Stability of LiNi$_{0.6}$Mn$_{0.2}$Co$_{0.2}$O$_2$ as a Cathode Material for Lithium-Ion Batteries against Air and Moisture

Jae-hoon Park, Joon-ki Park, and Jae-won Lee*

Department of Energy Engineering, Dankook University, Cheonan 330-714, Korea.
*E-mail: jwlee7@dankook.ac.kr

Received September 8, 2015, Accepted November 18, 2015, Published online February 14, 2016

LiNi$_{0.6}$Mn$_{0.2}$Co$_{0.2}$O$_2$ (C622), a Ni-rich cathode material, was prepared and its durability tested in air and moisture. For the test, C622 was stored in a glovebox and in a humidity chamber at 50% RH. For each sample, the cell performance was tested in terms of the specific capacity, rate capability, and cycling stability; the changes in the crystal structure were also investigated. The results indicate that when C622 is stored in a humidity chamber, severe degradation occurs in all measurements relating to the cell performance, whereas when it is stored in a glovebox, no degradation is seen. This indicates that C622 is very sensitive to air and moisture. A larger quantity of residual lithium compounds, which are by-products of the reaction between the cathode material, CO$_2$, and moisture in the air, could be seen on the surface of the C622 that was stored in a humidity chamber when compared to the one stored in a glovebox. The formation of residual lithium compounds and the corresponding changes in the crystal structure of C622 kept in the humidity chamber may be the reason for the degradation in the cell performance.

Keywords: Ni-rich cathode, Storage, Stability, Moisture, Air

Introduction

Today, most mobile IT devices, including smartphones and laptop PCs, have adopted the use of lithium-ion batteries as their power source because of their advantages, including high energy density, long cycle life, and lack of a memory effect. Much attention has been paid to next-generation batteries, including lithium-air, lithium-sulfur, and sodium-ion batteries, but these still face numerous technical problems. There-
(003)/(104) and [(006) + (102)]/(101) reflections were calculated to estimate the degree of cation disorder and the hexagonal ordering of the sample.

The amount of residual lithium compounds that was present on the surface of the cathode particles was measured using Warder’s method. The cathode material powder 10 g was placed in 100 mL of DI (deionized) water and was stirred vigorously. After stirring for 10 min, the cathode material powder was separated by vacuum filtration, and the filtrate was titrated with 1.0 N HCl solution. Phenolphthalein and methyl orange were used as indicators for the titration.

To measure the electrochemical performance, 2016 coin-type half-cells were assembled in an Ar-filled glovebox with a moisture content that was controlled below 1.0 ppm. The lithium metal was used as a counter electrode, and the cathode was fabricated by casting a slurry with a formulation of 90 wt % active material, 5 wt % acetylene black, and 5 wt % poly(vinylidene difluoride) (PVdF) binder on an aluminum foil. The electrolyte consisted of a 1.0 M LiPF6 solution in 3:7 (vol %) ethylene carbonate (EC)/diethyl carbonate (DEC). The specific capacity was measured at 0.1 C-rate, and a rate capability test was conducted at various current densities (0.1, 1.0, 3.0, 5.0 and 7.0 C-rate). The cells were cycled for 100 cycles at 1.0 C-rate to examine the cycling stability.

**Results and Discussion**

Figure 1 shows the XRD patterns obtained for the cathode materials stored in the glovebox and in the humidity chamber for 7 and 15 days. The (003) and (104) peak positions shifted to a higher angle after storage in the humidity chamber while no changes in the peak position were observed for the sample stored in a glovebox. This means that the crystal structure changed after storage in the humidity chamber. CO2 and H2O in air have been reported to be likely to be absorbed on the LiNiO2-based cathode material as a result of the spontaneous reduction of Ni3+ to Ni2+ ion.10 Subsequently, Li+ forms Li2CO3 and LiOH on the surface of the cathode particles, reacting with the CO2 and H2O molecules and leaving the Li site vacant. Subsequently, the vacant site may accommodate nickel ions from the transition-metal layer, resulting in cation mixing. According to Choi et al., the lowering of c/a is an indicator of cation mixing,11 and the results of our XRD analysis showed a slight decrease in the c/a value as the storage time in the humidity chamber increased.

In order to investigate the variation in the degree of cation mixing after storage, the relative intensities I(003)/I(104) (= $R_w$) and I(006) + I(102)/I(101) (= $R_f$) were plotted against the storage time. $R_w$ and $R_f$ have been reported to represent the degree of cation mixing and hexagonal ordering, respectively.12,13 The correlation between these factors and the storage time in the glovebox and in the humidity chamber is shown in Figure 2. The $R_w$ value of C622-C-x decreases as the storage time increases, while that of C622-G-x does not show any discernable variation in the storage time, which indicates that the degree of cation mixing for C622 increases upon exposure to moisture and air. In the meantime, the storage of the cathode material in a humidity chamber appears to degrade the hexagonal ordering, considering that the $R_f$ of C622-C-x increased from 0.44 to 0.46 after 15 days while that of C622-G-x remained almost constant. These observations indicate that the cell performance of the cathode stored in the humidity chamber may be degraded as the storage time increases because the cell performance is highly related to the crystal structure.

The amounts of the residual lithium compounds (Li2CO3, LiOH) on the surface of the cathode materials were estimated using Warder’s method, and the results are shown in Figure 3.
The LiOH and Li₂CO₃ concentrations of the fresh C622 were measured to be approximately 2000 and 3000 ppm, respectively. After storage in the humidity chamber for 15 days, the concentration of Li₂CO₃ increased to 15 000 ppm while that of LiOH decreased to almost 0 ppm. Li₂CO₃ and LiOH are the products of the reaction of lithium ions in C622 with CO₂ and water molecules, respectively. The data suggests that the formation reaction for Li₂CO₃ seems to be much more likely to occur than that for LiOH when C622 is exposed to air. The reason for this could be that Li₂CO₃ forms more easily from LiOH and CO₂ in air at room temperature, as expected from the Gibbs free energy of the following reaction:

\[
2 \text{LiOH} + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{H}_2\text{O}, \\
\Delta G^\circ = -97 \text{kJ/mol Li}_2\text{CO}_3
\]  

(1)

LiOH is widely used as a carbon dioxide absorbent.

The amount of residual lithium compounds on the surface should be minimized, since it may cause swelling of the battery during charge–discharge cycling and gelation of the slurry during the manufacturing process of the electrode.¹⁴

The specific discharge capacities of the samples were measured, which are displayed in Figure 4. Fresh C622 exhibited a discharge capacity of 189 mAh/g, which decreased to 184 and 179 mAh/g after 7 and 15 days, respectively. In contrast, a much smaller drop in capacity could be observed with C622-G-ₓ. The irreversible formation of the residual lithium compounds would consume the lithium ions in the lattice of C622, thus reducing the amount of lithium ions available to participate in the intercalation and de-intercalation, which is associated with the capacity fading in the C622-C-ₓ samples along with an alteration in the crystal structure of the cathode material.

The rate capability of the samples was measured under various current densities (0.1, 1, 3, 5, 7 C-rate) in order to examine the effect of the storage atmosphere on the kinetics of the intercalation/de-intercalation processes of the lithium ions (Figure 5). As can be seen in the figure, C622-C-7 and -15 show drastic capacity fading with increase in the current density, while C622-G-ₓ did not show any significant decrease in capacity even at high C-rates. At the 7 C-rate, fresh C622 retained approximately 82% of the capacity at 0.1 C, but only 8–13% of the capacity could be obtained at the same current density after storage in the humidity chamber. Moreover, C622-C-7 and -15 showed an almost similar degradation in
the rate capability, which indicates that C622 could deteriorate in the early stages of exposure to air and moisture. The severe degradation in the rate capability of C622-C-x may be interpreted as due to two reasons: a high resistance due to the formation of a layer of residual lithium compounds, and a high degree of cation mixing of C622-C-x. The layer of residual lithium compounds may act as an insulating layer for electron and lithium-ion conduction, and Ni atoms located at the Li site would also retard the motion of the lithium ions.15

The cycling stability of the cathode materials is shown in Figure 6. The cells were charged and discharged at a 1 C-rate, and the initial capacity for C622-C-7 and -15 was approximately 150 mAh/g, which is much lower than that of the fresh sample due to the poor rate capability of these samples. C622-C-7 and -15 showed a capacity retention of only 58% and 43% after 100 cycles, respectively, while the fresh sample retained 92% of the initial capacity. However, C622-G-7 and -15 retained 92% and 93% of the initial capacity, which is almost the same retention rate as the fresh one. Moreover, C622-G-x showed initial capacities with a much smaller difference from the fresh sample at the 1 C-rate. The change in the crystal structure and the formation of residual lithium compounds during storage in a humidity chamber are believed to be the cause of the poor cycling stability of the C622-C-x samples.

The results given above indicate that storage of C622 in air should be avoided and that the storage conditions should be strictly controlled. In particular, the concentration of CO2 should be controlled at a low level in order to prevent the formation of Li2CO3 on the surface of the cathode material.

Conclusion

C622 was stored in a humidity chamber at constant temperature and humidity for certain periods. The electrochemical performance of the samples was measured in order to examine the stability of the material against moisture and air. For the control group, C622 was stored in a glovebox filled with argon with strictly controlled moisture content. Storage in the humidity chamber resulted in changes in the crystal structure, including cation mixing and hexagonal ordering. This also caused the formation of more residual lithium compounds on the surface of the cathode particles. In particular, a large amount of Li2CO3 was formed, while the quantity of LiOH decreased. On the contrary, C622 stored in the glovebox did not show any significant changes in the crystal structure and in the amount of residual lithium compounds. As a result of these changes, a severe degradation in the cell performance in terms of the specific capacity, rate capability, and cycling stability could be observed with C622 stored in the humidity chamber compared to that stored in the glovebox, and this degradation was closely associated with a change in the crystal structure. All of these results indicate that the Ni-rich cathode materials for the lithium-ion batteries should be handled in a controlled atmosphere of moisture and CO2.

References

2. N. V. Kosova, E. T. Devyatkina, V. V. Kaichev, J. Power Sources 2007, 174, 965.
12. X. Zhang, W. J. Jiang, A. Mauger, Qilu, F. Gendron, C. M. Julien, J. Power Sources 2010, 195, 1292.