Reactivity of Electrolyte with the Surface of 5-V Cathode Materials for Li-ion Batteries

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An electrolyte for high voltage lithium secondary batteries simultaneously meets at least these four requirements [1-4]: (i) stability for charging voltage of over 5 V, (ii) high specific conductivity over a wide temperature range, (iii) high current discharge, (iv) quick recharge and discharge at low temperature. Hayashi et al. [1] reported physical properties of solvents used in Li-ion batteries. However, it is accepted that practically, the anodic limit of these standard electrolyte solutions is around 4.5 V vs. Li/Li⁺. Markovsky et al. [4] demonstrated that LiMn_{1.5}Ni_{0.5}O₄ (LNM) electrodes which redox potential is around 4.8 V can work well even at elevated temperatures in some compositions of standard solutions.

In this work, we examine the reactivity of various LiPF₆-based electrolytes including various solutes as ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC) and 1,2-dimethoxyethane (DME) with the surface of LiNi_{0.45}Mn_{1.45}O₄ (Toda commercial grade) in the voltage range $3.0{\text -}4.9~V~vs.~\text{Li}^+/\text{Li}$.

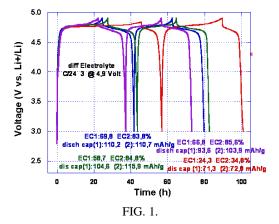


Figure 1 shows the typical voltage profiles of $\text{Li}/\text{Li}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ coin cells charged and discharged at C/24 rate using 1M LiPF₆ based electrolytes with solutes. The detrimental effect on battery performance is also analysed using various electrolyte additives. Electrolytes were (i) EC:DEC

(3:7), (ii) EC:DMC:adiponitrile (39:39:22), (iii) EC:DMC:methoxypropionitrile and (iv) EC:DMC: sebaconitrile. From these studies, we conclude that the appropriate electrolyte for the LNM cathode material could be 1M LiPF₆ EC:DMC (1:1) for which the surface layer appeared to be stable. Discharge capacity after the first formation cycle is also mentioned in the figure for the different electrolytes.

References

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