Effect of Tungstate Additive into NMC Cathode for Li-Ion Batteries

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Higher-power and -energy Li-ion batteries (LIBs) are required for electric and hybrid electric vehicles. To achieve better battery performance, much effort has been devoted to developing electrode materials. Electrode performance of layered transition metal oxides as positive electrode materials is generally improved by changing particle size and morphology, partial metal-doping, surface coating with carbon or electrochemically inactive oxides and fluorides, and so on. These improvement methods need costly process for modification of the electrode materials, resulting in increase in the production cost. Recently, an effect of small amount of Li_4WO_5 powder as an electrode additive in slurry of $Li_{1.02}Ni_{0.82}Co_{0.15}Al_{0.03}O_2$ (NCA) composite electrode before coating was reported to decrease resistance of the graphite/NCA full cells and results in higher rate performance [1]. In this study, in order to further enhance the additive effect and elucidate the reaction mechanism, we prepared a new electrode additive Li_4MgWO_6 (LMW) and investigated the influence on electrochemical properties in $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ (NMC111)//graphite full cells.

LMW was synthesized by a conventional solid-state reaction and the ball-milled powder was added and mixed with NMC111, Super P, polyvinylidene fluoride (PVdF) at a weight ratio of 1:88:6:5 with N-methyl-2-pyrrolidone (NMP) solvent. Figure 1 shows capacity retention of graphite/1 mol dm^{-3} $LiPF_6$ EC:DMC (= 1:1 v/v)/NMC111 full cells with or without LMW additive in a NMC111 positive electrode. Despite both full cells deliver almost the same reversible capacity of 150 mAh g^{-1} after a pre-cycle, the LMW-added cell shows better cycle performance than additive-free one after 500 cycles. Furthermore, the LMW-added cell shows lower direct current resistance than that of additive-free one in Figure 2. In the past report, Mo-doping in NMC622 also shows better cycle performance. To elucidate the reaction mechanism, NMC and graphite electrodes were analyzed before and after cycles by using SEM, XPS, and XRD. The results and reaction mechanism of LMW-addition will be presented in detail.

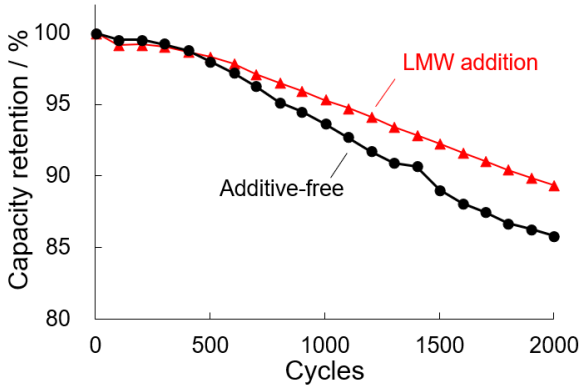

Fig. 1 Cycle performance of graphite//NMC Li-ion full cells with or without LMW additive in the NMC electrode.

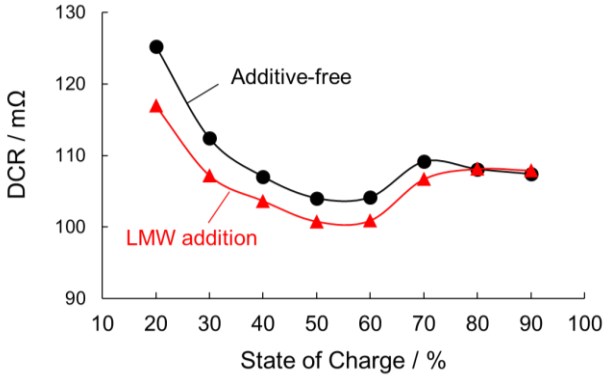

Fig. 2 Direct current resistance of graphite//NMC Li-ion full cells with or without LMW additive in the NMC electrode at different state of charge.

Reference:

[1] R. Kokado *et al.*, PCT International Publication No. WO 2013/125426 A1.