The Li[Ni0.8Co0.15Al0.05]O2 (NCA) cathode containing an aqueous binder for Li ion batteries was fabricated by the CO2 gas treatment method using the cavitation effect (CTCE) with the continuous mixing device process. The CTCE is a simple process for decreasing the pH value of the cathode slurry containing an aqueous binder from the alkaline region to neutral region. In our studies, we have recently developed a simple method to remove the alkaline species in the cathode slurry, i.e., the pressurized CO2 gas treatment (PCT), in which the carbonate layer suppressed the electrolyte decomposition and stabilized the surfaces. These phenomena lead to improvement of the cyclability. The PCT is a batch process. Therefore, it is expected that the PCT is demanded that the CO2 gas treatment can be a continuous process for mass production.

Thereafter, we have developed a CO2 gas treatment using the cavitation effect (CTCE) as a continuous process in the present study. In the CTCE, the CO2 gas is simply flowed from the aperture parts of the mixing equipment using the cavitation effect while the cathode slurry is produced by this method. A lot of the bubbles containing the CO2 gas expand and contract by the cavitation effects because of the dynamic change in the pressure. The intense movement of the fluid makes dissolution of the CO2 gas in the slurry very rapid, resulting in a decrease in the pH of the slurry in a short time. This method can achieve a uniform dissolution of CO2 in the slurry because many bubbles containing the CO2 gas can be generated and dissolved in the slurry. Moreover, a lot of the slurry can be treated in a short time by use of the CTCE.

The capacities for the NCA electrode were significantly improved for all the cycles, and a 92% retention rate of the discharge capacity for 49 cycles was achieved using the CTCE with the continuous process.

Experimental

Production of the NCA slurry by the CTCE.—The NCA powder (92 wt%) was mixed with carbon black (CB) (4 wt%) and an acrylic polymer (4 wt%) in water (acrylic binder) by a mixing device using the cavitation effect (Jet Paster, Nihon Spindle Manufacturing Co., Ltd.) along with adding the CO2 gas (1.0 L/min). The pH value of the slurry after the CTCE indicated 8.5.

Production of the NCA slurry with the PCT.—CB and the acrylic binder were agitated by a planetary centrifugal mixer. The dispersion was mixed under CO2 gas at 0.55 MPa for 4 minutes in order to dissolve the CO2 in the dispersion. The NCA powder was added to the dispersion and stirred by the mixer. The slurry was then again mixed under the CO2 gas at 0.55 MPa for 4 minutes to further neutralize the alkaline species. The weight ratio of NCA/CB/binder was the same as the CTCE. The pH value of the slurry after the PCT indicated 8.5.
Fabrication and electrochemical evaluation of the NCA electrodes.— These slurries were pasted on Al foil current collectors and dried at 90°C in air and at 160°C under vacuum for 13 hours. The foil was cut into a circular shape (11-mm diameter). The capacity density of the NCA electrodes was ~1.3 mA/h cm².

The NCA electrode was used as the working electrode with lithium foil as the counter electrode with a polypyrrole porous micro membrane (Celgard #2325, Celgard, LLC.) as the separator in CR2032-type coin cells. The electrolyte consisted of 1 M LiPF₆ in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume).

The charge (delithiation)-discharge (lithiation) cycle tests were done using a battery charge and discharge unit (BLS series, Keisokuki Center Co., Ltd.) between 4.2 and 2.7 V for 50 cycles at 0.2°C. The charge and discharge currents were 18 mA/g (~0.1C) for the 1st cycle and 36 mA/g (~0.2C) for the additional 49 cycles. Cyclic voltammetry (CV) profiles were obtained by an electrochemical workstation (Solartron) between 4.6 and 2.7 V at 30°C. The AC impedance spectra were measured using the electrochemical workstation (Solartron) from 100 kHz to 0.1 Hz at 4.0 V with a 10 mM amplitude perturbation.

The transmission electron micrograph (TEM) images were obtained by a Tecnai G20 FEI with the 200 kV transmission electron microscope incident electron energy.

Results and Discussion

Fig. 1 shows TEM images of the NCA particle surfaces with the CTCE using the mixing device and the cavitation effect (a and b) and PCT using the planetary centrifugal mixer for production of the slurry (c and d).

On the other hand, with the PCT (Fig. 2b), the slurry was mixed by the planetary centrifugal mixer. However, a part of the NCA powder and CB was not uniformly dispersed with only rotation and revolution, leading to an uneven distribution of part of the NCA powder and CB in the slurry (b-ii). Furthermore, the CO₂ gas in the slurry flowed only from a certain direction (b-iii). This phenomenon caused part of the NCA particle surfaces to be partly coated with the existing Li₂CO₃ layer (b-iv).

Results and Discussion

Fig. 1 shows TEM images of the NCA particle surfaces with the CTCE using the mixing device and the cavitation effect (Figs. 1a and 1b) and PCT using the planetary centrifugal mixer for production of the slurry (Figs. 1c and 1d). After both treatments, most of the NCA particle surfaces were covered with the coating layer that was mainly composed of Li₂CO₃ because three different lattice distances of the particle surfaces were covered with the coating layer that was mainly the slurry (Figs. 1c and 1d). After both treatments, most of the NCA electrode was used as the working electrode with lithium foil as the counter electrode with a polypyrrole porous micro membrane (Celgard #2325, Celgard, LLC.) as the separator in CR2032-type coin cells. The electrolyte consisted of 1 M LiPF₆ in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume).

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The transmission electron micrograph (TEM) images were obtained by a Tecnai G20 FEI with the 200 kV transmission electron microscope incident electron energy.

Results and Discussion

Fig. 1 shows TEM images of the NCA particle surfaces with the CTCE using the mixing device and the cavitation effect (Figs. 1a and 1b) and PCT using the planetary centrifugal mixer for production of the slurry (c and d).
Figure 2. Proposed mechanisms of the dispersion of the NCA powder and CB, and formation of the Li$_2$CO$_3$ layer on the NCA particle surfaces with CTCE using the mixing device and the cavitation effect (a) and PCT using the planetary centrifugal mixer for production of the slurry (b).

The intercept, semicircles in the high and middle frequencies, and a quasi-straight line in the low frequency region. The value of the intercept with $Z_{Re}$ corresponds to the series resistance ($R_s$). The diameter of the small semicircle at the high frequency is assigned to the Li ion transport resistance through the film layer on the NCA electrode surfaces ($R_f$). The diameter of the large semicircle in the middle frequency corresponds to the charge transfer resistance ($R_{ct}$). The quasi-straight line corresponds to the Warburg impedance ($Z_{w}$).

Figure 3. Discharge capacities of the NCA electrodes ($\sim 1.3$ mAh/cm$^2$) with the CTCE using the mixing device and the cavitation effect and PCT using the planetary centrifugal mixer for production of the slurry.

| Sample | 1st | 2nd | 50th | (50th/1st) | (50th/2nd) |
|--------|-----|-----|------|------------|------------|
| w/ the CTCE | 183 | 175 | 161 | 92 | 88 |
| w/ the PCT | 171 | 161 | 144 | 84 | 89 |
Figure 4. CV profiles of the NCA electrodes (\(~1.3\, mAh/cm^2\)) after the 50th cycle with the CTCE using the mixing device and the cavitation effect (a) and PCT using the planetary centrifugal mixer for production of the slurry (b) at different scan rates.

Figure 5. Nyquist plots of the NCA electrodes (\(~1.3\, mAh/cm^2\)) after the 1st, 30th, and 50th cycles with the CTCE using the mixing device and the cavitation effect (a) and PCT using the planetary centrifugal mixer for production of the slurry (b).

Table II. Cell Voltage difference ($\Delta V$) between the anodic and cathodic peaks in the CV curves for the NCA electrodes with the CTCE and PCT.

|          | $\Delta V_{0.2}$ | $\Delta V_{0.4}$ | $\Delta V_{0.6}$ |
|----------|------------------|------------------|------------------|
| w/ the CTCE | 0.039V         | 0.27V            | 0.39V            |
| w/ the PCT   | 0.095V         | 0.31V            | 0.46V            |

Figure 6. $R_f$ (a) and $R_{ct}$ (b) values of the NCA electrodes (\(~1.3\, mAh/cm^2\)) with the CTCE using the mixing device and the cavitation effect and PCT using the planetary centrifugal mixer for production of the slurry.

Surfaces with the CTCE was more stabilized than that with the PCT as described later.

Fig. 7 shows the proposed structure for the NCA electrodes with the CTCE (Fig. 7a) and PCT (Fig. 7b) before the cycling. The NCA particle was almost totally covered with the Li$_2$CO$_3$ coating layer before the cycling (Fig. 1). It is known that Li$_2$CO$_3$ is electronically insulating because the bandgap of the Li$_2$CO$_3$ is calculated to be 7.07 eV. Therefore, the electrical conductivity of the surfaces was very low due to the formation of the Li$_2$CO$_3$ layer on the surfaces.
This phenomenon caused the increasing $R_l$, resulting in decreasing the capacity. However, with the CTCE (Fig. 7a), a part of the Li$_2$CO$_3$ layer on the NCA particle surfaces contained CB. Therefore, the electrical conductivity of the NCA powder was significantly improved. Therefore, the $R_l$ after the 1st cycle was lower than that with the PCT (Fig. 6). Moreover, the $R_c$ with the CTCE after the 1st cycle was also lower than that with the PCT (Fig. 6). This result was most probably due to the improvement of the dispersion of CB by the mixing device using the cavitation effect (Fig. 2). These results increased the capacities of the initial cycles and improvement of the rate characteristics. Furthermore, the surface areas of the NCA powder partially covered with the Li$_2$CO$_3$ layer before the cycle were lower than those with the PCT (Fig. 1). It is known that the Li$_2$CO$_3$ layer formed on the cathode powder and cathode can prevent the electrolyte decomposition and stabilize the cathode particle surfaces during the cycling. Thus, the NCA electrode with the CTCE has greater suppression effects on the electrolyte decomposition and reaction of the electrolyte with the surfaces during the cycling than that with the PCT. These phenomena suppressed the increasing of the $R_l$ and $R_c$ values during the cycling (Fig. 6), leading to improvement of the capacities for all the cycles (Table 1 and Fig. 3).

Conclusions

We studied the NCA electrode containing the aqueous binder with the CO$_2$ gas treatment using the cavitation effect (CTCE). The CTCE is a simple method for decreasing the pH values of the aqueous cathode slurry. The retention rate of the discharge capacity during the 49 cycles reached 92%. It was observed that almost all the NCA particle surfaces were covered with the Li$_2$CO$_3$ layer after the CTCE. This result suppressed the increasing of the $R_l$ and $R_c$ values with an increase in the cycle number because the Li$_2$CO$_3$ layer prevented the electrolyte decomposition and reaction of the NCA particle surfaces with the electrolyte. These phenomena lead to improvement of the cyclability. Furthermore, a part of the CB was absorbed in the Li$_2$CO$_3$ layer formed on the NCA particle surfaces before the cycling. This result improved the electrical conductivity of the NCA powder, leading to increasing capacities for all the cycles. Therefore, the CTCE will be an effective treatment of the NCA cathodes containing the aqueous binder with the continuous process for mass production.

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