Rate Discharge Characteristics of $LiNi_xCo_{1-x}O_2$/EC:DMC, 1M $LiPF_6$/LiC_6 Lithium Ion Batteries

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Abstract: *$LiNi_xCo_{1-x}O_2$ with $0.7 \leq x \leq 0.9$ were used to fabricate lithium ion batteries. The rate discharge capabilities versus 0.2C of the batteries were studied by measuring the discharge profile of the batteries. From the results obtained, the battery fabricated from $LiNi_{0.7}Co_{0.3}O_2$ showed the best performance at room temperature. At -10^oC this battery was able to sustain more than 85% of its discharge capacity at room temperature. At $60\ ^oC$ the battery was able to sustain almost all its discharge capacity at room temperature.*

Key words: $LiNi_xCo_{1-x}O_2$, Lithium ion battery, rate discharge, discharge profile

1. INTRODUCTION

In rechargeable lithium ion or lithium polymer battery production, $LiCoO_2$ is normally used instead of other lithiated transition metal oxides. This is because $LiCoO_2$ is easy to handle and process, does not pose any safety issue and has longer cycle life compare to other lithiated metal oxides. However, $LiCoO_2$ have limited capacity, within the range of 130 to 140 mAh/g and cobalt is very expensive.

To overcome the above disadvantages, new materials have been developed, such as $LiNiVO_4$, $LiCoPO_4$, $LiCoVO_4$, $LiPtO_3$, $LiFe_2(SO_4)_3$, $LiNiO_2$ and $LiMnO_2$. Among these materials, $LiNiO_2$ shows the highest energy density [1,2] and is more economical than the other materials. However, these other materials are not without limitations. $LiNiO_2$ has structural instability upon cycling and show severe capacity fading [3, 4]. This is closely related to the irreversible phenomena at insertion or de-insertion of Li^+ ions into the $LiNiO_2$ lattice. Unlike $LiCoO_2$ which has a high order of Li and Co

sublattices, the Ni atom of $LiNiO_2$ can sit on Li atom or vice versa. This Li and Ni atomic disorders hinder the intercalation and transport of Li^+ during charge and discharge processes. The higher the order of the atomic sublattices, the higher is the reversible capacity [5].

$LiNiO_2$ also reacts with the electrolyte [6, 7, 8]. Unlike $LiCoO_2$, during the charging mode $LiNiO_2$ decomposes at about 200^oC, releasing heat and oxygen due to the free energy or enthalpy of the reaction [9, 10].

In the attempts to stabilize lithium nickelate, $LiNiO_2$ has been doped with transition or alkaline earth metals. For example, $LiNiO_2$ has been doped with magnesium (Mg) [11, 12], cobalt (Co) [13-21], manganese (Mn) [16, 22, 23], titanium (Ti) [16], aluminum (Al) [6], iron (Fe) [24], combination of titanium and magnesium [25], gallium (Ga) and magnesium (Mg) [26]. It is expected that the dopant atoms will provide supports to prevent the nickel atoms from being displaced from their lattice so as not to block the lithium ion pathways.

In addition doped $LiNi_xCo_{1-x}O_2$ shows improved thermal stability, higher rate capability and therefore good cycling

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behavior [5]. The dopant atoms in the lithium nickel cobalt oxide material do not participate in the electrochemical reaction within the charge and discharge voltage range of the lithium ion cell. These substituting elements, being inactive, reduce the specific capacity of lithium nickel cobalt oxide [27]. Among the many materials that have been doped and studied, the $LiNi_xCo_{1-x}O_2$ systems have been identified as one of the most attractive materials since they are iso-structural in the solid state for all range of x values.

Literature has reported on the studies of $LiNi_{0.85}Co_{0.15}O_2$ [REF] and $LiNi_{0.75}Co_{0.25}O_2$ [ref] and their derivatives in which Co was substituted with other atoms, such as Mg, Ti, Mn and Al. Most of the studies mainly concentrated on the stability of lithium nickelate and the production of lithium nickelate based materials with higher capacity. However, the rate discharge capabilities of these half cells were not reported. It is important to know the rate discharge capabilities of these cells so that the stoichiometric composition nickel in the lithiated nickel cobalt oxide that will provide the best performance in a wide discharge current range and in a wide temperature range can be determined. Li and Currie [Ref] has reported that $LiNi_xCo_{1-x}O_2$ in which $0.7 < x < 0.9$ have excellent electrochemical performance including low fade rate at ambient and elevated temperatures and good rate capabilities at 1C for 50 cycles. In this work, the discharge rate is varied from 0.2C to 3.0C. The batteries were also discharge at 0.2C at various temperatures.

2. EXPERIMENTAL

The $LiNi_xCo_{1-x}O_2$ compounds with $0.7 \leq x \leq 0.9$ were characterized using X-ray diffraction (XRD) technique. The XRD, Brand Bruker, Model D8 Advance with 40 kV Cu Ka radiation source and a scan rate of 4 °/min over 10 to 90° range.

The $LiNi_xCo_{1-x}O_2$ powder was mixed with PVdF, conductive carbon and binder, and dissolved in electronic grade acetone. The mixed materials were then vigorously blended until a uniform slurry was formed and cast onto an aluminum foil. The same procedure was carried out to get the anode done. The cast materials were then cut into the size of 31 mm in width, 53 mm in length and 0.6 mm in thickness. The cathode and anode active materials were stacked and wound with polyethylene, PE separator. The battery was activated by dispensing in EC:DMC (1:1 v/v), 1 M $LiPF_6$ electrolyte, which makes about 30 % of the total electrode weight. The electrochemical performance of the battery was done using a Maccor 4000 system.

3. RESULTS AND DISCUSSION

The XRD pattern of $LiNi_xCo_{1-x}O_2$ for x = 0.7, 0.8 and 0.9 is shown in Figure 1. The 2q value of the XRD peak for these samples is similar, but different in the intensity. The intensity ratio of peak (003) and (104) peak in the XRD pattern shows that the materials have excess lithium stoichiometry, Table 1. Excess lithium is used to compensate for lithium ion losses

due to irreversibility and inability of lithium ions to deintercalate due to structural instabilities. The (006)-(102) and (108)-(110) doublet peaks in the XRD is definite indication of rhombohedral-hexagonal structure [27].
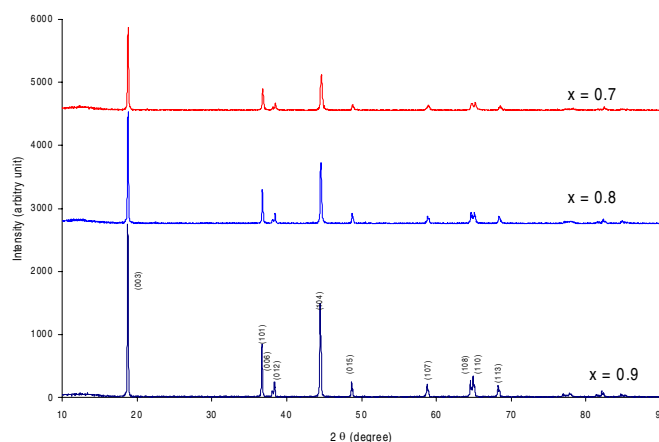

Figure 1. The XRD pattern of the $LiNi_xCo_{1-x}O_2$ materials for x = 0.7, 0.8 and 0.9.

Table 1. The cation mixing in the $LiNi_xCo_{1-x}O_2$ materials for x = 0.7, 0.8 and 0.9.

x in $LiNi_xCo_{1-x}O_2$	Intensity of Peak (cps)		y in $Li_yNi_xCo_{1-x}O_2$
	(003)	(104)	
0.9	2734	1499	1.82
0.8	1823	961	1.90
0.7	1323	568	2.33

Figure 2 shows a charge and discharge profile of $LiNi_xCo_{1-x}O_2$/ EC:DMC, 1M $LiPF_6$/LiC_6 battery. The battery was charged using C/2 current up to 4.2V and further charged with constant voltage until the current retreats to C/10 or 50mA. The battery was discharged at constant current, C/2 until a cut-off voltage was reached at 2.5V.

This profile has been used during the formation and stabilization of the solid electrolyte interface (SEI) layer on MCMB material and the definition of battery capacity was taken during the third cycle discharge. The specific capacity of $LiNi_xCo_{1-x}O_2$/EC:DMC, 1M $LiPF_6$/LiC_6 battery is shown in Table 2. These data clearly shows that by increasing the molar fraction of Ni atom will increase the battery capacity. These results are in reasonable agreement with the work of Li et. al.,[29] who studied on lithium nickel cobalt oxide materials with mole fraction, x = 0.67, 0.75, 0.85 and 1.00. The discharge capacity of these materials as reported by Li et. al. [29] is 164 mAh, 175 mAh, 183 mAh and 200 mAh
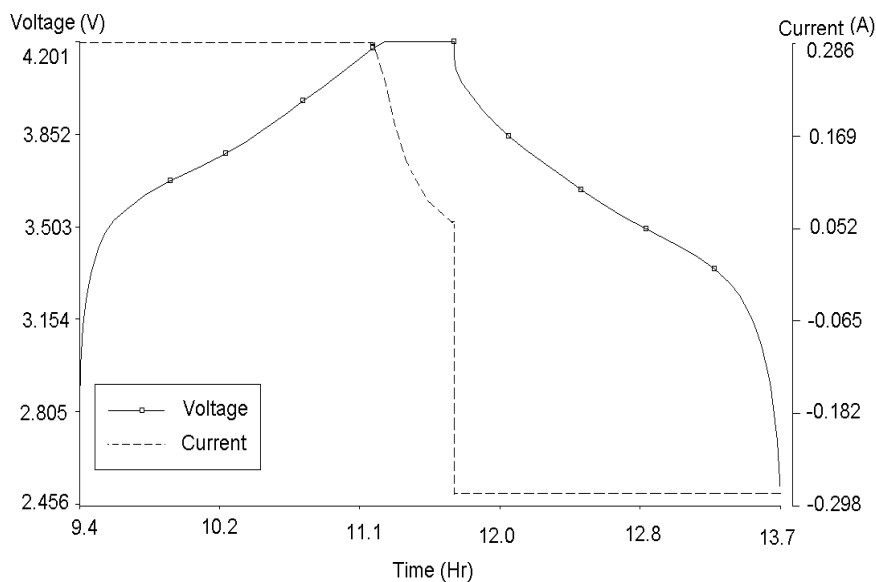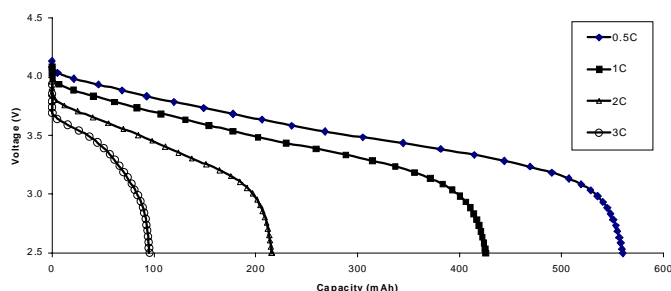
Figure 2. Charge and discharge profile of LiNi$_x$Co$_{1-x}$O$_2$/EC:DMC, 1M LiPF$_6$/LiC$_6$ battery.

Table 2. Capacity of LiNi$_x$Co$_{1-x}$O$_2$/EC:DMC, 1M LiPF$_6$/LiC$_6$ battery.

x in LiNi$_x$Co$_{1-x}$O$_2$	Specific Capacity, mAh/g	% versus LiCoO$_2$ (140 mAh/g)
0.70	150	7.1
0.75	153	9.0
0.80	160	14.3
0.85	182	30.2
0.9	185	32.0

Figure 3. Typical of rate discharge profile of of LiNi$_x$Co$_{1-x}$O$_2$/EC:DMC, 1M LiPF$_6$/ LiC$_6$ battery.

respectively [29]. The difference between their work and the present work is that in the former half cells (vs Li metal) were used, whereas in the present work graphite was used as the anode.

Typical rate discharge profile of LiNi$_x$Co$_{1-x}$O$_2$/EC:DMC, 1M LiPF$_6$/LiC$_6$ battery is shown in Figure 3. Unlike, LiCoO$_2$, the LiNi$_x$Co$_{1-x}$O$_2$ material has no plateau region in the discharge profile.

Figure 4 shows the rate discharge of LiNi$_x$Co$_{1-x}$O$_2$/EC:DMC, 1M LiPF$_6$/LiC$_6$ battery for $0.7 < x < 0.9$. It is clear that the capacity of LiNi$_x$Co$_{1-x}$O$_2$ materials is highly affected at high C rates. The same trend of result was shown by H.X Yang et al [30]. By comparing performance of batteries utilizing these cathodic materials, it can be observed that the battery with LiNi$_{0.7}$Co$_{0.3}$O$_2$ cathode active material managed to sustain most of the capacity discharged at 0.2C. Although this material has the lowest capacity compared to LiNi$_x$Co$_{1-x}$O$_2$ with $0.75 \leq x \leq 0.9$, its stability has reduced capacity fading compared with batteries fabricated with lithiated nickel cobalt oxide with higher nickel content.

For the various temperature performance studies, the battery was charged at C/2 current at room temperature and stored for 4 hours at that particular temperature and discharged using C/4 current. The discharge capacity of the LiNi$_x$Co$_{1-x}$O$_2$/ EC:DMC, 1M LiPF$_6$/LiC$_6$ battery is shown in Figure 5. At low
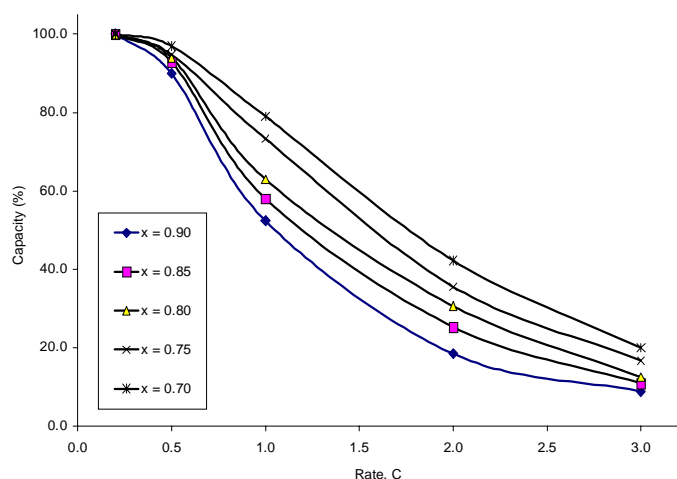
Figure 4. Rate discharge of LiNi$_x$Co$_{1-x}$O$_2$/EC:DMC, 1M LiPF$_6$/LiC$_6$ battery for x = 0.7, 0.8 and 0.9.

temperature, -10 ^{o}C the discharge capacity is 87.3 %, 72.1% and 64.0% of the discharge capacity at 0.2C for the batteries utilizing LiNi$_x$Co$_{1-x}$O$_2$ with x = 0.7, 0.8 and 0.9 respectively. The same trend can also be observed at high temperatures, 60 ^{o}C, the discharge capacity is 98.5%, 95.0% and 92.5 % of the capacity at 0.2C for x = 0.7, 0.8 and 0.9 respectively. These data show that the discharge capacity for x = 0.7 always superior to inferior than others. LiNi0.7Co0.3O2 can then be stabilized further by doping with Mg, Al, Mn, Ti etc.
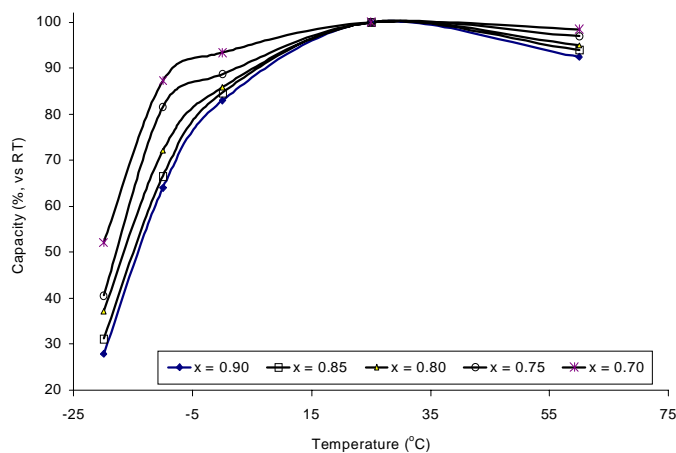
Figure 5. Various temperature performance of LiNi$_x$Co$_{1-x}$O$_2$/EC:DMC, 1M LiPF$_6$/LiC$_6$ battery for x = 0.7, 0.8 and 0.9.

4. CONCLUSIONS

The X-ray diffraction pattern on the synthesis of LiNi$_x$Co$_{1-x}$O$_2$ (x = 0.7, 0.8 and 0.9) materials shows that, the powder is well synthesized with rhombohedral-hexagonal structure. The capacity study on LiNi$_x$Co$_{1-x}$O$_2$/EC:DMC, 1M LiPF$_6$/LiC$_6$ battery for x = 0.7, 0.8 and 0.9 show improvement in capacity

over that of LiCoO$_2$. The discharge capacity at different discharging current rate and different temperature show that the cathode material with x = 0.7 gives the best batteries performance. The results show that LiNi$_{0.7}$Co$_{0.3}$O$_2$ should be selected for improved stability.

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