Gas solubility and vapor pressure of electrolytes based on alkylcarbonates containing LiTFSI, LiFAP, and LiPF$_6$ lithium salt: Measurement and prediction

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Most liquid electrolytes used in commercial lithium-ion batteries are composed by alkylcarbonate mixture containing lithium salt. The decomposition of these solvents by oxidation or reduction during cycling of the cell, induce generation of gases (CO$_2$, CH$_4$, C$_2$H$_4$, CO …) increasing of pressure in the sealed cell, which causes a safety problem [1] The prior understanding of parameters, such as structure and nature of salt, temperature pressure, concentration, salting effects and solvation parameters, which influence gas solubility and vapor pressure of electrolytes is required to formulate safer and suitable electrolytes especially at high temperature.

We present in this work the CO$_2$, CH$_4$, C$_2$H$_4$, CO solubility in different pure alkylcarbonate solvents (PC, DMC, EMC, DEC) and their binary or ternary mixtures as well as the effect of temperature and lithium salt LiX (X = LiPF$_6$, LiTFSI or LiFAP) structure and concentration on these properties. Furthermore, in order to understand parameters that influence the choice of the structure of the solvents and their ability to dissolve gas through the addition of a salt, we firstly analyzed experimentally the transport properties (Self diffusion coefficient ($D$), fluidity ($\eta^{-1}$), and conductivity ($\sigma$) and lithium transport number ($t_{Li}$) using the Stock-Einstein, and extended Jones-Dole equations. Furthermore, measured data for the of CO$_2$, C$_2$H$_4$, CH$_4$ and CO solubility in pure alkylcarbonates and their mixtures containing LiPF$_6$, LiFAP; LiTFSI salt, are reported as a function of temperature and concentration in salt. Based on experimental solubility data, the Henry’s law constant of gases in these solvents and electrolytes was then deduced and compared with values predicted by using COSMO-RS methodology within COSMOthermX software. From these results, the molar thermodynamic functions of dissolution such as the standard Gibbs energy, the enthalpy, and the entropy, as well as the mixing enthalpy of the solvents and electrolytes with the gases in its hypothetical liquid state were calculated and discussed. Finally, the analysis of the CO$_2$ solubility variations with the salt addition was then evaluated by determining specific ion parameters $H_i$ by using the Setchenov coefficients in solution. This study showed that the gas solubility is entropy driven and can been influenced by the shape, charge density, and size of the anions in lithium salt.

References