Li$_3$PO$_4$ 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$_2$TiO$_3$ and LiMnO$_2$, which is reformulated as Li$_{1.2}$Ti$_{0.8}$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$_3$PO$_4$ is targeted. A binary system of $x$ Li$_3$PO$_4$ - (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$_3$PO$_4$ 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$_3$PO$_4$ ($x$ = 1). The electrode properties of samples in Li cells are shown in Fig. 2. The sample of $x$ = 0.2 (Li$_{1.8}$P$_{1/6}$Mn$_{23}$/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$_3$PO$_4$-based electrode materials as positive electrode materials with oxide ion redox for rechargeable lithium batteries.

![XRD patterns of $x$ Li$_3$PO$_4$ - (1 - $x$) LiMnO$_2$ binary system ($x$ = 0, 0.1, 0.2, 0.3 and 1.0).](image)

![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.](image)

References: