Li_3PO_4 integrated $LiMnO_2$ as High-Capacity Positive Electrode Materials

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The use of solid-state redox reaction of oxide ions is an important strategy to further increase in energy density of rechargeable lithium batteries. Recently, our group has reported that binary system of Li_2TiO_3 and $LiMnO_2$, which is reformulated as $Li_{1.2}Ti_{0.4}Mn_{0.4}O_2$, delivers large reversible capacity of 300 mA h g^{-1}. The capacity observed is much larger than that of the theoretical capacity calculated based on the Mn^{3+}/Mn^{4+} redox reaction, and the extra capacity originates from reversible contribution of oxide ion redox.[1]

In this study, this concept is extended into other lithium excess compounds, and the use of Li_3PO_4 is targeted. A binary system of x Li_3PO_4 – (1 – x) $LiMnO_2$ is studied as a new series of high capacity positive electrode materials. Since the molar mass of P is much smaller than that of Ti, and improved irreversibility for oxide ion redox on the basis of strong chemical bonding with oxygen is anticipated. The binary system was synthesized from a mixture of Li_3PO_4 and $LiMnO_2$ by mechanical milling. An X-ray diffraction study reveals that the samples are classified as a cation-disordered rocksalt-type structure as shown in Fig. 1, except pure Li_3PO_4 (x = 1). The electrode properties of samples in Li cells are shown in Fig.2. The sample of x = 0.2 ($Li_{7/6}P_{1/6}Mn_{2/3}O_2$) shows a high reversible capacity of approximately 300 mA h g^{-1} with relatively good capacity retention.

From these results, we will discuss the possibility of Li_3PO_4-based electrode materials as positive electrode materials with oxide ion redox for rechargeable lithium batteries.

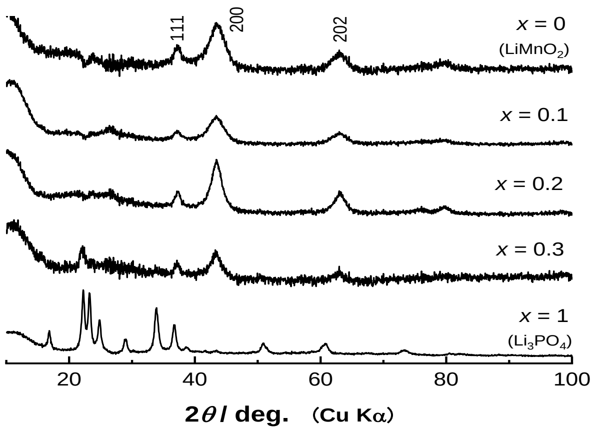

Fig. 1. XRD patterns of x Li_3PO_4 – (1 – x) $LiMnO_2$ binary system (x = 0, 0.1, 0.2, 0.3 and 1.0).

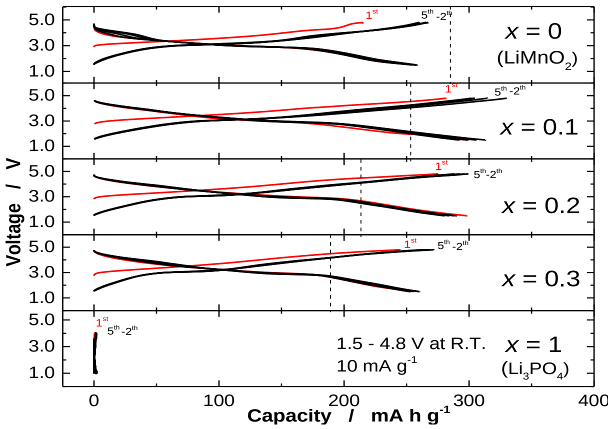

Fig. 2. Charge/discharge curves of the binary system (x = 0, 0.1, 0.2, 0.3 and 1.0) in Li cells. Dotted lines indicate the theoretical capacities based on Mn^{3+}/Mn^{4+} redox reaction.

References:
[1] N. Yabuuchi *et al.*, *Nature Commun.*, **7**, 13814 (2016).