

# Ionic Limiting Molar Conductivity Calculation of Li-Ion Battery Electrolyte Based on Mode Coupling Theory

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A method is proposed based on mode coupling theory in which the ion transference number is introduced into the theory. The ionic limiting molar conductivities of LiPF<sub>6</sub>, LiClO<sub>4</sub>, LiBF<sub>4</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, Li(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>N, LiC<sub>4</sub>F<sub>9</sub>SO<sub>3</sub>, and LiAsF<sub>6</sub> in PC(propylene carbonate), GBL(gamma-butyrolactone), PC(propylene carbonate)/EMC(ethylmethyl carbonate), and PC(propylene carbonate)/DME(dimethoxyethane) are calculated based on this method, which does not involve any adjustable parameter. The results fit well to the literature data which are calculated by an empirically adjusted formula. This presents a potential way to calculate the conductivities of Li-ion battery electrolytes.

## 1. Introduction

The conductance of the electrolyte solution is one of the most important factors in a lithium ion battery, where the electrolyte consists of lithium salt in organic solvent solution. The theory of the electrolyte is the subject of much interest.<sup>1–3</sup> The ionic limiting molar conductivities of lithium salts in organic solvents are obtained based on electrochemical experiments<sup>4</sup> and empirically adjusted formulae.<sup>5</sup> So far, no theory is presented to calculate them.

However, among physical chemists, the most popular expressions have been the Debye–Hückel limiting laws (DHLL) and expressions derived therefrom.<sup>6</sup> Among others, geochemists have extensively used Pitzer's modifications of DHLL to describe departures from ideality in concentrated ionic mixtures.<sup>7,8</sup> Another theory that is fundamentally connected to the DHLL is the mean spherical approximation (MSA), but the simple variational derivations exist nowadays.<sup>9–13</sup>

Recently, A. Chandra and B. Bagchi<sup>14–18</sup> have developed a new theoretical formulation to study ion conductance in electrolyte solutions, based on a mode coupling theory (MCT) treatment of the electrolyte friction. This new theory provides expressions for both the ion atmosphere relaxation and electrophoretic contributions to the total electrolyte friction that acts on a moving ion. While the ion atmosphere relaxation term arises from the time-dependent microscopic interaction of the moving ion with the surrounding ions in the solution, the electrophoretic term originates from the coupling of the ion's velocity to the collective current mode of the ion atmosphere. Mode coupling theory, combined with time-dependent density

functional theory of ion atmosphere fluctuations, leads to self-consistent expressions for these two terms which also include the effects of self-motion of the ion under consideration. These expressions have been solved for the concentration dependence of electrolyte friction and ion conductance. It is shown that in the limit of very low ion concentration, the MCT reduces to the well-known Debye–Hückel–Onsager limiting law which predicts a linear dependence of conductance on the square root of ion concentration  $c$ . At moderate and high concentrations, the MCT predicts a significant nonlinear and weaker dependence on root  $c$  which is in very good agreement with experimental results. Being self-contained, the MCT does not involve any adjustable parameter.

In this study, the ion transference number is introduced into the formula describing the relationship between ionic limiting molar conductivity and ionic concentration based on the MCT. The ionic limiting molar conductivities of LiPF<sub>6</sub>, LiClO<sub>4</sub>, LiBF<sub>4</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, Li(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>N, LiC<sub>4</sub>F<sub>9</sub>SO<sub>3</sub> and LiAsF<sub>6</sub> in PC, GBL, PC/EMC, and PC/DME are calculated by the proposed method.

## 2. Theory

Based on the MCT, the following expression of the microscopic electrolyte friction  $\delta\zeta_{s,\text{mic}}(c)$  is given in the following equation:<sup>15</sup>

$$\zeta_{s,\text{mic}}(c) = \frac{k_B T}{3(2\pi)^3} \int_0^\infty dt \int_{-\infty}^\infty dk k^2 [C_s][G(k,t)][C_s]^\dagger(k) F_s(k,t) \quad (1)$$

where,  $[C_s]$  is a  $(1 \times 2)$  matrix with elements  $\sqrt{\rho_i} c_{si}(k)$ ,  $i=1, 2$ ;  $c_{si}(k)$  is the wavevector ( $\mathbf{k}$ ) dependent direct correlation function between the tagged ion and an ion of species  $i$ , and  $\rho_i$  is the number density of the  $i$ th species.  $[\xi_s(k)]^T$  is the transpose of  $[C_s(k)]$ .  $F_s(k,t)$  is the self-dynamic structure factor of the

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tagged ion, assuming to be equal to  $\exp(-D_s k^2 t)$ , as we are interested in the zero-frequency friction. Thus, eq 1 calls for a self-consistent solution.  $[G(k, t)]$  is the  $(2 \times 2)$  van Hove function matrix with elements  $G_{ij}(k, t)$ . The elements of the van Hove function matrix can be calculated by using an extension of the molecular hydrodynamic theory.<sup>19</sup> The time integral can be carried out analytically to derive an expression for  $\delta\xi_{s, \text{mic}}(c)$  in terms of an integral over the wavevector  $\mathbf{k}$ .

The hydrodynamic contribution is due to the coupling of the ion velocity to the relevant current modes of the solution. Mode coupling theory directly provides an expression of the contribution of the currents or flows of the system to the diffusion coefficient, that is, inverse of the friction. Since the current modes of the solution consist of both solvent and ion currents, the hydrodynamic contribution to the diffusion ( $D_{s, \text{hyd}}$ ) can be expressed as the sum of a solvent contribution  $D_{s, \text{hyd}}(c = 0)$ , which is again assumed to be concentration independent, and a concentration dependent ion contribution  $\delta D_{s, \text{hyd}}(c)$ . The ion contribution to the hydrodynamic term is the so-called electrophoretic effect. By taking the basic ideas of mode coupling theory and considering the coupling of the ion velocity with the charge density and current modes of ion atmosphere, a general (and somewhat complicated) expression can be derived for the hydrodynamic (or the electrophoretic) term which (in the limit of equal sized ions) provides the following rather simple expression:

$$\delta D_{s, \text{hyd}}(c) = \frac{1}{3\pi^2 \rho N} \int_0^\infty dt \int_0^\infty dk k^2 [\rho_1 G_{11}^d(k, t) - \rho_2 G_{12}^d(k, t)] C^T(k, t) \quad (2)$$

where  $\rho$  is the total ion density and  $N$  is the total number of ions present in the solution.  $G_{ij}^d(k, t)$  is the distinct van Hove function between ionic species  $i$  and  $j$ , and  $C^T(k, t)$  is the Fourier transform of the transverse current time correlation function. The above integral can be evaluated by making the so-called viscous approximation for the decay of  $C^T(k, t)$ .<sup>20</sup> Since the relaxation of the transverse current correlation function occurs much faster than the decay of distinct van Hove functions, the distinct van Hove functions in eq 2 can be replaced by the corresponding pair correlation functions and the time integral of eq 2 can then be evaluated analytically. The long-range Coulombic interactions among ions and the effects of screening enter naturally in the formulation through the ion-ion correlation functions of eqs 1 and 2.

Closed-form expressions for the wavevector integrals of both eqs 1 and 2 can be obtained in the limit of very low concentration where the exact asymptotic expressions for the ionic pair correlation functions can be used. Equations 2 and 3 then lead to the following novel and essentially exact nonlinear equation for the conductance of  $i$ th species of a strong binary electrolyte at the low concentration

$$\Lambda_i(c_i) = \Lambda_i^0 - \left[ \frac{\sqrt{2\pi N_0} q_i^2 F}{3\pi\eta(1000\epsilon k_B T)^{1/2}} + \frac{\sqrt{2\pi N_0} q_i^2 |q_i| w_i}{3\sqrt{1000}(\epsilon k_B T)^{3/2} \Lambda_i^0} \right] \sqrt{c_i} \quad (3)$$

where,  $\Lambda_i$  is molar conductivity of ion  $i$ ,  $\Lambda_i^0$  is limiting molar conductivity of ion  $i$ ,  $q_i$  is the charge of an ion of species  $i$ ,  $N_0$  is the Avogadro number,  $F$  is Faraday constant,  $\eta$  is viscosity of solvent,  $\epsilon$  is dielectric constant of solvent,  $T$  is temperature,

$c_i$  is the molar concentration by volume and  $k_B$  is the Boltzmann constant.

$$w_i = 2 \left[ 1 - \left( \frac{1}{2} \sum_j \frac{\Lambda_i}{\Lambda_i + \Lambda_j} \right)^{1/2} \right] \quad (4)$$

where,  $j$  includes all ions in the solution. In the deriving eq 3, the relation between the diffusion coefficient and the conductance and also between the concentration  $c_i$  and the number density  $\rho_i$ .<sup>15</sup> It is to be solved self-consistently to obtain the numerical values of the conductance of positive and negative ions at the low concentration. That  $w_i$  goes over exactly to the DHO value  $(2 - \sqrt{2})$  for a symmetric binary electrolyte can be seen if one assumes  $\Lambda_i = \Lambda_j$ . More importantly, in the same limit eq 3 becomes identical with the DHO limiting law.<sup>21–23</sup> Furthermore, the above equation reduces to the expression of Friedman and co-workers<sup>24</sup> when one replaces  $\Lambda_i$  terms in the right-hand side of the above equation by  $\Lambda_i^0$ . This is exact to the order of  $\sqrt{c_i}$ . Equation 3 is valid even when the mobilities of the constituent ions of a binary electrolyte are different. This is almost always the case for real electrolytes. The original DHO limiting law does not reflect this asymmetry.

If parameters  $A$  and  $B$  are defined as

$$A = (\sqrt{2\pi N_A} q_\alpha^2 F / 3\pi\eta(1000\epsilon k_B T)^{1/2})$$

$$B = (\sqrt{2\pi N_A} q_\alpha^2 |q_\alpha| / 3\sqrt{1000}(\epsilon k_B T)^{3/2}) \quad (5)$$

the total conductivity of electrolytes could be decomposed with the conductivity of cationic and anionic species.<sup>25</sup> The cationic transference number  $t_+$  is defined as the net number of faradays of charge carried across the reference plane by cation constituent in the direction of the cathode, during the passage of 1 faraday of charge across the plane.  $t_-$  is the anionic transference number.  $\Lambda_+ = \Lambda_m t_+$  and  $\Lambda_- = \Lambda_m t_-$ . Thus, combining the definition of ion transference number, eq 3 can be rewritten as

$$\Lambda_m t_+ = \Lambda_+^0 - (A + B w_+ \Lambda_+^0) \sqrt{c_+} \quad (6)$$

where,  $t_+$  is the cationic transference number,  $\Lambda_m$  is the molar conductivity of the solution,  $\Lambda_+^0$  is the cationic limiting molar conductivity,  $c_+$  is the molar volume concentration of cation, and  $w_+$  is  $w_i$  when ion  $i$  is cation. Equation 4 is rewritten as

$$w_+ = 2 \left( 1 - \left( \frac{1}{2} \left( \frac{1}{2} + t_+ \right) \right)^{1/2} \right) = 2 - \sqrt{2} \left( \frac{1}{2} + t_+ \right)^{1/2} \quad (7)$$

thus, eq 6 becomes

$$\Lambda_m t_+ = \Lambda_+^0 - \left( A + B \Lambda_+^0 \left( 2 - \sqrt{2} \left( \frac{1}{2} + t_+ \right)^{1/2} \right) \right) \sqrt{c_+} \quad (8)$$

In the above equation,  $A$  and  $B$  are the coefficients determined by the solvent properties, the charge on the ions, and the temperature.  $\Lambda_m$  is the molar conductivity of the solution with concentration  $c_+$ . They can be measured by experiments. The unknown values are cationic limiting molar conductivity  $\Lambda_+^0$  and cationic transference number  $t_+$ , and can be calculated by regression of eq 8 using a group experimental data of  $\Lambda_m$  and  $c_+$ .

### 3. Results and Discussion

The molar conductivities of lithium salts in PC, GBL, PC/EMC, and PC/DME at 25 °C over the concentration range of  $10^{-3}$  to  $10^{-4}$  mol dm<sup>-1</sup>, and the physical properties of the

**TABLE 1: Ionic Limiting Molar Conductivities in PC (298 K)**

salt	$\Lambda_+^0/\text{S cm}^2 \text{mol}^{-1}$			$\Lambda_-^0/\text{S cm}^2 \text{mol}^{-1}$		
	calc. value	lit. value <sup>5</sup>	RD %	calc. value	lit. value <sup>5</sup>	RD %
LiClO <sub>4</sub>	8.43	8.43	−0.71	18.93	18.93	0.00
LiBF <sub>4</sub>	8.13			20.43	20.43	0.00
LiPF <sub>6</sub>	8.43			17.86	17.86	0.00
LiAsF <sub>6</sub>	8.43			17.57	17.58	−0.05
LiCF <sub>3</sub> SO <sub>3</sub>	8.43			16.89	16.89	0.00
Li(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> N	8.43			14.40	14.40	0.00
LiC <sub>4</sub> F <sub>9</sub> SO <sub>3</sub>	8.43			13.03	13.03	0.00
Average	8.37					0.01

**TABLE 2: Ionic Limiting Molar Conductivities in GBL (298 K)**

salt	$\Lambda_+^0/\text{S cm}^2 \text{mol}^{-1}$			$\Lambda_-^0/\text{S cm}^2 \text{mol}^{-1}$		
	calc. value	lit. value <sup>5</sup>	RD %	calc. value	lit. value <sup>5</sup>	RD %
LiClO <sub>4</sub>	13.99	13.99	−0.07	28.45	28.45	0.00
LiBF <sub>4</sub>	13.99			30.77	30.77	0.00
LiPF <sub>6</sub>	13.99			26.70	26.70	0.00
LiAsF <sub>6</sub>	13.99			25.92	25.92	0.00
LiCF <sub>3</sub> SO <sub>3</sub>	13.99			24.93	24.93	0.00
Li(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> N	13.95			20.53	20.55	−0.01
LiC <sub>4</sub> F <sub>9</sub> SO <sub>3</sub>	13.99			18.66	18.66	0.00
Average	13.98					0.00

**TABLE 3: Ionic Limiting Molar Conductivities in PC/EMC (298 K)**

salt	$\Lambda_+^0/\text{S cm}^2 \text{mol}^{-1}$			$\Lambda_-^0/\text{S cm}^2 \text{mol}^{-1}$		
	calc. value	lit. value <sup>5</sup>	RD %	calc. value	lit. value <sup>5</sup>	RD %
LiBF <sub>4</sub>	18.71	18.71	0.00	28.49	28.49	0.00
LiClO <sub>4</sub>	18.71			27.26	27.26	0.00
LiPF <sub>6</sub>	18.71			26.92	26.92	0.00
LiCF <sub>3</sub> SO <sub>3</sub>	18.71			26.67	26.68	−0.04
Li(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> N	18.71			23.07	23.07	0.00
Average	18.71					0.01

**TABLE 4: Ionic Limiting Molar Conductivities in PC/DME (298 K)**

salt	$\Lambda_+^0/\text{S cm}^2 \text{mol}^{-1}$			$\Lambda_-^0/\text{S cm}^2 \text{mol}^{-1}$		
	calc. value	lit. value <sup>5</sup>	RD %	calc. value	lit. value <sup>5</sup>	RD %
LiBF <sub>4</sub>	27.96	27.96	0.00	38.15	38.15	0.00
LiClO <sub>4</sub>	27.96			37.06	37.06	0.00
LiPF <sub>6</sub>	27.96			36.77	36.77	0.00
LiCF <sub>3</sub> SO <sub>3</sub>	27.96			35.61	35.61	0.00
Li(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> N	27.96			32.58	32.58	0.00
Average	27.96					0.00

solvents in refs 5 and 6 are used to validate eq 8. Adopting eq 8, the two parameters  $\Lambda_+^0$  and  $t_+$  are calculated by multivariable nonlinear least-squares regression from a group experimental data of  $\Lambda_m$  and  $c_+$ .

The calculation results of limiting molar conductivity of lithium salts in PC and GBL are listed in Tables 1 and 2, respectively.  $\Lambda_+^0$  is limiting molar conductivity of lithium ion.  $\Lambda_-^0$  is limiting molar conductivity of anion. The values of  $\Lambda_+^0$  and  $\Lambda_-^0$  are from ref 5, where they are calculated from experimental data of molar conductivities by empirical formula. The calculation presents good agreement with the data from ref 5, showing very low relative deviations (RD).

Tables 3 and 4 present the calculation results of limiting molar conductivity of lithium salts in mixture solvents of PC/EMC and PC/DME, respectively.  $\Lambda_+^0$  is the limiting molar conduc-

tivity of lithium ion.  $\Lambda_-^0$  is the limiting molar conductivity of anion. The values of  $\Lambda_+^0$  and  $\Lambda_-^0$  are from ref 4, where they are calculated from transport number measured by the electrochemistry cells. The calculation shows very good fittings, and the relative deviations are close to zero.

The agreement between the literature data, which are calculated from empirically adjusted equation, and the results calculated from our proposed calculation method is quite impressive given that we have employed a theoretical approach that does not involve any adjustable parameter. This spectacular agreement may result from the fact that both literature data and our results are calculated from the same experimental data by regression calculation.

Both the literature data and calculation results show that the different lithium salts present almost same cationic limiting molar conductivity in the same solvent system, although their anionic limiting molar conductivities are different, as shown in Tables 1–4. This indicates that there is very small interaction among ions, causing tiny effect on each other in a dilute electrolyte solution. The ionic limiting molar conductivity depends mainly on the ion itself and the solvent.

Regardless of the lithium salt or solvent, or whether the solvent is single or mixture, the calculation results by the proposed method in this study are in good agreement with the reported data. This indicates that the proposed method in this study is a promising alternative to calculate the ionic limiting molar conductivities of Li-ion battery electrolytes.

#### 4. Conclusions

The ionic limiting molar conductivities of LiPF<sub>6</sub>, LiClO<sub>4</sub>, LiBF<sub>4</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, Li(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>N, etc. in PC (propylene carbonate), GBL (gamma-butyrolactone), PC (propylene carbonate)/EMC (ethylmethyl carbonate), and PC (propylene carbonate)/DME (dimethoxyethane) have been calculated based on the mode coupling theory, in which the ion transference number is introduced. This approach does not involve any adjustable parameter. The results fit well to the literature data, which are calculated by empirically adjusted formula from experimental data. This presents a potential way to calculate the conductivities of Li-ion battery electrolytes.

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