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

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ABSTRACT

The methane solubility in five pure electrolyte solvents and one binary solvent mixture for lithium ion batteries – such as ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC) and the (50:50 wt%) mixture of EC:DMC was studied experimentally at pressures close to atmospheric and as a function of temperature between (280 and 343) K by using an isochoric saturation technique. The effect of the selected anions of a lithium salt LiX (X = hexafluorophosphate, PF_6^-; tris(pentafluoroethane)trifluorurophosphate, FAP^-; bis(trifluoromethylsulfonyl)imide, $TFSI^-$) on the methane solubility in electrolytes for lithium ion batteries was then investigated using a model electrolyte based on the binary mixture of EC:DMC (50:50 wt%) + 1 $mol \cdot dm^{-3}$ of lithium salt in the same temperature and pressure ranges. Based on experimental solubility data, the Henry's law constant of the methane in these solutions were then deduced and compared together and with those predicted by using COSMO-RS methodology within COSMOthermX software. From this study, it appears that the methane solubility in each pure solvent decreases with the temperature and increases in the following order: EC < PC < EC:EMC (50:50 wt%) < DMC < EMC < DEC, showing that this increases with the van der Walls force in solution. Additionally, in all investigated EC:DMC (50:50 wt%) + 1 $mol \cdot dm^{-3}$ of lithium salt electrolytes, the methane solubility decreases also with the temperature and the methane solubility is higher in the electrolyte containing the LiFAP salt, followed by that based on the LiTFSI one. From the variation of the Henry's law constants with the temperature, the partial molar thermodynamic functions of solvation, such as the standard Gibbs free energy, the enthalpy, and the entropy where then calculated, as well as the mixing enthalpy of the solvent with methane in its hypothetical liquid state. Finally, the effect of the gas structure on their solubility in selected solutions was discussed by comparing methane solubility data reported in the present work with carbon dioxide solubility data available in the same solvents or mixtures to discern the more harmful gas generated during the degradation of the electrolyte, which limits the battery lifetime.

1. Introduction

For the last decade, lithium ion battery and its safety have engaged more scientific consideration especially in respect with reduction requirement of CO_2 emission, as this technology may potentially substitute in short-term the currently used fossil energy. However, some safety problems associated with the utilisation of lithium ion batteries occur, which are mainly contributed by thermal runaway causing fire and explosion [1]. Briefly, lithium-ion battery electrolytes are composed of a dissolved lithium salt in a specific alkylcarbonate mixture. Currently, the most suitable electrolytes for lithium ion battery is the mixture of the lithium hexafluorophosphate, $LiPF_6$ with cyclic carbonates like ethylene carbonate (EC) or propylene carbonate (PC) and linear esters such as dimethyl carbonate (DMC), ethyl methyl carbonate (EMC) and diethyl carbonate (DEC) [2]. However, it is reported in the literature that $LiPF_6$ decomposes in LiF and PF_5, as well as, that $LiPF_6$ and PF_5 can react with residual water to form HF [1,3–5]. Despite these issues, $LiPF_6$ is still used as the reference salt in Li-ion batteries because of its unique properties in Li-ion devices providing a good transport properties of the electrolyte, as well as, based-on its ability to passivate an aluminium current collector [6–8].

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However, to date, many research groups investigate novel and safer lithium salts during the electrolyte formulation to substitute the unsafe $LiPF_6$ but this change influences in fact the physical, thermal and transport properties of the electrolyte [9,10]. For example, the lithium tris(pentafluoroethane)trifluorurophosphate LiFAP, is currently investigated by several groups due to its structure similarity with the $LiPF_6$ to limit potentially these properties changes [7]. Additionally, to improve the chemical and thermal stability of the electrolyte, many research groups formulated solutions using the lithium bis(trifluoromethylsulfonyl)imide, LiTFSI, salt since this salt is more stable and safer than the $LiPF_6$ one [11]. Nevertheless, it was clearly pointed-out into the literature that LiTFSI salt is more corrosive than $LiPF_6$ towards aluminium collector [12–15]. However, the performance of a lithium ion battery depends also to a great extent on the stability of solvents used during the formulation of the electrolyte solution, because the high voltage of the battery may cause the decomposition not only of lithium salt but also of the organic solvents [1,16–18]. This decomposition of the electrolyte limits in fact the battery lifetime [1,19,20]. For example, it is well reported into the literature that the oxidation reaction of the Li-ion electrolyte leads to the formation of gases like the carbon dioxide and light alkanes (methane, ethane) or alkenes (ethylene, propene, *etc.*) when high potentials are applied to the electrode, which increases the pressure inside the sealed cell [1,20–22]. The generation of these gases may drive also some changes of the composition of the electrolyte driven by the solubility of the each generated gas in the liquid solution. These effects caused by the formation of these gases can be evaluated with the prior knowledge of their solubility in electrolyte solutions. Many efforts in this field have been devoted to study the (liquid + vapour) equilibria of (CO_2 + alkylcarbonate) systems,[23–39] even if, generally, these studies are basically focused on pure alkylcarbonate solvents and on their mixtures without the presence of lithium salt, for example. As reported by our group previously [24], whatever the temperature and selected carbonate solvent or mixture, a clear salting out effect is observed in the case of the dissolution of $LiPF_6$ salt in each selected solution. In the case of LiTFSI or LiFAP, no salting, salting in or salting out effects are observed depending of the temperature, or structure of the carbonate solution. In other words, it appears that the salting effect depends mainly of both lithium salts and solvents structures and their interactions in solution. However, the CO_2 is not the solely gas generated during the decomposition of the electrolytes [1]. As the temperature increases, heat from SEI decomposition reaction causes the reaction of intercalated lithium with the organic solvents used in the electrolyte releasing also flammable hydrocarbon gases (methane, ethane, *etc.*) [1]. For example, the SAFT group has recently conducted different tests using their own commercial batteries containing classical carbonates solvent mixture and a lithium salt kept at 4 V and 60 °C. Based on these findings, it appears that after one month the generation of CO_2 in the gas phase (200 mL) is up to 61% (in volume fraction), while the CH_4 generation can be neglected. Interestingly, after eight months, the total volume of the gas phase increases up to 360 mL and contains a volume fraction of CO_2 and CH_4 close to 74% and 2%, respectively [40].

Nevertheless, to date very few hydrocarbon gas solubility data in alkylcarbonate are available in the literature [30,41,42], especially for solutions containing lithium salts [43]. During this work, we decided to investigate the methane solubility in different pure solvents and electrolytes as it is one of the gases found in the cells and it seems very important to know its behaviour *vs.* electrolyte, mainly its solubility in order to predict the pressure build up and the swelling of the cell and to adapt mechanically the safety vent for efficient protection in abuse condition.

Herein, we report at first, the vapour pressure of five pure carbonate solvents and one binary mixture, namely the ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC) and the (50:50 wt%) mixture of EC:DMC, as well as in three lithium ion batteries based electrolytes containing $1\ mol \cdot dm^{-3}$ of lithium salt, $LiPF_6$, LiTFSI, or LiFAP, dissolved in a (50:50 wt%) mixture of EC:DMC as a function of temperature from (283 to 345) K determined by using an isochoric saturation technique along their comparison with available data in the literature. Secondly, the solubility data of methane in these eight solutions are presented at pressure close to the atmospheric and as a function of temperature from (283 to 345) K. The comparison of these experimental data along with those reported previously by our group in the case of the CO_2 solubility in these solutions [23,24] permits then the quantification of the effect of the structure of the gas on their absorptions by each solution. Thirdly, each CH_4 solubility data was rigorously determined to investigate then the Henry's law constants and dissolution properties like the Gibbs free energy, the standard enthalpy and entropy of dissolution, as well as the mixing enthalpy of the solvent with CH_4 in its hypothetical liquid state. The characterization of the saturation properties of the mixture provides then insights about the molecular mechanisms involved during the solvation of the gas in the liquid mixture. Finally, the CH_4 solubility in these electrolytes has been then calculated by the COSMO-RS methodology by using directly the COSMOthermX chemical engineering software by following the same methodology already reported by our group [23,24]. These calculated values are then compared with experimental data to evaluate the predictive capability of the CH_4 solubility in electrolytes for Li-ion batteries applications.

2. Experimental

2.1. Materials and mixtures preparations

Highly pure (GC grade, mole 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.

The solvent mixture studied, EC:DMC (50:50 wt%), was prepared by mass at $T = 298.15$ K 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.

Based on this binary mixture, prepared electrolytes containing the lithium salt, LiX (with $X = PF_6^-$, or $TFSI^-$), were then prepared under a dry atmosphere in a glove box by mass at $T = 298.15$ K with an accuracy of $\pm 1 \cdot 10^{-4}$ g by dissolving a known quantity of salt into a well-known quantity of the solvent mixture to reach a weight fraction of EC, DMC and lithium salt in solution close to 0.44305, 0.44305 and 0.11390, or close to 0.40227, 0.40227 and 0.19546, for $LiPF_{6^-}$ or LiTFSI-based electrolyte, respectively. In each case, the electrolyte composition corresponds to a mole fraction of EC, DMC and lithium salt close to 0.4702, 0.4597 and 0.0701, respectively. This mixture composition corresponds to a concentration of the selected lithium salt ($LiPF_6$, or LiTFSI) in each solution close to $1\ mol \cdot dm^{-3}$. To simplify their notation, these electrolytes are then denoted as EC:DMC (50:50 wt%) + $1\ mol \cdot dm^{-3}$ LiX (with $X = PF_6^-$, or $TFSI^-$). These electrolytes were then kept inside the glove box before further analyses.

However, the electrolyte containing the LiFAP salt, denoted EC:DMC (50:50 wt%) + $1\ mol \cdot dm^{-3}$ LiFAP, was purchased directly from Merck within a mole fraction purity higher than 0.9999.