Facile synthesis of high performance LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_4$ and LiNi$_{0.5}$Mn$_{1.4}$Al$_{0.1}$O$_4$ by a low temperature solution combustion synthesis method

Guiyang Liu$^{1,2,*}$, Hongyan Sun$^{1,2}$, Xin Kong$^{1,2}$, Yannan Li$^{1,2}$, Baosen Wang$^{1,2}$

$^1$ Lab of New Materials for Power Sources, College of Science, Honghe University, Mengzi 661199, Yunnan, China.
$^2$ Local Characteristic Resource Utilization and New Materials Key Laboratory of Universities in Yunnan, Honghe University, Mengzi 661199, Yunan, China.
E-mail: liuguiyang@tsinghua.org.cn

Received: 15 April 2015 / Accepted: 28 May 2015 / Published: 24 June 2015

LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_4$ and LiNi$_{0.5}$Mn$_{1.4}$Al$_{0.1}$O$_4$ was synthesized by a low temperature solution combustion synthesis method at 700 °C in 30 min. Both of the two products are non-stoichiometric and disordered LiNi$_{0.5}$Mn$_{1.5}$O$_4$ spinels. The two products exhibit similar reversible capacity and excellent cycling stability at 1C rate at room temperature. The initial reversible capacity of LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_4$ and LiNi$_{0.5}$Mn$_{1.4}$Al$_{0.1}$O$_4$ are 114 mAh/g and 113 mAh/g, and remain 100.0% and 98.9% after 100 cycles at 1C, respectively. LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_4$ shows better rate capability and much better cycling stability at 10C rate than these of LiNi$_{0.5}$Mn$_{1.4}$Al$_{0.1}$O$_4$. At 10C rate, the capacity retention of LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_4$ is near 100% after 100 cycles, but the capacity retention of LiNi$_{0.5}$Mn$_{1.4}$Al$_{0.1}$O$_4$ is only 80%. LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_4$ also displays better cycling stability at 55 °C than that of LiNi$_{0.5}$Mn$_{1.4}$Al$_{0.1}$O$_4$. The excellent electrochemical performance of LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_4$ is attributed to its higher crystallinity, larger Li$^+$ diffusion coefficient and lower charge transfer resistance.

Keywords: Lithium ion batteries, LiNi$_{0.5}$Mn$_{1.5}$O$_4$ spinels, cathode materials, doping

1. INTRODUCTION

LiNi$_{0.5}$Mn$_{1.5}$O$_4$ spinel is one of the most promising cathode materials for lithium ion batteries because of its high operating voltage, good rate capability and low cost [1]. However, for practical applications, especially the application in electric vehicles (EVs) or hybrid electric vehicles (HEVs), the electrochemical performances of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ including cycling stability especially at elevated temperatures and rate capability need to be significantly improved [2].
Doping has been proved to be one of the most efficient routes to improve the electrochemical performance of LiNi_{0.5}Mn_{1.5}O_4 [3, 4]. In the literatures, LiNi_{0.5}Mn_{1.5}O_4 spinels doped by Mg [5], Al [6], Ti [7], Ga [8] and W [9] have been reported and exhibit improved electrochemical performance. Among them, Mg and Al are more attractive because of their light weight and high efficiency for improving the performance of LiNi_{0.5}Mn_{1.5}O_4 [10-12].

For the preparation of doped LiNi_{0.5}Mn_{1.5}O_4, it is important that the raw materials must be mixed homogeneously. Different synthesis methods such as solid-state method [13], sol-gel method [14] or co-precipitation synthesis [15] producing doped LiNi_{0.5}Mn_{1.5}O_4 with different electrochemical performance have been reported. Although solid-state method is the simplest, the mixture of raw materials is non-homogeneous. In order to prepare single phase doped LiNi_{0.5}Mn_{1.5}O_4, high temperature and long time are needed. However, high temperature generally results in increased grain size and impurities such as Li_{x}Ni_{1−x}O in the final product, leading to rate capability declining and capacity fading [16]. Other methods such as sol-gel method and co-precipitation method can obtain homogenous precursors and the electrochemical performance of the products can be improved, but the processes of them are complicated, resulting in the limitation in practical manufacturing applications.

Solution combustion synthesis method is a simple method to synthesize metal oxides at low temperature [17]. Due to the ionic level’s mixture of the raw materials in solution, doping could be easily carried out. In this paper, we introduced a modified low temperature solution combustion synthesis method to prepare Al and Mg doped LiNi_{0.5}Mn_{1.5}O_4. Based on the optimization of the experimental conditions of the improved solution combustion synthesis method [18, 19], doped LiNi_{0.5}Mn_{1.5}O_4 spinels with excellent electrochemical performance could be synthesized at 700°C in only 30 min. The total process took no more than 1 h. Although Mg and Al doping in LiNi_{0.5}Mn_{1.5}O_4 synthesized by other methods have been widely reported, to our knowledge, it has not been reported that Mg and Al doped LiNi_{0.5}Mn_{1.5}O_4 spinels with such excellent performance could be synthesized in such a short time. The electrochemical performances including capacity, cycling stability, rate capability of the products have been studied in details.

2. EXPERIMENTAL

2.1 Synthesis

For the synthesis of LiNi_{0.5}Mn_{1.4}Mg_{0.1}O_4 (or LiNi_{0.5}Mn_{1.4}Al_{0.1}O_4), raw materials of LiNO_3, CH_3COOLi, Mn(NO_3)_2, (CH_3COO)_2Mn, Ni(NO_3)_2, (CH_3COO)_2Ni and Mg(NO_3)_2 (or Al(NO_3)_3) (AR, 99%, Aladdin) with the mole ratio of 0.5:0.5:0.7:0.7:0.25:0.25:0.1 were firstly dissolved in distilled water to obtain a solution. Then, the solution was combusted in a muffle furnace preset at 700°C directly for 30 minutes. And then the product was taken out and cooled down to room temperature in air. The final LiNi_{0.5}Mn_{1.4}Mg_{0.1}O_4 (or LiNi_{0.5}Mn_{1.4}Al_{0.1}O_4) was obtained.
2.2 Phase composition and morphology

The phase composition and structure of the products were determined by X-ray diffraction (XRD, D/max-rB, Cu-Kα radiation) and Fourier transform infrared spectroscopy (FTIR, Perkin Elmer, with KBr pellets). The morphologies of the products were observed by scanning electron microscope (SEM, XL30ESEM-TMP, Philips).

2.3 Electrochemical performance test

The electrochemical performance of the as-prepared LiNi_{0.5}Mn_{1.5}O_{4} powders was tested in a standard CR2032 coin cell, which was composed of a cathode, lithium anode, a Celgard polypropylene separator, and LiPF6 in 1:1 ethylene carbonate/diethylene carbonate (EC/DEC) as electrolyte. The cathode electrode was composed of 80 wt.% active material, 12 wt.% conductive carbon, and 8 wt.% polyvinylidene fluoride binder. The cells were assembled in an argon-filled glove box and cycled at room temperature and 55 °C in the voltage range of 3.5 - 5.0 V (versus Li/Li⁺) at different C rate (in this paper, 1C=150mA/g). Cyclic voltammograms (CV) and electrochemical impedance spectroscopy (EIS) of the products were carried out by an electrochemical workstation (Autolab PGSTAT302N, Metrohm, Switzerland). The scan rate was from 0.1 to 0.5 mV/s between 3.5-5.0 V, and the frequency range was 10 kHz to 0.1 Hz with an AC amplitude of 5 mV. Before EIS test, the cell was charged to 5V at 100% state.

3. RESULTS AND DISCUSSION

3.1 Phase structure and micro-morphologies

XRD patterns of the products were shown in Fig.1. It can be seen that all peaks of the products correspond to LiNi_{0.5}Mn_{1.5}O_{4} (JCPDS 80-2162) and no evident other peaks appeared, suggesting that single phase LiNi_{0.5}Mn_{1.5}O_{4} spinels were obtained. Because of the larger ionic radius of Mg^{2+} than that of Al^{3+} [20, 21], the calculated lattice parameter of LiNi_{0.5}Mn_{1.4}Mg_{0.1}O_{4} is 0.81939 nm, larger than 0.81784nm of the LiNi_{0.5}Mn_{1.4}Al_{0.1}O_{4}. Because the ionic radius of Al^{3+} is smaller than that of Mn^{3+} [21], the lattice parameter of the LiNi_{0.5}Mn_{1.4}Al_{0.1}O_{4} should be smaller than 0.817nm of the standard pristine LiNi_{0.5}Mn_{1.5}O_{4}. However, the calculated lattice parameter of the LiNi_{0.5}Mn_{1.4}Al_{0.1}O_{4} is larger, suggesting that the as-prepared Al^{3+} doped LiNi_{0.5}Mn_{1.5}O_{4} spinel is non-stoichiometric and disordered [22]. There are two types of LiNi_{0.5}Mn_{1.5}O_{4} spinel, disordered Fd₃m or ordered P₄₃₃₂ [4]. In the stoichiometric and ordered LiNi_{0.5}Mn_{1.5}O_{4} spinel, Ni^{2+} and Mn^{4+} ions exhibit a cation site ordering over two distinct octahedral positions at 4a and 16d sites, respectively [6]. For the non-stoichiometric LiNi_{0.5}Mn_{1.5}O_{4,δ}, because of the loss of oxygen, part of the inactive Mn^{4+} ions would be reduced to Mn^{3+} to keep charge neutrality. Because the ionic radius of Mn^{3+} is larger than that of Mn^{4+}, the lattice parameters of the non-stoichiometric LiNi_{0.5}Mn_{1.5}O_{4,δ} generally increase with increasing Mn^{3+} in the lattice [23].
The cation ordering of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ can be determined by FT-IR spectroscopy effectively [24]. When the cation ordering of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ increases, the intensity of Ni–O band at 588 cm$^{-1}$ will increase and the intensity of Mn–O band at 620 cm$^{-1}$ will decrease [25]. For example, a typical highly ordered structure shows a higher intensity of Ni–O band at about 588 cm$^{-1}$ than that of Mn–O band at 620 cm$^{-1}$ [26]. As shown in Fig. 2, the band intensity of all the products at 585 cm$^{-1}$ is lower than that at 620 cm$^{-1}$, suggesting that the two products have disordered structure with space group of Fd$_{3}$m.

Figure 1. XRD patterns of (a) LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_4$ and (b) LiNi$_{0.5}$Mn$_{1.4}$Al$_{0.1}$O$_4$.

Figure 2. FT-IR spectra patterns of (a) LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_4$ and (b) LiNi$_{0.5}$Mn$_{1.4}$Al$_{0.1}$O$_4$. 
Figure 3. SEM images of (a) LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_{4}$ and (b) LiNi$_{0.5}$Mn$_{1.4}$Al$_{0.1}$O$_{4}$.

The SEM micro morphologies of the products are shown in Fig.3. It can be found that the micro morphologies of LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_{4}$ (as shown in Fig.3a) exhibit developed grains with ~300-500nm in size. The surface facets are very clear, indicating that the sample is well crystallized. Differently, besides developed grains, LiNi$_{0.5}$Mn$_{1.4}$Al$_{0.1}$O$_{4}$ also shows lots of small agglomerated particles, as shown in Fig.3b. From the small particles, typical octahedral surface facets of the spinel cannot be found, suggesting that some grains of LiNi$_{0.5}$Mn$_{1.4}$Al$_{0.1}$O$_{4}$ are not well developed.

3.2 Electrochemical performance

The initial charge/discharge curves of the LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_{4}$ and LiNi$_{0.5}$Mn$_{1.4}$Al$_{0.1}$O$_{4}$ are shown in Fig.4a. There are two voltage plateaus the curves. The main plateau at 4.7 V is attributed to Ni$^{4+}$/Ni$^{3+}$ and Ni$^{3+}$/Ni$^{2+}$ redox reactions, and the minor plateau at 4.0 V is ascribed to the redox reaction between the Mn$^{3+}$ and Mn$^{4+}$ couple [27]. The initial discharge capacities from the products of LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_{4}$ and LiNi$_{0.5}$Mn$_{1.4}$Al$_{0.1}$O$_{4}$ are around 114 mAh/g and 113 mAh/g, respectively. The capacity contribution from the 4.0 V plateau could be calculated from the capacity between 3.80 and 4.25 V, which could qualitatively reflect the relative concentration of Mn$^{3+}$ ions in the spinels [22].
The calculated capacities from 4.0V of LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_4$ and LiNi$_{0.5}$Mn$_{1.4}$Al$_{0.1}$O$_4$ are 27 and 28 mAh/g, respectively. The considerable capacities from 4.0V plateaus of the products reveal that there are considerable Mn$^{3+}$ ions in the products, and also indicate that the products are non-stoichiometric and disordered, which can support the results of XRD and FT-IR.

Figure 4. (a) Initial charge/discharge curves of the products. The cell was firstly charged to 5.0 V at 0.2C and held for 10min at 5.0 V, and then discharged to 3.5 V at 0.2C. (b) Cycling stabilities of the products. The cell was charged at 0.5C and discharged at 1C in 3.5-5.0V. (c) The discharge curves of the products of the 1st cycle and the 100th cycle.

Fig.4b shows the cycling performances of the products. The capacity retentions of LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_4$ and LiNi$_{0.5}$Mn$_{1.4}$Al$_{0.1}$O$_4$ after 100 cycles are 100.0% and 98.9%, respectively. Both the products exhibit excellent cycling stabilities, especially the Mg$^{2+}$ doped one. Moreover, after 100 cycles at 1C discharge rate, the plateau voltage in the discharge curve of the two products change little (Fig.4c), also suggesting the stable cycling performance of the products. Noticeably, the calcination temperature and time of the products are only 700°C and 30min. To our knowledge, no reported LiNi$_{0.5}$Mn$_{1.5}$O$_4$ could possess such high capacity retention in such short synthesis time. Compared with the doped LiNi$_{0.5}$Mn$_{1.5}$O$_4$ prepared by co-deposition method [5], sol-gel method [10] or self-sacrifice template method [26], the capacity retentions of the as-prepared products in this paper are also superior. Zhong [6], Lafont [10] and Ooms [28] reported that Mg and Al doping can stabilize...
the host structure against repeated de-intercalation of the Li$^+$ ion therefore can enhance the cycling stability of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$.

**Figure 5.** (a) Rates capabilities of the products. (b) Capacity retentions at different rates of the products. (c) Charge/discharge curves of LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_4$ at different rate. (d) Charge/discharge curves of LiNi$_{0.5}$Mn$_{1.4}$Al$_{0.1}$O$_4$ at different rate. (e) Cycling performance of the products at 10C rate. The cell was charged at a slow rate of 0.5C when discharge rate is ≥ 0.5C.

Fig.5 shows the rate capabilities of the products. The product LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_4$ shows excellent capacity retention with increasing C rate (as seen in Fig.5a). Even at a high rate of 20C, the capacity of LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_4$ is also 84 mAh/g. However, for LiNi$_{0.5}$Mn$_{1.4}$Al$_{0.1}$O$_4$, at 5C, the capacity appears an obvious drop, and at 20C, the capacity becomes only about 40 mAh/g. The capacity retentions at different C rate relative to the capacity at 0.2C are shown in Fig.5b. It can be seen from Fig.5b that the capacity retention of LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_4$ is much better than that of LiNi$_{0.5}$Mn$_{1.4}$Al$_{0.1}$O$_4$. 
It can be seen from Fig.5c and Fig.5d that the polarizations from 0.2C to 2C of the two products are small, revealing that at lower rate, the two products show good rate capabilities. However, when the rate is above 5C, the voltage drop of LiNi₀.₅Mn₁.₄Al₀.₁O₄ is larger than that of LiNi₀.₅Mn₁.₄Mg₀.₁O₄. At 20C, LiNi₀.₅Mn₁.₄Mg₀.₁O₄ still maintains an operation voltage close to 4.2V. Contrastively, the operation voltage of LiNi₀.₂Mn₁.₄Al₀.₁O₄ badly drops to 3.7V. LiNi₀.₅Mn₁.₄Mg₀.₁O₄ shows smaller polarization with increasing C rate.

LiNi₀.₅Mn₁.₄Mg₀.₁O₄ displays much better cycle stability than that of LiNi₀.₅Mn₁.₄Al₀.₁O₄. As shown in Fig.5c, the capacity retentions of LiNi₀.₅Mn₁.₄Mg₀.₁O₄ are near 100%, but the capacity retention of LiNi₀.₅Mn₁.₄Al₀.₁O₄ is only 80% at 10C rate after 100 cycles. Mg doping is more efficient for improving the rate capability of LiNi₀.₅Mn₁.₄O₄ than Al doping. Moreover, because the two products are non-stoichiometric and disordered, and the presence of oxygen defect and Mn³⁺ ions in the two products could improve their rate capabilities [22, 24, 29], the as-prepared LiNi₀.₅Mn₁.₄Al₀.₁O₄ and LiNi₀.₅Mn₁.₄Mg₀.₁O₄ exhibit better rate capabilities than many previously reported LiNi₀.₅Mn₁.₅O₄ spinels [30, 31].

Voltammetry measurements of LiNi₀.₅Mn₁.₄Mg₀.₁O₄ and LiNi₀.₅Mn₁.₄Al₀.₁O₄ were performed to further study the electrochemical performance. Fig.6a and Fig.6b show the cyclic voltammograms (CVs) of LiNi₀.₅Mn₁.₄Mg₀.₁O₄ and LiNi₀.₅Mn₁.₄Al₀.₁O₄ scanned from 0.1 to 0.5mV/s, respectively. Two regions at 4.0V and 4.7V appear in the CVs. The two redox pairs in 4.0V regions of the products are evident, suggesting the existence of the Mn⁴⁺/Mn³⁺ couple in the products, which confirm the results of charge/discharge curves. When the scan rates increase from 0.1 to 0.5 mV/s, the change of voltage gaps between each redox couple of LiNi₀.₅Mn₁.₄Mg₀.₁O₄ is smaller than that of LiNi₀.₅Mn₁.₄Al₀.₁O₄. It suggests that the polarization of LiNi₀.₅Mn₁.₄Mg₀.₁O₄ is smaller than that of LiNi₀.₅Mn₁.₄Al₀.₁O₄.

Fig.6a and Fig.6b also show that as the scanning rate (v) is increased, the peak current (iₚ) increases. Fig.6c shows the iₚ vs. the square root of the scan rates (v½) of the products. All of them display linear increase, which suggests that the intercalation reaction is a solid-state diffusion controlled reaction [32]. Moreover, the diffusion coefficient of Li⁺ (D_Li⁺) can be approximately determined by the dependence of iₚ on v½ based on the following equation [33]:

\[
iₚ = 2.69 \times 10^5 n^2 A C_{Li⁺} D_{Li⁺}^{3/2} v^{1/2}
\]  

(1)

Where n is the number of electrons per reaction species (for lithium-ion n=1), A is the total surface area of the electrode (2 cm² in this case), and C_Li⁺ is the bulk concentration of Li⁺ in the electrode (given as 0.02378 mol/cm³) [34, 35]. From the slope of linear fit of iₚ vs. v½ in Fig.6d, the diffusion coefficients (D_Li⁺) of LiNi₀.₅Mn₁.₄Mg₀.₁O₄ and LiNi₀.₅Mn₁.₄Al₀.₁O₄ have been calculated as 5.30×10⁻¹²cm²/s and 2.00×10⁻¹²cm²/s respectively. The calculated D_Li⁺ values are in accord with to the values reported previously [36, 37]. It has been reported that disordered (Fd₃m) LiNi₀.₅Mn₁.₅O₄ shows 1-2 order of magnitude larger D_Li⁺ than ordered LiNi₀.₅Mn₁.₅O₄ (P4₃m) [38]. The calculated D_Li⁺ values of our products are 1-2 order of magnitude higher than those ordered LiNi₀.₅Mn₁.₅O₄ reported previously, suggesting that the phase structure of the products are disordered structure. The result is in agreement with the analysis of FTIR above. D_Li⁺ is an important factor for improving the rate capability.
[36], the larger $D_{Li}$ of LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_4$ results in better rate capability than that of LiNi$_{0.5}$Mn$_{1.4}$Al$_{0.1}$O$_4$. Theoretically, the bond strength of Al-O is stronger than those of Mg-O [21], which may result in more difficult lithium ion diffusion in the lattice, therefore leads to the larger $D_{Li}$.

Figure 6. Cyclic voltammogram (CV) of (a) LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_4$ and (b) LiNi$_{0.5}$Mn$_{1.4}$Al$_{0.1}$O$_4$ at different scan rate. (c) The plotting of peak current vs. square root of the scan rate for the products.

The EIS of the cell with LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_4$ and LiNi$_{0.5}$Mn$_{1.4}$Al$_{0.1}$O$_4$ as electrodes are shown in Fig.7. The EIS spectrums consist of two semicircles in high-to-medium frequency region and an inclined line in low frequency region. The two semicircles are lithium-ion migration resistance ($R_i$) and the charge transfer resistance ($R_{ct}$), respectively, and the inclined line in the low frequency region is the Warburg impedance of solid phase diffusion ($\sigma_w$) [39-41]. Apparently, it can be seen from Fig.7 that the $R_{ct}$ of LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_4$ is lower than that of LiNi$_{0.5}$Mn$_{1.4}$Al$_{0.1}$O$_4$. Lower $R_{ct}$ value of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ implies a lower electrochemical polarization, which leads to better rate capability [4], and higher $R_{ct}$ means more capacity loss at the higher charge/discharge rate [41]. Combining the EIS with the CV analysis, it is clear that due to the larger $D_{Li}$ and lower $R_{ct}$, LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_4$ exhibit better rate capability and better cycle stability at high rate than those of LiNi$_{0.5}$Mn$_{1.4}$Al$_{0.1}$O$_4$, which are in good agreement with the C-rate investigation.
Figure 7. (a) EIS spectra of LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_4$ and LiNi$_{0.5}$Mn$_{1.4}$Al$_{0.1}$O$_4$ in the frequency range between 0.1 Hz and 100 kHz. (b) The equivalent circuit of the EIS.

The main drawback of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$-based cathodes is the severe capacity loss when cycling is carried out at elevated temperature [42]. The cycling performances at 55 °C of the products are shown in Fig. 9. Although the initial capacities of the products are similar with the results at 25 °C, the capacity fading of the products is more obvious at 55 °C. The capacity retention after 100 cycles at 1C at 55 °C of LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_4$ is 88.6%, higher than that of 82.3% of LiNi$_{0.5}$Mn$_{1.4}$Al$_{0.1}$O$_4$. The higher capacity retention at 55 °C of LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_4$ than that of LiNi$_{0.5}$Mn$_{1.4}$Al$_{0.1}$O$_4$ may be attributed to the higher crystallinity of LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_4$ [43]. Although the capacity loss of the two products at 55°C is larger than that at 25 °C, they are still better than many doped LiNi$_{0.5}$Mn$_{1.5}$O$_4$ spinels [6,44].

Figure 8. Cycling performance of LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_4$ and LiNi$_{0.5}$Mn$_{1.4}$Al$_{0.1}$O$_4$ at 55°C. The cell was charged at 0.5C and discharged at 1C at 55°C in the voltage range of 3.5-5.0V.

4. CONCLUSION

Single phase disordered LiNi$_{0.5}$Mn$_{1.4}$Mg$_{0.1}$O$_4$ and LiNi$_{0.5}$Mn$_{1.4}$Al$_{0.1}$O$_4$ were synthesized successfully by an optimized solution combustion synthesis method at 700 °C in only 30min. The two
products exhibit similar reversible capacity and cycling stability at 1C rate at room temperature, but LiNi0.5Mn1.4Mg0.1O4 shows better rate capability, better cycling stability at 10C rate and better elevated-temperature cycling stability than these of LiNi0.5Mn1.4Al0.1O4. LiNi0.5Mn1.4Mg0.1O4 delivers an initial reversible capacity of 114 mAh/g and remains 100.0% after 100 cycles at 1C. At 10C, the capacity is still 91 mAh/g and remains also 100.0% after 100 cycles. The excellent electrochemical performance of LiNi0.5Mn1.4Mg0.1O4 is attributed to its higher crystallinity, larger Li+ diffusion coefficient and lower charge transfer resistance.

ACKNOWLEDGEMENT
The present work was supported by the National Natural Science Foundation of China (No. 51362012), Natural Science Foundation of Yunnan Province (2012FB173) and the Key Construction Disciplines of Chemistry for Master Degree Program in Yunnan.

Reference

44. J.J. Shiu, W.K. Pang, S.g Wu, *J. Power Sources*, 244 (2013) 35.

© 2015 The Authors. Published by ESG (www.electrochemsci.org). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/).