



Electrical conductivity of solutions of lithium bis(fluorosulfonyl)imide in mixed organic solvents and multi-objective solvent optimization for lithium-ion batteries



Johannes Neuhaus, Esther Forte, Erik von Harbou*, Hans Hasse

Laboratory of Engineering Thermodynamics (LTD), University of Kaiserslautern, Erwin-Schrödinger Str. 44, D-67663, Kaiserslautern, Germany

HIGHLIGHTS

- High electrical conductivity for mixtures of planar and cyclic carbonates.
- Multi-objective optimization for the rational design of electrolyte solutions.
- Cost and performance optimization under constraints.

ARTICLE INFO

Keywords:

Lithium bis(fluorosulfonyl)imide
Lithium-ion battery
Multi-objective optimization
Pareto
Electrolyte solution
LiFSI

ABSTRACT

Lithium bis(fluorosulfonyl)imide (LiFSI) is an interesting novel electrolyte for lithium-ion batteries. In the present work, the electrical conductivity of solutions of LiFSI in binary and ternary mixtures of the solvents dimethyl carbonate (DMC), ethylene carbonate (EC) and propylene carbonate (PC) was studied experimentally for concentrations of LiFSI up to 0.2 mol mol^{-1} at ambient pressure and temperatures between 293 and 333 K. Information on the electrical conductivity of LiFSI in the pure solvents DMC, EC, and PC is available from previous work. An empirical correlation of the electrical conductivity σ of the studied solutions of LiFSI is presented that describes the dependence of σ on the LiFSI concentration, the solvent composition, and the temperature. Based on this correlation, a multi-objective optimization of the LiFSI concentration and the solvent composition was carried out with two conflicting objectives relevant to the performance and costs of batteries: maximizing electrical conductivity and minimizing the amount of the expensive electrolyte LiFSI. The solubility limits of the ternary solvent system DMC-EC-PC were included in the optimization as constraints. The multi-objective optimization applied here, is shown to be useful for obtaining a rational basis for decision-making in the design of electrolyte solutions for batteries.

1. Introduction

Lithium-ion batteries (LiB) are well established for the safe and efficient storage of electrical energy and there is a continuously growing demand for both smaller and more powerful devices [1–3]. Advanced electrolyte solutions can contribute to the progress in the field of LiB-technology [4–11].

A promising new electrolyte for LiB is lithium bis(fluorosulfonyl)imide (LiFSI). LiFSI has a higher electrical conductivity in organic solvents that are commonly used in LiB than the benchmark electrolyte LiPF_6 [12]. Further, LiFSI has other advantages like a better stability regarding hydrolysis and lower aluminium corrosion [13–18].

Commonly used solvents in LiB are dimethyl carbonate (DMC),

ethylene carbonate (EC), and propylene carbonate (PC) [19]. We have recently presented a comprehensive study on physico-chemical properties of LiFSI in these solvents, which includes data on the electrical conductivity [12]. However in that study, only pure solvents were investigated. For solutions of LiFSI in solvent mixtures, up to now, only spotty data is available. Table 1 gives an overview of literature data on physico-chemical properties of solutions of LiFSI in solvent mixtures.

In the present work, a systematic experimental study on the electrical conductivity of solutions of LiFSI in binary and ternary solvent mixtures of DMC, EC, and PC, was carried out for concentrations of LiFSI up to 0.2 mol mol^{-1} at ambient pressure and temperatures between 293 and 333 K. Based on the new data and that from our previous work [12], an empirical correlation of the dependence of the electrical

* Corresponding author.

E-mail address: erik.vonharbou@mv.uni-kl.de (E. von Harbou).

Table 1

Overview of literature data on physico-chemical properties of solutions of LiFSI in organic solvents mixtures.

Solvent (mixture) ^a	c_{LiFSI}/M	T/K	Properties	Reference
DEC-EC (7:3)	1.0	253–293	σ, η	Takekawa et al. [20]
DMC-EC (1:1, 9:1)	1.0	298	σ, η	Uchida and Ishikawa [21]
DMC-EC (1:1)	0.6–5.3	303	σ, η, ρ	Wang et al. [18]
DMC-EMC (3:7)	1.0	223–323	σ	Li et al. [22]
EMC-EC (7:3)	1.0	253–333	σ, η	Han et al. [13]
DMC-EMC-EC (2:3:5)	1.0	253–323	σ	Li et al. [22]

σ electrical conductivity, ρ density, η shear viscosity.

Abbr.: DEC: diethyl carbonate; DMC: dimethyl carbonate; EC: ethylene carbonate; EMC: ethyl-methyl carbonate.

^a Volume ratio.

conductivity on the temperature and composition of the electrolyte solution was developed.

The identification of an optimal composition of the electrolyte solution for LiB is a challenging task. The electrical conductivity and the costs of the electrolyte solution depend strongly on the concentration of the conductive salt (LiFSI). Furthermore, solid precipitation may occur at temperatures relevant for technical applications. Hence, there are multiple goals, which are conflicting. We solve this multi-objective optimization problem by the calculation of so-called Pareto sets. A Pareto set is defined as a set comprising all solutions in which an improvement in any objective can only be achieved by accepting a decline in at least one other objective [23–26]. The conflicting objectives that are considered here are the electrical conductivity that should be high and the LiFSI concentration that should be low, as LiFSI is expensive. The solubility limit of the ternary solvent system DMC-EC-PC is included in the optimization as a constraint. The liquid phase non-idealities are described by means of the NRTL model [27]. The NRTL model was parametrized in this work using experimental data of the solid-liquid equilibria of the binary solvent systems DMC-EC, DMC-PC, and EC-PC, reported by Ding et al. [28].

The multi-objective optimization strategy applied here can be extended to include more objectives and constraints. The present study provides an example that shows that multi-objective optimization is a powerful tool for optimizing battery electrolyte solutions.

2. Electrical conductivity





2.1. Chemicals and sample preparation

Lithium bis(fluorosulfonyl)imide (LiFSI, $\geq 0.999 \text{ g g}^{-1}$) was supplied by Budan Process UG. Dimethyl carbonate (anhydrous, $\geq 0.999 \text{ g g}^{-1}$), ethylene carbonate (anhydrous, 0.99 g g^{-1}), and propylene carbonate (anhydrous, 0.997 g g^{-1}) were purchased from Sigma Aldrich. All chemicals were used as received. The water content of the pure components was determined by coulometric Karl-Fischer titration (Metrohm 831 KF coulometer) and were found to be below $50 \cdot 10^{-6} \text{ g g}^{-1}$ for all solvents, and below $30 \cdot 10^{-6} \text{ g g}^{-1}$ for LiFSI. All chemicals were handled in an inert gas glove box (GS Glovebox Technik) that maintained an nitrogen atmosphere with a water content of less than $2 \cdot 10^{-6} \text{ g g}^{-1}$. A laboratory balance (Mettler-Toledo AG204) with an accuracy of $\pm 0.0001 \text{ g}$ according to the calibration protocol was used for the gravimetric sample preparation. The total mass of each prepared sample was larger than 30 g. The samples were hermetically sealed in 40 ml glass vials. The uncertainty of the mass fraction of the components is estimated to be $\pm 0.00015 \text{ g g}^{-1}$.

Some relevant physico-chemical properties of the employed solvents and LiFSI are shown in Table 2, wherein M is the molar mass, T_{mmp} and T_{nbp} are the normal melting point and the normal boiling point, respectively, ρ is the density, η is the shear viscosity, D is the self-diffusion coefficient and ϵ is the dielectric constant.

Table 2

Overview of pure component physico-chemical properties of substances that were used in the present work. The numbers for ρ , η , and ϵ for DMC, EC, and PC refer to the liquid state at 313.15 K and ambient pressure.

Property	DMC	EC	PC	LiFSI
				
$M / \text{g mol}^{-1}$	90.1	88.1	102.1	187.1
$T_{\text{mmp}} / \text{K}$	278.2 ^a	311.2 ^a	220.3 ^a	418.2 ^k
$T_{\text{nbp}} / \text{K}$	363.15 ^b	517.15 ^b	513.15 ^b	
$\rho / \text{g cm}^{-3}$	1.0434 ^c	1.3216 ^d	1.1893 ^e	
$\eta / \text{mPa s}$	0.4880 ^f	1.9000 ^g	1.9120 ^e	
$D / 10^{-9} \text{ m s}^{-2}$	26.0 ^{h,*}	8.0 ^h	5.8 ^{h,*}	
ϵ	3.2 ⁱ	89.7 ^j	61.4 ^j	

References: ^a[28], ^b[29], ^c[30], ^d[31], ^e[32], ^f[33], ^g[34], ^h[35], ⁱ[36], ^j[37], ^k[13].

*Measured at 303.15 K.

2.2. Method of measurement

A conductivity meter (Mettler-Toledo Seven Multi equipped with an inLab 720 probe) was used for the measurements of the electrical conductivity. The measurements were carried out at ambient pressure. The conductivity meter was calibrated at 298.15 K using aqueous solutions of NaCl with a maximum concentration of NaCl of 0.3 mol l^{-1} . The reference data were taken from Ref. [38]. The maximum relative deviation of an individual result from the calibration curve was 0.8%. That number is taken for the uncertainty of the measurement of the electrical conductivity. The temperature was controlled using a thermostat (Julabo F32 HE) and measured with the built-in thermometer provided by the instruments supplier which was calibrated in our laboratory using a certified standard. The uncertainty of the temperature measurement is $\pm 0.1 \text{ K}$. Before and after each set of measurements the apparatus was cleaned with toluene, water, and ethanol and flushed with dry nitrogen.

2.3. Correlation

For correlating the electrical conductivity of the studied electrolyte solutions, a Taylor-series type expression shown in Eq. (1) was found to be suitable.

$$\left(\frac{\sigma}{\text{mS cm}^{-1}}\right) = \sum_{k=1}^m \tilde{x}_k \sigma_{\text{LiFSI},k} + \sum_{k=1}^m \sum_{j \neq k}^n \tilde{x}_k \tilde{x}_j C_{k,j} \quad k, j = (\text{DMC, EC, PC}) \quad (1)$$

The first term describes the normalized sum of the electrical conductivity of solutions of LiFSI in the pure solvents, wherein \tilde{x}_k is the normalized mole fraction of solvent k that are defined in Eq. (2).

$$\tilde{x}_k = \frac{n_k}{n_{\text{DMC}} + n_{\text{EC}} + n_{\text{PC}}} \quad (2)$$

where n_i is the mole number of substance i .

The description of the electrical conductivity of solutions of LiFSI in the pure solvent k $\sigma_{\text{LiFSI},k}$ is adapted from our previous work and shown in Eq. (3).

$$\left(\frac{\sigma_{\text{LiFSI},k}}{\text{mS cm}^{-1}}\right) = A_{0,k} + A_{1,k} X_{\text{LiFSI}} + A_{2,k} X_{\text{LiFSI}}^2 + A_{3,k} X_{\text{LiFSI}}^3 + A_{4,k} X_{\text{LiFSI}}^4 \quad (3)$$

where X_{LiFSI} is the apparent molar loading of the solvent (mixture) with LiFSI.

Download English Version:

<https://daneshyari.com/en/article/7724663>

Download Persian Version:

<https://daneshyari.com/article/7724663>

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