

Effect of Salt on Electrochemical Performance of LiMn_2O_4 Cathode

Mo-Hua Yang, Hung-Chun Wu and Zheng-Zhao Guo

Materials Research Laboratories, Industrial Technology Research Institute, Chutung, Hsinchu, Taiwan

LiMn_2O_4 as cathode materials are of great interest for the replacement of LiCoO_2 in the Li-ion batteries due to its safety, low cost and environmental advantages. The obstacle that prevented it from being commercialized is the rapid capacity fading, especially at elevated temperatures. While it has generally been recognized that the poor cyclability is mainly associated with (1) the Jahn-Teller (J-T) distortion and (2) Mn dissolution induced by acids generated. In the later issue, the decomposition of electrolyte solution can be a significant effect for inducing this undesirable reaction. The thermal instability of electrolyte system for generating the acid species is believed mainly due to the electrolyte solute lithium hexafluorophosphate (LiPF_6) that the most Li-ion battery industry uses.

In this study, a new boron-based anion, bis(oxalate)borate (BOB), was investigated for comparing its stability with LiPF_6 in the LiMn_2O_4 Li-ion battery system. A cylindrical 18650 type lithium ion battery was investigated by using LiMn_2O_4 as cathode and MCMB as anode materials. In order to compare the salt effect, 1.0 M LiPF_6 and 0.6 M LiBOB are prepared to add into the EC/EMC solvent to form the electrolyte, respectively.

The results of charge-discharge cycle test in these two different electrolyte systems at 25°C and 55°C were shown in fig. 1 and fig, respectively. The LiMn_2O_4 cell was almost the same cycling performance in LiPF_6 and LiBOB electrolyte systems at 25°C, but it was fading rapidly in LiPF_6 electrolyte system at 55°C.

In order to understand the capacity fading mechanism, XRD, ICP and XPS analysis were used to characterize the surface of cathode and anode after the cycle test. From the ICP analysis, it was found the Mn content 296 and 1778 ppm on the MCMB surface in LiPF_6 and LiBOB electrolyte systems, respectively after cycling test at 55°C. Therefore, the dissolution of Mn from LiMn_2O_4 and then deposited on MCMB was not the major capacity fading mechanism for $\text{LiMn}_2\text{O}_4/\text{MCMB}$ battery during cycling. On the other hand, from the dynamic XPS surface analysis, it was found that the anode SEI film for the LiPF_6 electrolyte system is thicker than that of LiBOB electrolyte system after cycling. From the observation of different thickness property of SEI film on the MCMB surface, it was concluded that the capacity fading during cycle testing mainly due to the easily decomposition of LiPF_6 electrolyte system. The thermal stability of

LiBOB electrolyte system is superior to LiPF_6 for the Li-ion battery by using LiMn_2O_4 .

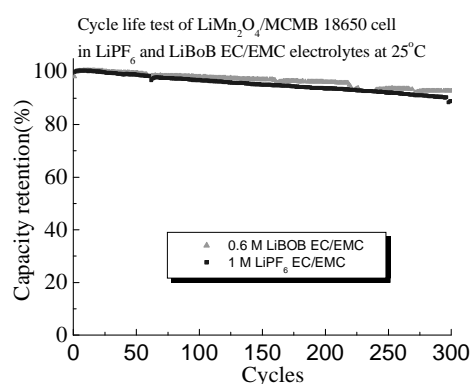


Figure 1. Cycle Life Test of LiMn_2O_4 cells at 1C Charge-Discharge Rate (4.2-2.8V) at 25°C

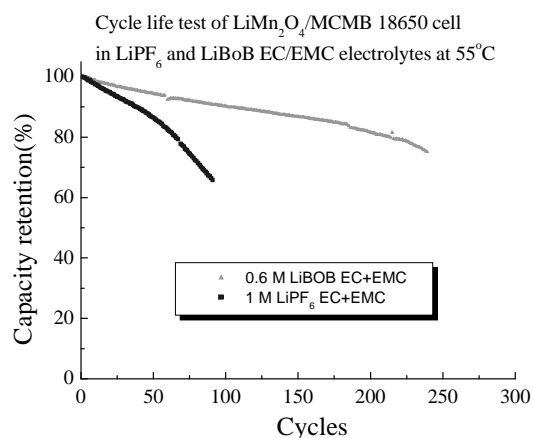


Figure 2. Cycle Life Test of LiMn_2O_4 cells at 1C Charge-Discharge Rate (4.2-2.8V) at 55°C