMENTAL

Polymer electrolytes were prepared by standard solution-casting techniques [16]. PEO (MW = 600,000, Acros Organics) was used as host polymer matrix, lithium hexaflurosphosphate (LiPF₆) (Aldrich) as the salt for complexation and ethylene carbonate (EC) (Alfa Aesar) as plasticizer. Amorphous carbon nanotube (α CNT) was prepared by chemical route at low temperature [24]. Prior to use, PEO was dried at 50 °C for 48 hours. Appropriate quantities of PEO, LiPF₆, EC and α CNT were dissolved separately in acetonitrile (Fisher) and stirred well for 24h at room temperature to form

a homogeneous solution. All samples were stored under dry conditions. An electronic digital caliper was used for measuring films thickness and average thickness for films is 0.76mm. The ionic conductivities of the samples were measured at temperature ranging from 298 to 373 K using HIOKI 3531 LCR Hi-Tester with frequency range of 50 Hz to 5 MHz.

3. BAYESIAN NEURAL NETWORK

Neural network are parallel-distributed information processing systems used for empirical regression and classification modelling. Their flexibility enables the discovery of complex relationships in data compared with traditional linear statistical models. A neural network consists of a number of highly interconnected processing elements operated into layers, whereby the geometry and functionality of the network is quite similar to the human brain as 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, and is able to infer automatically the appropriate complexity of

the model [21 - 23]. This helps to avoid problems of over-fitting the very flexible equations used in the neural network models. The output variable is expressed as a linear summation of activation functions h_i with weights w_i and bias θ_i .

$$y = \sum_{i} w_{i} h_{i} + \theta \tag{1}$$

and the activation function for a neuron *i* in the hidden layer is given by:

$$h_{\rm i} = \tanh\left(\sum_{\rm j} w_{\rm ij} x_{\rm j} + \theta_{\rm i}\right) \tag{2}$$

with weights w_{ij} and biases θ_i . The weightings are simplified by normalising the data within the range ±0.5 using the normalisation function

$$x_{\rm j} = \frac{x - x_{\rm min}}{x_{\rm max} - x_{\rm min}} - 0.5 \tag{3}$$

where x is the value of the input and x_j is the normalised value. In the Bayesian neural network [21 - 23], training is achieved by altering the parameters by back-propagation to optimise an objective function which combines an error term in order to assess how good the fitting is, and regularisation term to penalise large weights:

$$M(w) = \beta \left(\frac{1}{2} \sum_{i} (t^{(i)} - y^{(i)})^2 + \alpha \left(\frac{1}{2} \sum_{i} w_i^2 \right) \right)$$
(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 network 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 quantify the model's certainty about its predictions.

4. RESULTS AND DISCUSSION

4.1. Various of LiPF₆ salt concentrations

Fig. 2 shows the plot of conductivity dependence temperature at various weight percent of LiPF_6 . The temperature dependence of the ionic conductivity is not linear and obeys the VTF (Vogel-

Tamman-Fulcher) relationship. The conductivity of salted polymer electrolytes is found to increase with temperature, from 303 to 373K. At higher temperature, the thermal movement of polymer chain segments and the dissociation of salts were enhanced the ionic conductivity [25].



Figure 2. Conductivity dependence temperature of polymer electrolytes at various wt% of $LiPF_6$ (a) 5 ; (b) 10 ; (c) 15 ; (d) 20.

4.2. Various of EC plasticizer concentrations



Figure 3. Conductivity dependence temperature of complexes at various wt% of EC (a) 5 ; (b) 10 ; (c) 15.

Fig. 3 shows the plot of ionic conductivity temperature dependence at various wt% of EC. The temperature dependence of the ionic conductivity is not linear and obeys the VTF (Vogel-Tamman-Fulcher) relationship.

The conductivity increases with increasing temperature upon the addition of 5 and 10wt% of EC, as shown in Fig. 3. It is evident that the ionic conductivity increases with an increase in plasticizer content and temperature. This can be explained in terms of two factors, first: an increase in the degree of interconnection between the plasticizer-rich phases due to an increase in the volume fraction of these phases; and second, increase in the free volume of the plasticizer rich phase due to an increase in the relative amount of the plasticizer compared with that of PEO. At higher concentrations of plasticizer, the transport of ions may be expected to take place along the plasticizer-rich phase.

Although the improvement in conductivity in certain electrolyte systems has been interpreted in terms of plasticization of the polymer structure [26] or an alteration in the ion transport mechanism [27], other effects related to the viscosity of the ionic environment may also contribute. As the amount of plasticizer is increased, an optimum composition is reached whereby ion interactions between the solubilizing polymer and the plasticizer are such that ion mobility is maximized. A further increase in plasticizer content may eventually cause displacement of the host polymer by plasticizer molecules within the salt complexes and a decrease in ionic mobility.

4.3. Various of CNT filler concentrations

Fig. 4 shows the temperature dependence of conductivity for polymer electrolytes between 298 to 373K. It is evident that the room temperature conductivity increases with different wt% of aCNTs. When the organic filler was added to the polymer electrolytes, new interfaces were connected with the filler surface such as the α CNTs/polymer spherulite interfaces, which provide more effective paths for the migration of the conductivity ions [28]. Moreover, the nanosize α CNTs improve the conduction of the mobile ions due to their extremely high surface energy [28-33]. This, prevents local PEO chain reorganization with the result of freezing at ambient temperature and a high degree of disorder, which in turn favours fast ionic transport. As the α CNTs concentration increases, the conductivity also increases due to more mobile ions which can be transported in nanocomposite polymer electrolytes. The conductivity values at room temperature for 1wt% of α CNTs is 2.2 x 10⁻⁴ Scm⁻¹ and increases to 1.3 x 10^{-3} Scm⁻¹ when 5wt% of α CNTs were added into polymer complexes. The conductivity value increases by an order of magnitude with the increase of α CNTs concentrations. However, there is a possibility of increased proton conductivity with increases a CNTs concentrations. It is well known that α CNTs are very good electronic conductors [34, 35], but the effect on proton conductivity is less studied. It is also suggested that structural modifications occuring at the aCNT surface due to the specific action of the polar surface groups of the organic filler act as Lewis acid-base interaction centers with the electrolyte ionic species [34]. Thus, it is expected that lowering ionic coupling promotes salt dissociation via a sort of ion-filler complex formation.



Figure 4. Temperature dependence conductivity for polymer electrolyte at different wt% of αCNTs of (a) 1 and (b) 5.

4.4. Optimum concentration of polymer electrolytes.

Fig. 5 shows the temperature dependence of conductivity for various electrolytes between 298 and 373K. It is evident that the room temperature conductivity increases with different chemical composition. The conductivity increases by 5 orders of magnitude with the addition of LiPF₆, 4 orders of magnitude with the addition of EC and 3 orders of magnitude with the addition of α CNTs. The sudden increase of conductivities is due to the role of lithium ions in the PEO, the increase in flexibility of the polymer chain due to the EC and high electrical conductivity properties of α CNTs on polymer electrolytes.

There is a sudden increase in conductivity for pure PEO electrolyte at 313 - 323K (Fig. 5(a)). However, the ionic conductivity increases linearly beyond 323K. With the addition of LiPF₆, EC and α CNTs, the thermal effects are clearly observed in Fig. 5(b) – (d), which show a slight increase in conductivity in a wide temperature range. When EC was added into the system, more salts are dissociated into ions, which have low viscosity and therefore increases ionic mobility. The addition of α CNTs increases the conductivity by inhibiting recrystallization of the PEO chains and providing Li⁺ conducting pathway at the filler surface through Lewis Acid base interaction among different species in the electrolytes [36]. A transportation lithium ion within the polymer matrix requires low energy and hence increases the conductivity. This is possibly due to size of the filler and plasticizer molecule compared to the polymer molecule, which can penetrate easily into the polymer matrix requires low energy at ambient temperature (298K ~ 373K). A transportation lithium ion within the polymer matrix requires low energy at ambient temperature (298K ~ 373K). A transportation lithium ion within the polymer matrix requires low energy and hence increases the conductivity. This is possibly due to size of the filler and plasticizer molecule compared to the polymer molecule, which can penetrate easily into the polymer matrix requires low energy and hence increases the conductivity. This is possibly due to size of the filler and plasticizer molecule compared to the polymer molecule, which can penetrate easily into the polymer matrix requires low energy and hence increases the conductivity. This is possibly due to size of the filler and plasticizer molecule compared to the polymer molecule, which can penetrate easily into the polymer matrix requires low energy and hence increases the conductivity. This is possibly due to size of the filler and plasticizer molecule compared to the polymer molecule, which can penetrate easily into



Figure 5. Conductivity dependence temperature of nanocomposite polymer electrolytes at optimum compositions (a) PEO; (b) PEO -20 wt% LiPF₆; (c) PEO -20 wt % LiPF₆ - 15 wt % EC (d) PEO -20 wt% LiPF₆ - 15 wt% EC -5 wt% α CNTs.

4.5. Differential Scanning Calorimetry (DSC) studies



Figure 6. DSC curves of (a) PEO; (b) PEO-5wt% LiPF₆; (c) PEO-10wt% LiPF₆; (d) PEO-15wt% LiPF₆; (e) PEO-20wt% LiPF₆; (f) PEO-20wt% LiPF₆-5wt%EC; (g) PEO-20wt% LiPF₆-10wt%EC; (h) PEO-20wt% LiPF₆-15wt%EC; (i) PEO-20wt% LiPF₆-5wt%EC-1wt% αCNTs; (j) PEO-20wt% LiPF₆-5wt%EC-5wt% αCNTs.

DSC was utilized to examine the thermal behaviour of PEO based polymer complexed systems. The DSC thermograms of various compositions of (PEO), LiPF₆, EC, α CNTs systems are shown in Fig. 6. Table 1 compiles the values of glass transition temperature (T_g), melting temperature (T_m), percentage of crystallinity and conductivity values at 298K. The glass transition temperature (T_g) provides insight regarding the miscibility of strength of molecular interactions within the complex. Below the T_g the polymer chains are considered to be static, whereas the chains are dynamic above the T_g . A sharp endothermic peak was observed at a temperature near 69 °C for pure PEO during the heating process, as shown in Fig. 6a. The decrease in T_g and X_c will increase the flexibility of the PEO chains and the ratio of amorphous PEO, respectively. It is observed that the addition of salt into the PEO results in an increase in T_g , which suggests a significant reduction in PEO chain mobility. It is seen that the T_m of the PEO phase within the salt complex decreases significantly compared with pure PEO. The decrease in T_g and T_m of the PEO upon the addition of LiPF₆ also indicates the complexation between LiPF₆ and PEO.

Sample	T_g (°C)	$T_{\rm m}$ (°C)	$X_c(\%)$	σ (Scm ⁻¹) at 298K
Pure PEO PEO-5wt% LiPF ₆ PEO-10wt% LiPF ₆ PEO-15wt% LiPF ₆ PEO-20wt% LiPF ₆ -5wt% EC PEO-20wt% LiPF ₆ -10wt% EC PEO-20wt% LiPF ₆ -15wt% EC PEO-20wt% LiPF ₆ -15wt% EC -1wt% α CNT	-66.01 -67.98 -68.00 -70.05 -72.00 -72.01 -74.01 -76.03 -78.03	68.8 67.4 65.1 64.4 63.5 63.2 63.1 62.9 62.0	84.87 67.82 58.46 55.03 47.52 59.47 51.27 47.35 46.21	3.25×10^{-10} 1.20×10^{-6} 9.03×10^{-6} 1.82×10^{-5} 4.10×10^{-5} 5.93×10^{-5} 1.43×10^{-4} 2.06×10^{-4} 2.20×10^{-4}
PEO-20wt% L1PF ₆ -15wt% EC -5wt% α CNT	-80.04	61.0	27.12	1.30×10^{-3}

Table 1. Thermal parameters and conductivity values of PEO-xLiPF₆-xEC-xαCNTs

The T_g and T_m further decrease with the addition of plasticizer (EC). The plasticization effect is related to a weakening of the dipole-dipole interaction due to the presence of ion clusters between the PEO chains. The decrease in glass transition temperature (T_g) facilitates softening of the polymer backbone and increases its segmental motion. Such segmented motion produces voids, which facilitates flow of ions through the polymer chain network in the presence of an applied electric field. Ferry et al. [38] reported a similar plasticizing effect of LiClO₄ in TPU-LiClO₄ polymer electrolytes. Similar plasticizing effect of ion pairs and ion multiplets were also reported by Silva et al. [39] and Chiodelli et al. [40] for poly(trimethylenecarbonate) with LiBF₄ and PEO–LiBF₄ polymer electrolytes, respectively. The curves show that the addition of α CNTs influences the T_g and T_m of polymer electrolytes.

The peaks broaden and shift slightly towards lowers temperatures. The nanosized α CNTs interact with the PEO polymer matrix to suppress the crystallization of PEO. This leads to an increase in ionic conductivity, especially at temperatures lower than its melting point [41]. A similar behaviour was also observed in PEO polymer electrolytes containing fillers such as SiO₂ and TiO₂ [41, 42]. The conductivity enhancement is contributed by the structural modifications associated with the polymer host caused by the filler. A dominant contribution to the conductivity enhancement by the filler at temperatures below T_g and T_m should possibly be due to this effect.

4.6. Neural Network Model

The database compiled from experimental data consists of 5 inputs including the chemical compositions and temperature, as shown in Table 2.

 Table 2. Conductivity values of different composition polymer electrolyte samples at elevated temperature

PEO (wt%)	LiPF ₆ (wt%)	EC (wt%)	CNT (wt%)	Temp (K^{-1})	Conductivity (S cm ⁻¹)
100	0	0	0	3.35402	2 -21.8472
100	0	0	0	3.29870) -21.3619
100	0	0	0	3.24517	7 -20.3656
100	0	0	0	3.19336	5 -19.9035
100	0	0	0	3.14317	7 -16.5504
100	0	0	0	3.09454	4 -16.2984
100	0	0	0	3.04739	9 -15.8950
100	0	0	0	3.00165	5 -15.6734
100	0	0	0	2.95727	7 -15.2018
100	0	0	0	2.91418	3 -14.9211
100	0	0	0	2.87233	3 -13.7957
100	0	0	0	2.83166	5 -13.6085
100	0	0	0	2.79213	3 -13.4302
100	0	0	0	2.75368	3 -13.3027
100	0	0	0	2.71628	3 -12.7967
100	0	0	0	2.67989	-12.7717
100	5	0	0	3.35402	2 -13.6310
100	5	0	0	3.29870) -13.3716
100	5	0	0	3.24517	7 -12.5725
100	5	0	0	3.19336	5 -11.6943
100	5	0	0	3.14317	7 -9.47620
100	5	0	0	3.09454	4 -8.87486
100	5	0	0	3.04739	-8.32398
100	5	0	0	3.00165	5 -5.51057
100	5	0	0	2.95727	7 -5.44313
100	5	0	0	2.91418	-5.43535
100	5	0	0	2.87233	-5.49597

100	5	0	0	2.83166	-5.48116
100	5	0	0	2.79213	-5.48859
100	5	0	0	2.75368	-5.49597
100	5	0	0	2.71628	-5 48859
100	5	0	0	2.71020	-5 48116
100	10	0	0	3 35/02	-11 6154
100	10	0	0	3.33402	10 8720
100	10	0	0	3.29070	-10.8729
100	10	0	0	5.24517 2.10226	-9.93411
100	10	0	0	3.19330	-9.12474
100	10	0	0	3.14317	-8.11/20
100	10	0	0	3.09454	-7.62530
100	10	0	0	3.04739	-7.47011
100	10	0	0	3.00165	-7.21983
100	10	0	0	2.95727	-7.07010
100	10	0	0	2.91418	-7.04993
100	10	0	0	2.87233	-5.91742
100	10	0	0	2.83166	-5.20805
100	10	0	0	2.79213	-5.16630
100	10	0	0	2.75368	-5.13286
100	10	0	0	2.71628	-5.10347
100	10	0	0	2.67989	-5.15405
100	15	0	0	3.35402	-10.9114
100	15	0	0	3.29870	-9.81122
100	15	ů 0	ů 0	3 24517	-9 15581
100	15	ů 0	0	3 19336	-7 60044
100	15	0	0	3 14317	-6 92684
100	15	0	0	3.09/5/	-1 93584
100	15	0	0	3.07730	4 00384
100	15	0	0	3.04757	4 86741
100	15	0	0	2.05727	-4.80741
100	15	0	0	2.93727	-4.80234
100	15	0	0	2.91410	-4.84332
100	15	0	0	2.87233	-4.84352
100	15	0	0	2.83166	-4.841/9
100	15	0	0	2.79213	-4.83658
100	15	0	0	2.75368	-4.82257
100	15	0	0	2.71628	-4.84179
100	15	0	0	2.67989	-4.81727
100	20	0	0	3.35402	-10.1023
100	20	0	0	3.29870	-9.30859
100	20	0	0	3.24517	-8.50518
100	20	0	0	3.19336	-6.87561
100	20	0	0	3.14317	-5.10705
100	20	0	0	3.09454	-5.06966
100	20	0	0	3.04739	-5.06966
100	20	0	0	3.00165	-5.05043
100	20	0	0	2.95727	-5.05043
100	20	0	0	2.91418	-5.05043
100	20	0	0	2.87233	-5.06966
100	20	0	0	2.83166	-5.06009
100	20	0	0	2.79213	-5.06009

100	20	Ο	0	2 75368	-5 00783
100	20	0	0	2.75508	-5.09783
100	20	0	0	2.71028	-3.09783
100	20	0	0	2.07969	-3.10929
100	20	5	0	5.55402 2.20870	-9.75212
100	20	5	0	5.29870	-9.07921
100	20	5	0	3.24517	-8.18058
100	20	5	0	3.19336	-7.84160
100	20	5	0	3.14317	-7.57361
100	20	5	0	3.09454	-7.40133
100	20	5	0	3.04739	-7.22931
100	20	5	0	3.00165	-7.16757
100	20	5	0	2.95727	-7.11998
100	20	5	0	2.91418	-7.11998
100	20	5	0	2.87233	-7.11817
100	20	5	0	2.83166	-7.21463
100	20	5	0	2.79213	-7.28898
100	20	5	0	2.75368	-7.20970
100	20	5	0	2.71628	-7.10544
100	20	5	0	2.67989	-7.00130
100	20	10	0	3.35402	-8.85455
100	20	10	0	3.29870	-8.08584
100	20	10	Ő	3 24517	-7 53347
100	20	10	0	3 19336	-7 30017
100	20	10	0	3 14317	-6 97964
100	20	10	0	3 09454	-5 56302
100	20	10	0	3 04739	-5 36315
100	20	10	0	3 00165	5 33624
100	20	10	0	2 05727	5 37106
100	20	10	0	2.93727	-3.37190
100	20	10	0	2.91410	-3.30313
100	20	10	0	2.07255	-3.33420
100	20	10	0	2.85100	-3.30313
100	20	10	0	2.79213	-5.35420
100	20	10	0	2.75368	-5.3/196
100	20	10	0	2./1628	-5.36315
100	20	10	0	2.67989	-5.40645
100	20	15	0	3.35402	-8.48561
100	20	15	0	3.29870	-7.96573
100	20	15	0	3.24517	-7.76506
100	20	15	0	3.19336	-7.57437
100	20	15	0	3.14317	-7.39641
100	20	15	0	3.09454	-7.30940
100	20	15	0	3.04739	-7.23554
100	20	15	0	3.00165	-7.17852
100	20	15	0	2.95727	-7.13254
100	20	15	0	2.91418	-7.09931
100	20	15	0	2.87233	-6.95413
100	20	15	0	2.83166	-6.91266
100	20	15	0	2.79213	-6.89292
100	20	15	0	2.75368	-6.79894
100	20	15	0	2.71628	-6.75986

100	20	15	0	2.67989	-6.67681	
100	20	15	1	3.35402	-8.42083	
100	20	15	1	3.29870	-7.69855	
100	20	15	1	3.24517	-7.38929	
100	20	15	1	3.19336	-7.19753	
100	20	15	1	3.14317	-7.04879	
100	20	15	1	3.09454	-7.00047	
100	20	15	1	3.04739	-6.93712	
100	20	15	1	3.00165	-6.85699	
100	20	15	1	2.95727	-6.72915	
100	20	15	1	2.91418	-6.69749	
100	20	15	1	2.87233	-6.65784	
100	20	15	1	2.83166	-6.72264	
100	20	15	1	2.79213	-6.77112	
100	20	15	1	2.75368	-6.69480	
100	20	15	1	2.71628	-6.65364	
100	20	15	1	2.67989	-6.59004	
100	20	15	5	3.35402	-6.64774	
100	20	15	5	3.29870	-6.39311	
100	20	15	5	3.24517	-6.21264	
100	20	15	5	3.19336	-6.04334	
100	20	15	5	3.14317	-5.95460	
100	20	15	5	3.09454	-5.87469	
100	20	15	5	3.04739	-5.81026	
100	20	15	5	3.00165	-5.76295	
100	20	15	5	2.95727	-5.74536	
100	20	15	5	2.91418	-5.73145	
100	20	15	5	2.87233	-5.72543	
100	20	15	5	2.83166	-5.79537	
100	20	15	5	2.79213	-5.81946	
100	20	15	5	2.75368	-5.86073	
100	20	15	5	2.71628	-5.90204	
100	20	15	5	2.67989	-5.89866	

The network model for the ionic conductivity consists of 5 input nodes, a number of hidden nodes and an output node representing the ionic conductivity. The complexity of the model is controlled by the number of hidden units (Fig. 1) and the values of the the 7 regularisation constants σ_w , one associated with each of the 5 inputs, one for biases and one for all weights connected to the output. Fig. 7 shows that the inferred noise level decreases as the number of hidden units increases. However, the complexity of the model also increases with the number of hidden units. A high degree of complexity may not be justifiable. To select the correct complexity, it is necessary to examine how the model generalises on previously unseen data in the test data set using the test error. The latter is defined as:

$$T_{\rm e} = 0.5 \sum_{\rm n} (y_{\rm n} - t_{\rm n})^2$$
(5)

where y_n is the predicted ionic conductivity and t_n is its measured value. Fig. 8 shows that the test error first decreases, but begins to increase again as a function of the number of hidden units. Figs. 9 - 10 show the behaviour of the training and test data which exhibit a similar degree of scatter in both graphs, indicating that the complexity of this particular model is optimum. The error bars in Figs. 9 - 10 include the error bars of the underlying function and the inferred noise level in the dataset σ_v . The test error is a measure of the performance of a model. Another useful measure is the "log predictive error", for which the penalty for making a wild prediction is accompanied by an appropriately large error bar. Assuming that for each example *n*, the model gives a prediction with error (y_n, σ_n^2) , the log predictive error(LPE) as shown in equation 6:

$$LPE = \sum_{n} \left[\frac{\frac{1}{2} (t_n - y_n)^2}{\sigma_n^2} + \log(\sqrt{2n\sigma_n}) \right]$$
(6)

Fig. 9 shows the log predictive error as a function of hidden units.



Figure 7. A variation in (the model perceived level of noise in the data) as function of number of hidden units



Figure 8. Test error as a function of the number of hidden units



Figure 9. Log predictive error as a function of the number of hidden units



Figure 10. Typical performance of the trained model on training data



Figure 11. Typical performance of the trained model on test data



Figure 12. Test error as a function of the number of members in a committee

When making predictions, MacKay [9 - 11] recommended the use of multiple good models instead of just one best model. This is called 'forming a committee'. The committee prediction \overline{y} is obtained using the expression:

$$\overline{y} = \frac{1}{L} \sum_{i} y_{i}$$
⁽⁷⁾

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 is used to make more reliable predictions. The models are ranked according to their log predictive error. Committees are 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. 12. A committee of the best three models gives the minimum error. Each constituent model of the committee is therefore retrained on the entire dataset, beginning with the weights previously determined. Fig. 13 shows the results from the new training on the entire dataset. Consistent with the reduction in test error illustrated in Fig. 12, it is evident that the committee model outperforms the single best model. The retrained committee is then used for all further work.



Figure 13. Training data for the best committee model (training is carried out on whole dataset)

A comparison of the measured and predicted conductivity is presented in Figs. 14 - 19. In these cases it can be seen that the measured values lie completely within the predicted values. The model is found to be capable of generalising sufficiently to reproduce the general trends in the data and is capable of making useful predictions of unseen composition and temperature.



Figure 14. Experimental and neural network curves of pure PEO conductivity according to temperature



Figure 15. Experimental and neural network curves of pure PEO - Salt conductivity according to temperature



Figure 16. Experimental and neural network curves of PEO-Salt-EC conductivity according to temperature



Figure 17. Experimental and neural network curves of PEO-Salt-EC-CNT conductivity according to temperature



Figure 18. Temperature-dependent conductivity of polymer electrolyte system from experimental data



Figure 19. Temperature-dependent conductivity of polymer electrolyte system obtained from neural network's prediction

5. CONCLUSION

Novel composite solid polymer electrolytes were synthesized successfully via solution-casting technique. It has been demonstrated in this paper that the addition of various weight percent of salt, plasticizer and filler into the PEO matrix enhances conductivity. DSC thermographs exhibit a decrease in T_m , T_g and X_c values, which leads to increased conductivity for composite polymer electrolytes at 298K. A neural networks model has been developed, which can predict the ionic conductivity of nanocomposite polymer electrolyte systems (PEO - LiPF₆ - EC - CNT). The generalized capability of the neural network is the primary consideration of this paper. The Bayesian neural network is found to be successful in predicting of experimental results rather that of time-consuming studies.

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