Electrochemical properties of Li$_2$MnO$_2$ based cathode materials prepared by reduction-ion exchange method

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1. Introduction

Lithium-rich layered cathode materials Li$_2$MnO$_2$-LiMnO$_2$ (M = Ni, Co, Fe) with large specific capacity (~250mAh g$^{-1}$) have been studied intensively as next generation cathode materials for LIBs. However, this kind material shows large irreversible capacity at the initial cycle. It is necessary to improve the first cycle efficiency of this cathode material before the practical application. In this study we tried to synthesize Li$_2$MnO$_2$ based material from P3 type Na$_2$Ni$_{1/3}$Mn$_{2/3}$O$_2$ through a simultaneous reduction and lithium exchange in molten salts. By employing this method, extra Li can be incorporated into the Na$_2$Ni$_{1/3}$Mn$_{2/3}$O$_2$ than the traditional ion-exchange method. The as-prepared Li$_2$Ni$_{1/3}$Mn$_{2/3}$O$_2$ exhibited similar XRD patterns and charge and discharge profiles as those of Li$_2$MnO$_2$ based cathode material. Moreover, the Li$_2$Ni$_{1/3}$Mn$_{2/3}$O$_2$ showed extremely small irreversible capacity and good cycleability. The effect of metal substitution on the properties of the as-prepared Li$_2$Ni$_{1/3}$Mn$_{2/3}$O$_2$ compound was also investigated.

2. Experimental

The precursor P3 Na$_2$Ni$_{1/3}$Mn$_{2/3}$O$_2$ was prepared through a simple combustion method. Typically, stoichiometric amounts of nickel nitrate (Ni(NO$_3$)$_2$), manganese nitrate (Mn(NO$_3$)$_2$) and sodium nitrate (NaNO$_3$) were mixed in triethylene glycol. The mixture was fired at around 350°C and ash like powder can be obtained after the vigorous decomposition of organic materials. The decomposed powder was ball-milled for 1h and was subsequently calcinated at 700°C in air for 10h to form P3 type Na$_2$Ni$_{1/3}$Mn$_{2/3}$O$_2$ precursor. For the synthesis of P3 Na$_2$Ni$_{1/3}$Mn$_{2/3}$O$_2$ (M=Al, Co, Fe, Mg) precursors, the same procedure was used except for the added amount of the metal nitrate. Reduction-Ion exchange was done by using the molten salt of mixture of LiNO$_3$ and LiI at 280°C in air.

CR2032 type coin cells were assembled to evaluate the electrochemical properties of the obtained compounds. The electrolyte used was a mixture of 1 M lithium phosphorus hexafluoride (LiPF$_6$) in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) volume ration of 1:2. The assembled cells were cycled at a current density of 20 mA/g between 2.5 V-4.7 V.

3. Results and discussion

The XRD patterns of P3 precursor Na$_2$Ni$_{1/3}$Mn$_{2/3}$O$_2$ and its ion exchanged samples are shown in Figure 1. All peaks of Na$_2$Ni$_{1/3}$Mn$_{2/3}$O$_2$ can be indexed to P3 layered structure without out impurity. After normal ion exchange, the XRD patterns of turned to O3 structure due to the successful Li to Na ion exchange. For precursors treated with LiI, additional peak around 22° appears, which is a characteristic peak of lithium-rich layered cathode materials. The XRD patterns of Li$_2$Ni$_{1/3}$Mn$_{2/3}$O$_2$ suggests that lithium-rich layered compound was formed after reduction-ion exchange.

Figure 2 presents the galvanostatic charge-discharge profiles of Li$_2$Ni$_{1/3}$Mn$_{2/3}$O$_2$ and Li$_2$Ni$_{1/3}$Mn$_{2/3}$O$_2$. It is obvious to observer that the first discharge capacity of Li$_2$Ni$_{1/3}$Mn$_{2/3}$O$_2$ is higher than the charge capacity. Also, the appearance of 3V plateau a typical feature of Li$_2$Ni$_{1/3}$Mn$_{2/3}$O$_2$. In contrast, Li$_2$Ni$_{1/3}$Mn$_{2/3}$O$_2$ shows exactly different potential-capacity profiles. This potential-capacity profile is similar to that of lithium-rich layered cathode materials. The first cycle capacity of Li$_2$Ni$_{1/3}$Mn$_{2/3}$O$_2$-Solid increased to around 240mAh g$^{-1}$. Furthermore, the first cycle irreversible capacity is extremely small compared to well-known lithium-rich layered cathode materials. It is also found that samples prepared from co-precipitation precursor Li$_2$Ni$_{1/3}$Mn$_{2/3}$O$_2$-Cop delivered much higher reversible capacity compared to that of solid state samples, which indicates that it is possible to further improve the capacity of the samples by optimizing the precursor. Electrochemical properties of metal substituted Li$_2$Ni$_{1/3}$Mn$_{2/3}$O$_2$ were also investigated and they showed good cycleability and rate performance.

References