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Low pressure carbon dioxide solubility in lithium-ion batteries based electrolytes as a function of temperature. Measurement and prediction

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ABSTRACT

We present in this study the effect of nature and concentration of lithium salt, such as the lithium hexafluorophosphate, $LiPF_6$; lithium tris(pentafluoroethane)-trifluorurophosphate LiFAP; lithium bis(trifluoromethylsulfonyl)imide, LiTFSI, on the CO_2 solubility in four electrolytes for lithium ion batteries based on pure solvent that include ethylene carbonate (EC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC), as well as, in the EC:DMC, EC:EMC and EC:DEC (50:50) wt.% binary mixtures as a function of temperature from (283 to 353) K and atmospheric pressure. Based on experimental solubility values, the Henry's law constant of the carbon dioxide in these solutions with the presence or absence of lithium salt was then deduced and compared with reported values from the literature, as well as with those predicted by using COSMO-RS methodology within COSMOThermX software. From this study, it appears that the addition of 1 $\text{mol} \cdot \text{dm}^{-3}$ $LiPF_6$ salt in alkylcarbonate solvents decreases their CO_2 capture capacity. By using the same experimental conditions, an opposite CO_2 solubility trend was generally observed in the case of the addition of LiFAP or LiTFSI salts in these solutions. Additionally, in all solutions investigated during this work, the CO_2 solubility is greater in electrolytes containing the LiFAP salt, followed by those based on the LiTFSI case. The precision and accuracy of the experimental data reported therein, which are close to (1 and 15)%, respectively. From the variation of the Henry's law constant with temperature, the partial molar thermodynamic functions of dissolution such as the standard Gibbs energy, the enthalpy, and the entropy, as well as the mixing enthalpy of the solvent with CO_2 in its hypothetical liquid state were calculated. Finally, a quantitative analysis of the CO_2 solubility evolution was carried out in the EC:DMC (50:50) wt.% binary mixture as the function of the $LiPF_6$ or LiTFSI concentration in solution to elucidate how ionic species modify the CO_2 solubility in alkylcarbonates-based Li-ion electrolytes by investigating the salting effects at $T = 298.15$ K and atmospheric pressure.

1. Introduction

Most liquid electrolytes used in commercial lithium-ion batteries are obtained by dissolving a lithium salt in a specific alkylcarbonate mixture. Currently, the most suitable electrolytes for lithium ion battery remain the mixture of the lithium hexafluorophosphate, $LiPF_6$ with 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) [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 $LiPF_6$ and PF_5 can react with residual water to form HF [2–4]. Despite these technological issues, $LiPF_6$ is still used as the reference salt in Li-ion batteries for more than a decade because of its unique properties in Li-ion devices providing good ionic conductivity of the electrolyte, as well as, based-on its ability to passivate an aluminium current collector, and to participate to the passivation layer on the negative electrode [5–7]. Furthermore, the selection of another safer lithium salt to be dissolved in alkylcarbonates is of great importance, but this change influences the physical, thermal and transport properties of the electrolyte [8,9]. According to the structure similarity between the hexafluorophosphate and tris(pentafluoroethane)-trifluorophosphate anions, the lithium tris(pentafluoroethane)-trifluorophosphate LiFAP, is currently investigated by several groups to limit potentially these property changes [6]. Lithium imide salts are also potentially a good alternative to $LiPF_6$ since these salts could both improve the chemical and thermal stability of the

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electrolyte. Particularly, the lithium bis(trifluoromethylsulfonyl)imide, LiTFSI salt, which is well known to be more stable and safer than $LiPF_6$ [10], even if it were clearly pointed-out in the literature that LiTFSI salt is more corrosive than $LiPF_6$ towards the aluminium collector [11–14]. Additionally, the performance of a lithium ion battery depends also to a great extent on the stability of electrolyte solution, because the high voltage of the battery may cause the decomposition of lithium salt or organic solvents [15–17]. This decomposition of the electrolyte limits the battery lifetime [18,19]. For example, it is reported in the literature that the oxidation reaction of the Li-ion electrolyte at high potentials leads to the formation of CO_2 when high potentials are applied to the electrode, which increases the pressure inside the sealed cell [19–21]. Furthermore, the carbon dioxide formation also changes the composition of the electrolyte driven by the solubility of the carbon dioxide in this solution. These effects caused by the formation of the carbon dioxide can be evaluated with the prior knowledge of the CO_2 solubility in electrolyte solutions. Furthermore, the salt selection and effects on the CO_2 solubility in electrolytes can be analyzed in detail by comparing the CO_2 solubility in solutions with or without a lithium salt. Many authors have reported in the literature the CO_2 solubility in classical alkylcarbonate solvents [22–38], but generally, these studies are basically focused on pure alkylcarbonate solvents and on their mixtures without the presence of lithium salt. However, the CO_2 solubility in classical Li-ion electrolytes depends not only on the pressure and temperature, but also on the salt structure and its concentration in solution. The salting effect in solvents containing a specific salt needs to be investigated, nevertheless, to date very few CO_2 solubility data in alkylcarbonate are available in the literature, especially for solutions containing lithium salts.

Herein, we report first, the solubility of carbon dioxide in eight lithium ion batteries based electrolytes containing 1 $mol \cdot dm^{-3}$ lithium salt, $LiPF_6$ or LiTFSI, dissolved in a pure alkylcarbonate solvent, EC, DMC, EMC, DEC, as a function of temperature from (283 to 353) K and atmospheric pressure. The comparison of these experimental results along with those reported previously by our group in the case of the CO_2 solubility in pure carbonate solvents [22,23] permits the quantification of the effect of the presence of lithium salt on the carbon dioxide absorption by the pure carbonate solvent. Secondly, by using the same methodology, we report in this paper the effect of the presence or the absence of 1 $mol \cdot dm^{-3}$ lithium salt ($LiPF_6$, LiTFSI or LiFAP) on the CO_2 solubility in three different (50:50) wt.% binary mixtures of alkylcarbonate solvents such as EC:DMC, EC:EMC and EC:DEC as a function of temperature. From these results, Henry's law constants and dissolution properties to include the Gibbs energy, the standard enthalpy and entropy of dissolution, as well as the mixing enthalpy of the solvent with CO_2 in its hypothetical liquid state were then deduced. Thirdly, we present a quantitative analysis of the CO_2 solubility evolution with the salting effects in the EC:DMC (50:50) wt.% binary mixture as the function of the $LiPF_6$ or LiTFSI concentration in solution. Finally, the CO_2 solubility in these electrolytes has been then calculated by the COSMO-RS methodology by using directly the COSMOThermX chemical engineering software. These calculated values are then compared with experimental values to evaluate the predictive capability of the CO_2 solubility in electrolytes for Li-ion batteries applications.

2. Experimental

2.1. Materials and mixtures preparations

Highly pure (GC grade, mass fraction purity > 0.9999) ethylene carbonate (EC), dimethylcarbonate (DMC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC) were obtained from Aldrich and were used as received. The highly pure (mass fraction 0.9999 lithium salts such as: lithium hexafluorophosphate ($LiPF_6$) and lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) purchased from Sigma Aldrich and from Solvionic, respectively, were kept and used under a dry atmosphere in a glove box. All electrolytes containing the LiFAP salt were purchased from Merck with mass fraction purity greater than 0.9999. All LiFAP electrolytes were kept and used under a dry atmosphere in a glove box and then were used as received from the manufacturer.

Studied solvents mixtures were prepared by mass with an accuracy of $\pm 1 \cdot 10^{-4}$ g using a Sartorius 1602 MP balance under a dry atmosphere in a glove box, and kept inside the glove box before further analyses. Alkylcarbonate mixtures studied into this work have been prepared by mass at 25 °C and are denoted in mass fraction as follow: EC:DMC (50:50) wt.%, EC:EMC (50:50) wt.%, and EC:DEC (50:50) wt.%. Based on these mixtures, electrolytes based on lithium salts, LiX (with X = PF_6^-, or $TFSI^-$), were then prepared by dissolving a salt into the solvent and the concentrations of lithium salts in solutions are reported in $mol \cdot dm^{-3}$.

As the experimental setup used to determine the amount of CO_2 dissolved in solutions is based on a chemical titration methodology, NaOH (0.5 $mol \cdot dm^{-3}$) and HCl (1 $mol \cdot dm^{-3}$) solutions, were used as received from Sigma Aldrich (Riedel-de Haen). Prior to any measurement, HCl (0.2 $mol \cdot dm^{-3}$) solutions, which were prepared using double distilled water and the HCl (1 $mol \cdot dm^{-3}$) commercial solution, were standardized from the NaOH commercial solution using potentiometric titration. Additionally, prior to any solubility measurement, solvents and electrolytes were analyzed for water content using coulometric Karl-Fischer (Coulometer 831 – Metrohm) titration. The water content of selected solvents and electrolytes, measured before and after their preparations, is close to $(10 \pm 1)\ 10^{-6}$.

The gases used (AGA/Linde Gaz) have the following specifications: carbon dioxide, mole fraction purity of 0.99995; and argon, mole fraction purity of 0.999997. All gases were used as received from the manufacturer. Information (*i.e.*, source, abbreviation, purity, and water content) for each chemical sample studied in this paper are summarized in table 1.

2.2. Experimental methods

The density of pure liquids, binary liquid mixtures and investigated electrolytes were measured by using a pycnometer (5 cm^3) immersed in a water bath at T = 298.15 K. The temperature control is ensured within ± 0.01 K by means of a JULABO thermostated bath. The pycnometer was firstly calibrated at T = 298.15 K with degassed water at atmospheric pressure using reference data from Wagner and Pruss [39]. More than three measurements were performed for each density measurement reported therein. The accuracy of the reported density values is better than $\pm 5 \cdot 10^{-2}\ g \cdot cm^{-3}$.

The experimental apparatus used during the CO_2 solubility measurements reported in this present work is based on a chemical titration technique, which was already described by our group elsewhere [22,23], and schematically represented herein in figure 1. Under a dry atmosphere in a glove box, a known quantity of electrolyte, determined gravimetrically with an accuracy of $\pm 1 \cdot 10^{-4}$ g using a Sartorius 1602 MP balance, was first placed into equilibrium cell (EqC) equipped with a septum to avoid air and moisture contaminations during measurements. The EqC was then immersed in a water bath maintained at constant temperature, $T_{exp.}$ using a PID temperature controller and accurately measured with a calibrated 100 platinum resistance thermometer within accuracy better than ±0.1 K. The electrolyte was then saturated with CO_2 at atmospheric pressure by dissolving the gas in the liquid phase at constant temperature during 1 h to reach the