Reaction Mechanisms of Aromatic Compounds as an Overcharge Protection Additive For 4 V Class Lithium Ion Rechargeable Cells

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Lithium ion cells are now widely used for portable PC, cellular phones, camcorders etc., due to their small size, light weight, and high capacity. On the contrary, they have some problems from the viewpoint of safety. Particularly, the overcharge protection is an urgent problem, since the overcharge causes the deformation and heat generation of the cells, which may result in the ignition and explosion. The heat generation and the change in the cell voltage under the overcharge conditions were reported.[1-3)]

To prevent overcharging the cell, some aromatic compounds such as biphenyl (BP), cyclohexylbenzene (CHB), etc. are added into the electrolyte solutions.[4,5)] However, their reaction mechanisms of the overcharge protection additives haven't been clarified yet.

2 wt% of BP, CHB, or partially hydrogenated m-terphenyl (HmTP) were added into a 1.0 mol dm^{-3} $LiPF_6$/ethylene carbonate (EC)-ethyl methyl carbonate (EMC) (3:7 in volume ratio) electrolyte solution, respectively. Figs. 1-3 show anodic cyclic voltammograms of these electrolytes at room temperature using a Pt working electrode (1.6 mm in diameter), a Li reference electrode, and a Li counter electrode. The measurement was carried out over a potential range from open circuit voltage to 5.0 V *vs.* Li^+/Li at a sweep rate of $5mVs^{-1}$.

We have observed that the onset oxidation potentials of 2nd and 3rd cycles were less than that of 1st cycle in all voltammograms. This behavior indicates that the oxidation products are more oxidizable than the original aromatic compounds. Black precipitates were observed on the surface of the working electrodes (Pt or $LiCoO_2$) after the cyclic voltammetry tests.

We will report various analytical results on the oxidation products by electrochemical and surface analysis techniques such as TPD-MS and MALDI-TOF MS. A reaction mechanism of these aromatic compounds will be presented based on these results.

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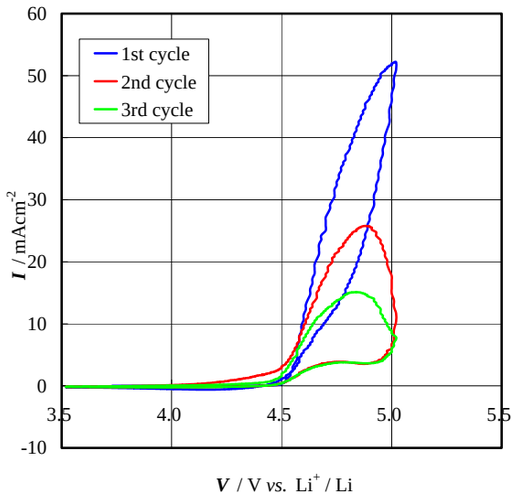

Fig. 1 Cyclic voltammogram of BP (2 wt%) in 1.0 mol dm^{-3} $LiPF_6$/EC-EMC (3:7).

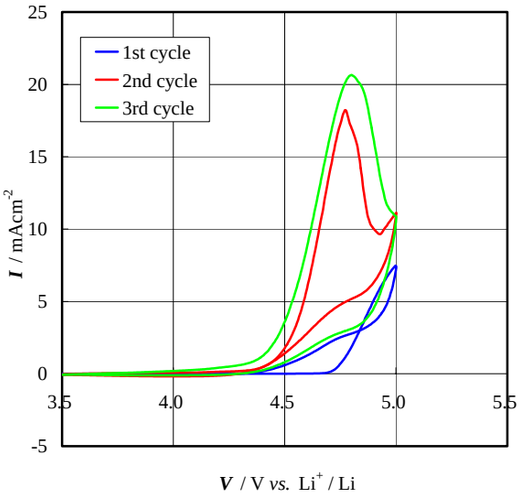

Fig. 2 Cyclic voltammogram of CHB (2 wt%) in 1.0 mol dm^{-3} $LiPF_6$/EC-EMC (3:7).

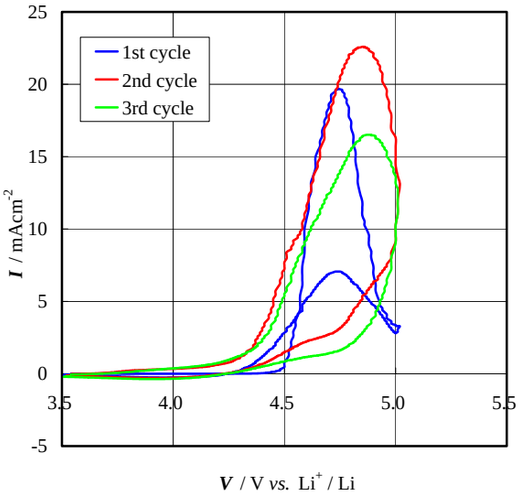

Fig. 3 Cyclic voltammogram of HmTP (2 wt%) in 1.0 mol dm^{-3} $LiPF_6$/EC-EMC (3:7).