



Washing Effect of a $\text{LiNi}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}\text{O}_2$ Cathode in Water

Jisuk Kim,^a Youngsik Hong,^{b,d} Kwang Sun Ryu,^{b,*} Min Gyu Kim,^c and Jaephil Cho^{a,*z}

^aDepartment of Applied Chemistry, Kumoh National Institute of Technology, Gumi, Korea

^bIonics Device Team, Electronics and Telecommunications Research Institute, Daejeon, Korea

^cBeamline Research Division, Pohang University of Science and Technology, Pohang, Korea

The formation of LiOH and Li_2CO_3 impurities on high Ni content $\text{LiNi}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}\text{O}_2$ powders due to H_2O and CO_2 absorption from the air can be reduced without structural degradation by washing in water. Although the as-synthesized sample had a moisture content of 570 ppm immediately after firing, this level increased rapidly to 1270 ppm in air with a relative humidity of 50%. However, its content was decreased to 210 ppm after washing twice in water, followed by heat-treatment at 700°C. It is believed that this improvement was due to the decreased level of Li_2CO_3 and LiOH impurities on the particles. This was highlighted by the decreasing swelling of the Li-ion cell at 90°C, and the thickness of the cell containing the washed samples was decreased by 50% compared with the bare sample.

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Since the 1200 mAh Li-ion cell in a cylindrical 18650R size was developed in 1991, its capacity has been increasing by 7-10% each year, and a 2400 mAh Li-ion cell was commercialized in 2004. Despite the fact that the electrode materials used were graphite and LiCoO_2 , the capacity has increased by 100% compared with the capacity 12 years ago. The achievement of such a high capacity was made possible by the maximum utilization of the dead spaces within the cell, decreasing the amount of binder and conducting agents, and using LiCoO_2 with a high electrode density 3.7 g/cm³. However, increasing the capacity beyond 2400 mAh can only be made possible using new high capacity active materials, such as Si, Sn, or $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ with a 4.2 V cutoff.¹⁻⁵ One of the fundamental problems of the $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$, where $1 - x - y$ is >0.8 (high Ni content) is the rapid reaction with air resulting in the formation of Li_2CO_3 and LiOH on the surface.⁶⁻⁸ Zhuang et al. reported the presence of Li_2CO_3 on the surface of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder exposed to air, and the long-term exposure of the cathode produced a dense Li_2CO_3 coating, approximately 10 nm in thickness, which severely reduces the capacity and increased the irreversible capacity, according to the following equation $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2 + 4x\text{O}_2 + 2x\text{CO}_2 \rightarrow \text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2 + 2x\text{Li}_2\text{CO}_3$. Moshtev et al. also reported the formation of LiOH on the LiNiO_2 as a result of oxygen evolution: $\text{LiNiO}_2 + y\text{H}_2\text{O} \rightarrow \text{Li}_{1-y}\text{NiO}_{2-y/2} + y\text{LiOH}$.⁸ In addition, the extraction of Li from $\text{Li}_{1-x}\text{NiO}_2$ in water led to a rapid decrease in capacity, and the discharge capacity of the washed powder was reduced to 150 mAh/g from 181 mAh/g.⁹ Recently, Yang et al. reported that surface-active oxygen O^{2-} from an impurity NiO phase that combined with CO_2 and H_2O in air to form CO_3^{2-} and OH^- , and suggested the following surface reaction mechanism: $2\text{Li}^+ + \text{CO}_3^{2-}/2 \text{OH}^- \rightarrow \text{Li}_2\text{CO}_3/2\text{LiOH}$.¹⁰

The presence of such impurities led to severe cell swelling during the formation process in the Li-ion cell manufacturing and at 90°C storage at the 4.2 V charged state. Therefore, this study investigated the effect of washing on an air-exposed $\text{LiNi}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}\text{O}_2$ powder on the structural and electrochemical properties.

Experimental

The co-precipitated $\text{Ni}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}(\text{OH})_2$ powder with spherical grains was prepared by dissolving metal nitrates in water and adjusting the pH ~ 11 using NaOH and NH_4OH . The detailed experimental procedures are described elsewhere.¹¹ $\text{Ni}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}(\text{OH})_2$ powder and $\text{LiOH}\cdot\text{H}_2\text{O}$ with a molar ratio

of 1:1.02 was mixed thoroughly and fired at 480 and 740°C for 4 and 15 h, respectively. After sieving, powders with an average particle size of 13 μm were used for further analyses. The Li content of the as-prepared sample was 1.0, as confirmed by inductively coupled plasma-mass spectroscopy (ICP-MS) analysis. In order to determine the moisture content (OH^-) in the sample, a Karl-Fisher moisture titrator was used at 250°C (prior to measuring, the sample was vacuum-dried at 150°C for 2 h to remove the H_2O molecules adsorbed on the sample). The change in the pH of the powder immersed in water was monitored by adding 20 g of the powder to 50 mL purified water (pH ~ 7) with constant stirring with a magnetic stirrer. The pH was measured over a 30 to 40 min period. The powder was recovered by filtration when the pH had stabilized. This procedure was repeated in order to compare the pH evolution with the previously washed powder. Finally, the first and second washed powders were either dried or fired at 150 and 700°C, respectively. The amounts of the dissolved Li were estimated by titration. Since the Li_2CO_3 was also dissolved in water in a basic solution, most of the Li sources are believed to originate from LiOH and Li_2CO_3 . The total carbon content C in Li_2CO_3 was measured using an element analyzer.

The electrochemical properties were tested in a coin-type 2016R cell with lithium metal as an anode, and the cathode consisted of the following active material: Super P carbon black: polyvinylidene fluoride (PVDF) binder with a weight ratio of 94:3:3. The electrolyte for the coin-type half-cells (2016 type) was 1 M LiPF_6 with ethylene carbonate/diethylene carbonate/ethyl-methyl carbonate (EC/DEC/EMC) (30:30:40 vol %) (Cheil Industries, Korea). The capacity and capacity retention were measured between 3 and 4.3 V at a rate of 0.1 C and 0.3 C, respectively (1C = 18 mA/g).

Results and Discussion

Table I shows the moisture and carbon content of the $\text{LiNi}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}\text{O}_2$ powders only [Brunauer-Emmett-Teller (BET) surface area = 1.1 g/m²] and with LiCoO_2 (average particle size = 10 μm , BET surface area = 1.0 g/m² at different storage conditions in open air with a relative humidity of 50% and in dry air with a relative humidity of 10%, respectively). When the CO_2 in air reacts with H_2O , H_2CO_3 is formed, which decreases the pH to ~ 5.5 .¹² Acidic CO_3^{2-} ions then attack the particle surface, and Li^+ ions can be easily leached from the bulk, forming LiOH and Li_2CO_3 . Hence, the amounts of LiOH and Li_2CO_3 are expected to increase with increasing air exposure time. On the other hand, it was reported that the spontaneous reduction of Ni^{3+} to Ni^{2+} in LiNiO_2 and the evolution of oxygen species from the surface also contributed to the formation of LiOH and Li_2CO_3 .¹⁰

When the as-prepared $\text{LiNi}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}\text{O}_2$ was stored in a dry

* Electrochemical Society Active Member.

^d Present address: Department of Science Education, Seoul National University of Education, Seoul, Korea.

^z E-mail: jpcho@kumoh.ac.kr

Table I. Moisture and carbon contents in the $\text{LiNi}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}\text{O}_2$ and LiCoO_2 powders as function of the washing time.

	$\text{LiNi}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}\text{O}_2$		LiCoO_2 (10 μm)		Amounts of Li sources ^a g (± 0.001)
	A (ppm)	B (ppm)	A (ppm)		
	Moisture	Carbon	Moisture	Carbon	
Bare (before washing)	1270	1300	570	490	
After annealing at 700°C without washing	2576	2670	250	210	
After 1st washing, (1)	1139		220		0.024
(1) and annealed at 700°C	870	540	150	140	
After 2nd washing, (2)	994		246		0.015
(2) and annealed at 700°C	210	120	110	70	

A: after heat-treatment, the powders were stored in air with a relative humidity of 50% for 48 h.

B: after heat-treatment, the powders were stored in a dry keeper with a relative humidity of 10% for 48 h.

^a $\text{LiNi}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}\text{O}_2$.

Table II. Rietveld analysis results of the $\text{LiNi}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}\text{O}_2$ as a function of the washing time.

	a (Å)	c (Å)	c/a	O_z	B_M B_O (Å ²)	R_p R_{wp} R_B (%)	Ni in Li sites
Bare (before washing)	2.8633(2)	14.165(1)	4.947	0.24125(5)	0.8(1) 0.5(2)	12.5 13.4 3.2	0.01
After 1st washing (1) and annealed at 700°C	2.8626(2)	14.170(2)	4.950	0.2407(5)	0.8(1) 0.5(2)	12.6 13.0 2.8	0.01
After 2nd washing (2) and annealed at 700°C	2.8629(2)	14.174(2)	4.951	0.2411(4)	0.8(1) 0.6(2)	11.7 13.0 2.7	0.01

holder, the moisture content was 570 ppm, which increased to 1270 ppm after exposure to air for 2 days. In contrast, the moisture content from LiCoO_2 in air was 100 ppm, indicating that Li in the LiCoO_2 is more stable against CO_3^{2-} attack, and less Li^+ ions are leached out from the LiCoO_2 than $\text{LiNi}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}\text{O}_2$.

When the air-exposed $\text{LiNi}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}\text{O}_2$ was heat-treated at 700°C for 2 h, the moisture content in the powder stored in a dry keeper was 250 ppm, but its value rapidly increased to 2576 ppm after being exposed to air again. On the other hand, the moisture content of LiCoO_2 was 310 ppm under the same conditions. This indicates that Li_2O formed after heat-treatment accelerated the reaction with the moisture. Even though LiCoO_2 shows a similar behavior to $\text{LiNi}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}\text{O}_2$, the moisture content of the as-synthesized powder was 100 ppm. However, the moisture contents of the annealed sample after the first wash and subsequent heat-treatment after being stored in a dry holder and in air were 150 and 870 ppm, respectively, indicating that some portion of the Li_2CO_3 and LiOH had been washed away by water. The moisture content of LiCoO_2 was 200 ppm under the same test conditions. Even after the second wash and subsequent heat-treatment, $\text{LiNi}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}\text{O}_2$ in air still had a slightly higher moisture content than LiCoO_2 , highlighting the intrinsic chemical instability of $\text{LiNi}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}\text{O}_2$. However, the moisture and carbon content of $\text{LiNi}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}\text{O}_2$ stored in the dry holder was 110 and 80 ppm, respectively, which remained relatively constant after 1 week. This indicates that the washing frequency and moisture level in air were the key factors for reducing such impurities.

In order to measure the actual amount of LiOH and Li_2CO_3 on the $\text{LiNi}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}\text{O}_2$ dissolved in water, the total weight of the Li sources was measured using a titration method. Figure 1 shows

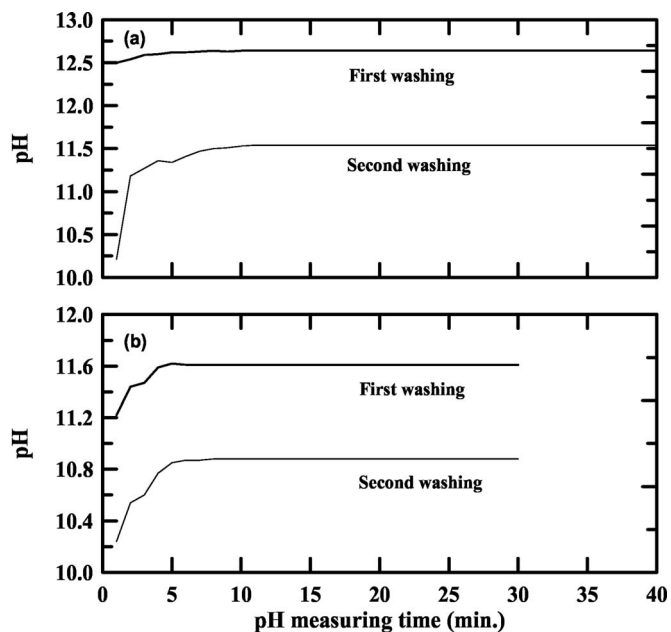


Figure 1. Plot of pH vs the measuring time of the immersed cathode powders (a) $\text{LiNi}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}\text{O}_2$, (b) LiCoO_2 in water. After the first wash, the powders were filtered and the pH measurement was repeated under the same conditions used in the first wash.

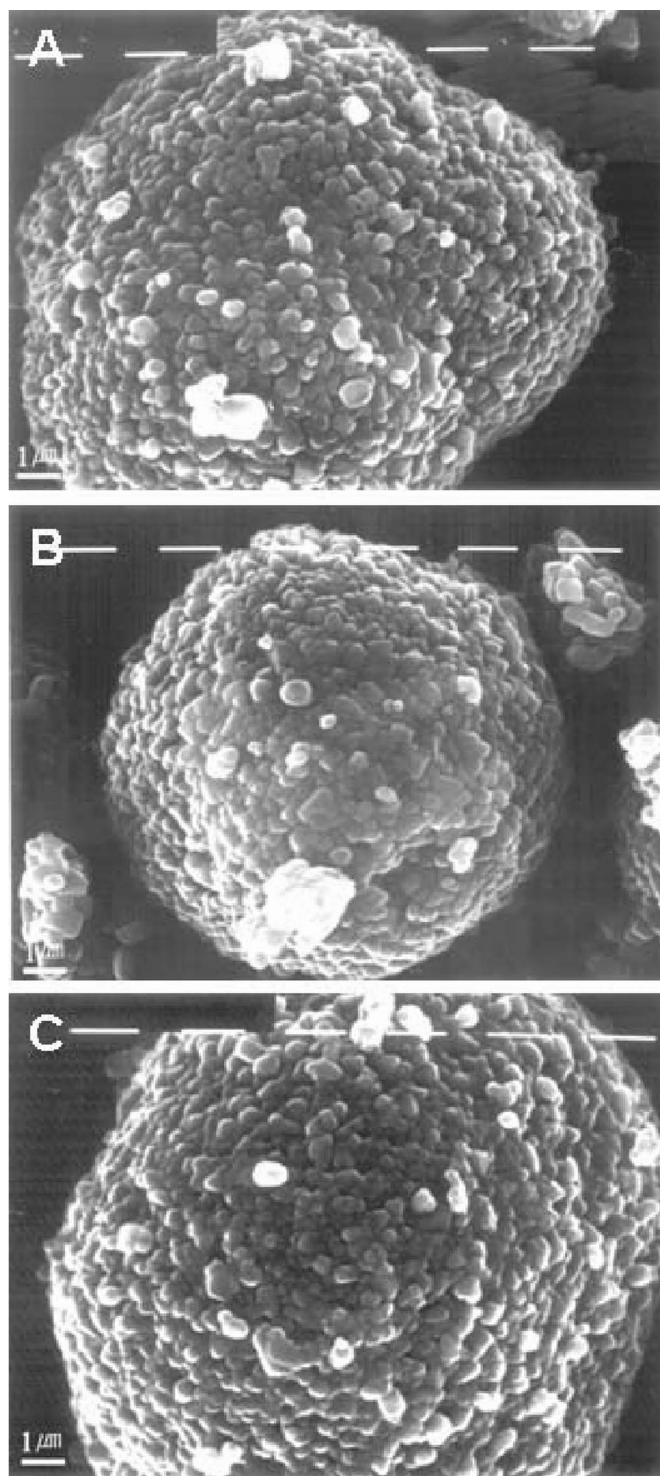


Figure 2. SEM micrographs of (a) bare, (b) first washed, and (c) second washed $\text{LiNi}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}\text{O}_2$ powders.

the pH changes in the $\text{LiNi}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}\text{O}_2$ and LiCoO_2 as a function of time. As soon as the powder had been placed into the water, the pH rapidly increased to 12.5 and at this value was stabilized. In the case of the second wash, the pH increased slowly, and the pH leveled off at 11.5 after 10 min, which was a factor of 1 lower than the first wash. The amounts of dissolved Li were 0.024 and 0.015 g after the first and second wash, respectively. Total amounts of washed Li_2CO_3 and LiOH was 0.039 g. Therefore, a loss of Li in $\text{Li}_{1.0}\text{Ni}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}\text{O}_2$ is expected, causing a slight Li deficiency

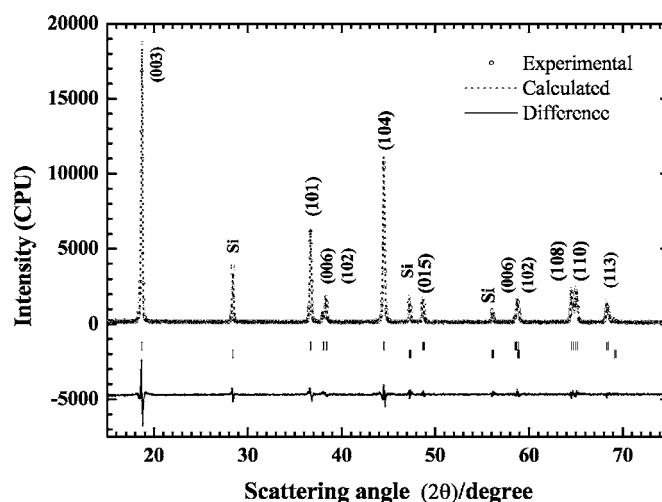


Figure 3. Observed, calculated, and difference XRD patterns of the 2nd washed $\text{LiNi}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}\text{O}_2$. Si was used for the reference powder. The difference pattern is shown at the bottom of each plot.

on the surface. However, this weight loss corresponds to 0.004 mole of the total lithium in the sample. This is well supported by the inductively coupled plasma-Auger electron spectroscopy (ICP-AES) result, and the chemical composition of the samples after second wash was $\text{Li}_{0.995}\text{Ni}_{0.827}\text{Co}_{0.147}\text{Al}_{0.02}\text{O}_2$. The washed and heat-treated samples were more resistant to H_2O and CO_2 than the as-prepared

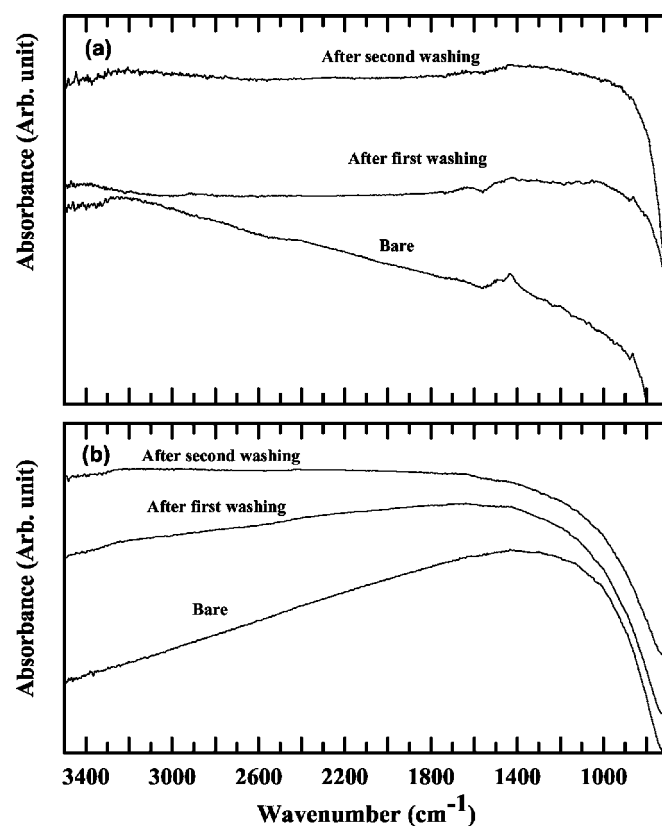


Figure 4. Reflection FTIR spectra of the (a) bare, the first-washed, and second-washed $\text{LiNi}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}\text{O}_2$ powders, and (b) bare, the first-washed and second-washed LiCoO_2 powders.

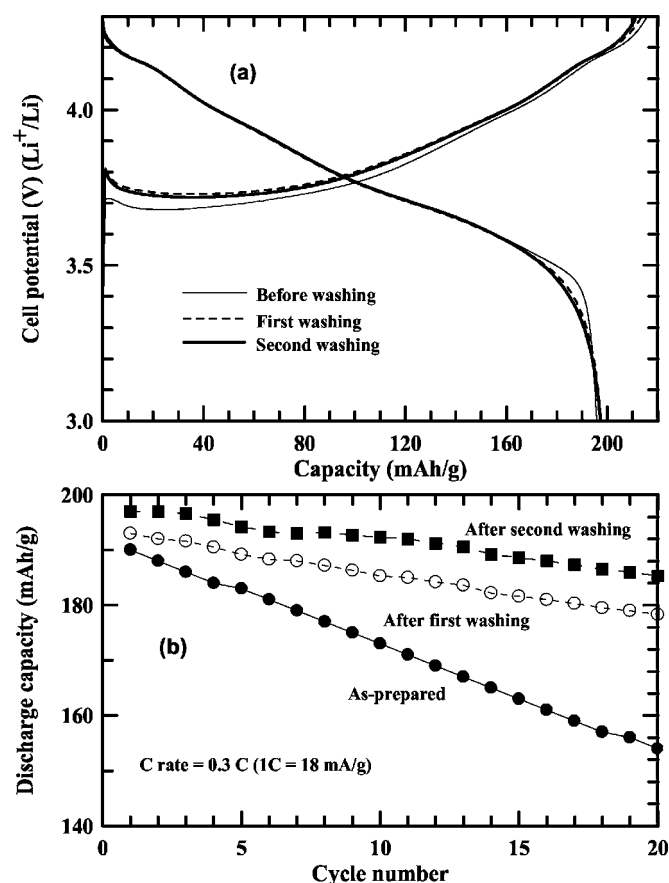


Figure 5. (a) Voltage profiles vs capacity in a coin-type half cell with a lithium metal anode and $\text{LiNi}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}\text{O}_2$ cathode. The cells were charged and discharged at a rate of 0.2 C between 4.3 and 3 V. (b) Plot of the discharge capacity vs cycle number in the coin-type half cells. The cathodes were bare, and the first and second washed $\text{LiNi}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}\text{O}_2$ cathodes at a rate of 0.3 C.

sample, which is believed to be due to the surface composition of the samples. The partial lithium deficiency on the surface significantly reduced the reactions with H_2O and CO_2 .

On the other hand, LiCoO_2 shows a very stable trend, compared with $\text{LiNi}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}\text{O}_2$, and the pH was stabilized at 11.6 after the first wash. The amounts of the dissolved Li sources were 0.005 and 0.002 g after the first and second wash, indicating that the dissolved Li concentration was negligible. Figure 2 shows a comparison of the scanning electron microscopy (SEM) micrographs of the bare, first, and second washed samples, which do not show any change in morphology after washing. This indicates that the impurities may exist as a thin film. Zhaung et al. reported that Li_2CO_3 forms as a ~ 3 nm thin film.⁸ The structural changes in the cathodes before and after washing were estimated using Rietveld refinement (Table II). Figure 3 shows the observed, calculated, and difference XRD patterns of the second washed powder. The formation of a rhombohedral layer structure was indicated by the large intensity ratio of (003) to (104) and the split (108) and (110) reflections. Table II summarizes the refinement result. The lattice constant and the c/a ratio were not influenced by washing, which showed that washing does not increase the level of disorder of the layered structure.

Using reflection Fourier transform infrared (FTIR) spectroscopy (Fig. 4), the evolution of the Li_2CO_3 or LiOH vibration peaks was investigated with increasing washing frequency. Initially, there was a band $3500\text{--}3000\text{ cm}^{-1}$, which was assigned to the O-H stretching vibration from LiOH , and two peaks at 1450 and 870 cm^{-1} , which were assigned to the CO_3 vibration from Li_2CO_3 , respectively. After

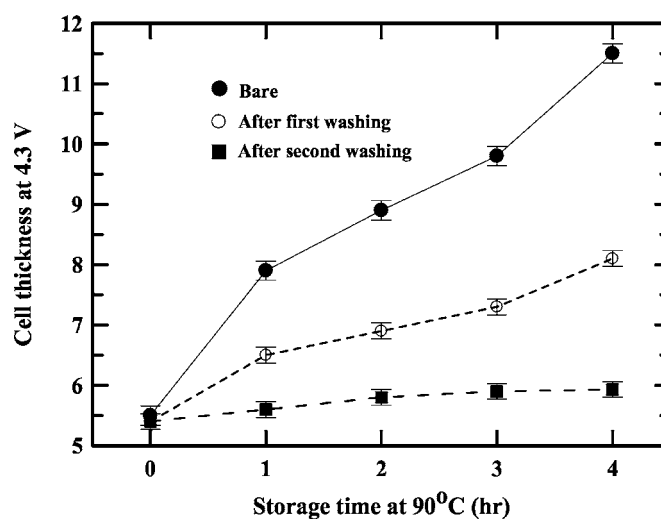


Figure 6. Evolution of the cell thickness of the Li-ion cell after 4.2 V charging as a function of the storage time at 90°C.

washing, the Li_2CO_3 and LiOH peaks disappeared, suggesting that both Li_2CO_3 and LiOH had been rinsed away by the water. On the other hand, LiCoO_2 did not contain any Li_2CO_3 and LiOH peaks in the spectra, suggesting a negligible amount of these phases.

The initial capacities and cycling life of the bare and washed samples (after heat-treatment at 700°C) were compared in order to determine the effect of washing on the electrochemical properties, as shown in Fig. 5. The bare sample shows an initial discharge capacity of 197 mAh/g with an irreversible capacity of 90%. On the other hand, the first and second washed samples show no capacity changes and a decrease in the irreversible capacity by 3%, indicating that the insulators, Li_2CO_3 and LiOH , influence the initial capacity. Furthermore, the initial capacities at the 0.3 C rate and the cycling stability out to 20 cycles were also improved by washing, and the second washed sample showed a 20% improved capacity retention after 20 cycles.

Finally, the evolution of the cell thickness after storage at 90°C at the 4.2 V charged condition was compared after washing (Fig. 6) using a 200 mAh pouch-type Li-ion cell with a cell thickness of 5 mm in order to observe the affect of the LiOH and Li_2CO_3 content on cell swelling. H_2 and CO or CO_2 gases as a result of the decomposition of Li_2CO_3 and LiOH are the main sources for cell swelling at 90°C at the charged state.⁹ Accordingly, the removal of these impurities should reduce the level of cell swelling. The cathodes used were the bare, and the first and second washed cathodes heat-treated at 700°C (the powders were stored for 2 days in air). Figure 6 shows that the cell thickness of all the cathodes was 5.3 mm (± 0.1 mm), but the cell containing the bare cathode rapidly increased to 10 mm. In contrast, the cell thickness of the cell containing the first and second washed cathodes was 7.8 and 5.8 mm, respectively. The cell thickness swelling ratio of the cell containing the second washed cathode was half that of the bare cell. Accordingly, removing the LiOH and Li_2CO_3 phases on the particle surfaces by washing substantially decreases the level of cell swelling at 90°C storage.

Conclusions

When the as-synthesized $\text{LiNi}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}\text{O}_2$ was exposed to air, the amounts of LiOH and Li_2CO_3 were found to increase rapidly as a result of H_2O and CO_2 adsorption. However, simple washing led to the easy removal of these impurities on the particles and made them much more resistant to H_2O and CO_2 , without showing any bulk structural defects and decreasing the capacity. In contrast, the cycle life and level of cell swelling at 90°C were improved by sub-

sequent washing. Even though washing requires extra cost, it is essential if Ni-based cathode materials are to be used in Li-ion cells.

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