Synthesis and Electrochemical Properties of Olivine-type Cathode Materials Containing Fine Carbon for Lithium Batteries

Masao Kohzaki, Yoshio Ukyo
TOYOTA Central R&D Labs., Inc
Nagakute, Aichi, 480-1192, Japan

Mitsuharu Tabuchi
National Institute of Advanced Industrial Science and Technology, KANSAI
1-8-31 Midorigaoka, Ikeda, Osaka, 563-8577, Japan

Introduction
Among the known Li-insertion materials, phospho-olivine LiFePO$_4$ is one of the attractive candidates for the active cathode material of a lithium ion secondary battery because of the low cost, the environmental compatibility and the thermal stability due to the strong covalent bonding within the (PO$_4$)$^{3-}$ polyanion. These matters are favorable for large batteries to be used in an electric vehicle. However, owing to the very poor electric conductivity, the practical capacity decreased at high current density. In the present paper, we investigate the influence of Mn substitution for Fe and carbon dispersion into the LiFePO$_4$ particle on the electrochemical performance of the LiFePO$_4$ cathode materials with various grain size and crystallinity.

Experimental
The Li$_{1-x}$Mn$_x$PO$_4$ cathode materials containing fine carbon (LFMP-C) have been synthesized by solid-state reaction in an Ar atmosphere to prevent the oxidation of Fe(II) starting material. The synthesis of the material was carried out in stepwise method. First, the mixtures of starting materials containing fine carbon particle were pre-sintered at 350°C for 6 hours. After grinding and homogenizing the pre-sintered materials, they were fired in the temperature range from 600 to 900°C. The grain size of LFMP-C was observed by scanning electron microscopy and X-ray powder diffraction with Cu Kα radiation was used to identify the phases and to examine their crystallinity. $^{57}$Fe Mössbauer spectra were recorded at room temperature, and α-Fe was used for velocity calibration. Electrochemical properties of the LFMP-C were measured with a coin-type cell versus a Li metal or carbon anode. The cathode was fabricated as a mixture of LFMP-C / carbon black / polytetrafluoroethylene binder with weight ratio 70/25/5. The electrolyte used in this work was 1M solution of LiPF$_6$ in a mixture of ethylene carbonate and diethyl carbonate with volume ratio 1/1.

Results and discussion
We have succeeded to disperse well fine carbon particles in Phospho-olivine Li$_{1-x}$Mn$_x$PO$_4$ in the case of low carbon content. LFMP-C prepared beyond 650°C had olivine structure with good crystallinity and the grain of the LFMP-C became larger than 1μm in diameter. Mössbauer studies implied that Fe$^{3+}$/Fe$^{2+}$ ratios decreased by adding carbon particles although those ratios in LFMP-C were independent of Mn contents and of the anneal temperatures. Mn substitution for Fe had improved the cycle-life of LiFePO$_4$ even at high temperature as shown in Fig.1. Moreover, LFMP-C showed larger capacity and excellent cycle-life performance. The electrochemical properties of LFMP-C at higher current density were drastically improved even when the grain size was larger than 2μm in diameter. This may be due to the relatively high conductivity of LFMP-C achieved by dispersion of fine carbon.

References

Fig.1 Cycle-life performance of LiFePO$_4$, LiFe$_{0.85}$Mn$_{0.15}$PO$_4$ and LiFe$_{0.85}$Mn$_{0.15}$PO$_4$-C$_{0.10}$ evaluated with carbon anode cells at 60°C.