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Materials

Forecasting conductivities of LiBOB-EC/DEC electrolytes by the mass triangle model

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Abstract: Conductivities of lithium bis(oxalato)borate (LiBOB)-ethyl carbonate (EC)/diethyl carbonaten (DEC) electrolytes at 25°C and 50°C were studied. The electrolyte component with the highest conductivity at each temperature was obtained through changing the concentration of LiBOB and the ratio of EC/DEC. The mass triangle model was applied to calculate the conductivity of LiBOB-EC/DEC ternary system at 25°C and 50°C. The results show that the calculated and experimental results have reached a good agreement. Therefore, it is expected that the experimental work can be vastly reduced by introducing the mass triangle model.

Key words: lithium bis(oxalato)borate (LiBOB); electrolyte; conductivity; mass triangle model

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1. Introduction

Demand is now increasing for rechargeable lithium-ion batteries with a high energy density and a long life cycle since they have a wide application ranging from batteries for small-size devices to power sources for electrical vehicles. The temperature stability of lithium-ion batteries is related to the electrolyte component. Lithium salt is one of the most important components in the electrolytes, which affects the electrolyte properties. The most widely used electrolyte salt, $LiPF_6$, cannot meet these requirements because of its poor thermal stability. Therefore, in recent years many researches focus on the development of new salts [1-4], among which lithium bis(oxalato)borate (LiBOB) is regarded as the most promising salt for lithium-ion batteries [5-6]. It can effectively stabilize the graphite structure in pure propylene carbonate (PC) [7] and the lithium-ion cells with it as electrolyte solute exhibit excellent cycling capability even at 70°C [8]. Many researches have been performed on this kind of salt [9-13] in order to improve the cell performance.

Conductivity is a key property of the battery electrolyte, which determines the inner resistance and the rate discharge capability of lithium-ion batteries. LiBOB is a novel salt, thus it is necessary to optimize the conductivity of LiBOB electrolytes for the battery applications. Because the conductivity of electrolyte is dependent on temperature, lithium salt concentration and solvent composition, a lot of time and work will be taken to optimize conductivity if experimental measurement is the only method to rely on. Therefore, it is necessary to develop a model that can predict the conductivity based on some limited experimental data. Recently, a new method, so called the mass triangle model, has been developed for calculating physicochemical properties in a ternary system with a limited homogeneous region [14]. The characterization of this new model is that the theory is reasonable, practical applications are reliable, and using in computerized thermodynamic and phase diagram calculation is realistic. In this article, the conductivities of LiBOB-ethyl carbonate (EC)/diethyl carbonaten (DEC) electrolytes at two different temperatures were studied and the optimal electrolyte components were obtained. Based on the above results, the mass triangle model was adopted to calculate and predict the conductivities of electrolytes.

2. Experimental and theoretical calculation

2.1. Materials and instrument

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LiBOB was synthesized and purified in the lab through the procedures as Ref. [15]. Both EC and DEC were battery grade. LiBOB was dissolved in EC/DEC binary solvents to get electrolytes. The ionic conductivity was measured using a conductivity meter (DDSJ-308A, Shanghai, China).

2.2. Principle of mass triangle model

For a ternary system, when the physicochemical properties of three corresponding binaries were given, a geometrical model could be used to calculate these properties for the whole ternary area [16-18]. Nevertheless, if the given data were inside the ternary system instead of in the corresponding binaries, as Chou *et al.* pointed out, the traditional geometrical model could not be helpful to compute its physicochemical properties. Instead, it was suggested to use the mass triangle model [14]. In this article, this method was extended to calculate the electrolyte conductivity.

Fig. 1 is the schematic representation of the mass triangle model, the dashed circle within Δ123 represents the boundary, along which the physicochemical properties are known. Based on this information, the mass triangle model indicates that the conductivity of the point O (λ_O) can be expressed as

$$\lambda_O = W_{A'}\lambda_{A'} + W_{B'}\lambda_{B'} + W_{C'}\lambda_{C'},$$

where $\lambda_{A'}$, $\lambda_{B'}$, and $\lambda_{C'}$ represent the experimental conductivity of electrolyte at three points (A', B', C'); $W_{A'}$, $W_{B'}$, and $W_{C'}$ indicate the weight factors of probability, which can be calculated as

$$W_{A'} = \frac{S_{\Delta OB'C'}}{S_{\Delta A'B'C'}}, W_{B'} = \frac{S_{\Delta OA'C'}}{S_{\Delta A'B'C'}}, \text{ and } W_{C'} = \frac{S_{\Delta OA'B'}}{S_{\Delta A'B'C'}},$$

where $S_{\Delta ijk}$ represents the area of triangle with i, j, k as its three vertexes.

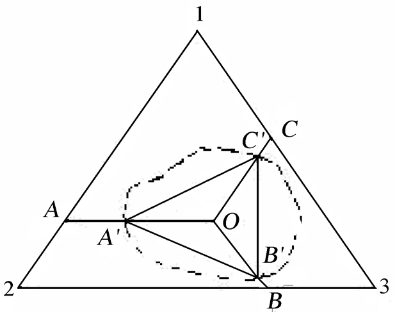

Fig. 1. Sketch map of the limited solubility region of the ternary system.

According to above formulae, a program for the mass triangle model was programmed by using C++ language which was successfully used in calculating surface tension [19] and density [20]. It was easy to apply this program to a practical system. Input the data of the known conductivities and the corresponding coordinates of boundary, the isoline of conductivity could be obtained directly.

3. Results and discussion

3.1. Experimental measurement of conductivity

A series of conductivities of LiBOB-EC/DEC electrolytes at 25°C and 50°C were studied. The results are shown in Figs. 2(a)-(b). LiBOB was dissolved in six groups of solvents with the corresponding compositions (EC:DEC=1:4, 3:7, 2:3, 1:1, 3:2, and 4:1) to get electrolytes. The concentration of LiBOB was ranged from 0.4 mol·L^{-1} to 0.8 mol·L^{-1}.

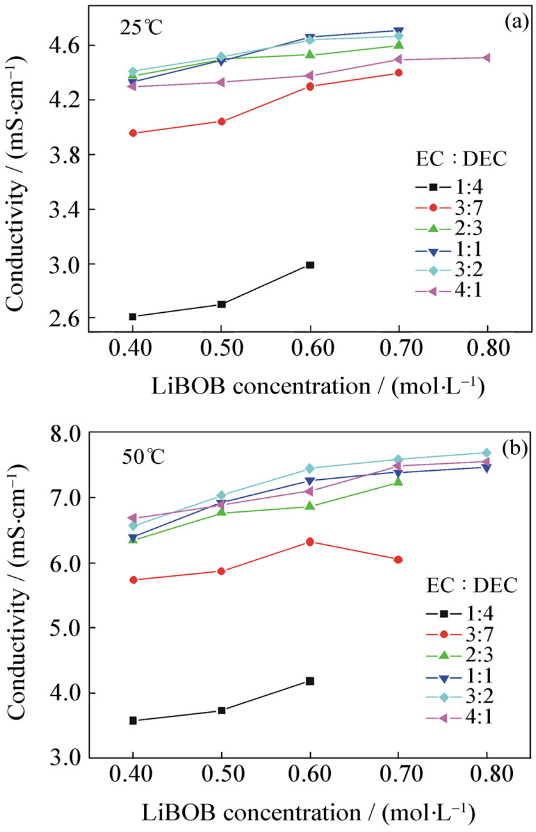

Fig. 2. Conductivities of LiBOB-EC/DEC electrolytes: (a) at 25°C; (b) at 50°C.

The conductivities of electrolytes at 25°C are shown in Fig. 2(a). With various ratios of EC:DEC, the conductivity sizes were σ(1:1)>σ(3:2)>σ(2:3)>σ(4:1)>σ(3:7)>σ(1:4). The 0.7 mol·L^{-1} LiBOB-EC/DEC (1:1) electrolyte had the highest conductivity of 4.71 mS·cm^{-1} at 25°C. The conductivities of LiBOB EC/DEC electrolytes at 50°C are shown in Fig. 2(b). With various ratios of EC:DEC, the conductivity sizes were σ(3:2)>σ(1:1)>σ(4:1)>σ(2:3)>σ(3:7)>σ(1:4). The conductivity of electrolytes increased as the LiBOB concentration increased, and 0.8 mol·L^{-1} LiBOB EC:DEC (3:2) electrolyte had the highest conductivity of 7.68 mS·cm^{-1} at 50°C.

The conductivity difference between 25°C and

50°C was related to some main factors, such as viscosity and dielectric constant of solvent, and the anion diameter of lithium salt. In general, at low concentration, the solvent with a higher dielectric constant contributed to the dissociation of the electrolyte, and the solvent with a lower viscosity favored ionic migration. Thus, high electrolytic conductance was expected in solutions consisting of the mixture of solvents with high dielectric constant and low viscosity. Cyclic carbonate EC with high viscosity had high dielectric constant, so lithium salt would disassociate easily in it. Linear carbonate DEC with low dielectric constant had low viscosity, then lithium ions could migrate freely in it. In practice, EC and DEC often mixed together in order to attain a good property of electrolyte. EC and LiBOB with large anions had the effect of increasing the viscosity of electrolyte and decreasing the migratory speed of lithium ions. In order to obtain appropriate ionic motion, a lower EC content and LiBOB concentration could get a higher conductivity at a lower temperature such as 25°C. This fact indicated that at a lower temperature, the viscosity of the solution was the main factor affecting conductivity. At a higher temperature such as 50°C when both the EC content and LiBOB concentration were higher, the higher conductivity was obtained. Here, the dielectric constant of solvent predominated the conductivity.

3.2. Cell test

The electrolyte conductivity was closely related to the rate property of the cell. Three different component electrolytes, 0.7 mol·L^{-1} LiBOB-EC/DEC (1:1), 0.7 mol·L^{-1} LiBOB-EC/DEC (2:3), and 0.6 mol·L^{-1} LiBOB-EC/DEC (1:4) were chosen to use in $LiMn_2O_4$/Li cells. The rate properties of cells were investigated. The results are shown in Fig. 3. The discharge capacity of the cell using 0.7 mol·L^{-1} LiBOB-EC/DEC (1:1) electrolyte was higher than that of the cell using 0.7 mol·L^{-1} LiBOB-EC/DEC (2:3) electrolyte. Under low discharge rate (0.2 C and 0.5 C), the discharge capacity of the cell using 0.6 mol·L^{-1} LiBOB-EC/DEC (1:4) electrolyte is higher than those of using other two electrolytes. When the discharge rate is 1 C, the discharge capacity decreases abruptly to only about 40 mAh·g^{-1}. In Fig. 2, the conductivities of 0.7 mol·L^{-1} LiBOB-EC/DEC (1:1) electrolyte and 0.7 mol·L^{-1} LiBOB-EC/DEC (2:3) electrolyte at 25°C were 4.71 mS·cm^{-1} and 4.60 mS·cm^{-1}, respectively. Among the three electrolytes, 0.6 mol·L^{-1} LiBOB-EC/DEC (1:4) electrolyte had the lowest conductivity of 2.99 mS·cm^{-1}.

The 0.6 mol·L^{-1} LiBOB-EC/DEC (1:4) electrolyte contained the least LiBOB and least EC among the three kinds of electrolytes, so the viscosity of the electrolyte and the number of free lithium ions were the lowest. A lower viscosity made the electrolyte immerge the cathode easily, and lithium ions could diffuse to the interior of the electrode easily. Consequently, under low discharge rate, the cell using 0.6 mol·L^{-1} LiBOB-EC/DEC (1:4) electrolyte had high discharge capacity. When the discharge rate was improved to 1 C, concentration polarization was generated while cycling due to the lowest number of free lithium ions in the 0.6 mol·L^{-1} LiBOB-EC/DEC (1:4) electrolyte, the discharge capacity of the cell decreased. The performance of the cell using 0.7 mol·L^{-1} LiBOB-EC/DEC (1:1) electrolyte, which had the highest conductivity at 25°C, was the best.

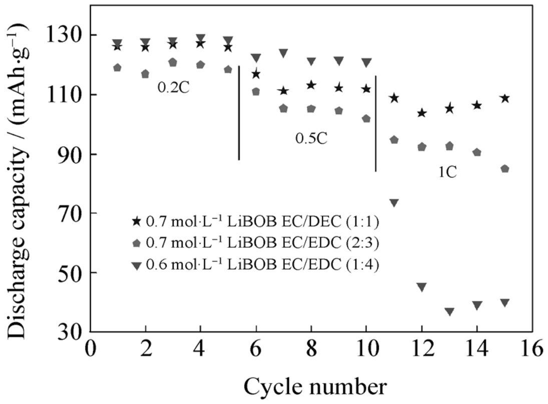

Fig. 3. Discharge capacities of $LiMn_2O_4$/Li cells with LiBOB electrolytes.

3.3. Theoretical calculation of conductivity

Although the optimal conductivity could be obtained through the above experimental measurements, lots of time and jobs were taken. The application of the mass triangle model to ternary and multicomponent electrolyte systems for calculating the conductivity of an electrolyte would save the time and energy.

Nine experimental conductivities were chosen as boundary data, which enclosed a close area. The mass triangle model was adopted to calculate conductivity in this area. The conductivity of LiBOB-EC/DEC electrolyte at 25°C and 50°C were calculated and plotted in an orthogonal reference frame in Figs. 4(a)-(b), respectively.

In Fig. 4(a), the calculated conductivities of the electrolytes achieved the highest value of 4.7 mS·cm^{-1} at 25°C when the mass fraction of LiBOB was 0.105 and the mass fraction of EC was 0.45-0.52. These calculated results were identical to experimental data shown in Fig. 2(a). Two electrolytes with different components, A (0.6 mol·L^{-1} LiBOB-EC/DEC (1:1)) and B (0.5 mol·L^{-1} LiBOB-EC/DEC (2:3)), were acted as verified points, the corresponding experimental results were 4.62 mS·cm^{-1} and 4.53 mS·cm^{-1}, respectively. From Fig. 4(a), it can be confirmed that the calculated conductivities of A and B were 4.62 mS·cm^{-1} and 4.55 mS·cm^{-1}, respectively, which were perfectly consistent with the experimental results. These indicated that it was feasible to predict the conductivities of LiBOB-EC/DEC electrolytes at 25°C by using the mass triangle model.

Fig. 4(b) showed in the area of LiBOB≈0.105wt%-0.118 wt%, EC≈0.505 wt%-0.581 wt%, *i.e.* near the area of 0.8 mol·L^{-1} LiBOB EC/DEC (3:2), that the conductivity was the highest. There was a good consistency between the calculated results and the experimental results as shown in Fig. 2(b). The conductivities of A (0.7 mol·L^{-1} LiBOB-EC/DEC (1:1)) and B (0.6 mol·L^{-1} LiBOB -EC/DEC (2:3)) at 50°C measured by experiment were 7.38 mS·cm^{-1} and 7.06 mS·cm^{-1}, whereas the calculated conductivities of A and B were 7.38 mS·cm^{-1} and 7.14 mS·cm^{-1}, respectively. Therefore, the calculated and the experimental conductivities at 50°C were also in a good agreement with each other.

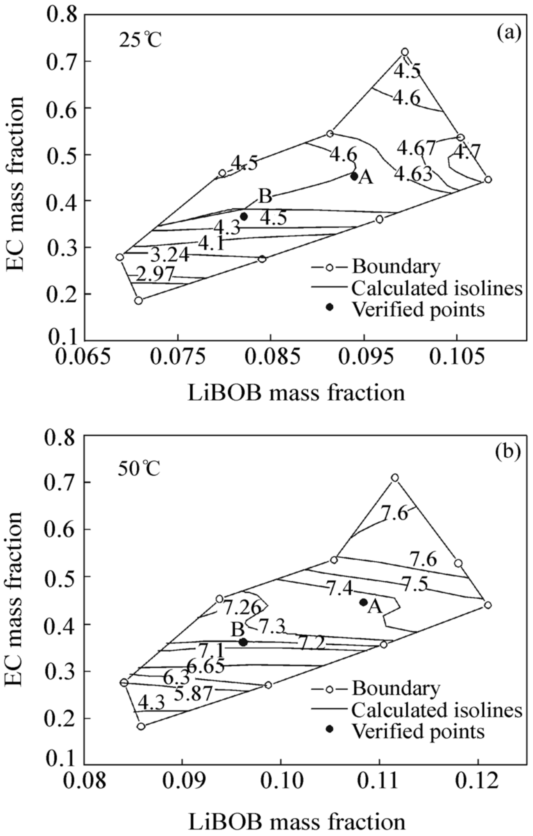

Fig. 4. Calculation and test of the mass triangle model for the conductivity of the LiBOB EC/DEC system: (a) at 25°C; (b) at 50°C.

Clearly, the mass triangle model was simple and helpful for calculating the electrolyte conductivity. The calculated results had a perfect consistency with the experimental ones at both low temperature and high temperature. Consequently, it could be concluded that the mass triangle model could offer a good prediction for the conductivity of the LiBOB-EC/DEC system.

4. Conclusion

An optimal electrolyte component is obtained through changing the concentration of LiBOB and the ratio of EC/DEC. The results shows that the 0.7 mol·L^{-1} LiBOB-EC/DEC (1:1) electrolyte has the highest conductivity of 4.71 mS·cm^{-1} at 25°C, and the 0.8 mol·L^{-1} LiBOB-EC/DEC (3:2) electrolyte has the highest conductivity of 7.68 mS·cm^{-1} at 50°C. When different electrolytes are used in $LiMn_2O_4$/Li cells at 25°C, the 0.7 mol·L^{-1} LiBOB-EC/DEC (1:1) electrolyte exhibits the best performance. The mass triangle model is applied to the LiBOB-EC/DEC ternary system for calculating the conductivity at 25°C and 50°C. The good agreements between experimental data and theoretical calculation show that this method is feasible and can play a useful role for predicting the conductivity of an electrolyte.

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