

Safe carbonate-based electrolytes for lithium-ion batteries

Zhengqi Wang^{a,b}, Andreas Hofmann^a and Thomas Hanemann^{a,b}

^a *Department Materials and Processes, Institute for Applied Materials (IAM-WK), Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany*

^b *Laboratory for Materials Process Technology, Department of Microsystems Engineering (IMTEK), University of Freiburg, Georges-Köhler-Allee 102, 79110 Freiburg, Germany*

E-mail: zhengqi.wang@kit.edu

Lithium-ion batteries (LIBs) can provide rechargeable energy for various applications. The currently widely used state-of-art non-aqueous electrolytes are composed of lithium salts dissolved in organic carbonate-based solvents. While proceeding to drive down costs and boost capacity, LIBs face challenges in several issues, such as the storage reliability, the cell safety in terms of thermal runaway and burning, and the work stability of the electrolyte. Our focus is therefore the prevention of these main risks associated with electrolytes.

For preparation of suitable “salt-in-solvent” electrolyte mixtures, several selected thermal stable conducting salts, e.g. lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), lithium tetrafluoroborate (LiBF₄) and lithium difluoro(oxalato)borate (LiDFOB) were dissolved in carbonates with boiling points above 200 °C. In this case, carbonates of different structures are available, e.g. cyclic ethylene carbonate (EC), propylene carbonate (PC), 1, 2-butylene carbonate (1, 2-BC), fluoroethylene carbonate (FEC) and linear dibenzyl carbonate (DBC) and dipropyl carbonate (DPrC). Various possibilities inspired the interest to understand the relationship between molecular structures, composition of components and the properties of the electrolyte mixtures.

For practical use, the solubility and chemical stability of salt-carbonate mixtures were investigated. Furthermore, we measured physicochemical properties (phase transition behavior, temperature dependent density and the viscosity values) to draw a picture of interaction between ions and solvent molecules. The temperature dependent viscosity and ionic conductivity of the mixtures is presented by the empirical Vogel-Fulcher-Tammann (VFT) equation and correlated by the fractional Walden rule. The flow activation energy E_a was calculated and compared with each other, regarding to Angell’ fragility concept [1]. The electrochemical stability obtained by the cyclic voltammetry showed the oxidative potentials of mixtures. The role of additives (e.g. lithium bis(oxalato)borate LiBOB) on the aluminum (Al) corrosion of mixtures was investigated by cell-cycling versus Li/Li⁺. [2]

Charge-discharge cycling performance of the electrolyte mixtures were investigated by full-cell tests using LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ and graphite as electrode materials. Due to the electrochemical damage or the Al corrosion, unstable cycling results are observed in some cases (e.g. irreversible loss of discharge capacity (mAh/g) and capacity conservation). These phenomena were significantly improved by utilizing LiBOB as additive, which forms a passivation film on the electrode surfaces. Besides, the flash point (> 140 °C) and the burning tests of the selected mixtures showed the improved safety beneficial to the practical aspects such as the vapour-leakage of the boiled electrolytes. In summary, the properties of mixtures were influenced by the structure/composition and the electrochemical measurements and the cell tests in coin cell and pouch-bag configuration indicated that the novel electrolyte mixtures can be regarded as more stable and temperature-robust compared to state-of-the-art electrolyte mixtures while maintaining the cell performance at moderate current rates.

References:

[1] A. Hofmann, M. Migeot, T. Hanemann, J. Chem. Eng. Data. 61 (2016) 114–123.

[2] A. Hofmann, M. Schulz, V. Winkler, T. Hanemann, Electrochim. Acta. 116 (2014) 388–395.