



Direct relations between ion diffusion constants and ionic conductivity for lithium electrolyte solutions



Kikuko Hayamizu

Institute of Applied Physics, University of Tsukuba, Tsukuba 305-8573, Japan

ARTICLE INFO

Article history:

Received 4 July 2017

Received in revised form 5 September 2017

Accepted 10 September 2017

Available online 14 September 2017

Keywords:

Organic lithium electrolyte solution

Ion diffusion constant

Ionic conductivity

Carrier number

Li secondary battery

ABSTRACT

Lithium cation and anion diffusion constants (D_{Li} and D_{Anion}) are plotted versus ionic conductivity (σ) (σ - D relation) for lithium organic electrolyte solutions which are important to investigate Li secondary batteries. Lithium salts studied are LiPF_6 , LiBF_4 , $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ (LiTFSA), $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$ (LiBETI), LiC_4BO_8 (LiBOB), LiSO_3CF_3 and $\text{Li}_2\text{B}_{12}\text{F}_{12}$. Main organic solvents are propylene carbonate (PC), ethylene carbonate (EC), γ -butyrolactone (GBL), diethyl carbonate (DEC), four glymes and polyethylene glycol (PEG) dimethyl ethers of average molecular weights of 400 and 1,000. Mixing effects of two solvents are shown for EC-DEC- LiPF_6 systems. In total, about 20 organic electrolyte solutions were studied. In addition, for six binary ionic liquid systems, σ - D relations are plotted. Values for the degree of apparent ion dissociation (α) were calculated from the D_{Li} , D_{Anion} and σ using the Nernst-Einstein (NE) relation and are plotted against σ (σ - α relation). The number of charge-carrying ions (N_{carrier}) was estimated from the α and salt concentration, and plotted versus σ (σ - N_{carrier} relation). To estimate the velocity of ions, the σ - D_{solvent} relations are plotted. Also, the apparent lithium transference number (t_{Li}) obtained simply from the D_{Li} and D_{anion} values are plotted versus σ (σ - t_{Li} relation). While we have already reported all the data in our previous papers, we did not plot directly the ion diffusion constants and other parameters versus ionic conductivity. In this paper, the importance of the direct relations of σ - D , σ - α , and σ - N_{carrier} is demonstrated to understand functions of lithium electrolyte solutions.

The numerical data are freely available in Supplementary Information (SI), covering broad aspects of the fundamental and practical lithium electrolyte solution systems. We believe that they will contribute to the research and development for next generation Li battery systems.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

In this paper, we focus on the direct relationships between ionic conductivity (σ) and lithium ion and anion diffusion constants (D_{Li} and D_{Anion}) for lithium organic electrolyte solutions including ionic liquids. Generally, the relationship between σ and D is investigated by the Nernst-Einstein (NE) equation. For over a decade, we have studied lithium electrolytes to measure D and σ values and to analyze the data using the NE relation, however, we did not plot directly D versus σ . Experimental σ and D values are sensitive to salt concentration and temperature. The measurements of σ and D values were performed for the same samples prepared by adding a lithium salt to a solvent. The diffusion constants of the lithium, anions and solvent (D_{solvent}) were measured using pulsed-gradient spin-echo (PGSE) ^7Li , $^{19}\text{F}/^{11}\text{B}$, and ^1H NMR resonances, respectively. We have published these data in 13 papers from 1999 to 2012 [1–

13]. These studies provided values for σ , D_{Li} , D_{Anion} and D_{solvent} in lithium organic electrolyte solutions and binary ionic liquids, in which the dependences of the transport parameters were discussed precisely for numerous solvents with different property, various anions, salt concentrations, and temperatures. The data were separately plotted against temperature or salt concentration. The relations between σ and D were investigated through the degree of apparent ionic dissociation derived by the NE equation.

Recently, we noticed that the direct relations between σ and D (σ - D relation) are important in developing various types of new lithium electrolyte systems. In this paper, using the data that have already been published in our research papers [1–13], direct plots of D_{Li} and D_{Anion} versus σ are presented. Extensive datasets have been compiled for various electrolyte solution systems and the numerical data are provided in Supplementary Information (SI). Some of numerical data have already been made available on the Internet in Japanese [14], but the direct plots of D versus σ shown in this paper have not previously been presented elsewhere. The acronym, chemical name, chemical structure, molecular formula

E-mail address: hayamizu.k3@gmail.com (K. Hayamizu).

and molecular weight are provided for each solvent, anion and cation in ionic liquid described in this paper are shown in the SI.

From the experimental data we can calculate the so-called apparent lithium transference number t_{Li} as

$$t_{Li} = \frac{D_{Li}}{D_{Li} + D_{Anion}} \quad (1)$$

The Nernst-Einstein (NE) relation for a monovalent solution of completely isolated ions is given in Eq. (2),

$$\sigma_{NE} = \frac{e_0^2 N}{kT} (D_+ + D_-), \quad (2)$$

where e_0 is electric charge ($1.602 \times 10^{-19}C$), N is Avogadro's number ($6.022 \times 10^{23} \text{ mol}^{-1}$), and k is the Boltzmann constant ($1.380 \times 10^{-23} \text{ JK}^{-1}$) for complete ion dissociation. The NE relation for the observed ionic conductivity σ_{AC} is given by Eq. (3) for the lithium electrolyte solutions,

$$\sigma_{AC} = \frac{e_0^2 N}{kT} (D_{Li} + D_{Anion}) (1 - \xi). \quad (3)$$

Usually, σ_{AC} is observed in $S \text{ cm}^{-1}$, N is the number of ions in cm^3 , and the D_{Li} and D_{Anion} must be [$\text{cm}^2 \text{ s}^{-1}$] in this equation. ξ is the degree of ion association. To obtain N , density measurements may be necessary, except for a sample prepared by molar concentration M (mol/L). The ion diffusion constants measured are the weighted average of isolated ions having charge and the paired ions without charge. Simply, we calculated the ionic conductivity from the ion diffusion constants using Eq. (4)

$$\sigma_{calculated} = \frac{e_0^2 N}{kT} (D_{Li} + D_{Anion}). \quad (4)$$

The $\sigma_{calculated}$ values are always larger than the experimental σ_{AC} values. The degree of apparent ion dissociation α can be estimated by Eq. (5), which is smaller than unity.

$$\alpha = \frac{\sigma_{AC}}{\sigma_{calculated}}. \quad (5)$$

Electrochemically, the number of charge-carrying ions ($N_{carrier}$) is important and here was simply calculated from the α and M in the unit of mol/L as following

$$N_{carrier} = \alpha \times M. \quad (6)$$

Electrochemical studies on various electrolyte solutions have been done over a long period [16]; however, experimental values of diffusion constants for cation, anion and solvent have not been obtained. We also measured the D_{Li} , D_{Anion} and σ for polymer gel and solid polymer electrolytes intended for use in Li batteries [17–21].

Initially, 12 typical lithium electrolyte solutions were prepared using lithium bis(trifluoromethanesulfonyl)amide ($\text{LiN}(\text{SO}_2\text{CF}_3)_2$, LiTFSA) as a lithium salt [1]. Twelve organic solvents with small molecular weight studied in this study were characterized as having two types of properties: high dielectric constant to dissociate a lithium salt, and low viscosity to promote ion transport. Typical solvents with the former characteristic are propylene carbonate (PC) and ethylene carbonate (EC), and γ -butyrolactone (GBL), and those typical for the latter are dimethylcarbonate (DMC) and 1,2-dimethoxyethane (DME). Since the electrodes in Li batteries are sensitive to moisture, the solvents must be extremely well controlled to ensure that they are non-hydrophilic. The solvation effects around Li^+ , degree of ion dissociation α and lithium transference number t_{Li} were estimated [1].

Experimental confirmation of the NE relation was performed by observing σ , D_{Li} , D_{Anion} and $D_{solvent}$ near infinitesimal

concentration region for four electrolyte solutions composed of two lithium salts (LiTFSA or LiBF_4) and two solvents (PC or GBL) [2]. Historically, the NE equation has been discussed mainly in aqueous solutions [16]. It is important to confirm that the NE relation is valid in organic electrolyte solutions including lithium salts. The experimental σ and D_{ion} 's values were extrapolated to infinite dilution and it was verified that the NE relation holds in organic lithium solutions.

The effects of anions on the D_{Li} were studied using six lithium salts (LiBF_4 , LiPF_6 , LiTFSA, $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$ (LiBETI) and lithium bis(oxalate)borate (LiBOB)) in GBL [3] and a lithium divalent salt, $\text{Li}_2\text{B}_{12}\text{F}_{12}$ in PC [4,5].

Since ideal solvents with high dielectric constant and low viscosity cannot be found, two or more solvents are mixed to afford such functions for use as lithium electrolyte solutions. We studied two binary solvent systems composed of PC-DEC (diethylcarbonate) and PC-DME with LiTFSA to clarify the roles of two solvents having different properties [6]. Binary solvent systems of EC-DEC- LiPF_6 were studied in the temperature range between -20 and 80°C [7], because they are important basic lithium electrolyte solution systems used in practical Li batteries. Note that actual lithium electrolyte solutions used in commercial Li batteries are complicated mixtures of many materials to serve various purposes [22].

As models of polyethylene oxide (PEO)-based polymer electrolytes, we observed σ , D_{Li} , D_{Anion} and $D_{solvent}$ for the $\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{OCH}_3$ systems; diglyme (DG, $n=2$), triglyme (TG, $n=3$), tetraglyme (TeG, $n=4$), pentaglyme (PG, $n=5$), and dimethyl polyethylene-oxide of molecular weights 400 (P4, $n \approx 11$) and 1,000 (P10, $n \approx 24$) doped with LiTFSA and showed clear interactions of Li^+ and $\text{CH}_2\text{CH}_2\text{O}$ chains [8,9]. The results supported our studies on lithium ion and anion diffusion in PEO-based polymer gel and solid polymer electrolytes [17–20] (data not shown in this paper, because the long-term structure relaxation exists and ion diffusion constants varied [21]). Experimentally, the D_{Li} and D_{anion} in polymer electrolytes depend on measuring time and we are sure that they differ from those in electrolyte solutions and their numerical data cannot be treated as physical constants.

The possibility of using ionic liquids (IL) in Li batteries was considered. To support the manufacture of batteries, the diffusion constants of lithium, cation and anion were measured for six binary systems; Emim-TFSA-Li, Emim-FSA-Li, P13-TFSA-Li, P13-FSA-Li, DEME-TFSA-Li and Emim- BF_4 -Li, where Emim; 1-ethyl-3-methylimidazolium, P13: *N*-methyl-*N*-propyl pyrrolidinium, DEME: *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium and FSA: bis(fluorosulfonyl)amide [10–13]. Direct plots of D_s versus σ for the lithium doped binary ILs are presented in this paper.

In the present paper all the data used were our own measurements. An important purpose is to open numerical values in 35 tables of Supplementary Information to the worldwide electrochemistry community.

2. Experimental

A lithium electrolyte solution was prepared by adding a weighed amount of lithium salt to organic solvent/ionic liquid. The battery-grade organic solvents and lithium salts (if available) were used and the preparation of the electrolyte solutions was made in a dry room or in a glove box. NMR samples were prepared to fill a 5 mm (o. d.) NMR microtube (BMS-005J, Shigemi, Tokyo) to a height of less than 5 mm to prevent convection effects at high temperatures. For diffusion measurements of non-viscous diglyme solutions at high temperatures, a special donut-type microtube was used [9]. The diffusion constants were measured using the

Download English Version:

<https://daneshyari.com/en/article/6469789>

Download Persian Version:

<https://daneshyari.com/article/6469789>

[Daneshyari.com](https://daneshyari.com)