$LiBF_4$/TFEP Electrolyte Solutions for 5 V $LiNi_{0.5}Mn_{1.5}O_4$ Positive-Electrodes in Lithium-Ion Batteries

Romain Taccori [a], Michihiro Hashinoguchi [a], Takayuki Doi [a], Minoru Inaba [a]
[a] *Doshisha University, 1-3 Tataramiyakodani, Kyotanabe, Kyoto 610-0321, Japan*

Email: ctwb3701@mail4.doshisha.ac.jp

Introduction

To improve the safety of the lithium ion batteries (LIB), remediating the issue of flammability while enhancing the energy density with the development of additives has been researched in recent years. Usage of phosphorous solvents as additives have been proven to be effective for their flame retardant properties in high potential working cathodes such as $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) [1]. Tris(2,2,2-trifluoroethyl) phosphate (TFEP) possess such properties and also a low melting point which makes it an interesting candidate for improving the safety of the LIB. Furthermore, it is also stable at high voltages due to the presence of fluorinated group. Thus, the properties of TFEP as a main solvent coupled with the LNMO were investigated. The results were compared to the conventional electrolyte 1M $LiPF_6$/EC+DMC (1:1 vol.%).

Experimental

The LNMO-composite electrode was composed of $LiNi_{0.5}Mn_{1.5}O_4$ powder with poly [(vinylidenefluoride)-co-chlorotrifluoroethylene] (P(VdF-CtFE)) (10 mass%) as a binder and Ketjenblack (10 mass%) as a conductor in N-methyl-2-pyrrolidone (NMP) on an Al current collector. Li foil was used as the counter electrode. The test cells were assembled in an Ar filled glove box. Charge and discharge tests were performed galvanostatically between 3.5 and 5.0 V at 30ºC at C/10 rate for 50 cycles.

Results and discussion

The LNMO electrode delivered a discharge capacity of 131.7 mAh g^{-1} in 0.58 mol kg^{-1} $LiBF_4$/TFEP at the 1st cycle. The capacity retention at the 50th cycle was as high as that of the reference electrolyte solution: 96.2 and 96.1% for 0.58 mol kg^{-1} $LiBF_4$/TFEP and 1 M $LiPF_6$/EC+DMC, respectively. On the other hand, the average Coulombic efficiency was high in 0.58 mol kg^{-1} $LiBF_4$/TFEP (97.9%), compared to the reference electrolyte solution (94.4%). TFEP should oxidatively decompose at the LNMO electrode to form a protective surface film in the initial cycles, limiting the further decomposition of the electrolyte solution [2]. Nevertheless, LNMO exhibited the larger polarization on charge/discharge reactions in 0.58 mol kg^{-1} $LiBF_4$/TFEP than in 1 M $LiPF_6$/EC+DMC (1:1 vol.%). Then, propylene carbonate (PC) was added as a co-solvent to obtain 1.98 mol kg^{-1} $LiBF_4$/PC+TFEP (1:2 vol.%) electrolyte solution. The initial discharge capacity was higher (133 mAh g^{-1}) than the reference (126.2 mAh g^{-1}). The capacity retention was improved to 97.3% and an average Coulombic efficiency of 95.9% was achieved. The polarization was reduced as comparison with 0.58 mol kg^{-1} $LiBF_4$/TFEP. Thus, the usage of TFEP as a main solvent has improved the charge/discharge performance of the $LiNi_{0.5}Mn_{1.5}O_4$ and usage of a co-solvent such as PC might further improve the properties of the cell. We believe that the TFEP acted as a sacrificial solvent protecting the electrolyte from further decomposition.

Reference :

[1] : Yoo E Hyung, Donald R Vissers, Khalil Amine, J. Power Source, 119-121 (2003) 383-387

[2] : K. Matsumoto, M. Martinez, T. Gutel et al., J. Power Source, 273 (2015) 1084-1088