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Database and models of electrolyte solutions for lithium battery

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Abstract

Transport and thermodynamic properties of electrolyte solutions are very essential for development and design of lithium ion or lithium polymer batteries. An electrolyte database for lithium battery, which includes a quite number of organic solvents, lithium electrolytes and possible by-products (e.g. CO₂), has been compiled. Appropriate models have been evaluated for representing the variety of properties for solvents and electrolyte solutions, such as, conductivity, transference number, diffusivity, dissociation constant and so on. Particular attention has been given on conductivity in this paper, considering its essential importance for battery; several typical examples have been presented and discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lithium battery; Electrolyte solution; Transport property; Database; Model

1. Introduction

Electrolyte solutions are essential for lithium battery; even in the case of lithium polymer battery, liquid electrolytes are extensively employed by incorporation into polymer matrix, known as gel polymer electrolytes. There is evidence that polymer is likely to have very little effects on the conductive performance of liquid electrolytes entrapped in polymer gel when the content of polymer is small, e.g. <30–35 wt.% [1–3]. Therefore, the optimal design of gel polymer electrolytes can also be somewhat reduced to the basis of optimizing liquid electrolyte compositions, which is same as that for lithium ion battery.

The strategy of our researches for the properties of electrolyte solutions is to develop an algorithm for quickly screening potential solvents/electrolytes, systemically optimizing the compositions of liquid electrolytes, and further supporting the optimization and design of the whole lithium battery. The working scheme is shown in Fig. 1. We believe that a systematic approach is very important, because many factors are highly interacted. For example, conductivity (κ) is function of viscosity (η) and dissociation constant (K_a), and further linked to dielectric constant (ϵ), ionic activity coefficients (γ_{\pm}) and others.

2. Liquid electrolyte database

A reliable database of liquid electrolytes is always very useful for the research and development of lithium battery. Collection of experimental data is hard work and time consuming, because data are widely spread in a variety of literature [4], and many researches that are not directly contacted to lithium battery, e.g. electrolyte thermodynamics, corrosion, electrochemistry and material science, could provide useful information. An electrolyte database for lithium battery, which covers equilibrium properties, transport properties, thermal properties as well as electrochemical properties, have been compiled. Organic solvents are classified in terms of functional groups, such as, carbonate, ether, ester, amide, alcohol, acid and so on; electrolytes are mainly lithium salts, e.g. LiPF₆, LiBF₄, LiAsF₆, LiC(SO₂CF₃)₃, LiN(SO₂CF₃)₂, LiCF₃SO₃ and LiClO₄. In addition, some by-products/impurities, for example, light gases like CO₂, CH₄, CO and H₂ are also included. In addition to the data collected from the open literature, our measuring data have also been included. In view of the fast developing for lithium cells and the valuable information, at least on the order of magnitude, provided by the experimental results reported only with diagrams/equations, some data deduced from the plots/fitting equations have also been compiled in the databank. However, a special symbol (!) has been assigned to these data so as to remind the users to use them with caution. The compiled data can be retrieved by name, or molecular formula, or CA registry number, and displayed in

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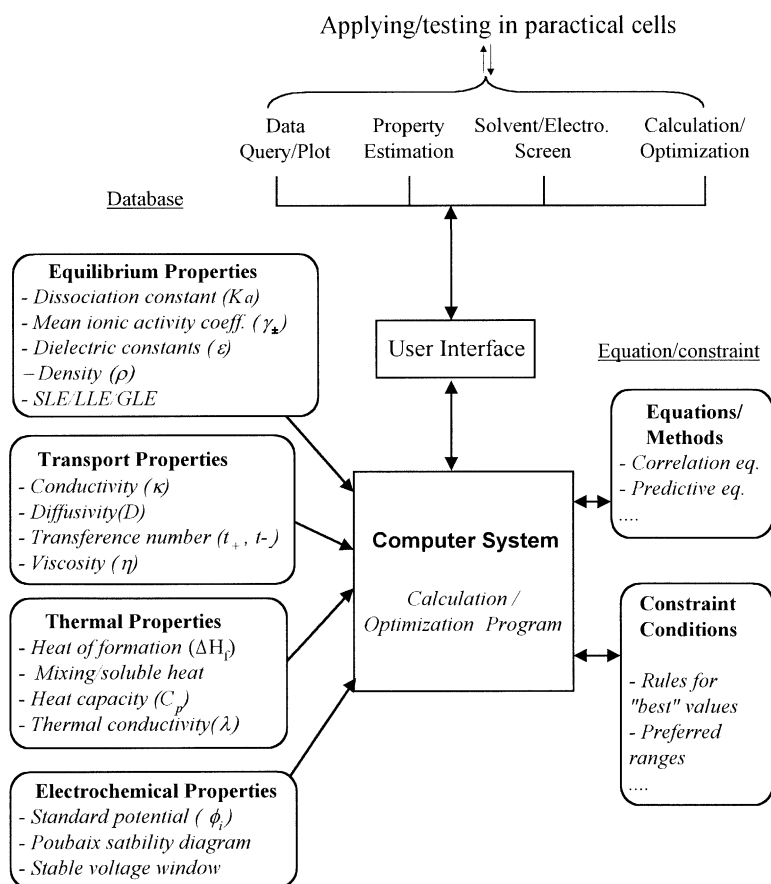


Fig. 1. A scheme of strategic researches for electrolyte database, property models and optimal design of electrolyte solutions for lithium battery.

either table or diagram, or other forms. It is worthy of mention here that our electrolyte database is more specific and closely serving for our practical R&D, therefore, somewhat different from the strategies of the general databases, e.g. electrolyte data Regensburg (ELDAR) [4] and Dortmund databank (DDB) [17].

3. Electrolyte property models

The reliability and accuracy of property models in terms of composition, concentration, temperature and sometimes also pressure are usually crucial for the systematical optimization of lithium cells. Furthermore, a good correlation equation could be served as a tool for evaluation of the quality of experimental data from various sources. A number of correlation equations are available for representation of a variety of properties, e.g. density (ρ), viscosity (η), permittivity (ϵ), conductivity (κ), diffusivity (D) and transference number (t), for pure solvents as well as electrolyte solutions. Reviews or discussions about various models and underlying theories could be found in [4–7], yet beyond the scope of this paper. Considering the limited pages, it is impossible to discuss all the models for various properties. Hence, the particular attention is given on conductivity models here.

Numerous conductivity equations, such as, Fuoss equation [8], Pitts equation [9], Lee-Wheaton equation [10,11], MSA equation [6,12] and various modified equations [13], are in use today. Most of the theoretical based equations are valid only in dilute region (e.g. $c < 0.01/0.1 \text{ mol dm}^{-3}$), one big advantage of these models is that their parameters have physical meanings, for example A_0 , K_a and R (Gurney radius, or center–center distance). On the other hand, the practical applications often require that the conductivity models be reliable and accurate in a wide range of concentration and temperature. In order to meet the different purposes, several models have to be chosen/developed for representation of the conductivity data.

3.1. Conductivity at dilute region ($c < 0.01$, or 0.1 mol dm^{-3})

$$A = \alpha[A^\infty - S(c\alpha)^{0.5} + E c \alpha \ln(c\alpha) + J_1 c \alpha - J_2 (c\alpha)^{1.5}],$$

$$K_a = \frac{1 - \alpha}{\alpha^2 c} \frac{1}{y_{\pm}}, \quad \ln(y_{\pm}) = -\frac{\kappa_D q}{1 + \kappa_D R} \quad (1)$$

where S , E , J_1 and J_2 have the usual meanings [6]. The useful properties, e.g. A^∞ , and K_a , could be obtained by fitting the conductivity data at dilute solutions with Eq. (1).

3.2. Conductivity at wide concentration region (up to several mol kg⁻¹)

In order to keep the model consistency from very dilute to concentrated solutions, an empirical modification of Fuoss-type equation (Eq. (1) with the assumption of $\alpha = 1$) has been adopted by us.

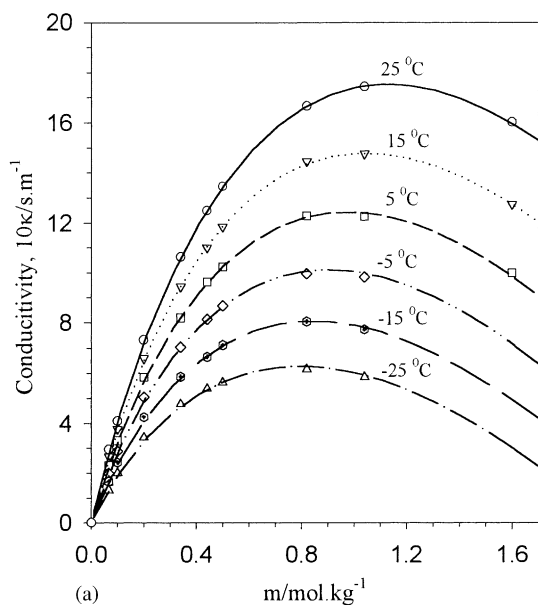
$$\frac{\kappa}{c} = A^\infty - Sc^{0.5} + Ec \ln c + J'_1 c - J'_2 c^{1.5} + Fc^2 + Hc^{3.5} \quad (2)$$

where κ is the conductivity in s m^{-1} , c the molarity in mol m^{-3} . The last two terms are empirically added for concentrated solutions, F and H are fitting parameters. A^∞ can be determined by fitting conductivity in dilute solutions with Eq. (1), or estimated from ionic limiting conductivity, or fitted to experimental data with the other parameters altogether. S and E are calculated with the usual expressions [6] as that in Eq. (1). J'_1 and J'_2 can be obtained either by the usual expressions [6] with R as adjustable parameters, or by treating themselves as fitting parameters when the latter allows a better fitting.

The advantage of Eq. (2) is the consistency from limiting to concentrated solutions while still keeping some parameters with physical meanings. It has been proved to be effective. An example was shown in Fig. 2a and b, where the conductivity (κ) and molar conductivity (Λ) for LiAsF₆ in PC (32 wt.%):DME were accurately represented by Eq. (2).

It is worthy of mention Casteel-Amis equation [14] here, the expression is as follows:

$$\frac{\kappa}{\kappa_{\max}} = \left(\frac{m}{\mu}\right)^a \exp\left[b(m - \mu)^2 - \frac{a}{\mu} \left(\frac{m}{\mu}\right)\right] \quad (3)$$



where k_{\max} , μ , a and b are adjustable parameters. Casteel-Amis equation is capable of fitting conductivity data for concentrated solutions, however, it is not meaningful for dilute solutions. Moreover, Eq. (3) is not applicable for electrolyte systems with more than one maxima of κ versus c , for example, two conductivity maxima for LiCF₃SO₃ in polyethylene oxide (PEO) [15,16], although, it is not common for liquid electrolyte systems without polymer.

3.3. Temperature dependency of conductivity

The temperature dependency of conductivity is particularly important for development of lithium cells, especially for those applied at very low/high temperature environment, e.g. -30 or 120°C . The Vogel-Tamma-Fulcher (VTF) equation generally provides a better description.

$$\kappa = AT^n \exp\left[-\frac{E_a}{R(T - T_0)}\right] \quad (4)$$

where A , E_a and T_0 are fitted parameters. T_0 can be associated to the glass transition temperature; and E_a a pseudo-activation energy. R is the gas constant. The superscript “ n ” can be used as adjustable parameter, usually $n = -1/2, +1/2, 1$ or 0 . Eq. (4) reduces to the usual Arrhenius-type relation when $n = 0$.

In Fig. 3 the variations in conductivity versus inverse temperature for lithium salts in mixed solvents (A and B), gel polymer (C) and polymer (D and E) have been shown. In the cases, A–C, Eq. (4) with $n = 1/2$ provides accurate correlation. In the cases, E and D, both the curves show a knee around the transition temperatures, and separate into two regions. For curve E the two regions follow Arrhenius

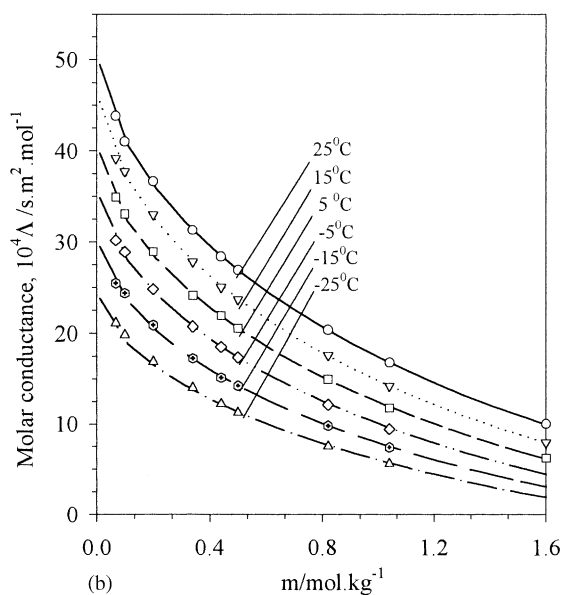


Fig. 2. (a) Comparison of calculated conductivity (line) and experimental data (symbol) [4] for LiAsF₆ in PC (32 wt.%):DME; (b) comparison of calculated molar conductivity (line) and experimental data (symbol) [4] for LiAsF₆ in PC (32 wt.%):DME.

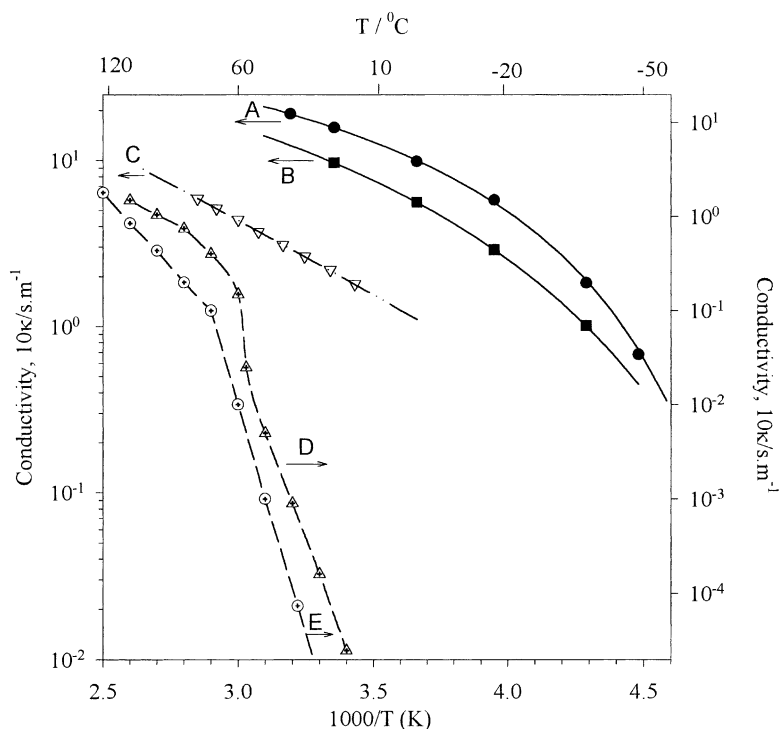


Fig. 3. Variations in conductivity vs. inverse temperature (lines: calculated by VTF Eq. (4); symbols: experimental data). (A) LiPF_6 (1 mol dm^{-3})/EC:DMC:MA (1:1:1 volume) [18]. (B) LiPF_6 (1 mol dm^{-3})/EC:DMC:DEC (1:1:1 volume) [18]. (C) LiPF_4 (1 mol kg^{-1})/EC:PC:Kynar (20 wt.%) [19]. (D) LiClO_4 /PEO (O/Li = 40) [15]. (E) LiClO_4 /PEO (O/Li = 6) [15]. EC = ethylene carbonate; PC = propylene carbonate; DMC = dimethyl carbonate; DEC = diethyl carbonate; MA = methyl acetate; PEO = polyethylene oxide.

relationship (i.e. Eq. (4) with $n = 0$); for curve D the upper region can be accurately described by VTF equation while the lower region by Arrhenius relation.

4. Conclusions

An electrolyte database is the basis for the development of electrolyte models; electrolyte models further support the simulation and optimization as well as the design and scale-up of battery. A systematic approach will essentially speed up the R&D of battery, and further lead to a better cell.

Reliable models in terms of electrolyte concentrations, temperatures and sometimes also pressures are essentially important for guaranteeing the quality of the simulation and optimization of battery. In this paper particular attention has been given on the conductivity models, because of its essential importance. From the practical viewpoint, it is necessary to use one equation to describe the conductivity performance over a wide range of electrolyte concentration (from dilute to several molalities) as well as temperature (e.g. from -50 to 130°C). Furthermore, some systems may show an unusual behavior in the relation of κ versus c , for example, two maxima for LiAsF_6 , LiClO_4 and LiCF_3SO_3 in PEO [15]. Such widely applicable equations, which must be

function of both concentration and temperature, are usually empirical. Due to the limited pages, the details will not be described here. One of such conductivity equations was presented in [16].

By the way, the readers, if interested, may refer to [17] for acquiring the electrolyte UNIFAC model for prediction of thermodynamic properties, such as, γ_{\pm} , CO_2 solubility, solid–liquid equilibria (SLE), and so on.

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