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Comparative study on transport properties for LiFAP and $LiPF_6$ in alkyl-carbonates as electrolytes through conductivity, viscosity and NMR self-diffusion measurements

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ABSTRACT

We present in this work a comparative study on density and transport properties, such as the conductivity (σ), viscosity (η) and self-diffusion coefficients (D), for electrolytes based on the lithium hexafluorophosphate, $LiPF_6$; or on the lithium tris(pentafluoroethane)-trifluorophosphate, LiFAP dissolved in a binary mixture of ethylene carbonate (EC) and dimethylcarbonate (DMC) (50:50 wt%). For each electrolyte, the temperature dependence on transport properties over a temperature range from 10 to 80 °C and 20 to 70 °C for viscosity and conductivity, respectively, exhibits a non-Arrhenius behavior. However, this dependence is correctly correlated by using the Vogel-Tamman-Fulcher (VTF) type fitting equation. In each case, the best-fit parameters, such as the pseudo activation energy and ideal glass transition temperature were then extracted. The self-diffusion coefficients (D) of the Li^+ cation and PF_6^- or FAP^- anions species, in each studied electrolyte, were then independently determined by observing ^3Li, ^{19}F and ^{31}P nuclei with the pulsed-gradient spin-echo (PGSE) NMR technique over the same temperature range from 20 to 80 °C. Results show that even if the diffusion of the lithium cation is quite similar in both electrolytes, the anions diffusion differs notably. In the case of the $LiPF_6$-based electrolyte, for example at $T \approx 75\,^\circ C$ (high temperature), the self-diffusion coefficients of Li^+ cations in solution ($D(Li^+) \approx 5 \times 10^{-10}\ m^2\ s^{-1}$) is 1.6 times smaller than that of PF_6^- anions ($D(PF_6^-) = 8.5 \times 10^{-10}\ m^2\ s^{-1}$), whereas in the case of the LiFAP-based electrolyte, FAP^- anions diffuse at same rate as the Li^+ cations ($D(FAP^-) = 5 \times 10^{-10}\ m^2\ s^{-1}$). Based on these experimental results, the transport mobility of ions were then investigated through Stokes–Einstein and Nernst–Einstein equations to determine the transport number of lithium t_{Li^+}, effective radius of solvated Li^+ and of PF_6^- and FAP^- anions, and the degree of dissociation of these lithium salts in the selected EC/DMC (50:50 wt%) mixture over a the temperature range from 20 to 80 °C. This study demonstrates the conflicting nature of the requirements and the advantage of the well-balanced properties as ionic mobility and dissociation constant of the selected electrolytes.

1. Introduction

Electrolytes used in commercial lithium-ion batteries are mainly formulated by the dissolution of the lithium hexafluorophosphate, $LiPF_6$ in cyclic carbonates like ethylene carbonate (EC) or propylene carbonate (PC) and linear carbonates such as dimethyl carbonate (DMC), ethyl methyl carbonate (EMC) and diethyl carbonate (DEC), which are, to date, the most sustainable electrolytes, dealing with their cost and properties, for lithium-ion battery applications, LiBs [1]. However, it is well described into the literature that $LiPF_6$ is thermally unstable and decomposes in LiF and PF_5, as well as, that PF_5 can be hydrolyzed in presence of residual water to form HF and PF_3O [2–4]. Furthermore, the battery lifetime is often linked to the quantity of these decomposition products, as they are highly reactive to both negative and positive electrodes in LiBs [5,6]. Despite these technological issues, $LiPF_6$ is still used as the reference salt in LiBs till more than a decade because of its unique properties in Li-ion devices providing a good ionic conductivity of the electrolyte, as well as, based-on its ability to passivate an aluminum current collector, and to participate to the passivation layer on the negative electrode [7–9]. Therefore, the selection of another safer

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lithium salt to be dissolved in alkyl-carbonates operating over a wide temperature range has received increasing attentions [10,11]. Among this and according to the structure similarity between the hexafluorophosphate, $LiPF_6$ and tris(pentafluoroethane)-trifluorophosphate, $LiPF_3(CF_2CF_3)_3$ (denoted herein LiFAP) anions, electrolytes-based on the LiFAP, which are now commercially available from many suppliers as the Merck company [12], are currently investigated by several groups [13,14], because the substitution of three fluorine atoms by three $-(CF_2CF_3)$ groups seems to improve both the hydrolytic and thermal stabilities of this lithium salt series. Additionally, several works demonstrated that LiFAP-based electrolytes containing common alkyl-carbonates such as EC, DMC or DEC have better LiBs properties than those reported for $LiPF_6$, lithium bis[(trifluoromethyl)sulfonyl]imide, LiTFSI or lithium bis[(pentafluoroethyl)sulfonyl]imide, LiBeti solutions [8]. For examples, both LiBs anodes and cathodes perform better in LiFAP solutions as higher capacity and lower capacity fading upon cycling than those using other lithium salt-based electrolytes are described in the literature [8,13–15]. Furthermore, it was also observed that both electrodes are stabilized faster upon repeated lithiation–delithiation cycling in LiFAP than in $LiPF_6$ solutions [8]. Gnanaraj et al. [8] suggest that the absence of HF and the relatively higher stability and lower reactivity of the FAP^- anion in comparison with the PF_6^- prevent detrimental solution-electrode interactions and allow the development of surface films originating from solvent reactions that well protect the electrode's active mass. Furthermore, even if the conductivity of LiFAP-based electrolytes is generally 30% lower than that of $LiPF_6$ ones, better LiBs performances are reported [8,13–15]. Therefore, it is necessary to compare the transport properties of both lithium salts dissolved in a common alkyl-carbonate-based lithium electrolytes solvent or mixture to understand the key parameters which explain observed differences on their cycleability, properties and LiBs performances. In the present study, we first compared the physical properties: density, ionic conductivity and viscosity of two lithium ion batteries based electrolytes containing 1 mol L^{-1} of lithium salt, $LiPF_6$ or LiFAP, dissolved in the alkyl-carbonates EC/DMC (50:50 wt%) mixture as a function of temperature from 20 to 80 °C. Secondly, pulsed-gradient spin-echo NMR technique has been applied to measure the self-diffusion coefficients of lithium, fluorine, and phosphorus nuclei in order to detect the differences on the ions mobility between the two selected electrolytes. Finally, by using the Stokes–Einstein and Nernst–Einstein equations, the temperature dependence on the self-diffusion coefficients and on the viscosity has been investigated to determine the effective radius of lithium cations, PF_6^- and FAP^- anions in each electrolyte, as well as the degree of dissociation of each salt in the selected EC/DMC (50:50 wt%) mixture.

2. Experimental

2.1. Materials and mixtures preparations

Highly pure (GC grade, molecular purity > 99.99%) ethylene carbonate (EC), and dimethylcarbonate (DMC), purchased from Aldrich, were used as received. The alkyl-carbonate mixture studied into this work has been prepared by mass with an accuracy of $\pm 1 \times 10^{-4}$ g using a Sartorius 1602 MP balance under a dry atmosphere in a glove box at 25 °C and is denoted in mass fraction as follow: EC/DMC (50:50 wt%).

The highly pure (99.99%) lithium hexafluorophosphate ($LiPF_6$) purchased from Sigma–Aldrich was kept and used under a dry atmosphere in a glove box. The electrolyte based on 1 mol L^{-1} of $LiPF_6$ salt dissolved in EC/DMC (50:50 wt%) was prepared by mass using a Sartorius 1602 MP balance under a dry atmosphere in a glove box, and kept inside the glove box before further analyses. Firstly, the mixture of EC/DMC (50:50 wt%) was prepared by mass and its density measured as a function of temperature. Secondly, a precise quantity of EC/DMC mixture has been placed in a precise volume vessel at constant temperature (*e.g.* 25 °C) and an appropriate quantity (in mass) of $LiPF_6$ was dissolved in it to reach a $LiPF_6$ salt composition of 1 mol L^{-1} of solution. Finally, the density of this electrolyte was measured as a function of temperature. The electrolyte containing the 1 mol L^{-1} of LiFAP salt in EC/DMC (50:50 wt%) was purchased, as is, from Merck within a molecular purity higher than 99.99%. This commercial electrolyte was kept and used as received from the manufacturer under a dry atmosphere in a glove box. Additionally, prior to any measurement, electrolytes were analyzed for water content using coulometric Karl-Fischer (Coulometer 831 – Metrohm) titration. The water content of selected electrolytes is lower than (20 ± 1) ppm.

2.2. Experimental and theoretical methods

The optimized 3D structure of each investigated ion and solvent was carried out by using DFT calculations within Gaussian software (Gaussian version 03-D1, DFT-B3LYP-DGTZVP) [16], to generate then each COSMO file (Turbomole version 5.7, BP-DFT-Ahlrichs-TZVP) [17] by using the same methodology as already presented previously by our group [18–20] Additionally, COSMO volume and sigma profile of investigated species were obtained by using the COSMOthermX software (version 2.1, release 01.08) [21]. Briefly, as the COSMO-RS theory (from Conductor-like Screening Model for Real Solvents) uses the concept of an ideally screened molecule energy and charge distribution on surface of molecule, the molecule being embedded in a virtual conductor with an infinite permittivity = ∞ [21]. For COSMO-RS calculations, knowledge of COSMO parameters describing the 3D chemical structure of the molecules is required. The interaction energy is then expressed by local surface descriptors calculated from quantum chemical methods. The principal descriptor and a key parameter for molecular interactions in COSMO-RS methodology is the screening charge density σ at the surface of each molecule (*e.g.* the sigma profile of each molecule)", based on which affinity between species can be highlighted and depicted [18–21].

Conductivity measurements were performed by using a Crison (GLP 31) digital multi-frequencies conductometer between 1000 and 5000 Hz. The temperature control (from 10 °C to 80 °C) was carried out within an accuracy of 0.2 °C by means of a JULABO thermostated bath. Prior any measurement, the conductometer was first calibrated with a standard solution of known conductivity such as 0.1 and 0.01 mol L^{-1} KCl aqueous solutions, as well as, using a 1 mol L^{-1} of $LiPF_6$ salt dissolved in EC/PC/3DMC (20:20:60 wt%) as the electrolyte standard ($\sigma = 12\ \mathrm{mS\,cm^{-1}}$ at 25 °C) [7,22]. From this study the repeatability and the uncertainty of conductivity measurements did not exceed ±0.5% and ±1%, respectively.

Density and viscosity measurements were conducted from 20 to 70 °C using an Anton Parr digital vibrating tube densitometer (model 60/602, Anton Parr, France) and an Anton Parr rolling-ball viscometer (model Lovis 2000M/ME, Anton Parr, France), respectively. In both cases, the temperature in the cell was regulated within ±0.02 °C. Dynamic viscosity values reported herein were calculated by taking into account the effect of the sample density and the buoyancy of the ball in each sample as a function of temperature. Additionally, as specify by the constructor, density data is required to calculate a dynamic and kinematic viscosity by using the Lovis M/ME micro-viscosimeter. For that we decided to perform simultaneously density and viscosity measurements using the sample, as both instruments are connected with hoses and simultaneously filled with the same sample. Furthermore, the thermo-balance technology was used to obtain precise viscosity