

The Effects of C-Rate on the Discharge Capacities of $\text{LiNi}_{1-y}\text{M}_y\text{O}_2$ (M=Ni, Ga, Al and/or Ti) Cathodes

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$\text{LiNi}_{1-y}\text{M}_y\text{O}_2$ specimens with compositions of LiNiO_2 , $\text{LiNi}_{0.975}\text{Ga}_{0.025}\text{O}_2$, $\text{LiNi}_{0.975}\text{Al}_{0.025}\text{O}_2$, $\text{LiNi}_{0.995}\text{Ti}_{0.005}\text{O}_2$ and $\text{LiNi}_{0.990}\text{Al}_{0.005}\text{Ti}_{0.005}\text{O}_2$ were synthesized by wet milling and solid-state reaction method. All the synthesized samples possessed the $\alpha\text{-NaFeO}_2$ structure of the rhombohedral system (space group; $R\bar{3}m$) with no evidence of any impurities. Among the LiNiO_2 cathodes prepared with the weight ratios of LiNiO_2 :acetylene black:binder = 85:10:5, 85:12:3 and 90:7:3, the cathode with the weight ratio of 85:10:5 had the best cycling performance, with a discharge capacity degradation rate of 1.06 mAh/g/cycle and a discharge capacity at $n=20$ of 143.5 mAh/g. Among all the samples, $\text{LiNi}_{0.990}\text{Al}_{0.005}\text{Ti}_{0.005}\text{O}_2$ had the highest first discharge capacities at 0.1 C, 0.2 C and 0.5 C rates. That sample had the smallest R-factor value, indicating that it had the lowest degree of cation mixing. Among all the samples, $\text{LiNi}_{0.975}\text{Al}_{0.025}\text{O}_2$ showed the lowest rate of decrease in the first discharge capacity with C rate. The first discharge capacities at 0.1 C, 0.2 C and 0.5 C rates were 170.5 mAh/g, 155.0 mAh/g and 124.2 mAh/g, respectively.

Keywords: $\text{LiNi}_{1-y}\text{M}_y\text{O}_2$ (M=Ni, Ga, Al and/or Ti), solid-state reaction method, discharge capacity, C-rate, I_{003}/I_{104} , R-factor

1. INTRODUCTION

Transition metal oxides such as LiMn_2O_4 ,^[1-3] LiCoO_2 ,^[4-6] LiNiO_2 ,^[7-10] and $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ ^[11] have been intensively investigated in order to use them as the cathode materials of lithium secondary batteries. LiMn_2O_4 is comparatively inexpensive and does not bring about any environmental pollution, but its cycling performance is inadequate. LiCoO_2 has a large diffusivity and a high operating voltage, and it can be easily prepared. However, it has the disadvantage that it contains Co, an expensive element. LiNiO_2 is a very promising cathode material since it has a large discharge capacity^[12] and is excellent from the economic and environmental viewpoints. On the other hand, its preparation is very difficult compared with that of LiCoO_2 and LiMn_2O_4 .

It is known that $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ forms rather than the stoichiometric LiNiO_2 during synthesis^[13] due to cation mixing. Excess nickel occupies the Li sites, destroying the ideally layered structure and preventing the lithium ions from

undergoing the easy movement required for intercalation and deintercalation during cycling. This results in a small discharge capacity and poor cycling performance.

To improve the electrochemical properties of LiNiO_2 , Co,^[14] Al,^[15,16] Ti,^[17,18] Ga,^[12] Mn^[19] and Fe^[20,21] have been substituted for nickel by synthesis in oxygen. Guildmard *et al.*^[15] investigated the electrochemical performances of $\text{LiNi}_{1-y}\text{Al}_y\text{O}_2$ ($0.10 \leq y \leq 0.50$) specimens synthesized by a coprecipitation method. They showed that aluminum substitution suppressed all the phase transitions observed for the LiNiO_2 system. According to Gao *et al.*,^[17] the substitution of Ti for Ni resulted in a large discharge capacity and good cycling performance. Chang *et al.*^[18] detected partial disordering between the transition metal (Ni and Ti) layer and lithium by Rietveld refinement in $\text{Li}_x\text{Ni}_{1-y}\text{Ti}_y\text{O}_2$ ($0.1 \leq y \leq 0.5$) prepared by solid-state reaction. By considering the ionic radius and the Ni-O bond length, they concluded that the Ni(II) ions are partially stabilized in the lithium sites. Nishida *et al.*^[12] reported that gallium-doping into LiNiO_2 stabilizes the crystal structure during the charging process and leads to better cycling performance than LiNiO_2 .

In this work, $\text{LiNi}_{1-y}\text{M}_y\text{O}_2$ (M=Ni, Ga, Al and/or Ti) speci-

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mens were synthesized by solid-state reaction, and the effect of C-rate on the discharge capacities of the synthesized samples was investigated.

2. MATERIALS AND METHODS

$\text{LiNi}_{1-y}\text{M}_y\text{O}_2$ specimens with compositions of LiNiO_2 , $\text{LiNi}_{0.975}\text{Ga}_{0.025}\text{O}_2$, $\text{LiNi}_{0.975}\text{Al}_{0.025}\text{O}_2$, $\text{LiNi}_{0.995}\text{Ti}_{0.005}\text{O}_2$ and $\text{LiNi}_{0.990}\text{Al}_{0.005}\text{Ti}_{0.005}\text{O}_2$ were synthesized by wet milling and solid-state reaction method. These compositions were chosen because they had relatively good electrochemical properties in the previously reported works.^[22,23] $\text{LiOH}\cdot\text{H}_2\text{O}$ (Kojundo Chemical Lab. Co., Ltd, purity 99%), $\text{Ni}(\text{OH})_2$ (Kojundo Chemical Lab. Co., Ltd, purity 99.9%), Ga_2O_3 (Aldrich Chemical, purity 99%), $\text{Al}(\text{OH})_3$ (Kojundo Chemical Lab. Co., Ltd, purity 99.99%) and TiO_2 (Aldrich Chemical, purity 99%) were used as the starting materials. These were mechanically mixed by wet SPEX milling under distilled acetone for 1 h, and dried in a shaking incubator with 50 rpm at 50°C for 48 h. The mixtures were then preheated at 450°C for 5 h in air, pressed into pellets and calcined at 750°C for 30 h under an oxygen stream. The phase identification of the synthesized samples was carried out by X-ray powder diffraction analysis (Rigaku III/A diffractometer) using $\text{Cu K}\alpha$ radiation, a scanning rate of 6°min^{-1} and 2θ of $10^\circ \leq 2\theta \leq 80^\circ$. The electrochemical cells consisted of $\text{LiNi}_{1-y}\text{M}_y\text{O}_2$ as a positive electrode, Li foil as a negative

electrode and an electrolyte [Purelyte (Samsung General Chemicals Co., Ltd.)] prepared by dissolving 1 M LiPF_6 in a 1:1 (volume ratio) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The positive electrode consisted of synthesized materials, acetylene black and polyvinylidene fluoride (PVDF) binder dissolved in 1-methyl-2-pyrrolidone (NMP) with weight ratios of 85:10:5, 85:12:3 and 90:7:3. A Whatman glass-filter was used as a separator. The coin-type (2016) cells were assembled in an argon-filled dry box. All of the electrochemical tests were performed at room temperature with a potentiostatic/galvanostatic system. The cells were cycled between 2.7 and 4.4 V at the rates of 0.1 C, 0.2 C and 0.5 C.

Figure 1 shows the experimental procedure for the $\text{LiNi}_{1-y}\text{M}_y\text{O}_2$ electrodes prepared by the solid-state reaction method after wet milling.

3. RESULTS AND DISCUSSION

Figure 2 shows the XRD patterns of the samples LiNiO_2 , $\text{LiNi}_{0.975}\text{Ga}_{0.025}\text{O}_2$, $\text{LiNi}_{0.975}\text{Al}_{0.025}\text{O}_2$, $\text{LiNi}_{0.995}\text{Ti}_{0.005}\text{O}_2$ and $\text{LiNi}_{0.990}\text{Al}_{0.005}\text{Ti}_{0.005}\text{O}_2$ calcined at 750°C for 30 h in an O_2 stream (after milling for 1 h and preheating in air at 450°C for 5 h). All the samples possess the $\alpha\text{-NaFeO}_2$ structure of the rhombohedral system (space group; $\bar{R}3m$ structure is distorted in the c-axis direction of the hexagonal structure. This is reflected by the split of the 006 and 102 peaks and of the 108 and 110 peaks in the XRD patterns. The 108 and 110 peaks were split for all of the samples.

Ohzuku *et al.*^[24] reported that electrochemically reactive LiNiO_2 showed a larger integrated intensity ratio of the 003 peak to the 104 peak (I_{003}/I_{104}) and a clear split of the 108 and 110 peaks in its XRD patterns. The degree of cation mixing (displacement of nickel and lithium ions) is low if the value of I_{003}/I_{104} is large and the 108 and 110 peaks are split clearly. The value of $(I_{006}+I_{102})/I_{101}$, called the R-factor, is known to

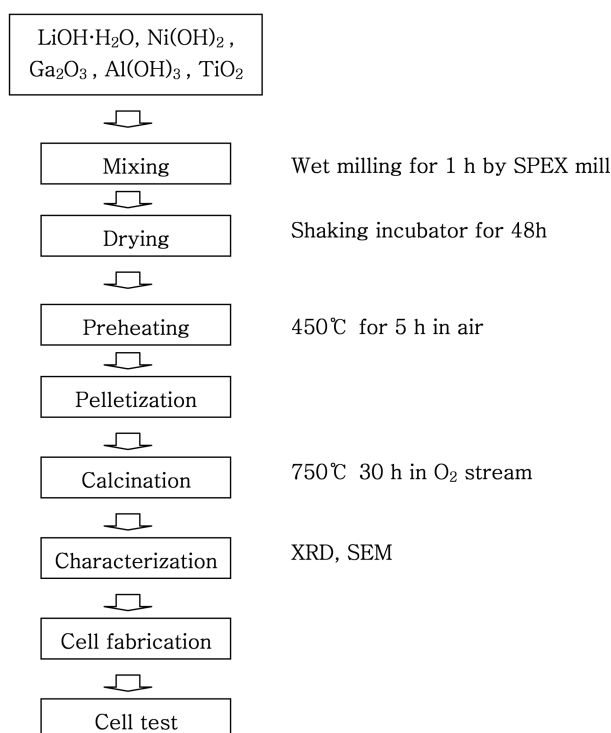


Fig. 1. Experimental procedure for $\text{LiNi}_{1-y}\text{M}_y\text{O}_2$ electrodes prepared by the solid-state reaction method after wet milling.

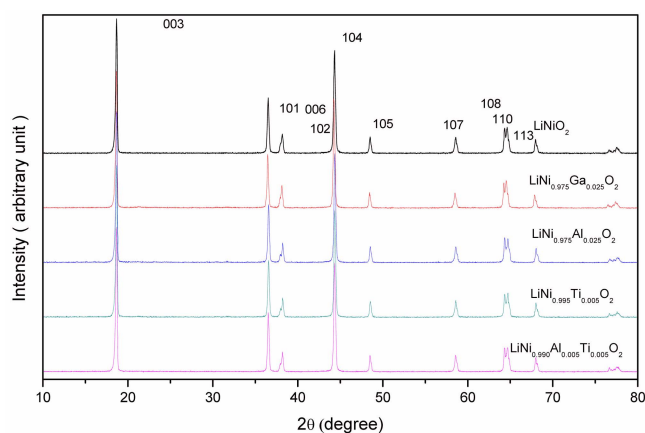


Fig. 2. XRD patterns of the samples calcined at 750°C for 30 h in an O_2 stream (after milling for 1 h and preheating in air at 450°C for 5 h).

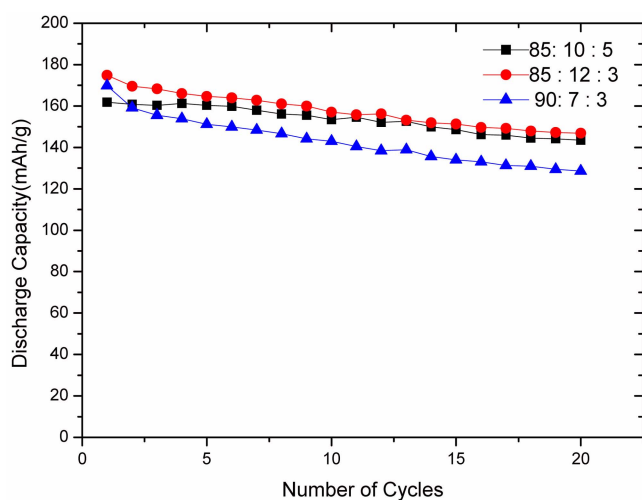
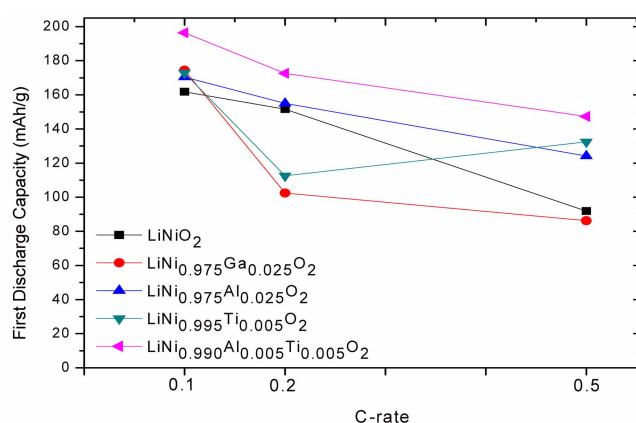
Table 1. Data calculated from XRD patterns of the samples calcined at 750°C for 30 h in an O_2 stream (after milling for 1 h and preheating in air at 450°C for 5 h)

	a(Å)	c(Å)	c/a	I_{003}/I_{104}	R-factor	Unit cell volume (Å ³)
LiNiO_2	2.876	14.253	4.956	1.31	0.36	102.09
$\text{LiNi}_{0.975}\text{Ga}_{0.025}\text{O}_2$	2.885	14.255	4.941	1.25	0.43	102.75
$\text{LiNi}_{0.975}\text{Al}_{0.025}\text{O}_2$	2.874	14.252	4.959	1.39	0.47	101.95
$\text{LiNi}_{0.995}\text{Ti}_{0.005}\text{O}_2$	2.877	14.239	4.949	1.43	0.47	102.07
$\text{LiNi}_{0.990}\text{Al}_{0.005}\text{Ti}_{0.005}\text{O}_2$	2.876	14.254	4.956	1.33	0.33	102.10

decrease as the unit cell volume of $\text{Li}_y\text{Ni}_{2-y}\text{O}_2$ decreases. The R-factor increases as y in $\text{Li}_y\text{Ni}_{2-y}\text{O}_2$ decreases for y near 1. This indicates that the R-factor increases as the degree of cation mixing increases.^[7]

Table 1 shows the values of a, c, c/a, I_{003}/I_{104} , R-factor, and unit cell volume calculated from XRD patterns of the samples calcined at 750°C for 30 h in an O_2 stream (after milling for 1 h and preheating in air at 450°C for 5 h). $\text{LiNi}_{0.995}\text{Ti}_{0.005}\text{O}_2$ has the largest value of I_{003}/I_{104} and its value decreases in the order of $\text{LiNi}_{0.975}\text{Al}_{0.025}\text{O}_2$, $\text{LiNi}_{0.990}\text{Al}_{0.005}\text{Ti}_{0.005}\text{O}_2$, LiNiO_2 and $\text{LiNi}_{0.975}\text{Ga}_{0.025}\text{O}_2$. $\text{LiNi}_{0.990}\text{Al}_{0.005}\text{Ti}_{0.005}\text{O}_2$ has the smallest R-factor value and its value increases in the order of LiNiO_2 , $\text{LiNi}_{0.975}\text{Ga}_{0.025}\text{O}_2$, $\text{LiNi}_{0.975}\text{Al}_{0.025}\text{O}_2$ and $\text{LiNi}_{0.995}\text{Ti}_{0.005}\text{O}_2$.

Figure 3 shows the variation of discharge capacity (at 0.1 C rate) with number of cycles n for the LiNiO_2 cathodes prepared with various weight ratios of LiNiO_2 :acetylene black:binder. The LiNiO_2 cathode prepared with weight ratio of 85:12:3 shows the highest discharge capacity of 174.8 mAh/g. The LiNiO_2 cathodes prepared with weight ratios of 90:7:3 and 85:10:5 have the first discharge capacities of 169.8 mAh/g and 161.9 mAh/g, respectively. The LiNiO_2 cathodes prepared with weight ratio of 85:10:5 has the best cycling performance, with the discharge capacity degradation rate of

**Fig. 3.** Variation of discharge capacity with number of cycles for the LiNiO_2 cathodes with various weight ratios of LiNiO_2 :acetylene black:binder.**Fig. 4.** Variation of the first discharge capacity with C-rate for LiNiO_2 , $\text{LiNi}_{0.975}\text{Ga}_{0.025}\text{O}_2$, $\text{LiNi}_{0.975}\text{Al}_{0.025}\text{O}_2$, $\text{LiNi}_{0.995}\text{Ti}_{0.005}\text{O}_2$, and $\text{LiNi}_{0.990}\text{Al}_{0.005}\text{Ti}_{0.005}\text{O}_2$.

1.06 mAh/g/cycle and the discharge capacity at n=20 of 143.5 mAh/g.

The effect of the C-rate on the discharge capacities of the synthesized samples was investigated by preparing cathodes with a weight ratio of LiNiO_2 :acetylene black:binder of 85:10:5.

Figure 4 shows the variations of the first discharge capacity with C-rate for LiNiO_2 , $\text{LiNi}_{0.975}\text{Ga}_{0.025}\text{O}_2$, $\text{LiNi}_{0.975}\text{Al}_{0.025}\text{O}_2$, $\text{LiNi}_{0.995}\text{Ti}_{0.005}\text{O}_2$ and $\text{LiNi}_{0.990}\text{Al}_{0.005}\text{Ti}_{0.005}\text{O}_2$. $\text{LiNi}_{0.990}\text{Al}_{0.005}\text{Ti}_{0.005}\text{O}_2$ has the highest first discharge capacities at three different C rates. $\text{LiNi}_{0.990}\text{Al}_{0.005}\text{Ti}_{0.005}\text{O}_2$ has the smallest value of R-factor, indicating that this sample has the lowest degree of cation mixing. $\text{LiNi}_{0.975}\text{Al}_{0.025}\text{O}_2$ shows the lowest decrease rate of the first discharge capacity with C-rate.

Figure 5 shows the variations of the discharge capacity at n = 20 with C-rate for LiNiO_2 , $\text{LiNi}_{0.975}\text{Ga}_{0.025}\text{O}_2$, $\text{LiNi}_{0.975}\text{Al}_{0.025}\text{O}_2$, $\text{LiNi}_{0.995}\text{Ti}_{0.005}\text{O}_2$ and $\text{LiNi}_{0.990}\text{Al}_{0.005}\text{Ti}_{0.005}\text{O}_2$. LiNiO_2 has the highest discharge capacities at 0.1 and 0.2 C rates, and $\text{LiNi}_{0.975}\text{Al}_{0.025}\text{O}_2$ has the highest discharge capacity. $\text{LiNi}_{0.975}\text{Al}_{0.025}\text{O}_2$ shows the lowest decrease rate of the discharge capacity at n=20 with C rate. Ohzuku *et al.*^[25] reported that the substitution of Al^{+3} for Ni forms an insulating material due to the fixed oxidation number and gives a resistive characteristic against overcharging, which limits the deintercalation of lithium ions at the later stage of charging. They also

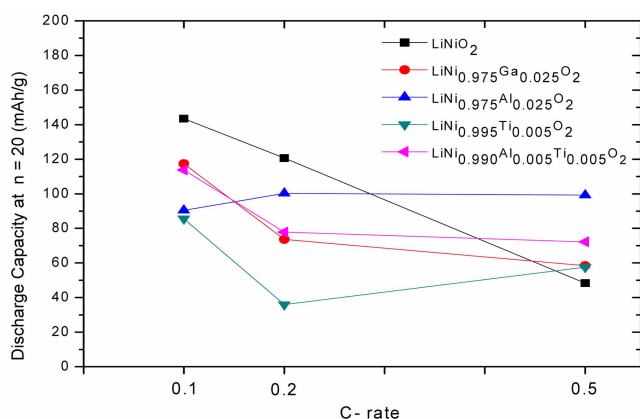


Fig. 5. Variation of the discharge capacity at $n=20$ with C-rate for LiNiO_2 , $\text{LiNi}_{0.975}\text{Ga}_{0.025}\text{O}_2$, $\text{LiNi}_{0.975}\text{Al}_{0.025}\text{O}_2$, $\text{LiNi}_{0.995}\text{Ti}_{0.005}\text{O}_2$, and $\text{LiNi}_{0.990}\text{Al}_{0.005}\text{Ti}_{0.005}\text{O}_2$.

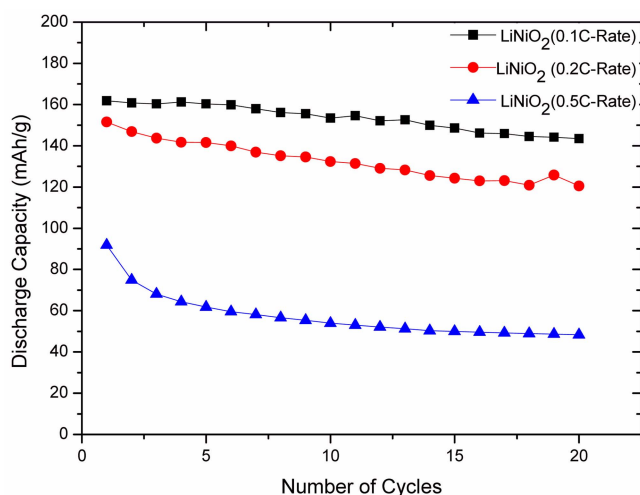


Fig. 6. Variation, with various C-rates, of the discharge capacity vs. number of cycles for LiNiO_2 .

reported that the substitution of Al^{3+} increases the structural stability by preventing the phase transition in the range of $0 < x \leq 1$ during charging and discharging. These two effects of the substitution of Al^{3+} are considered to lead to the lowest rate of decrease in the discharge capacity at $n=20$ with C rate.

Figure 6 shows the variation, with C-rate, of the plot discharge capacity vs. number of cycles for LiNiO_2 . The first discharge capacity decreases drastically as the C rate increases. Their values at 0.1 C, 0.2 C and 0.5 C rates are 161.8 mAh/g, 151.6 mAh/g and 91.8 mAh/g, respectively. At 0.5 C rate the discharge capacity decreases from $n=1$ to $n=4$, but after $n=5$ it has similar cycling performance to those at the other C rates.

Figure 7 shows the variation, with C-rate, of the plot discharge capacity vs. number of cycles for $\text{LiNi}_{0.975}\text{Al}_{0.025}\text{O}_2$. The first discharge capacities at 0.1 C, 0.2 C and 0.5 C rates

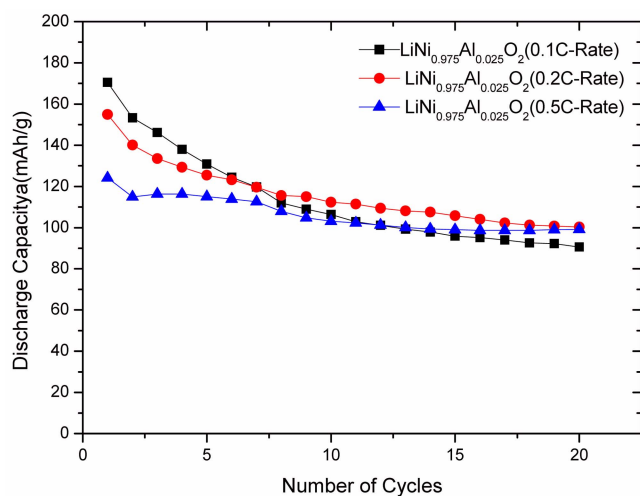


Fig. 7. Variation, with various C-rates, of the discharge capacity vs. number of cycles for $\text{LiNi}_{0.975}\text{Al}_{0.025}\text{O}_2$.

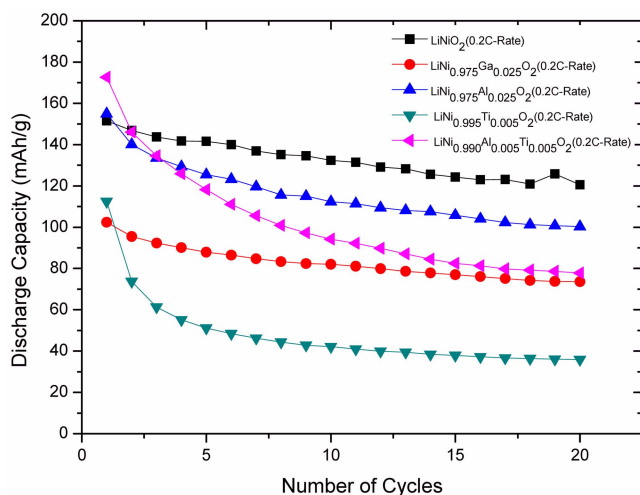


Fig. 8. Variations of the plot discharge capacity vs. number of cycles at 0.2 C rate for LiNiO_2 , $\text{LiNi}_{0.975}\text{Ga}_{0.025}\text{O}_2$, $\text{LiNi}_{0.975}\text{Al}_{0.025}\text{O}_2$, $\text{LiNi}_{0.995}\text{Ti}_{0.005}\text{O}_2$, and $\text{LiNi}_{0.990}\text{Al}_{0.005}\text{Ti}_{0.005}\text{O}_2$.

are 170.5 mAh/g, 155.0 mAh/g and 124.2 mAh/g, respectively. The cycling performance at 0.1 C rate is worse than at 0.2 C and 0.5 C rates. However, after $n=10$ similar discharge capacity and cycling performance are exhibited at the all C-rates.

Figure 8 shows the variations of the plot discharge capacity vs. number of cycles n at 0.2 C rate for LiNiO_2 , $\text{LiNi}_{0.975}\text{Ga}_{0.025}\text{O}_2$, $\text{LiNi}_{0.975}\text{Al}_{0.025}\text{O}_2$, $\text{LiNi}_{0.995}\text{Ti}_{0.005}\text{O}_2$ and $\text{LiNi}_{0.990}\text{Al}_{0.005}\text{Ti}_{0.005}\text{O}_2$. $\text{LiNi}_{0.990}\text{Al}_{0.005}\text{Ti}_{0.005}\text{O}_2$ has the highest first discharge capacity of 172.6 mAh/g, and those of LiNiO_2 , $\text{LiNi}_{0.975}\text{Ga}_{0.025}\text{O}_2$, $\text{LiNi}_{0.975}\text{Al}_{0.025}\text{O}_2$ and $\text{LiNi}_{0.995}\text{Ti}_{0.005}\text{O}_2$ are 151.6, 102.4, 155.0 and 112.6 mAh/g, respectively. At $n=20$ LiNiO_2 has the highest discharge capacity of 120.6 mAh/g, and those of $\text{LiNi}_{0.975}\text{Ga}_{0.025}\text{O}_2$, $\text{LiNi}_{0.975}\text{Al}_{0.025}\text{O}_2$, $\text{LiNi}_{0.995}\text{Ti}_{0.005}\text{O}_2$, $\text{LiNi}_{0.990}\text{Al}_{0.005}\text{Ti}_{0.005}\text{O}_2$ are 73.6, 100.3, 35.9 and

77.8 mAh/g, respectively. $\text{LiNi}_{0.975}\text{Ga}_{0.025}\text{O}_2$ has the best cycling performance, with a degradation rate of discharge capacity of 1.26 mAh/g/cycle between the first cycle and the 20th cycle.

4. CONCLUSIONS

$\text{LiNi}_{1-y}\text{M}_y\text{O}_2$ specimens with compositions of LiNiO_2 , $\text{LiNi}_{0.975}\text{Ga}_{0.025}\text{O}_2$, $\text{LiNi}_{0.975}\text{Al}_{0.025}\text{O}_2$, $\text{LiNi}_{0.995}\text{Ti}_{0.005}\text{O}_2$ and $\text{LiNi}_{0.990}\text{Al}_{0.005}\text{Ti}_{0.005}\text{O}_2$ were synthesized by wet milling and solid-state reaction method. The mixtures were preheated at 450°C for 5 h in air, pressed into pellets and calcined at 750°C for 30 h under an oxygen stream. All the synthesized samples possessed the $\alpha\text{-NaFeO}_2$ structure of the rhombohedral system (space group; $R\bar{3}m$) with no evidence of any impurities. Among LiNiO_2 cathodes prepared with the weight ratios of LiNiO_2 :acetylene black : binder of 85:10:5, 85:12:3 and 90:7:3, that with the weight ratio of 85:10:5 had the best cycling performance, with the discharge capacity degradation rate of 1.06 mAh/g/cycle and the discharge capacity at $n=20$ of 143.5 mAh/g. Among all the samples, $\text{LiNi}_{0.990}\text{Al}_{0.005}\text{Ti}_{0.005}\text{O}_2$ had the highest first discharge capacities at 0.1 C, 0.2 C and 0.5 C rates. $\text{LiNi}_{0.990}\text{Al}_{0.005}\text{Ti}_{0.005}\text{O}_2$ had the smallest R-factor value, indicating that this sample had the lowest degree of cation mixing. Among all the samples, $\text{LiNi}_{0.975}\text{Al}_{0.025}\text{O}_2$ showed the lowest rate of decrease in the first discharge capacity with C rate. $\text{LiNi}_{0.975}\text{Al}_{0.025}\text{O}_2$ also showed the lowest rate of decrease in the discharge capacity at $n=20$ with C-rate probably because the substitution of Al^{+3} led to a resistive characteristic against overcharging and an increase in the structural stability.

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