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Synthesize and electrochemical characterization of Mg-doped Li-rich layered $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ cathode material

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ABSTRACT

Mg-doped $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ as a Li-rich cathode material of lithium-ion batteries were prepared by co-precipitation method and ball-milling treatment using $Mg(OH)_2$ as a dopant. Scanning electron microscopy (SEM), ex situ X-ray powder diffraction (XRD), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvantatic charge/discharge were used to investigate the effect of Mg doping on structure and electrochemical performance. Compared with the bare material, Mg-doped materials exhibit better cycle stabilities and superior rate capabilities. $Li[Li_{0.2}Ni_{0.195}Mn_{0.595}Mg_{0.01}]O_2$ displays a high reversible capacity of 226.5 mAh g^{-1} after 60 cycles at 0.1 C. The excellent cycle performance can be attributed to the improvement in structure stability, which is verified by XRD tests before and after 60 cycles. EIS results show that Mg doping decreases the charge-transfer resistance and enhances the reaction kinetics, which is considered to be the major factor for higher rate performance.

1. Introduction

In recent years, the Li-rich solid solution (Li_2MnO_3-$LiMO_2$) [1] (M = Ni, Co and Mn) cathode materials have drawn a lot of attention due to their high capacity comparing to commercial $LiCoO_2$ [2]. Among them, the composite between Li_2MnO_3 and $LiNi_{1/2}Mn_{1/2}O_2$ [3,4] can deliver a high discharge capacity of 200–300 mAh g^{-1} in the voltage range of 2.0–4.8 V and exhibit an excellent cycling performance [5], which make it an ideal candidate cathode material to realize extensive industrial application, especially in the field of electric vehicles or hybrid electric vehicles.

Although Li_2MnO_3 is usually believed to be electrochemically inactive [6], it plays a critical role in storing excess lithium and stabilizing $LiMO_2$ component above 4.5 V [7,8], which makes high-voltage battery with high capacity possible. However, there are still several unsolved issues hindering its large-scale commercial popularization, such as large irreversible capacity loss in the initial cycle, poor structural stability at high cutoff potential and poor rate capability [9].

Surface coating and element doping are two effective methods to improve the electrochemical performance of cathode materials. Coating with $Al(OH)_3$ [9], MnO_2 [10], Li_2CO_3 [11], ZnO [12], ZrO_2 [13,14], $LiNiPO_4$ [15] and carbon [16] to improve cycle performance have been extensively investigated. Although the coated layer could suppress the undesired surface side reactions, some materials are generally with low lithium-ion conductivity and lead to the loss of rate or power capability [17]. The substitution of metal elements such as Al, Zn, Zr, Co, Mg and Cr [18–22] for transition element has also been studied to improve electrochemical performance. So far, Mg has been used successfully to improve the cycling stability of cathode materials such as $LiNi_{1-x}Co_xO_2$ [23] and $LiCoO_2$ [24]. The improved performance is attributed to the enhanced conductivity and structural stability [23]. In this paper, the effect of Mg doping on the structure and electrochemical performance of Li-rich layered cathode material $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ has been investigated.

2. Experimental

The $Ni_{0.25}Mn_{0.75}(OH)_2$ precursor was prepared beforehand by co-precipitation method [9] as follows: a 2 mol/L aqueous solution of $NiSO_4{\cdot}H_2O$ (>98.5% purity) and $MnCl_2{\cdot}4H_2O$ (>99% purity) and a 4 mol/L solution of NaOH with a required amount NH_4OH were separately dropped into a continuously stirred reactor under nitrogen atmosphere. The precursor was washed several times and then dried at 120 °C for 12 h. After mixing $Ni_{0.25}Mn_{0.75}(OH)_2$ precursor with different amount of $Mg(OH)_2$ and Li_2CO_3 by a planetary ball mill for 2 h (excess $LiCO_3$ should be added to compensate volatilized Li), the mixtures were calcinated at 550 °C for 5 h and 900 °C for 12 h in air to obtain the corresponding lithiated compounds $Li[Li_{0.2}Ni_{0.2-x}Mn_{0.6-x}Mg_{2x}]O_2$ ($2x = 0, 0.01, 0.02, 0.05$), which were named as QMg0, QMg1, QMg2 and QMg5 according to the value of $2x$.

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Table 1
The experimental and theoretical results of Ni/Mn/Mg and Li/(Ni + Mn + Mg) mole ratios of the $Li[Li_{0.2}Ni_{0.2-x}Mn_{0.6-x}Mg_{2x}]O_2$ materials.

Samples	Ni/Mn/Mg		Li/(Ni + Mn + Mg)	
	Theoretical	Experimental	Theoretical	Experimental
QMg0	0.20:0.60:0	0.201:0.599:0	1.200	1.197
QMg1	0.195:0.595:0.01	0.195:0.594:0.011	1.200	1.199
QMg2	0.190:0.590:0.02	0.191:0.589:0.020	1.200	1.202
QMg5	0.175:0.575:0.05	0.177:0.574:0.049	1.200	1.196

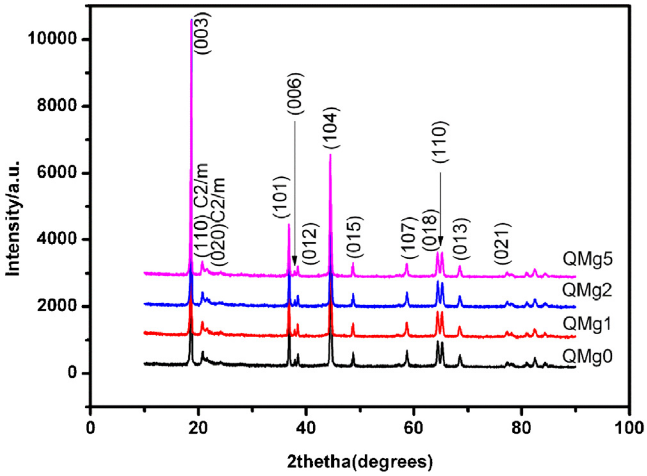

Fig. 1. XRD patterns of QMg0, QMg1, QMg2, and QMg5.

Inductively Coupled Plasma (ICP) was used to identify the contents of Ni, Mn, Mg in the materials. Powder X-ray diffraction (XRD) using a Bruker D8 ADVANCE diffractormeter was carried out from $2\theta = 10–90^\circ$ to analyze the crystalline phase. Scanning electron microscope (SEM, HITACHI S4800) was used to characterize the powder morphology. After 60 cycles, the cells were disassembled in a glovebox, and electrodes were washed with DMC solvent and dried at 100 °C. Then the dried electrodes were analyzed by ex situ XRD and SEM to evaluate structural and morphology changes of Mg-doped and undoped materials.

The cathodes were prepared by coating homogeneous slurries with 80 wt% active materials, 10 wt% carbon black, and 10 wt% poly(vinylidene difluoride) binder onto Al foils, and dried at 120 °C under vacuum for 10 h. All types of electrodes comprised 8 mg of active material on Al current collector and the thickness of the electrodes is 45 μm. CR2032 coin cells were assembled in a glovebox with the cathodes, Li anodes, Celgard 2300 polypropylene separators and electrolyte with 1 M $LiPF_6$ in EC:DEC:EMC (1:1:1 by volume). The cells were tested using a constant current method (CC) for charging to 4.8 V and holding at 4.8 V for 1.5 h, and a CC method for discharging to 2.0 V at different current rate at room temperature. Electrochemical impedance spectroscopy (EIS) was performed with an electrochemical workstation PARSTAT 2273 in the ac voltage of 10 mV over a frequency range of 10 mHz to 100 kHz. The cyclic voltammetry (CV) tests were conducted using an electrochemical workstation (CHI 660D) at a scan rate of 0.2 mV s^{-1} between 2.0 and 4.8 V (versus Li^+/Li).

3. Results and discussion

The ICP results in Table 1 are in accord with the target compositions. The powder X-ray diffraction (XRD) patterns of QMg0,

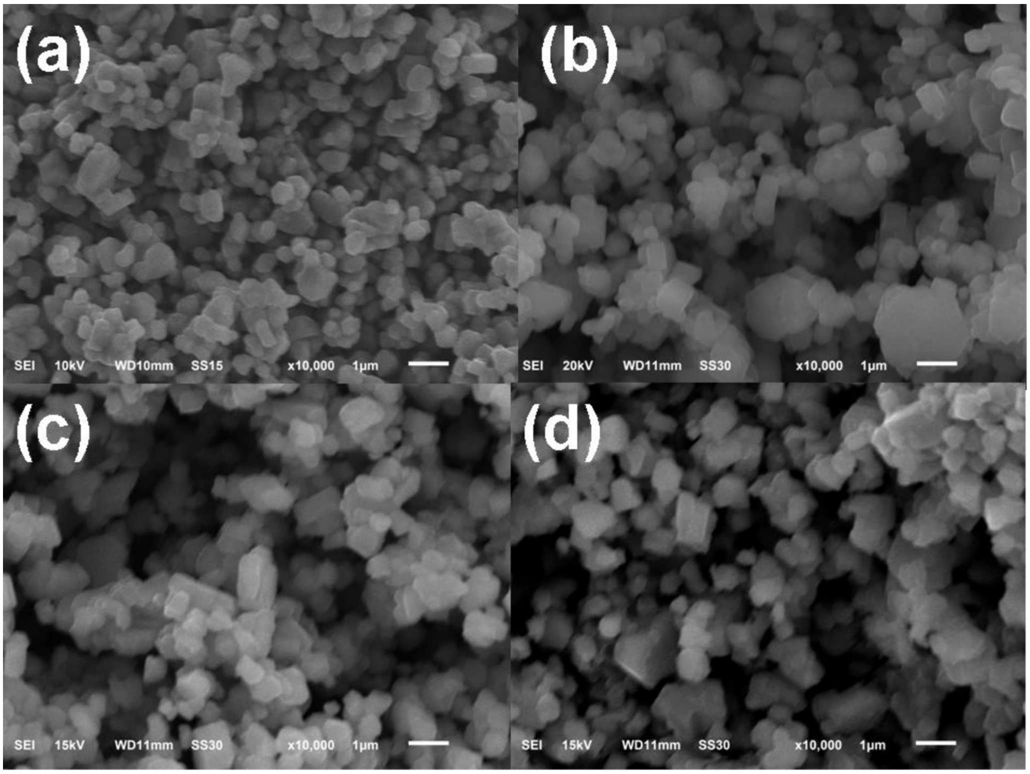

Fig. 2. SEM images of (a) QMg0, (b) QMg1, (c) QMg2, and (d) QMg5.