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Authors

Feng, Zhange

Higa, Kenneth

Han, Kee Sung

et al.

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Evaluating transport properties and ionic dissociation of LiPF_6 in concentrated electrolyte

Zhange Feng^a, Kenneth Higa^b, Kee Sung Han^c, and Venkat Srinivasan^a

^a *Argonne National Laboratory, Lemont, Illinois 60439, USA*

^b *Environmental Technologies Area, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

^c *Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington 99352, USA*

Abstract

The presence of lithium hexafluorophosphate (LiPF_6) ion pairs in carbonate-based electrolyte solutions is widely accepted in the field of battery electrolyte research and is expected to affect solution transport properties. No existing techniques are capable of directly quantifying salt dissociation in these solutions. Previous publications by others have provided estimates of dissociation degrees using dilute solution theory and pulsed field gradient nuclear magnetic resonance spectroscopy (PFG-NMR) measurements of self-diffusivity. However, the behavior of a concentrated electrolyte solution can deviate significantly from dilute solution theory predictions. This work, for the first time, instead uses Onsager–Stefan–Maxwell concentrated solution theory and the generalized Darken relation with PFG-NMR measurements to quantify the degrees of dissociation in electrolyte solutions (LiPF_6 in ethylene carbonate/diethyl carbonate, 1:1 by weight). At LiPF_6 concentrations ranging from 0.1M to 1.5M, the salt dissociation degree is found to range from 61% to 37%. Transport properties are then calculated through concentrated solution theory with corrections for these significant levels of ion pairing.

Keywords: electrolytes; transport properties; pulsed field gradient NMR; ionic dissociation; lithium ion battery; concentrated solution theory.

Introduction

Accurate prediction of lithium ion battery (LIB) performance is critically important in many battery applications,^{1,2} including the high-power, high-energy battery packs used in electric vehicles. Accurate model predictions by, for instance, the classical porous electrode model developed by John Newman,³ require accurate electrolyte solution transport properties.

Two types of theories have been widely applied in order to analyze the transport properties of binary electrolytes: Nernst-Planck dilute solution theory and Onsager–Stefan–Maxwell (OSM) concentrated solution theory.⁴ Many studies of LIB electrolyte transport properties employ dilute solution theory.^{5,6} However, OSM theory, which considers interactions among all solution components,⁷ should be used to analyze the transport properties of concentrated electrolyte solutions and improve accuracy of electrochemical models at high C-rates,⁸ which are associated with large concentration gradients. Monroe *et al.* calculated the conductivity of an aqueous binary electrolyte solution with both dilute solution theory and OSM theory, and demonstrated that results based on dilute solution theory can deviate significantly from concentrated solution theory at higher concentrations.⁴

However, the presence of ion pair, in addition to fully-dissociated electrolyte salt, complicates the application of concentrated solution theory. Few experimental techniques can quantitatively distinguish ion pairs from fully-solvated ions. However, the presence of solvated LiPF₆ ion pairs (which will be denoted as “Li-PF₆”) in carbonate electrolytes has been confirmed by infrared absorption spectroscopy and Raman spectroscopy.⁹

Ion pairs should not contribute to electrolyte solution conductivity because of charge neutrality, making it possible to calculate the degree of dissociation by comparing directly

measured conductivity values to those calculated by other means. Based on the Haven ratio¹⁰ of experimentally-measured conductivity and theoretical conductivity as calculated from the Nernst-Einstein equation, Hayamizu reported that the degree of LiPF₆ dissociation increased as the quantity of ethylene carbonate (EC) in the electrolyte solution was increased.¹¹ Stolwijk *et al.* isolated dilute-limit ionic diffusivities in polymer electrolyte based on the Nernst-Einstein equation and conductivity measurements.¹² Goward *et al.* adopted this framework to analyze the degree of LiPF₆ dissociation in carbonate electrolyte solutions commonly used in LIBs, e.g. LiPF₆/EC/dimethyl carbonate (DMC), and LiPF₆/EC/ethyl methyl carbonate (EMC), and reported a high degree of ion pairing even at a low salt concentration of 0.2M.¹³

Recently, our group reported a method for estimating OSM theory transport properties of LiPF₆/propylene carbonate (PC) electrolytes from the self-diffusivity values of both the salt and solvent under the assumption of that LiPF₆ is fully dissociated.¹⁴ The present work, for the first time, uses concentrated solution theory to provide a quantitative analysis of the degree of LiPF₆ dissociation in EC/diethyl carbonate (DEC) electrolyte with self-diffusivity values measured by pulsed field gradient nuclear magnetic resonance (PFG-NMR) and subsequently determines corrected diffusivity and transference number values.

Experiment

All electrolyte solution components used in this work were purchased from BASF. In an argon-filled glovebox (with 0.5 ppm oxygen and 0.2 ppm water), LiPF₆ was dissolved in a mixture of EC/DEC (1:1 by weight) to obtain electrolyte solutions of concentrations ranging from 0.1M to 1.5M. Solution conductivity values were measured with a VWR symPHony conductivity meter equipped with a titanium probe inside the glovebox at room temperature.

These solutions were then sealed in aluminum bottles for transport to the NMR facility and were transferred to NMR tubes and sealed a top with an epoxy in the glove box.

Self-diffusivities of Li^+ cation, PF_6^- anion and solvent molecules (EC and DEC) denoted as D_{Li} , D_{PF_6} , D_{EC} and D_{DEC} were measured by ^7Li , ^{19}F , and ^1H pulsed field gradient (PFG) NMRy at Larmor frequencies of 233.2 , 564.3, and 599.8MHz , respectively at temperatures ranging from 0 to 40°C. Since ^1H NMR peaks from EC and DEC are well separated in one-dimensional ^1H spectra from these solutions, it is possible to measure the D_{EC} and D_{DEC} using ^1H PFG-NMR at a same time. All measurements were performed on a 14.1 T (600 MHz ^1H) NMR spectrometer (Agilent) equipped with a 5 mm z-gradient probe (Doty Scientific), which can generate a maximum gradient strength of approximately 31 T/m. The echo heights, $S(g)$, recorded as a function of gradient strength, g , were fitted with the Stejskal-Tanner equation,¹⁵

$$S(g) = S(0)e^{\left[-D(\gamma g \delta)^2(\Delta - \delta/3)\right]}, \quad (1)$$

where D is the diffusion coefficient, γ is the gyromagnetic ratio of ^1H , ^{19}F , or ^7Li , g is the gradient strength, Δ is the diffusion delay and δ is the gradient length.

Theory

Darken's relation was proposed in the 1940s as a means of translating self-diffusivity into binary diffusivity in binary metallic systems.¹⁶ A generalized form was found to provide reasonable results by Krishna and Baten in molecular dynamics simulations of ternary and quaternary mixtures of linear alkanes.¹⁷ Recently, Kim applied this generalized Darken relation and OSM theory to solutions of LiPF_6 in PC and obtained reasonable OSM transport properties.¹⁴

For comparison with published OSM transport parameter values and for use with conventional electrochemical models, one may apply Kim's protocol¹⁴ under the assumption that no ion pairs are present in solution:

- I. As mentioned in the Experimental section, the self-diffusivity values D_{Li} , D_{PF6} , and D_{EC} ,

are measured by PFG-NMR. Under the assumption of complete salt dissociation, the D_{DEC}

first two are identical to the self-diffusivities of cations and anions denoted by D_+ and D_- . It

is assumed that the EC and DEC components can be described with a concentration-averaged

diffusion coefficient D_0 . These ideas are represented by the following equations:

$$D_0 = \frac{c_{EC}}{(c_{EC} + c_{DEC})} D_{EC} + \frac{c_{DEC}}{(c_{EC} + c_{DEC})} D_{DEC} \quad (2)$$

$$D_+ = D_{Li}$$

$$D_- = D_{PF6}$$

where the subscripted c symbols denote species concentrations.

- II. The generalized Darken relation, is used to translate the self-diffusivities D_0 , D_+ , and D_- into

binary diffusivities in OSM theory, D_{0+} , D_{0-} , and D_{+-} , for this binary electrolyte:

(3)

$$D_{0+} = \frac{x_0}{x_0 + x_+} D_+ + \frac{x_+}{x_0 + x_+} D_0$$

$$D_{0-} = \frac{x_0}{x_0 + x_-} D_- + \frac{x_-}{x_0 + x_-} D_0$$

$$D_{+-} = \frac{x_-}{x_- + x_+} D_+ + \frac{x_+}{x_- + x_+} D_-$$

where the subscripted x symbols are the molar fractions of solvent ($x_0 = c_0 / c_T$), cations ($x_+ = c_+ / c_T$), and anions ($x_- = c_- / c_T$); c_T is the total concentration, equal to the sum of c_0 , c_+ , and c_- .

and c_- .

III. The diffusivity D of the electrolyte based on thermodynamic driving force is determined by

the binary diffusivities from (see Reference 7, chapter 12.2):

$$D = \frac{v_- D_{0+} D_{0-}}{v_- D_{0+} + v_+ D_{0-}} = \frac{(z_+ - z_-) D_{0+} D_{0-}}{z_+ D_{0+} - z_- D_{0-}} \quad (4)$$

IV. The diffusivity D of the salt, often used in porous electrode model,^{3,8} is related to the

diffusivity D of the binary electrolyte from Equation (4) by:⁷

$$D = D_{c_T} \bar{V}_0 \left(1 + \frac{d \ln f_{+-}}{d \ln c} \right) \quad (5)$$

where \bar{V}_0 is the partial molar volume of the solvent (56.8 ml/mole),¹⁸ and the thermodynamic

factor $1 + \frac{d \ln f_{+-}}{d \ln c}$ is taken from literature as¹⁸

$$\frac{0.2731c_+^2 + 0.6352c_+ + 0.4577}{0.1291c_+^3 - 0.3517c_+^2 + 0.4893c_+ + 0.5713}$$

V. The cation transference number, t_+^0 and anion transference number t_-^0 are determined⁷ from

the binary diffusivities, D_{0+} and D_{0-} (Equation (3)):

$$t_+^0 = 1 - t_-^0 = \frac{v_- D_{0+}}{v_- D_{0+} + v_+ D_{0-}} = \frac{z_+ D_{0+}}{z_+ D_{0+} - z_- D_{0-}} \quad (6)$$

where subscripted z and v symbols indicate the charges and stoichiometric coefficients of the anions and cations.

VI. The ionic conductivity of the electrolyte, κ , as a function of the binary diffusivities and the

anion transference number, t_-^0 , is obtained from OSM theory⁷:

$$\frac{1}{K} = \frac{-RT}{F^2 z_+ z_- c_T} \left[\frac{1}{D_{+-}} + \frac{c_0 t_-^0}{c_+ D_{0-}} \right] \quad (7)$$

where R, T, and F are the universal gas constant, temperature, and Faraday's constant.

The above procedure can be modified to allow for the possible presence of Li-PF₆ ion pairs.⁷Li has the same NMR chemical shift in both Li⁺ and Li-PF₆, as does ¹⁹F in both PF₆⁻ and Li-PF₆. For this reason, the self-diffusivity values measured by PFG-NMR are averages of ion and ion pair self-diffusivity values, so one may write:

$$\begin{aligned} D_{Li} &= \alpha D_+ + (1-\alpha) D_p \\ D_{PF_6} &= \alpha D_- + (1-\alpha) D_p \end{aligned} \quad (8)$$

where D_{Li} and D_{PF_6} denote the self-diffusivities of Li⁺ cation and PF₆⁻ anion measured by ⁷Li

and ¹⁹F PFG-NMR, respectively, D_+ , D_- , and D_p are the self-diffusivities of Li⁺, PF₆⁻, and Li-PF₆ pairs, and α is the degree of salt dissociation and equal to $c_+/(c_+ + c_p)$, where c_p is the concentration of Li-PF₆ ion pairs. The form of these relations has been confirmed using weakly dissociating salts in polymer and EC/DMC electrolytes.^{12, 19} The degree of LiPF₆ dissociation and its effects on transport properties may then be obtained by using the following modified procedure:

- I. The neutral ion pairs Li-PF₆, which do not contribute to the conductivity of the electrolyte, are treated as if part of the solvent. Similarly to the earlier development, the self-diffusivity

of the solvent, D_0 , is calculated by molar average of the self-diffusivities of EC, DEC, and

Li-PF₆. D_+ and D_- , representing the Li⁺ and PF₆⁻, are obtained by rearranging Equation (8):

$$\begin{aligned}
 D_0 &= \frac{c_{EC}}{(c_{EC} + c_{DEC} + c_p)} D_{EC} + \frac{c_{DEC}}{(c_{EC} + c_{DEC} + c_p)} D_{DEC} + \frac{c_p}{(c_{EC} + c_{DEC} + c_p)} D_p \\
 D_+ &= \frac{D_{Li} - (1 - \alpha) D_p}{\alpha} \\
 D_- &= \frac{D_{PF_6} - (1 - \alpha) D_p}{\alpha}
 \end{aligned} \tag{9}$$

II. The assumption, $D_+ \approx D_p$, is taken in the analysis for the following reason: Molecular

dynamics simulations have suggested that Li-PF₆ exists mostly in the form of direct contact ion pairs in that PF₆⁻ ions are in direct contact with Li⁺ ions, as opposed to solvent-shared ion pair, and the solvation shell geometry remains similar in EC solvated Li⁺, a tetrahedral structure with four EC molecular, and EC solvated Li-PF₆, despite the substitution of one EC molecule by a PF₆⁻.^{20,21,22} It is therefore reasonable to assume that a EC solvated Li⁺ and a

contact ion pair have similar sizes and thus similar self-diffusivities: $D_+ \approx D_p$. This

assumption is further supported by electrochemical microcalorimetry, in which Li-PF₆ ion pairs show similar solvation behavior to EC solvated Li⁺²³ and has been applied in electrolyte research by Goward *et al.* recently.¹³

III. The binary diffusivities, D_{0+} , D_{0-} and D_{+-} are calculated by the generalized Darken relation

using the self-diffusivities obtained in Equation (9):

(10)

$$D_{0+} = \frac{x_0}{x_0 + x_+} D_{++} + \frac{x_+}{x_0 + x_+} D_{00}$$

$$D_{0-} = \frac{x_0}{x_0 + x_-} D_{--} + \frac{x_-}{x_0 + x_-} D_{00}$$

$$D_{+-} = \frac{x_-}{x_- + x_+} D_{++} + \frac{x_+}{x_- + x_+} D_{--}$$

where the molar fractions of solvent, cations and anions, denoted by x_0 , x_+ and x_- , are

given by:

(11)

$$x_0 = \frac{c_0}{c_T} = \frac{c_{EC} + c_{DEC} + c_p}{c_+ + c_- + c_{EC} + c_{DEC} + c_p}$$

$$x_+ = \frac{c_+}{c_T} = \frac{c_+}{c_+ + c_- + c_{EC} + c_{DEC} + c_p}$$

$$x_- = \frac{c_-}{c_T} = \frac{c_-}{c_+ + c_- + c_{EC} + c_{DEC} + c_p}$$

- IV. Equation (10) is substituted into Equation (6) to calculate the cationic transference number t_+ .
- V. For each concentration at which the conductivity is measured directly, its value, the transference number from step IV, and binary diffusivity from step III are substituted into

Equation (7), which is then solved to obtain the degree of dissociation α .

- VI. With the known degree of dissociation α at each concentration, the binary diffusivities (D_{0+}

and D_{+-}) and the transference number, t_+ are evaluated based on Equations (10), (11), (6).

- VII. The diffusivity D of the electrolyte is calculated from the binary diffusivities using Equation

(4).

VIII. The diffusivity D of the salt is calculated from the value of D obtained in the previous step

through Equation (5), using the same value of the partial molar volume of the solvent.

Results and Discussion

Assuming fully-dissociated $LiPF_6$. Shown in Figure 1 are the self-diffusivities of Li^+ , PF_6^- , EC, and DEC in the $LiPF_6/EC/DEC$ electrolyte solutions as measured by PFG-NMR at varying concentrations and temperatures. Inspection of the data immediately suggests the following trends:

- I. The self-diffusivities of all species decrease as the concentration increases or the temperature decreases, which is qualitatively consistent with the Stokes-Einstein equation, in which diffusivity is proportional to the temperature and inversely proportional to the viscosity (which increases with concentration),

$$D = \frac{kT}{c\pi\eta r_s} \quad (12)$$

where k is the Boltzmann constant, r_s is the Stokes radius of the diffusing species, η is

the viscosity, and the constant c ranges between 4 to 6 for slip and stick boundary conditions.

- II. At a given concentration and temperature, $D_{EC} \approx D_{DEC} > D_{PF_6} > D_{Li}$.

III. At 20 °C (see Figure 2), D_{Li} shows the weakest concentration dependence among all

species, while the concentration dependence of D_{PF_6} is more dramatic than other species at lower concentration, e.g. 0.1M to 0.75M.

Under the assumption that Li-PF₆ is not present in solution, the binary diffusivities D_{0+} ,

D_{0-} and D_{+-} , are calculated at 20 °C from the self-diffusivities in Figure 2 using Equation (3).

The resulting values are shown in Figure 3a. In general, the binary diffusivities decrease as the concentration increases, and $D_{0-} > D_{+-} > D_{0+}$ at all concentrations. In Figure 3b, the diffusivity

based on thermodynamic driving force calculated in equation (4) shows monotonously decreasing values as concentration increases.

Published activity coefficient¹⁸ and partial molar volume data¹⁸ are used with Equation (5)

to then evaluate the diffusivity D of the electrolyte, again with the assumption that LiPF₆ is

dissociated completely. The diffusivity values shown by the connected magenta squares are calculated in recognition of ion pairing and will be discussed in the next section. Overall, the

diffusivity values (black connected squares, Figure 4) decrease from 3.7×10^{-10} to 2.47×10^{-10} m²/s

as the concentration increases and compare well with those measured by others using electrochemical methods with similar electrolyte solutions over a wide range of concentrations. For example, Lundgren *et al.* reported that diffusivities of LiPF₆ in the same electrolyte decreased from $2.8 \times 10^{-10} \text{ m}^2/\text{s}$ to $2.0 \times 10^{-10} \text{ m}^2/\text{s}$ in the range of 0.5M to 1.5M by galvanostatic polarization experiments (red connected squares, Figure 4),¹⁸ and Valøen and Reimers measured the diffusion of LiPF₆ in a PC/EC/DMC mixture (blue connected squares, Figure 4).²⁴ However, the diffusivity values from the present work do not decrease monotonically; a smaller diffusivity value is observed at 0.5M than at 0.75M. This can be understood by examining equation (5). Taking its derivative with respect to concentration yields

$$\frac{dD}{dc} = \dot{V}_0 \left\{ \frac{d}{dc} c_T \left(1 + \frac{d \ln f_{\pm}}{d \ln c} \right) + \frac{d}{dc} \left[c_T \left(1 + \frac{d \ln f_{\pm}}{d \ln c} \right) \right] \right\} .$$

It can be seen in Figure 3b that the derivative of D is negative, while Figures 3c and 3d indicate that the derivative of the factor in square brackets is positive. All other terms on the right side are positive. The overall decrease in D shown in Figure 4 then indicates that the left term on the right side is generally dominant, particularly at higher concentrations since D decreases exponentially (Figure 3b). However, the derivative of D briefly becomes positive when the right term on the right side becomes dominant as the slope of the thermodynamic factor (Figure 3d) increases around 0.5M.

Shown in Figure 5 (black connected squares) is the transference number as a function of salt concentration, as computed from Equation (6) under the assumption of fully-dissociated LiPF_6 , where $z^+ = 1$ and $z^- = -1$ for Li^+ and PF_6^- in EC/DEC. The transference number values shown by the connected magenta squares (Figure 5) are calculated based on the degree of ion pairing and will be discussed in next section. Overall, the transference number increases with solution concentration, rising from 0.3 to 0.38 as concentration increases from 0.1M to 0.5M, and then shows relatively little change at higher concentrations. A reasonable comparison is found with values reported for different electrolyte solutions, e.g. PC/EC/DMC (green connected squares),²⁵ PC (blue connected squares)²⁶ and γ -butyrolactone (red connected squares).²⁶ However, as with the diffusivity of the salt, the transference number does not change monotonically with concentration. Taking the derivative of Equation (6) and simplifying yields

$$\begin{aligned}
 & \frac{0 - \dot{c}}{0 + \dot{c} + \square_{\dot{c}}} \\
 & \frac{\square_{\dot{c}}}{\dot{c}} \\
 & \frac{\dot{c}}{\dot{c}} \\
 & \frac{\dot{c}}{\dot{c}} \\
 & \frac{d \square_{0-\dot{c}}}{dc} \\
 & \frac{0 + \dot{c}}{\dot{c}} \cdot \text{The denominator is always positive, so the sign of the derivative is determined} \\
 & \frac{d \square_{0+\dot{c}}}{dc} - \square_{\dot{c}} \\
 & \frac{0 - \dot{c} \dot{c}}{\square_{\dot{c}}} \\
 & \frac{d \frac{t_{+\dot{c}}^0}{dc} = \dot{c}}{\dot{c}}
 \end{aligned}$$

only by the relative magnitudes of the terms in the numerator. The absolute value of the second term divided by the first term suggests a positive slope if the ratio is greater than 1, and a negative slope if less than 1. Writing this inequality and simplifying, one can conclude that the

slope is positive if $\frac{d \ln \frac{\square_{0-\dot{c}}}{dc}}{d \ln \frac{\square_{0+\dot{c}}}{dc}}$, or negative if the inequality holds in the opposite direction. This

can be determined immediately from Figure 3a, in which it the slope of the logarithm of D_{0-} is

clearly more severe than that of D_{0+} at high and low concentrations, corresponding to the increasing transference number values in Figure 5, but is approximately the same (and even smaller) at intermediate concentrations, at which the transference number dips slightly.

Figure 6 compares the ionic conductivity of LiPF₆ in EC/DEC (1:1 by weight) calculated from the binary diffusivities by Equation (7), again assuming fully-dissociated LiPF₆, with direct measurements. Both have maximum values around 1.0M and decrease at higher concentrations. The calculated ionic conductivities are higher than the directly measured values over the whole concentration range. This suggests the presence of neutral Li-PF₆, since the conductivity calculation assumes that LiPF₆ is fully dissociated, which would suggest a higher concentration of charge carriers. This is also consistent with Kim's conductivity calculations for LiPF₆ in PC,¹⁴ a solvent with a higher dielectric constant than EC/DEC, which showed a ratio of conductivity values that was much closer to unity (black bars, right panel of Figure 7).

Recognizing the presence of ion pairs. The degree of dissociation is important to quantify because it should also affect other transport properties. The ratio of measured conductivity and the conductivity calculated from the Nernst-Einstein equation, known as the Haven ratio¹⁰, is frequently used as an estimate of the degree of dissociation.¹¹ Another approach,^{12,13} again using the Nernst-Einstein equation, decomposes diffusivities into those of ions and ion pairs, the relative quantities of which yield the degree of dissociation in the dilute limit. The modified method described in the Theory section involves a similar approach, distinguishing ions from ion pairs, but incorporates concentrated solution theory and so is not limited to dilute conditions. The results of this analysis are shown by the red bars in the left panel of Figure 7. This shows that only 61% of salt molecules are dissociated at 0.1M. The presence of ion pairs in electrolyte

solutions containing similarly low concentrations of LiPF_6 has also been reported by other researchers,^{9,13} with comparable degrees of dissociation for a given LiPF_6 concentration found for $\text{LiPF}_6/\text{EC}/\text{DMC}$.¹³ The degree of LiPF_6 dissociation decreases to 0.37 at 1.25M and then appears to increase to 0.39 at 1.5M. However, at this high Li^+ concentration, the assumption $D_{++} \approx D_p$

might not hold because of the relatively low number of EC molecules available to solvate each lithium ion.

Also included for comparison in Figure 7 is the Haven ratio^{10,11} of experimental and theoretical conductivities (black bars, left panel), but calculated using OSM theory rather than the Nernst-Einstein equation. This is labeled as “Haven ratio/OSM,” and shows the same qualitative concentration dependence as obtained by the method developed here, but with larger values; this discrepancy quantifies the error in taking the Haven ratio as a direct estimate of the degree of dissociation.

Decreasing degrees of dissociation at higher concentrations and lower dissociation degrees than estimated from the Haven ratio/OSM (red bars, right panel of Figure 7) are also obtained by reanalyzing the LiPF_6/PC data reported by Kim¹⁴ with the present protocol. Further, the dissociation degree for LiPF_6/PC electrolyte is higher than that of $\text{LiPF}_6/\text{EC}/\text{DEC}$ at the same concentration, which is consistent with the larger dielectric constant of PC as discussed earlier.

With the degrees of dissociation now available, diffusivities and transference numbers of the dissociated LiPF_6 are then calculated as described in steps VIII and VI of the modified procedure described in the Theory section. The concentration-dependent diffusivities of the dissociated LiPF_6 (connected magenta squares, Figure 4) are slightly larger than those previously calculated under the assumption of no ion pairing.

The transference number values calculated in recognition of ion pairing (connected magenta squares in Figure 5) and those evaluated under the assumption of complete LiPF_6 dissociation (connected black squares) show similar trends. However, the former shows a much stronger dependence on concentration dependence. In this modified analysis, the cation self-

diffusivity values D_i^{+} remain identified with the ion pair self-diffusivity, leading to little

change in D_{0+} . However, the D_i^{-} values change more dramatically with concentration

because they have been corrected to remove the moderating contribution of the ion pair self-

diffusivity, leading to larger values of D_{0-} with more dramatic changes. The corrected

transference number values, which fall in the range 0.27 ± 0.03 , are also lower than that

previously calculated under the assumption of no ion pairing, as the increase in the value of D_{0-}

increases the size of the denominator of Equation (6). These smaller values are in agreement with those found by other researchers using a galvanostatic polarization method based on concentrated solution theory in a similar electrolyte, LiPF_6 in EC/DEC (3/7 wt).²⁷ However, to have a full understanding of the influence of ion pairs, the dynamics of ion pairing need to be explored.

While the experiments described in this work were limited to various concentrations of LiPF_6 in a single mixture of EC/DEC (1:1 by weight), the procedure outlined here could be applied to other electrolyte solutions to quantify the extent to which ion pairing affects conductivity through quantities such as binary diffusivities, concentrations, and transference numbers, as seen in Equation 7. In general, as other authors have noted,¹¹ ion pairing can be minimized by using solvents with high dielectric constants and electrolytes that dissociate readily.

Conclusion

A novel method for quantifying the degree of dissociation of LiPF_6 in carbonate electrolyte solutions, based on the generalized Darken relation and OSM theory, was presented and applied to solutions of LiPF_6 in EC/DEC (1:1 by weight). The degree of dissociation was found to decrease from 0.61 to 0.37 as concentration was increased from 0.1M to 1.25M. Similarly for LiPF_6 in PC, the dissociation degree was found to decrease from 0.675 and 0.51 over a concentration range of 0.5M to 2.0M. This information was then used to reevaluate transport property values.

While the assumption of complete LiPF_6 dissociation was observed to have a modest effect on diffusivity values, the effect on transference number values was found to be relatively large. These differences indicate that it can be important to consider salt dissociation when developing electrochemical models, as will be addressed in future research.

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Figure 1. Concentration and temperature dependence of self-diffusivity for Li^+ , PF_6^- , EC and DEC by PFG-NMR.

Figure 2. Concentration dependence of self-diffusivity for Li^+ , PF_6^- , EC and DEC at 20 °C

Figure 3. (a) Binary diffusivities (D_{0+} , D_{0-} and D_{+-}) calculated from self-diffusivities in Figure

2; (b) diffusivity of the electrolyte; (c) total concentration c_T ; (d) thermodynamic factor

$$1 + \frac{d \ln f_{+-}}{d \ln c}$$

Figure 4. Diffusivities of the electrolyte as a function of concentration, compared with previously reported experimental values. Black connected squares from this work under the assumption of no ion pairing. Magenta connected squares from this work, recognizing the presence of ion pairing. Red connected squares from Lundgren *et al.* (EC/DEC 1:1). Blue connected squares from Valøen and Reimers (PC/EC/DMC10:27:63).

Figure 5. Li^+ transference numbers as functions of concentration, compared with previously reported values. Black connected squares from this work, under the assumption of no ion pairing. Magenta connected squares from this work, recognizing the presence of ion pairing. Red connected squares from Aihara *et al.* (γ -butyrolactone). Green connected squares from Valøen and Reimers (PC/EC/DMC 10:27:63). Blue connected squares from Kim *et al.* (PC).

Figure 6. Calculated ionic conductivities of $\text{LiPF}_6/\text{EC}/\text{DEC}$ electrolyte solution (black connected points) and directly measured values (red connected points) as a function of salt concentration.

Figure 7. LiPF_6 dissociation degree in EC/DEC (left) and PC (right) calculated by Haven ratio/OSM (black bars) and by generalized Darken relation and OSM theory (red bars).













