電気学会論文誌●（●●●●●●●部門誌）
IEEJ Transactions on ●●●●●●●●●●●●●●●
Vol.●● No.● pp.●-●● DOI: ●.●●/ieejeiss.●●.●

Paper

Effect of Low Temperature Conditions on Diffusion Polarization Electrolyte of Positive Electrode in Lithium-Ion Battery Charging Process

LI Wenhua* member, DU Le* Non-member, FAN Wenyi* Non-member,
JIAO Zhipeng* Non-member,

(Manuscript received Jan. 00, 20XX, revised May 00, 20XX)

Abstract the charging performance of lithium-ion batteries is greatly affected by the ambient temperature. The problem of increasing the charging polarization voltage and lowering the charging capacity under low temperature conditions has always limited the development of lithium-ion batteries.Based on the theory of electrochemical kinetics, charge conservation, mass conservation and energy conservation, an electrochemical-thermal coupled transient calculation model based on $LiFePO_4$/graphite lithium-ion battery was established.The model studies the variation of the terminal voltage and the diffusion polarization voltage electrolyte of the positive electrode with the SOC during the charging process of lithium-ion battery under the three low temperature conditions of -5ºC, -10ºC and -15ºC. The variable P_{dep} is used to quantitatively analyze the effect of low temperature conditions on the diffusion polarization electrolyte of positive electrode. Finally, the cause of the polarization change is analyzed by the electrolyte salt concentration and the electrolyte current density.The results show that the low temperature condition will increase the diffusion polarization electrolyte of positive electrode of the lithium-ion battery to a certain extent, and the lower the temperature, the stronger the polarization effect, and the positive electrode electrolyte concentration and electrolyte current density can better characterize this phenomenon.

Keywords : lithium-ion battery, low temperature conditions, charging process, diffusion polarization in electrolyte, positive electrode

1. Introduction

Lithium-ion batteries have promoted the rapid development of hybrid vehicles and electric vehicles due to their high energy density, high power density and long cycle life [1-3]. The influence of ambient temperature on the charging of lithium-ion battery is very obvious , and the ambient temperature in most parts of northern China is below 0ºC for a long time. The low temperature environment changes the conductivity of the electrode material and the viscosity of the electrolyte, and changes the charging polarization characteristics of the lithium-ion battery to some extent. Charging in a severe low temperature environment, lithium dendrite is also formed inside the lithium-ion battery. It has a great impact on the safety of charge and discharge of lithium-ion batteries [4,5].

In view of the phenomenon of charging polarization and low temperature operation of lithium-ion batteries, relevant scholars have made some research. Feng et al. [6] designed a kind of polypropylene/hydrophobic silica-aerogel-composite (SAC) separator which provided a new way to improve the safety and simultaneously reduce the polarization of the lithium-ion batteries. Bo et al. [7] calculated the average variables such as lithium-ion concentration and reaction current density, and polarization due to different sub-processes, such as activation of electrochemical in each subdomain finding that microstructural inhomogeneity in the 3D model has significant impact on global polarization and polarization distribution in the electrode reactions (PAER) and charge transport of species. Yu et al. [8] introduced an approach to compensating the capacity loss of LTO based lithium-ion batteries at low temperature by increasing the charging cut-off voltage which enlarge the charging capacity of the LTO batteries at -20ºC.

In this paper, the electrochemical-thermal coupled transient calculation model of LiFePO4/graphite lithium-ion battery was built based on the model proposed Nyman et al. [9] using simulation software COMSOL Multiphysics 5.4. The diffusion polarization electrolyte of positive electrode during the 1C constant current charging of lithium-ion batteries at three low temperature environments of -5ºC, -10ºC and -15ºC were studied.

2. Coupled Electrochemical-thermal Model

2.1 Computational Domain and Model Assumptions

A cylindrical 18650 lithium-ion battery was used as the research object to establish a coupled electrochemical-thermal model. The model consists of a one-dimensional electrochemical component and a three-dimensional solid heat transfer component. The one-dimensional electrochemical component simulates the electrochemical reaction kinetics, mass transfer, and current balance of a lithium-ion battery [10,11]. The three-dimensional solid heat transfer component simulates the temperature field distribution of the battery and the heat transfer process with the external environment. The model couples the heat of the one-dimensional electrochemical component with the temperature of the three-dimensional heat transfer component, more realistically reflecting the effect of temperature on the charging process of the lithium-ion battery [12].

In the model, the negative current collector material is metal copper, the positive current collector material is metal aluminum,

a) Correspondence to: LI Shuang. E-mail:1069816489@qq.com
* Hebei University of Technology.
No.8, GuangRong Street, HongQiao District, Tianjin, China

the negative active material is graphite (C_6), the electrolyte is $LiPF_6$ solution (3:7 EC/EMC solvent), and the positive active material is lithium-ion phosphate (LFP)[13].The model assumes that the electrode active material consists of ideal spherical particles of uniform size, regardless of the electric double layer effect, the reaction occurs only at the electrode/electrolyte interface, and no secondary reactions occur in the reaction process, and no gas is generated [14]. The 18650 lithium-ion battery has a multi-layer winding structure [15]. The one-dimensional electrochemical component simplifies the battery into a linear structure on the model according to the main moving direction of lithium ions during the actual charging process of the battery, as shown in Figure 1.

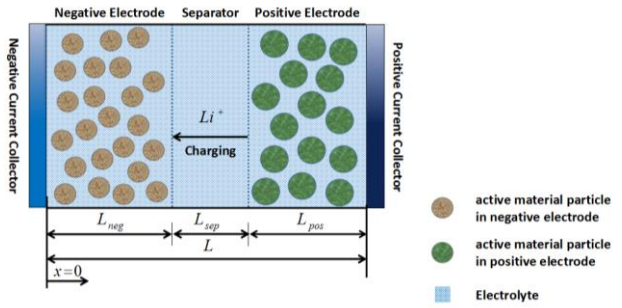

Fig.1. Electrochemical charging diagram of lithium-ion battery

During the charging process of the lithium-ion battery, the positive electrode material in the lithium-rich state undergoes oxidation reaction and loses electron-generated lithium ions. This part of lithium ions enters the electrolyte and diffuses through the separator to the negative electrode and electrolyte, and the electrons reach the negative electrode from the external circuit.During the charging process of the lithium-ion battery, the positive electrode material in the lithium-rich state undergoes oxidation reaction and loses electron-generated lithium ions [16-18]. This part of lithium ions enters the electrolyte and diffuses through the separator to the negative electrode electrolyte, and the electrons reach the negative electrode and the negative electrode from the external circuit. The lithium ion in the electrolyte undergoes a reduction reaction to form a solid lithium embedded in the negative electrode. Because the transmission speed of electrons in the external circuit is much larger than the movement speed of lithium ions in the electrolyte, this causes an imbalance in the ion concentration distribution inside the lithium ion battery to cause polarization phenomenon [19]. The equation for the above electrochemical process is as follows:

Positive Electrode :

$$Li_yFePO_4 \xrightarrow{charge} Li_{y-z}FePO_4 + zLi^+ + ze^- \quad \cdots\cdots (1)$$

Negative Electrode :

$$Li_{x-z}C_6 + zLi^+ + ze^- \xrightarrow{charge} Li_xC_6 \quad \cdots\cdots (2)$$

where x is the stoichiometric coefficient or the number of moles of lithium present in the graphite structure (C_6), y is the stoichiometric coefficient or the number of moles of lithium in the olivine structure of iron phosphate ($FePO_4$), Li^+ is the lithium-ion, z is the number of moles of lithium taking part in the electrochemical reaction.

2.2 Electrochemical Kinetics The Butler-Volmer equation in electrode dynamics gives a calculation of the local reaction current density:

$$j_n = j_0\{\exp[\frac{\alpha_a F}{RT}\eta] - \exp[-\frac{\alpha_c F}{RT}\eta]\} \quad \cdots\cdots (3)$$

where j_0 is the exchange current density, α_a and α_c are the charge transfer coefficients, F is the Faraday constant, R is the molar gas constant, T is the reaction thermodynamic temperature, η is the reaction overvoltage.

The exchange current density is given by

$$j_0 = Fk_0 c_l^{\alpha_a}(c_{s,\max} - c_{s,surf})^{\alpha_a} c_{s,surf}^{\alpha_c} \quad \cdots\cdots (4)$$

where k_0 is the reaction rate constant, c_l is the electrolyte salt concentration, $c_{s,max}$ is the maximum lithium concentration in the active electrodes, $c_{s,surf}$ is the surface lithium concentration in the active electrodes.

The reaction overvoltage is given by

$$\eta = \phi_s - \phi_l - U_{eq} \quad \cdots\cdots (5)$$

where ϕ_s is the solid phase potential, where ϕ_l is the liquid phase potential, U_{eq} is the electrode equilibrium potential.

2.3 Charge Conservation The governing equation of charge conservation in electrode can be described as follows:

$$\nabla \cdot i_s + \nabla \cdot i_l = 0 \quad \nabla \cdot i_s = -S_a j_n \quad \nabla \cdot i_l = -S_a j_n \quad \cdots (6)$$

where i_s is the electronic current density in the electrode, i_l is the ionic current density in the electrolyte, and S_a is the specific surface area.

2.3.1 Charge Conservation in Electrode The transport of electrons in the electrode follows Ohm’s law which can be expressed as follows:

$$i_s = -\sigma_s^{eff}\nabla\phi_s \quad \cdots\cdots (7)$$

Where σ_s^{eff} is the effective electrical conductivity of electrode.

2.3.2 Charge Conservation in Electrolyte The transport of lithium ions in electrolyte can be expressed as follows:

$$i_s = -\sigma_l^{eff}\nabla\phi_l + \frac{2RT\sigma_l^{eff}}{F}(1+\frac{\partial \ln f_{\pm}}{\partial \ln c_l})(1-t_+)\nabla(\ln c_l) \quad \cdots (8)$$

Where σ_l^{eff} is the effective electrical conductivity of electrolyte, $f_{\pm}$ is the average molar activity coefficient, t_+ is the transferring number of lithium ions in electrolyte.

2.4 Mass Conservation

2.4.1 Lithium in Electrode Material Active Particles

The mass conservation of lithium in electrode material active particles can be described by Fick’s law:

$$\frac{\partial c_s}{\partial t} + \frac{1}{r^2}\frac{\partial}{\partial r}(-r^2 D_s \frac{\partial c_s}{\partial r}) = 0 \quad \cdots\cdots (9)$$

where c_s is the concentration of lithium in electrode material active particles, t is the time, r is the radial coordinate inside a spherical particle of electrode material, D_s diffusion coefficient of lithium in the active material.

2.4.2 Lithium in Electrolyte

The mass conservation of lithium in electrolyte can be expressed as follows:

$$\varepsilon_l \frac{\partial c_l}{\partial t} + \nabla \cdot J_l = \frac{S_a}{F} \quad \cdots\cdots (10)$$

$$J_l = -D_l^{eff} \nabla c_l + \frac{i_l \cdot t_+}{F} \quad \cdots\cdots (11)$$

where ε_l is the electrolyte volume fraction in the electrode, Jl is the molar flux of lithium ions, D_l^{eff} is the effective diffusion coefficient of lithium ions in the electrolyte.

2.5 Energy Conservation Due to the different heat generation mechanism during charging and discharging, the heat of the lithium-ion battery is derived from reaction heat, Q_{rea}, ohmic heat, Q_{ohm}, activation polarization heat, Q_{act}. The energy conservation in the lithium-ion battery can be expressed as follows:

$$\rho C_p \frac{\partial T}{\partial t} - \lambda \nabla^2 T = Q_{rea} + Q_{act} + Q_{ohm} \quad \cdots\cdots (12)$$

where the ρ is the density, C_p is the heat capacity, λ is the thermal conductivity.

The reaction heat that due to electrochemical reaction can be expressed as follows:

$$Q_{rea} = S_a j_n T \frac{\partial U_{eq}}{\partial T} = S_a j_n T \frac{\Delta S}{F} \quad \cdots\cdots (13)$$

The ohmic heat that due to electrical ohmic losses in electrode and ionic losses electrolyte can be expressed as follows:

$$Q_{ohm} = -i_1 \cdot \nabla \phi_1 - i_2 \cdot \nabla \phi_2 \quad \cdots\cdots (14)$$

The activation polarization heat that due to electrochemical reaction polarization between the particle surface of the active material and the electrolyte can be expressed as follows:

$$Q_{act} = S_a j_n \eta \quad \cdots\cdots (15)$$

2.6 Diffusion Polarization Electrolyte of Positive Electrode According to the different generation mechanism, the charge and discharge polarization of lithium-ion batteries is divided into ohmic polarization, electrochemical polarization and concentration polarization [20]. The polarization phenomenon is closely related to the ambient temperature of the lithium-ion battery, the charge and discharge current, and the battery SOC [21-23]. Lithium-ion batteries belong to the electrochemical product so the generation of polarization voltage appears with charge and discharge and this phenomenon can not be eliminated.This paper focuses on the low temperature characteristics of the diffusion polarization electrolyte of the positive electrode.The average polarization voltage is as follows [7]:

$$P_v = -\frac{1}{J_t} \int_+ \frac{2RT}{c_l F} \kappa_c \frac{\partial c_l}{\partial x} J_l dx \quad \cdots\cdots (16)$$

where the J_t is the total current per cross-sectional area, κ_c is the concentration conductivity.

The total current per cross-sectional area can be expressed as follows:

$$J_t = \int_+ S_a j_n dx \quad \cdots\cdots (17)$$

2.7 Model Validation In order to verify the validity of the model, a Chinses manufacturer's LR1865EC lithium-ion battery (nominal voltage 3.2V, nominal capacity 1.3Ah, charge cut-off voltage 3.6V) was used as the test sample, and the Arbin-LBT battery test system and The temperature box is the test platform. The test samples are subjected to 1C constant current charging test under the three low temperature conditions of -5ºC, -10ºC and -15ºC respectively. The structure of the test platform is shown in the Figure 2.

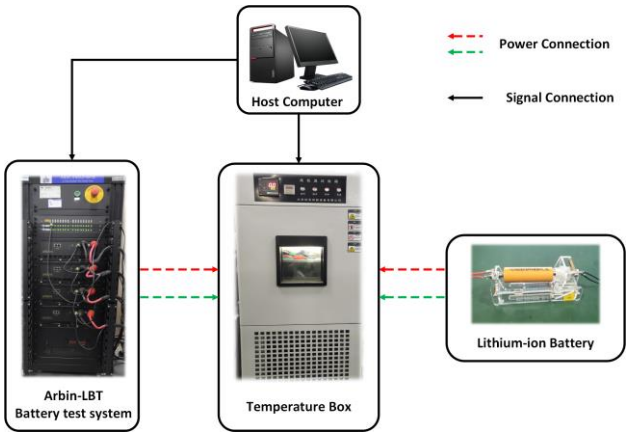

Fig. 2. Experimental setup of charging system in low temperature.

In the state of full battery, the commercial lithium-ion battery is surrounded by an outer protective shell, which is a very closed system. The data of the positive electrode, the separator, the negative electrode is difficult to collect.Therefore, in this paper, the validity of the model is verified from the side by comparing

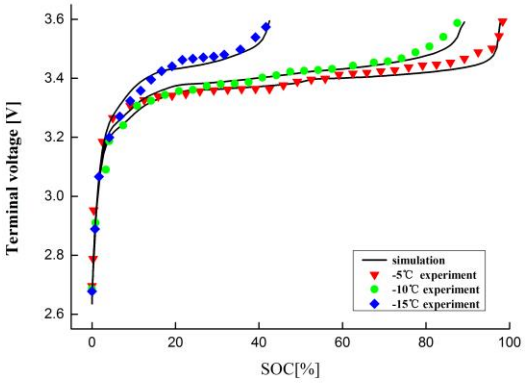

Fig. 3. -5ºC, -10ºC, -15ºC,1C charge validations.

IEEJ Trans. ●●, Vol.●●, No.●, ●●●

the experimental and simulated values of the charging terminal voltage curve of the lithium-ion battery [24,25]. At the same temperature, a total of 4 samples are tested simultaneously, and the average voltage of the four samples is taken at the same time. Figure 3 is a comparison of the test results and simulation results of the 1C constant current charging terminal voltage in three low temperature environments. It can be seen that the simulated values and experimental values are consistent at three temperatures, indicating that the model has good accuracy.

3. Results

3.1 Diffusion Polarization Voltage of Positive Electrode in Electrolyte Figure 4 shows the variation of diffusion polarization voltage of positive electrode in electrolyte with the overall SOC of the battery in three low temperature environments. It can be seen from the figure that the diffusion polarization voltage in electrolyte is divided into three stages: initial period, plateau period and rising period. These three stages together constitute a basic trend of rising first, then stabilizing and finally rising again, and the temperature decrease does not affect the trend of this polarization voltage , which indicates that diffusion polarization voltage of positive electrode in electrolyte is independent of the SOC of lithium-ion battery but is related to the charging process.

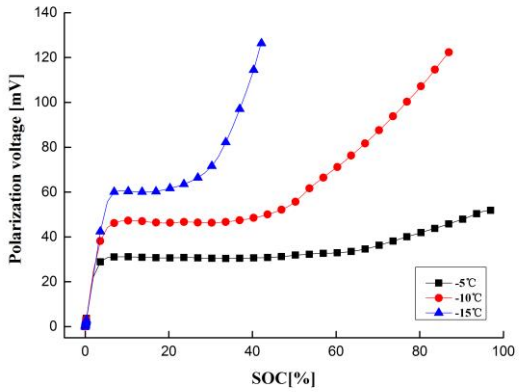

Fig. 4. -5ºC, -10ºC, -15ºC,1C charge validations.

The variables SOC_1, SOC_2, and SOC_3 are set to represent the initial battery SOC during the plateau period, the initial battery SOC and the charge end SOC of the rising period of diffusion polarization voltage of positive electrode in electrolyte, respectively; the variables V_{pp_ave} and V_{pr_max} are set to represent average polarization voltage value during the plateau period and the maximum polarization voltage value during the rise period, respectively.Table 1 shows the values of each variable under three low temperature conditions.

Table 1. Variable value table in polarization voltage curve.

Temperature	SOC_1	SOC_2	SOC_3	V_{pp_ave}	V_{pr_max}
-5ºC	5.28%	66.94%	96.94%	31.39 mV	51.85 mV
-10ºC	5.28%	50.28%	86.94%	47.82 mV	122.37 mV
-15ºC	6.94%	20.28%	42.14%	60.48 mV	126.35 mV

It can be seen from Table 4 that the decrease of the ambient temperature in the initial period will not affect the value of SOC_1, and this variable will only increase slightly at -15ºC. As the temperature decreases, average value of the polarization voltage during the plateau period V_{pp_ave} will gradually increase.The SOC interval of the platform period is gradually shortened, it can be seen the SOC interval width of the -15ºC in the platform period is only 21.63% at -5ºC, while the average value of the polarization voltage V_{pp_ave} is 192.67% at -5ºC. The polarization voltage will be significantly different in the three ambient temperatures during the rising period, the slowest rise and the minimum peak value of the polarization voltage appear at -5ºC, the fastest rise and the maximum peak value of polarization voltage appear at -15ºC, which indicates the lower temperature at this stage, the faster the polarization voltage changes, and the more severe the degree of diffusion polarization voltage of positive electrode in electrolyte.

The above variables can well explain the change about diffusion polarization voltage of positive electrode in electrolyte. In this paper, the dimensionless function P_{dpe} is used to characterize the degree of this kind polarizationat low temperature.Its definition is as follows.

$$P_{dpe} = \frac{V_{pp\_ave}}{SOC_2 - SOC_1} \frac{V_{pr\_\max} - V_{pp\_ave}}{SOC_3 - SOC_2} \quad \cdots\cdots\cdots (16)$$

It can be seen from the values in the Table 2 that the temperature decrease will enhance the diffusion polarization voltage of positive electrode in electrolyte, Especially when it reaches -15ºC, this phenomenon will increase significantly.When the ambient temperature is -10ºC and -5ºC, the value is 2.49% and 15.81% of the value at -15ºC, respectively.

Table 2. Variable value table in polarization voltage curve.

Temperature	-5ºC	-10ºC	-15ºC
P_{dpe}	0.34	2.16	13.66

3.2 Analysis of Positive Electrolyte Salt Concentration Gradient The main cause of diffusion polarization in electrolyte is the accumulation of lithium-ion concentration gradient in the electrolyte, and the main manifestation of this accumulation is the time-space distribution of the positive electrolyte salt concentration.

During charging, charge transferring and generation of a large amount of lithium ions occur simultaneously in the oxidation reaction of the positive electrode material.These lithium ions move toward the separator under the interaction of electric field force and concentration gradient, but the movement speed of lithium ions is relatively slow and the porous electrode material has a certain thickness，lithium-ions near the side of separator will preferentially enter the separator, and lithium ions near the side of the current collector will lag behind,which caused the phenomenon that the electrolyte salt concentration near the collector side will be higher than the side close to the separator in the positive porous electrode and the concentration gradient is thus formed.The decrease in temperature has a negative effect on the conductivity, activity dependence and diffusion coefficient of the electrolyte. Macroscopically, the viscosity of the electrolyte

increases, which makes the diffusion of ions slower and the diffusion polarization of positive electrode in electrolyte is more serious.

Figure 5, Figure 6 and Figure 7 show the change of electrolyte salt concentration with time in the thickness direction of the positive electrode under three low temperature conditions respectively.The conclusions we can draw are as follows.

(1)The electrolyte salt concentration in three low temperature environments has a process of first rising, then stabilizing, and finally rising again during charging progress.This is because the addition of lithium ions at the initial stage of charging causes a rapid increase in the initial concentration of the electrolyte.During the middle of charging,the generation and diffusion of lithium ions will balance the electrolyte salt concentration. However, as the degree of charging increases, the ability of the negative electrode to receive lithium ions decreases, and the salt concentration in the negative pore electrode increases, which cause the decreasing of concentration gradient in the lithium ion battery as a whole ,the reduction of diffusion effect in positive electrolyte and the accumulation of lithium ions in the positive electrode.As a result, the concentration of the positive electrolyte salt finally rises once.It can be seen from the following three figures that the gradual decrease in temperature causes the liquid phase diffusion ability of lithium ions in positive to decrease, resulting in an overall rise of electrolyte concentration in the middle and late charging stages.

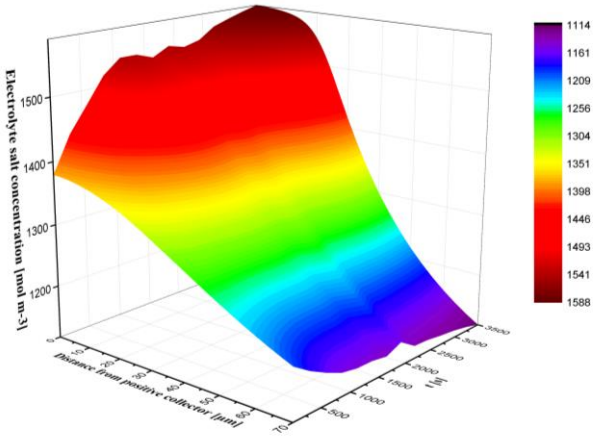

Fig. 5. Time and space distribution of electrolyte salt concentration at -5ºC.

(2) Time accumulation of electrolyte salt concentration: the overall level of electrolyte salt concentration under three low temperature conditions has greatly improved with time.It can be seen from Figure 5 that the electrolytic salt concentration will not exceed 1600 mol/m^3 during the entire charging process at -5ºC, but the electrolytic salt concentration within 150 s will reach or exceed this in the low temperature conditions of -10ºC and -15ºC.which can be seen from Figure 6 and Figure 7.This is due to the influence of low temperature on the diffusion coefficient and other parameters of positive electrolyte. As the charge progresses, the positive electrode continuously generates lithium ions by the charge transfer of the oxidation reaction, but as the temperature decreases, the parameters such as the liquid phase diffusion coefficient are continuously reduced.The generated lithium ions cannot be moved to the side close to the separator in time, so that the electrolyte salt concentration is increased as a whole.

(3) Spatial accumulation of electrolyte salt concentration:Since the continuously generated lithium ions cannot diffuse to the side of separator in time, as the temperature decreases, lithium ions will accumulate to a certain extent at the side of the current collector, which is evident in Figure 7.It can be seen from Figure 7 that a stable concentration appears near the end of the current collector at 600s, and as the charge progresses, this concentration increases in the thickness direction of the electrode to cause an electrolyte salt concentration platform which is also a certain manifestation in Figure 6.This indicates that under certain low temperature conditions, the lithium ions near the side of the current collector appear to diffusion stagnation. The phenomenon that the lithium ions are continuously generated but cannot be time-shifted greatly aggravates the diffusion polarization of positive electrode in electrolyte at low-temperature charging progress.

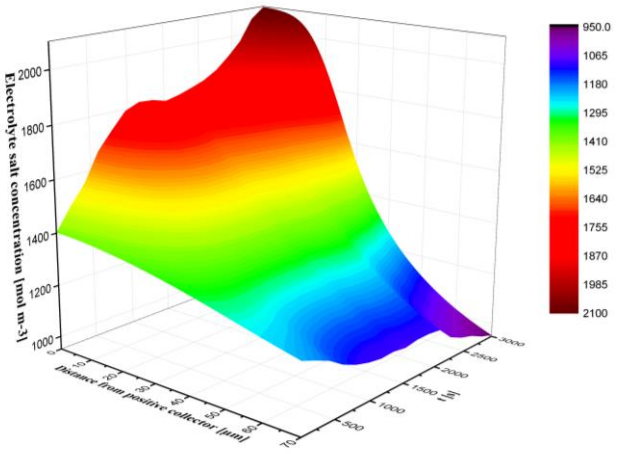

Fig. 6. Time and space distribution of electrolyte salt concentration at -10ºC

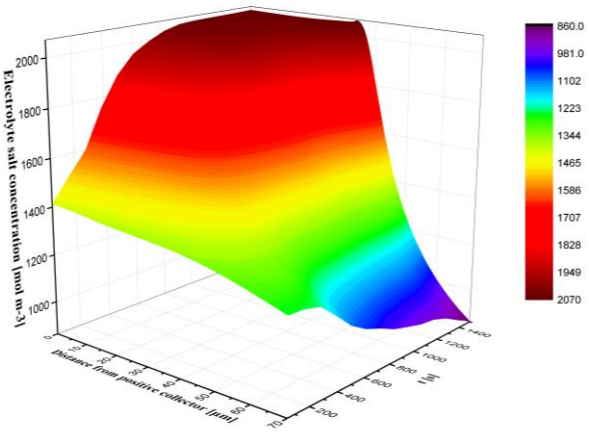

Fig. 7. Time and space distribution of electrolyte salt concentration at -15ºC

3.3 Analysis of Positive Electrolyte Current Density The current in the external circuit comes from the movement of electrons and the current in the electrolyte comes from the movement of lithium ions.The electrolyte salt concentration can only indicate the instantaneous distribution of lithium ions in the electrolyte and the electrolyte current density can indicate the rate

of movement of lithium ions in the electrolyte.The electrolyte salt concentration can only indicate the instantaneous distribution of lithium ions in the electrolyte and the electrolyte current density can indicate the rate of movement of lithium ions.This explains the accumulation of lithium ion concentration gradients in the electrolyte from another perspective, and also explains the diffusion polarization of positive electrode in electrolyte.

Figure 8 shows the distribution of electrolyte current density in the thickness direction of the positive electrode under three low temperature conditions at 300s. The positive electrode current density generally shows a tendency to grow from the current collector to the separator in the thickness direction, and the initial value and the peak value are consistent. This is because the positive electrode generates lithium ions simultaneously in the thickness direction while charging in the one-dimensional electrochemical model,but these lithium ions move toward one end of the separator.The greater the lithium ion flux near the end of the membrane, the greater the corresponding electrolyte current density, reaching a maximum at the junction where the positive electrode is connected to the separator.

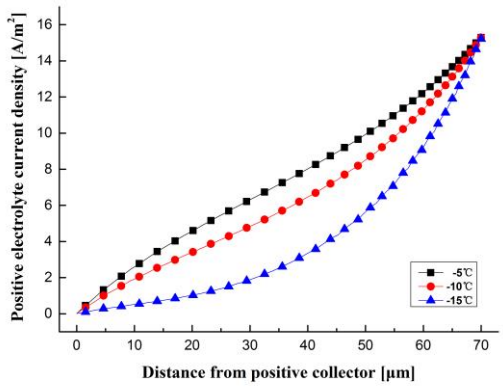

Fig. 8. Positive electrolyte current density at 300s

Figure 8 shows the distribution of electrolyte current density in the thickness direction of the positive electrode under three low temperature conditions at 300 s.

At 300s, the decrease in temperature will cause the current density of the positive electrolyte to decrease, resulting in the lowest electrode current density at the same thickness of the positive electrode at -15ºC, the highest at -5ºC. And this gap is the largest at the midpoint of the positive electrode thickness.On the other hand, the gradual decrease in temperature causes a certain increase in the growth rate of the electrolyte current density. From Figure 8, it can be seen that the electrolyte current density increases fastest at -15ºC. This is because the decrease in temperature increases the viscosity of the electrolyte, which causes the movement speed of lithium ions to be slower at the same thickness, so that the corresponding current density decreases as the temperature decreases. However, the decrease in temperature also aggravates the accumulation of lithium ion concentration in the liquid phase, so that the absolute value of the lithium ion flux on the adjacent back end unit is relatively large.Thus, the lower the temperature, the faster the current density of the positive electrode electrolyte grows.

Figure 9 is a distribution diagram of the current density of the positive electrode electrolyte. Under the three low temperature conditions, a certain current density platform appears in the positive electrolyte during charging, wherein the -5ºC and -10ºC corresponding platforms appear in the part near the separator, and the platform height is consistent with the maximum current density; and the -15ºC corresponding platform appears near the current collector, and the platform is close to zero.

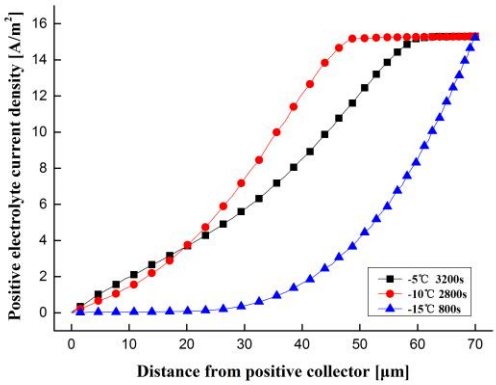

Fig. 9. Positive electrolyte current density at the end of charging

This is because the increase in electrolyte viscosity caused by the decrease of temperature has a cumulative phenomenon of electrolyte salt concentration. The above curve shows that the accumulation of -5ºC and -10ºC appears on the side close to the separator because the current density at the intersection of the separator and the electrode is constant but the accumulated lithium ion concentration near the side of the separator exceeds the requirement corresponding to the maximum current density, and the positive current has a maximum current density within a certain width near the side of the separator.At -15ºC, the electrolyte viscosity is further increased due to further decrease in temperature, and a large amount of lithium ions generated by the oxidation reaction on the side close to the current collector cannot be actively transported to the side of the separator, and the retention of lithium ions causes the electrolyte current density to be almost zero. The phenomenon, which at the same time corresponds to the electrolyte concentration platform in Figure 7.

4 Conclusions In this paper, the electrochemical-thermal model was used to study the variation of the diffusion polarization electrolyte of positive electrode in the low-temperature conditions under the constant-current charging process, and the degree of this polarization was characterized by the variable Pdpe, and the cause of this polarization change was analyzed further by the electrolyte salt concentration and electrolyte current density. The conclusion is as follows.

(1)The low temperature condition increases the diffusion polarization electrolyte of positive electrode in the process during constant current charging of lithium ion battery to a certain extent, and the lower the temperature, the greater the degree of influence.

(2)The spatial and temporal distribution of electrolyte salt concentration and electrolyte current density in the thickness

direction of the electrode explains the effect of the accumulation of concentration gradient on diffusion polarization of positive electrode in electrolyte from another point of view.

Acknowledgement

This research was financially supported by Natural Science Foundation of Hebei Province (E2016202206).

References

(1) Meng X, Zhang Z. Xia, et al. Two-dimensional electrochemical–thermal coupled modeling of cylindrical $LiFePO_4$ batteries. Journal of Power Sources. 2014, 256, 233-243.
(2) Jie L, Yun C, et al. 3D simulation on the internal distributed properties of lithium-ion battery with planar tabbed configuration. Journal of Power Sources. 2015, 293, 993-1005.
(3) Yilmaz M, Krein P.T. Review of battery charger topologies, charging power Transactions on Power Electronics,2013, 28(5), 2151-2169.
(4) Zhang S.S, Xu K, Jow T.R. A new approach toward improved low temperature performance of li-ion battery. Electrochemistry Communications. 2002 , 4(11), 928-932.
(5) Wang T, Wu X, et al. Performance of plug-in hybrid electric vehicle under low temperature condition and economy analysis of battery pre-heating. Journal of Power Sources. 2018, 401, 245-354.
(6) Feng G, Li Z, et al. Polypropylene/hydrophobic-silica-aerogel-composite separator induced enhanced safety and low polarization for lithium-ion batteries. Journal of Power Sources, 2018,376, 177-183.
(7) Bo Y, Lim C, et al. Analysis of polarization in realistic li ion battery electrode microstructure using numerical simulation. Electrochimica Acta. 2015, 185, 125-141.
(8) Yu W,Zhengyu C, et al. Overcharge durability of $Li_4Ti_5O_{12}$ based lithium-ion batteries at low temperature. Journal of Energy Storage, 2018,19, 302-310.
(9) Nyman A, Zavalis, T.G, et al. Analysis of the polarization in a Li-ion battery cell by numerical simulations. Journal of the Electrochemical Society, 2010, 157,1236–1246.
(10) Meng X, Choe S.Y. Dynamic modeling and analysis of a pouch type $LiMn_2O_4$/carbon high power li-polymer battery based on electrochemical-thermal principles. Journal of Power Sources,2012 218, 357-367.
(11) Amiribavandpour P, Shen W, et al. An improved theoretical electrochemical-thermal modelling of lithium-ion battery packs in electric vehicles. Journal of Power Sources, 2015,284, 328-338.
(12) Han X, Ouyang M, et al. A comparative study of commercial lithium ion battery cycle life in electrical vehicle: aging mechanism identification. Journal of Power Sources, 2014, 251(2), 38-54.
(13) Krieger E.M, Cannarella J, Arnold C.B. A comparison of lead-acid and lithium-based battery behavior and capacity fade in off-grid renewable charging applications. Energy, 2013, 60(4), 492-500.
(14) Li J, Wang L, et al. New method for parameter estimation of an electrochemical-thermal coupling model for $liCO_2$ battery. Journal of Power Sources, 2016,307, 220-230.
(15) Bahiraei F, Fartaj A, Nazri, G.A. Electrochemical-thermal modeling to evaluate active thermal management of a lithium-ion battery module. Electrochimica Acta, 2017, 254,59-71.
(16) Wu X, Viswanathan V.V, et al. Investigation on the charging process of Li_2O_2-based air electrodes in Li-O_2 batteries with organic carbonate electrolytes. Journal of Power Sources, 2011, 196, 3894-3899.
(17) Guo S, Li H, et al. Numerical simulation study on optimizing charging process of the direct contact mobilized thermal energy storage. Applied Energy, 2013,112, 1416-1423.
(18) Xue X, Wang S, et al. Hybridizing energy conversion and storage in a mechanical-to-electrochemical process for self-charging power cell. Nano Letters, 2012, 12(9), 5048-5054.
(19) Jie L, Yun C, et al.An electrochemical–thermal model based on dynamic responses forlithium iron phosphate battery. Journal of Power Sources, 2014, 255(6), 130-143.
(20) Yang S, Deng C, et al. State of Charge Estimation for Lithium-Ion Battery with a Temperature-Compensated Model. Energies, 2017, 10(10), 1560.
(21) Jiang J, Liu Q, et al.. Evaluation of acceptable charging current of power Li-Ion batteries based on polarization characteristics. IEEE Transactions on Industrial Electronics, 2014, 61(12), 6844-6851.
(22) Noelle D.J, Meng W, et al. Internal resistance and polarization dynamics of lithium-ion batteries upon internal shorting. Applied Energy, 2018, 212, 796-808.
(23) Bazak J.D, Krachkovskiy S.A, Goward G.R. Multi-temperature in situ magnetic resonance imaging of polarization and salt precipitation in lithium-ion battery electrolytes. Journal of Physical Chemistry C, 2017, 121(38).
(24) Severin L.H, Mathias S, et al. Quantitative validation of calendar aging models for lithium-ion batteries. Journal of Power Sources, 2018, 400, 402-414
(25) Ye Y, Shi Y, et al. Electro-thermal modeling and experimental validation for lithium ion battery. Journal of Power Sources, 2012, 199(1), 227-238.

Nomenclature

List of Symbols

x	Distance in porous electrode(m)
r	Particle radius(m)
L	thickness of battery component(m)
j_n	Local reaction current density(A m^{-2})
j_0	Exchange current density(A m-2)
j_t	Total current per cross-sectional area(A m^{-2})
T	Reaction thermodynamic temperature(K)
k_0	Reaction rate constant
c_s	Concentration of lithium in electrode material active particles(mol m^{-3})
c_l	Electrolyte salt concentration(mol m^{-3})
D_s	Diffusion coefficient of electrode
D_l	Diffusion coefficient of electrolyte
k	thermal conductivity (W (m K)$^{-1}$)
SOC	State of charge
Q_{rea}	Reaction heat(W m^{-3})
Q_{ohm}	Ohmic heat(W m^{-3})
Q_{act}	Activation polarization heat(W m^{-3})

Greek

η	Over potential(V)
α_a	Transfer coefficient in positive electrode
α_c	Transfer coefficient in negative electrode
ϕ_s	Solid phase potential(V)
ϕ_l	Liquid phase potential(V)
σ_s	Electronic conductivity of electrode(S m^{-1})
σ_l	Ionic conductivity of electrolyte (S m^{-1})
ε_s	Active material volume fraction
ε_l	Electrolyte volume fractioncon
κ_c	Concentration conductivity

Subscripts and Superscripts

neg	Negative electrode
sep	Separator
pos	Positive electrode
s	Solid phase
l	Liquid phase
t	Tota
eff	Effective value
surf	Surface of active material particle

Appendix A. Dynamic Variables

The model in this paper is calculated under three different low temperature conditions. Many important variables in the model will vary with temperature and electrolyte salt concentration. These variables are as follows:

Table A1. Variable expression that changes with temperature and electrolyte salt concentration.

Variable	Expression
$D_{s,neg}(T)$	$D_{s,neg}=3.9\times10^{-14}\exp(-\frac{E_{s,D,neg}}{R}(\frac{1}{T}-\frac{1}{T_{ref}}))$
$D_{s,pos}(T)$	$D_{s,pos}=\frac{1.18\times10^{-18}}{(1+y)^{1.6}}\exp(-\frac{E_{s,D,pos}}{R}(\frac{1}{T}-\frac{1}{T_{ref}}))$
$k_{s,neg}(T)$	$k_{s,neg}=3\times10^{-11}\exp(-\frac{E_{s,k,neg}}{R}(\frac{1}{T}-\frac{1}{T_{ref}}))$
$k_{s,pos}(T)$	$k_{s,neg}=3\times10^{-11}\exp(-\frac{E_{s,k,neg}}{R}(\frac{1}{T}-\frac{1}{T_{ref}}))$
$D_l(c_l,T)$	$D_l=1\times10^{-4}\times10^{-4.43-\frac{54.0}{T-229.0-0.005C}-2.2\times10^{-4}c_l}$
$k_l(c_l,T)$	$k_l=1.12\times10^{-4}(-8.2488+0.0532848T-2.9871\times10^{-5}T^2+0.26235c_l$ $-9.3063\times10^{-3}c_lT+8.069\times10^{-6}c_lT^2+0.22002{c_l}^2-1.765\times10^{-4}{c_l}^2T)$
$\nu(c_l,T)$	$\nu=0.601-0.24\sqrt{10^{-3}c_l}+0.982(1-0.0052(T-294.0)\sqrt{10^{-9}{c_l}^3})$
$t_+(c_l,T)$	$t_+=2.67\times10^{-4}\exp(\frac{833}{T})(\frac{c_l}{1000})+3.09\times10^{-3}\times\exp(\frac{653}{T})(\frac{c_l}{1000})+0.517\exp(-\frac{49.6}{T})$
$\sigma_l(c_l,T)$	$\sigma_l=10^{-4}c_l\times1.2544\times(-8.22c88+-0.053248T-2.987\times10^{-5}T^2+0.26235\times10^{-3}c_l$ $-9.3063\times10^{-3}\times0.001c_lT+8.069\times10^{-6}\times0.001c_lT^2+0.220022\times10^{-6}c_l^2T)^2$

Appendix B. List of Material Parameters in the Model

Table A2. Material parameters used in model.

Parameter	Unit	Negative Electrode	Separator	Positive Electrode
L	μm	34	25	70
r	μm	0.0365	-	3.5
ε_s		0.56	-	0.435
ε_l		0.268	0.54	0.306
$c_{s,max}$	mol m^{-3}	31370	-	22806
$c_{l,0}$	mol m^{-3}	-	1200	-
α_a		0.5	-	0.5
α_c		0.5	-	0.5
D_s	m^2 s^{-1}	Table A1	-	Table A1
D_l	m^2 s^{-1}	-	Table A1	-
k_s	$m^{2.5}mol^{-0.5}s^{-1}$	Table A1	-	Table A1
k_l	$m^{2.5}mol^{-0.5}s^{-1}$	-	Table A1	-
$E_{s,D}$	kj mol^{-1}	35	-	35

$E_{s,k}$	kj mol^{-1}	30	-	20
σ_s	S m^{-1}	100		0.1
Dl		-	Table A1	-
kl		-	Table A1	-
ν		-	Table A1	-
t_+		-	Table A1	-
σ_l		-	Table A1	-
k	W m^{-1} K^{-1}	1.04	1	1.48
ρ	Kg m^{-3}	2660	492	1500
cp,s	J kg^{-1} K^{-1}	1437	700	1260
cp,l	J kg^{-1} K^{-1}		2055	
T_{ref}	K		273.15	
F	C mol^{-1}		96487	