Study of nano-TiO₂ composite polymer electrolyte incorporating ionic liquid PP₁₂₀₁TFSI for lithium battery

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Abstract

A series of novel nano-composite polymer electrolytes (NCPEs) are prepared with the ionic liquid of N-methyl-N-methoxyethylpiperidiniumbis(trifluoromethanesulfonyl)imide (PP₁₂₀₁TFSI) as plasticizer and nano-sized TiO₂ as additive. The effect of the ratio of TiO₂ to Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) on the properties of the NCPEs are studied, such as the crystallinity and ionic conductivity. The results indicate that the nano-composite polymer electrolyte NCPE-2, that the ratio of TiO₂ to PVDF-HFP is 10%, exhibits the highest ionic conductivity of $2 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ with the lowest crystallinity. The LiFePO₄/NCPE-2/Li coin-typed cell cycled at 0.5 C shows the 1st discharge capacity of $127.9 \text{ mAh} \cdot \text{g}^{-1}$ and remains 97.6% of the initial discharge capacity on the 50th cycle.

Keywords: lithium polymer electrolyte, nano-composite polymer electrolyte, ionic liquid

1. Introduction

Compared to the traditional carbonate based liquid electrolytes used in lithium batteries, polymer electrolytes have attracted much attention due to their reliability, safety, and fabrication flexibility in shape and size for roll-up displays and portable electronic devices ^[1]. However, the solid polymer electrolytes (SPEs) show much lower ionic conductivity ($10^{-8} \sim 10^{-7} \text{ S} \cdot \text{cm}^{-1}$) than the conventional liquid electrolytes ^[2], which limits their application in batteries. By incorporating highly conductive organic solvents (plasticizers) into SPEs, the gel polymer electrolytes (GPEs) are developed to provide much higher ionic conductivity ($10^{-4} \sim 10^{-3} \text{ S} \cdot \text{cm}^{-1}$) compared to the SPEs ^[3,4].

The plasticizers used in the GPEs are mainly based on the commercial carbonate liquids, thus the safety problems still exist to some extent ^[5]. Room temperature ionic liquids (RTILs) have drawn much attention in electrochemical fields in recent years due to its high ionic conductivity and wide electrochemical window ^[6]. Using RTILs as the plasticizers in the GPEs can further improve the safety without sacrificing their electrochemical properties. The ionic liquids based on piperidinium cation have been reported intensively due to its wide electrochemical window and high cathode stability against metallic lithium, such as

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N-methyl-N-propylpiperidinium (PP13) salts ^[7], N-methyl-N-butylpiperidinium (PP14) salts ^[8] and N-butyl-N-ethylpiperidinium (PP24) salts ^[9], which are more suitable as electrolyte for lithium batteries. Among the piperidinium cation based ionic liquids, the ether-functionalized piperidinium ionic liquids present much lower viscosity and higher ionic conductivity compared to other functionalized groups ^[10].

Although the GPEs containing RTILs show many advantages, they still suffer from several problems, such as the interface instability between the polymer electrolyte and metallic lithium electrode, and relatively low ionic conductivity. Several methods have been proposed to solve the above problems, such as polymer bending ^[11] and the addition of several inorganic fillers ^[12]. It has been reported that the addition of nano-sized ceramic fillers to the polymer electrolytes may improve both the mechanical and thermal properties of the polymer electrolyte ^[13]. For example, TiO₂ nano-particles dispersed in a poly(ionic liquid) has been already studied as a hybrid electrolyte, resulting in better device performance and long-term stability^[14].

In this paper, the nano-composite polymer electrolytes based on PVDF-HFP were prepared with the ionic liquid of N-methyl-N-methoxyethylpiperidinium (PP₁₂₀₁) as cation and TFSI⁻ as anion. Nano-sized TiO₂ was dispersed in the nano-composite polymer electrolyte as an additive. The properties of the resulting nano-composite polymer electrolytes are systematically researched. The influence of the ratio of TiO₂ to PVDF-HFP on the properties of the NCPEs is discussed, such as the crystallinity and ionic conductivity of the NCPEs. The effect of TiO₂ addition into the gel polymer membrane on the electrochemical properties is discussed, such as the interfacial stability, with the aim to optimize the quality of the nano-composite polymer electrolyte.

2. Experiment

2.1. Materials

Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP, Kynar Flex 2801) and nano-TiO₂ particles (from Aladdin, average particle size 10 nm) were dried in vacuum at 80 °C for 24 hours prior to use. N-Methylpiperidine (from Aladdin, 97%) and 2-Bromoethyl methyl ether (from Sinopharm Chemical Reagent Co., Ltd) were stored with 4 Å molecular sieves to remove residual moisture prior to use. The LiFePO₄ (kindly provided by Changsha Yunchou Power Technology, China) comprises LiFePO₄ (91 wt%), conductive agent (5 wt%), and PVDF (4 wt%). LiTFSI (anhydrous, 99%), N,N-Dimethylformamide (anhydrous, 99.8%) and Acetonitrile(anhydrous, 99.9%) were purchased from Aladdin.

2.2. Preparation of ionic liquid

N-methyl-N-methoxyethylpiperidiniumbis(trifluoromethanesulfonyl)imide PP₁₂₀₁TFSI was produced by two-step synthesis. The mixture of 0.1 mol N-Methylpiperidine and 0.1 mol 2-Bromoethyl methyl ether was stirred

for 8 hours with acetonitrile as solvent at 80°C under N₂ atmosphere. After removing the residual solvent acetonitrile, the produced bromide was acquired and then dissolved in acetone. The obtained solution was evaporated under reduced pressure to remove the solvent acetone and thus the bromide PP₁₂₀₁Br was obtained. Then the ionic liquid PP₁₂₀₁TFSI was synthesized through ion-exchange by mixing PP₁₂₀₁Br with LiTFSI in deionized water. The crude PP₁₂₀₁TFSI was washed with deionized water till no residual Br ion in deionized water was detected. The ionic liquid (PP₁₂₀₁TFSI) was stored with 4Å molecular sieves in glove box prior to use. The water content in the synthesized PP₁₂₀₁TFSI was measured as 106 ppm by Coulometer (831KF, NETZSCH, Germany).

2.3. Preparation of nano-composite polymer electrolyte(NCPE)

The PVDF-HFP, nano-TiO₂, the ionic liquid of PP₁₂₀₁TFSI and LiTFSI were dissolved in the solvent of N, N-Dimethylformamide (DMF). The obtained solution was stirred at 50°C for 5 hours and then sonicated for 1 hour before casted on the poly(tetrafluoroethene) matrix. The solution in the matrix was evaporated under vacuum for 24 hours to generate the polymer membrane. Table 1 lists the composition of the different nano-composite polymer electrolytes and the abbreviation of the corresponding polymer electrolytes. The water content of the prepared nano-composite polymer electrolyte was measured as 92 ppm by Coulometer (831KF, NETZSCH, Germany).

2.4. Characterization of nano-composite polymer electrolytes

The crystallinity of the NCPEs was investigated by differential scanning calorimeter (DSC, DSC200F3, NETZSCH) in nitrogen ranging from 35 °C to 250°C at the scan rate of 10 °C ·min⁻¹.

2.5. Electrochemical characterization of Nano-composite polymer electrolytes

The ionic conductivity of the obtained NCPEs was measured with electrochemical impedance spectroscopy of PARSTAT 2273 in the frequency range from 0.1 Hz to 10⁶ Hz. The cell was assembled by sandwiching a piece of membrane between two stainless steel electrodes in the Argon-filled glove box. The ionic conductivity of the assembled cells were measured between 30 °C and 80 °C at every 10 °C.

The interfacial resistance between the electrolyte and lithium electrode was measured through A.C. impedance spectroscopy of PARSTAT 2273 in the frequency range of 0.1 Hz to 10⁶ Hz. The measured cells were assembled by sandwiching a piece of membrane between two lithium metals.

The lithium ion transference number (*t*₊) of the nano-composite polymer electrolyte was calculated according to the Evans and Abraham ^[15] method by applying 50 mV polarization to the cell, with the following Eq. (1),

$$t_+ = \frac{I_s R_{b,s} (\Delta V - I_0 R_{i,0})}{I_0 R_{b,0} (\Delta V - I_s R_{i,s})} \quad (1)$$

where ΔV is the potential applied across the cell, I_0 and I_s are the initial and steady-state dc current, $R_{b,0}$ and $R_{b,s}$ are the initial and final resistance of the electrolyte, and $R_{i,0}$ and $R_{i,s}$ are the initial and steady-state resistance of the passivating layer.

The electrochemical stability of the nano-composite polymer electrolyte was determined by linear sweep voltammetry (LSV) and cyclic voltammetry (CV) using Pt as the working electrode and Li as the counter/reference electrode with a coin cell. The LSV and CV scan were performed at the scan rate of $0.2 \text{ mV}\cdot\text{s}^{-1}$. There is very small distance around $50\mu\text{m}$ between the working and counter/reference electrode, and a thick piece of metallic lithium as reference/counter electrode to keep the voltage of counter/reference side constant. The IR drop in this experiment can be neglected. The Li/NCPE/LFP cell was assembled in the argon-filled glove box. The charge-discharge test were performed between 2.5 V and 4.0 V at 30°C , and the charge-discharge current density varied from 0.1 C to 1 C.

3. Result and discussion

3.1 The crystallinity of nano-composite polymer electrolytes

The crystallinity of the NCPE-X ($X=0, 1, 2, 3, 4$) was measured by DSC. Fig. 1 displays the DSC curves of the NCPE-X across the range of the tested TiO_2 contents from 0% to 20%. If the crystallinity of PVDF-HFP is assumed as 100%, the relative percentage of crystalline (X_c) can be calculated through the following Eq. (2),

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \times 100\% \quad (2)$$

where ΔH_m^0 is the heat of fusion of PVDF-HFP, $104.7 \text{ J}\cdot\text{g}^{-1}$ [16], ΔH_m is the heat of fusion of the prepared nano-composite polymer electrolyte NCPE-X. Table 2 summarizes X_c , ΔH_m and the crystalline melting temperature of T_m for all membranes. The variation of X_c and T_m for NCPE-X is caused by the TiO_2 content difference in the PVDF-HFP/PP₁₂₀₁TFSL/ TiO_2 system. In the nano-composite polymer electrolytes, X_c and T_m slightly decrease with the increasing content of TiO_2 first, then increase with TiO_2 , as seen in Table 2. The slight decrease may be related to the Lewis reaction between the nano-particles TiO_2 surface and the PVDF-HFP segments [17]. This interaction may induce the structure modification of polymer chains and break the crystal structure, leading to the formation of a favorable conductive path of Li^+ on the surface of nano- TiO_2 [18]. But with the further increase of TiO_2 amount, X_c and T_m increase slightly. The reason for this phenomenon is not clear, but as far as I can see, with the excessive TiO_2 addition on the PVDF-HFP/PP₁₂₀₁TFSL/ TiO_2 system, the excessive TiO_2 may hindered the movement of chain of PVDF-HFP, thus leading to the increase of the crystalline of NCPE-X ($X=3, 4$).

3.2 Ionic conductivity of nano-composite polymer electrolytes

The dependence of ionic conductivity on temperature for the NCPE-X was discussed in the temperature range from 30 °C to 80 °C and plotted in Fig. 2. Since high temperature not only enhances the ionic mobility, but also strengthens the mobility of the polymer chains which facilitates the ion migration. The ionic conductivity of all samples increases with the temperature.

The ionic conductivity of samples rises from 0.5×10^{-3} to $2 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ with the increase of TiO_2 content. NCPE-2 shows the maximum ionic conductivity of $2 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$. According to the EMT model proposed by Wiezonek ^[19], the ionic conductivity of the NCPE-X increases remarkably with the addition of TiO_2 , which is caused by the formation of highly conductive layers at the polymer chain-inorganic fillers interface. In addition, the crystalline of nano-composite polymer electrolyte decreases with the addition of TiO_2 , thereby improving the mobility of polymer chains and strengthening the ion migration ^[20].

The Arrhenius equation is used to calculate the activation energy, the minimum energy required for all ion transportation across the electrolyte. The linear relationship between ionic conductivity and temperature is expressed as Eq. (3),

$$\sigma = \sigma_0 \exp \left(\frac{-E_a}{RT} \right) \quad (3)$$

where σ is the ionic conductivity of the nano-composite polymer electrolyte, σ_0 is the pre-exponential factor, E_a is the activation energy, R is gas constant, and T is temperature. The E_a value decreases from 17 eV to 11 eV (Table 3) with the increase of TiO_2 content in the NCPE-X system. NCPE-2 shows the lowest activation energy of 11 eV. Besides, the E_a is directly correlated to the crystallinity of electrolyte and the formation of a new lithium ion conductive path by Lewis reaction, since low crystallinity corresponds to high mobility of the polymer chains and the new conductive path transmits more lithium ion.

3.3 Lithium transference number t_+

The lithium transference number, t_+ , is a key factor in the characterization of the polymer electrolyte. The bulk and interfacial resistance of the Li/NCPE-X/Li cell ($X=0, 2$) before and after polarization were measured by A.C. impedance. The results are plotted in Fig. 3. The inserted figure is the depolarization curve of the cell subjected to small DC polarization potential for sufficient time to reach steady-state. The data related to t_+ are summarized in Table 4. The measured t_+ value of the NCPE-2 is 0.56, which is higher than the value of NCPE-0 at 30 °C. This observation is consistent with a transport model based on the modification of polymer chains induced via Lewis reactions between the nano-particles TiO_2 surface and the PVDF-HFP segments ^[17]. In another word, the acid sites on the surface of TiO_2 may compete with Li^+ to form complex with the polymer chain of PVDF-HFP. Thus TiO_2 may act as cross-link center for PVDF-HFP segments, thereby lowering the reorganization tendency of

the polymer chains and promoting preferred Li^+ transport route ^[18]. Under these conditions, the enhancement of lithium transference number is expected.

3.4 Interface stability between lithium electrode and polymer electrolyte

The interfacial stability between lithium electrode and electrolyte is a key factor since uncontrollable passivation on the lithium electrode may cause serious safety issues. The prepared ionic liquid $\text{PP}_{1201}\text{TFSI}$ contains trace amount of residual impurities and/or moisture which may increase the interfacial resistance between lithium electrode and electrolyte. Here the interfacial stability of the nano-composite polymer electrolyte is explored by measuring the A.C. impedance of the $\text{Li}/\text{NCPE-X}/\text{Li}$ ($X=0, 2$) coin-typed cell stored at room temperature under open circuit potential condition. Fig. 4-1 and Fig. 4-2 present the Nyquist spectra of NCPE-0 and NCPE-2, respectively. Fig. 5 plots the change of interfacial resistance (R_{intf}) as the function of storage time. In this study, the bulk resistance (R_{bulk}) varies slightly with the storage time, while the interfacial resistance shows obvious difference. Generally, the interfacial resistance between the polymer electrolyte and the lithium electrode is around $10^3 \Omega$, due to the imperfect contact and the formation of passivation layer on the surface of lithium electrode. It can be seen (from Fig. 4-1 and Fig. 4-2) that the pristine interfacial resistance of NCPE-0 and NCPE-2 is 250Ω and 150Ω , respectively. However, the growth rate of R_{intf} for NCPE-2 is slower than NCPE-0.

In the first 12 days, the interfacial resistance of NCPE-0 increases sharply to 850Ω , which is attributed to the formation and growth of passivation layer. In the following 4 days, the interfacial resistance of NCPE-0 increases slightly along the time and reaches a stable value of 900Ω , implying that the NCPE-0 electrolyte is compatible with the lithium electrode well. In contrast, the interfacial resistance of NCPE-2 increases slowly to 300Ω in the first 8 days, then levels up to a stable value of 400Ω , which is smaller than NCPE-0. The fluctuation of R_{intf} for NCPE-0 and NCPE-2 can be ascribed to the reason that the residual impurities and moisture maybe trapped by capillary force with the addition of nano-particles, due to the high surface area of TiO_2 ^[20]. Therefore, the reaction between the impurities and the lithium electrode is inhibited and the growth of passivation layer is limited. The property comparison between NCPE-0 and NCPE-2 indicates that TiO_2 plays an important role in the compatibility between the polymer membrane and lithium electrode.

3.5 Electrochemical stability of nano-composite polymer electrolyte

In order to study the electrochemical stability of the obtained electrolyte, the linear sweep voltammetry and cyclic voltammetry scans were performed with Pt as the working electrode and metallic Li as the counter/reference electrodes. Fig. 6-1 presents the linear sweep voltammetry scans of NCPE-0 and NCPE-2. The NCPE-0 shows two oxidation peaks starting from 3.25 V and 5.25 V , respectively. While NCPE-2 doesn't show any obvious

decomposition reaction until 6 V. The small oxidation peak observed at around 4 V for NCPE-2 may be attributed to the oxidation of some residual from the synthesis of PP₁₂₀₁TFSI. It was reported that the decomposition voltage of the PP14 based ionic liquid is about 5.2 V^[8]. It can be concluded from Fig. 6-1 that the activity of PP₁₂₀₁TFSI is attenuated with the addition of nano-particles, thus improving the stability of the corresponding nano-composite polymer electrolyte^[22, 23].

Fig. 6-2 presents the cyclic voltammetry curve of NCPE-2. There is no reaction taking place in the potential range from -0.5 V to 3 V except the deposition and stripping of Lithium. The oxidation peak at 0.25 V is ascribed to the stripping of Lithium and the reduction peak at -0.4V is considered as the Lithium deposition on the Pt electrode. Thus, the nano-composite polymer electrolyte is suitable for the application in the lithium ion battery.

3.6 Cell Testing

The charge-discharge profiles of the Li/NCPE-2/LiFePO₄ 2032 coin type cell at different rates are shown in Fig. 7-1 (at 30°C). The discharge capacity of the coin cell is 142.3 mAh·g⁻¹, 140.3 mAh·g⁻¹, 127.9 mAh·g⁻¹, 109.8 mAh·g⁻¹ at 0.1 C, 0.2 C, 0.5 C, 1 C, respectively. The inserted figure of Fig. 7-1 shows the charge-discharge performance of NCPE-0 and NCPE-2 at 0.1C, the discharge capacity of NCPE-0 and NCPE-2 is 136.4 mAh·g⁻¹ and 142.3mAh·g⁻¹, respectively. Moreover, the voltage platform of NCPE-0 is lower than that of NCPE-2. The good performance of the coin cell based on NCPE-2, especially at low C-rates, is ascribed to the relatively high ionic conductivity of NCPE-2 (about 10⁻³ s·cm⁻¹) and good interfacial stability between the polymer electrolyte and lithium metal as well^[24]. The discharge capacity of NCPE-2 fades with the increase of C-rate, which is ascribed to slow Li⁺ diffusion within the LiFePO₄ electrode which is not witted by electrolyte, the relatively low ionic conductivity compared to liquid electrolytes, and the formation of barrier potential due to the anion accumulation in the vicinity of the anode-electrolyte interface, which further hinders the motion of Li⁺ during discharge^[25].

The cycling performance of the Li/NCPE-2/LiFePO₄ coin cell is plotted in Fig. 7-2. When the cell is cycled at 0.1C and 0.2C, the discharge capacity increases gradually during the first 5-10 cycle, which is attributed to the penetration of the ionic liquid from the polymer electrolyte to the porous electrode. However, when the NCPE-2 is cycled at 0.5 C and 1 C, the discharge capacity decreases and then stabilizes at 128 mAh·g⁻¹ and 109 mAh·g⁻¹, respectively, which remains 97.6% and 93.2% of the initial capacity after 50th cycle. The inserted figure of Fig. 7-2 presents the cycling performance of NCPE-0 and NCPE-2 at 0.1C, in which the discharge capacity of NCPE-0 decreases after several cycles which may be claimed to the decomposition of polymer electrolyte. While the NCPE-2 based cell exhibits good electrochemical performance at different C-rates, which may be attributed to its high lithium transference number. The high Lithium transference number of NCPE-2 ensures the high flux of Li⁺

and can effectively alleviate the cell polarization at even high C-rate, thus leading to better electrochemical performance.

4. Conclusions

The nano-composite polymer electrolyte PVDF-HFP/PP₁₂₀₁TFSL/TiO₂ system are synthesized and tested in this paper. The effect of TiO₂ amount in this system on the crystallinity and ionic conductivity of NCPEs are systematically explored. The nano-composite polymer electrolyte (NCPE-2) exhibits the lowest crystallinity of 7.4% and highest ionic conductivity of $2 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$, which is close to the liquid electrolyte. Meanwhile, the lithium transference number and the interfacial stability between the electrolyte and metallic lithium electrode are also promoted by the addition of TiO₂. NCPE-2 shows a relatively high lithium transference number of 0.56, and small interfacial resistance compared to NCPE-0. Moreover, NCPE-2 exhibits a stable potential window up to 6 V, which indicates that NCPE-2 can be applied to the practical lithium polymer battery. When the LiFePO₄/NCPE-2/Li coin-typed cell is cycled at 0.1 C, 0.2 C, 0.5 C, 1 C, the 1st discharge capacity is 142.3 mAh·g⁻¹, 140.3 mAh·g⁻¹, 127.9 mAh·g⁻¹, 109.8 mAh·g⁻¹, respectively. Moreover, the capacity retention remains 97.6% and 93.2% of the initial discharge capacity on the 50th cycle at 0.5 C and 1 C, respectively.

Acknowledgments

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Table Captions:

Table 1 The composition and abbreviation of the synthesized nano-composite polymer electrolytes

Table 2 Thermal properties of the nano-composite polymer electrolytes

Table 3 The calculated activation energy of Li^+ conduction for nano-composite polymer electrolytes

Table 4 The data related to lithium transference number of NCPE-X (X=0, 2)

Figure Captions:

Fig. 1 DSC curves of the nano-composite polymer electrolytes, (a) NCPE-0 (b) NCPE-1 (c) NCPE-2 (d) NCPE-3 (e) NCPE-4

Fig. 2 Temperature dependence of ionic conductivity of all synthesized nano-composite polymer electrolytes

Fig. 3-1 Impedance spectra of the Li/NCPE-0/Li cell measured before and after polarization at 30 °C. Inserted figure: depolarization curve of the cell.

Fig. 3-2 Impedance spectra of the Li/NCPE-2/Li cell measured before and after polarization at 30 °C. Inserted figure: depolarization curve of the cell.

Fig. 4-1 Impedance profile of a Li/NCPE-0/Li cell measured during various storage time

Fig. 4-2 Impedance profile of a Li/NCPE-2/Li cell measured during various storage time

Fig. 5 Time dependence profiles of the interfacial resistances for NCPE-0 and NCPE-2

Fig. 6-1 Linear sweep voltammetry curve of Li NCPE-0&NCPE-2 Pt cell at the scan rate of 0.2 mV·s⁻¹

Fig. 6-2 Cyclic voltammetry curve of Li/NCPE-2/Pt cell at the scan rate of 0.2 mV·s⁻¹

Fig. 7-1 The first charge/discharge curves of Li/NCPE-2/LiFePO₄ 2032 at various C-rates

Fig. 7-2 Cycling performance of Li/NCPE-2/LiFePO₄ 2032 at various C-rates

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Table 1 The composition and abbreviation of the synthesized nano-composite polymer electrolytes

	PVDF-HFP (g)	PP ₁₂₀₁ TFSI (g)	TiO ₂ (g)	LiTFSI (g)
NCPE-0	0.3	0.2	0	0.028
NCPE-1	0.3	0.2	0.015	0.028
NCPE-2	0.3	0.2	0.030	0.028
NCPE-3	0.3	0.2	0.045	0.028
NCPE-4	0.3	0.2	0.060	0.028

Table 2 Thermal properties of the nano-composite polymer electrolytes

	NCPE-0	NCPE-1	NCPE-2	NCPE-3	NCPE-4
T_m (°C)	150.8	148.8	146.5	149.0	150.7
ΔH_m (J·g ⁻¹)	9.249	8.921	7.78	12.06	14.18
X_c (%)	8.8	8.5	7.4	11.5	13.5

Table 3 The calculated activation energy of Li^+ conduction for nano-composite polymer electrolytes

Sample	Calculated activation energy E_a ($\text{kJ}\cdot\text{mol}^{-1}$)
NCPE-0	17.06
NCPE-1	16.79
NCPE-2	10.98
NCPE-3	14.96
NCPE-4	15.25

Table 4 The data related to lithium transference number of NCPE-X (X=0, 2)

Sampl	$R_{b,0}(\Omega)$	$R_{b,s}(\Omega)$	$R_{i,0}(\Omega)$	$R_{i,s}(\Omega)$	$I_0(\text{mA})$	$I_s(\text{mA})$	t_+
e			)	)	)	)	
NCPE	12.1	17.4	557	655	0.027	0.009	0.37
-0					66	15	
NCPE	9.0	11.0	191	289	0.026	0.012	0.56
-2					74	61	