Synthesis and Characterization of Cathode Materials for the Lithium Secondary Batteries by Spray Drying Method

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Abstract : It has been known that the synthesis of the cathode materials for the lithium rechargeable batteries by the sol-gel process has many advantages over the conventional solid-state method. It has been, however, a continuing issue that new additional steps should be introduced to commercialize this process. In this work, spray drying was introduced to the existing sol-gel process as a continuous mass production method of the pre-heat treatment precursor materials. The precursors of $LiCoO_2$ and $LiNi_{0.8}Co_{0.2}O_2$ were continuously produced through spray drying from the solution containing stoichiometric amount of lithium, cobalt, and nickel sources as well as a chelating agent. The process variables, such as pH of the starting solution, spray drying conditions, and calcination conditions were optimized. The XRD pattern for the synthesized material indicated a good crystallinity with a layered structure.

Key words : Cathode, Sol-gel, Spray drying, $LiCoO_2$, $LiNi_{0.8}Co_{0.2}O_2$, Continuous.

1. Introduction

Recently, lithium secondary batteries become main rechargeable power sources in modern portable electronic devices because of their high output voltage, high specific energy and long life cycle. Cathode materials of lithium batteries are usually made of $LiCoO_2$ with layered structure. But recently a number of other potential cathode materials such as layered $LiNi_{0.8}Co_{0.2}O_2$,[1] $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$,[2] spinel $LiMn_2O_4$[3] and olivine $LiFePO_4$[4] are being developed for their better electrochemical performance, lower cost and improved safety characteristics. The synthesis of these materials is usually very difficult and needs a careful preparation method other than conventional solid-state method.

Recently, various advanced chemical processes, such as sol-gel,[5] spray pyrolysis,[6] co-precipitation method,[7] mechanochemical process,[8] reflux reaction,[9] and hydrothermal process[10] have been tried to synthesize the high performance cathode active materials. Although most of these solution-based processes are able to produce materials with better homogeneity and higher electrochemical performance than the conventional solid-state reaction method, there is still a need for better understanding of the effects of the solution and process parameters on the morphology, the chemical composition, and the crystallinity of the synthesized materials in order to commercialize these processes. Among them, sol-gel synthesis has a lot of superior advantages over the conventional solid-state reaction process, such as preparation of compositional homogeneity of intermediate precursors in molecular level, shorter diffusion length to facilitate the generation of nanocrystalline materials during shorter calcination

process, easy control of particle size and favorable microstructure as well as excellent electrochemical performance of the calcined powders. However, it has been pointed out that commercialization of this process requires additional steps be introduced to make the overall process a continuous process for mass production of the materials.[11,12] It is also well known that electrochemical performance of these materials greatly depends on the specific synthesis route since any change of the conventional process can influence the performance of the final product.

In this work, spray-drying step was introduced to the existing sol-gel process with an aim to make the overall process a continuous process. And the prepared powders of $LiCoO_2$, and Li $Ni_{0.8}Co_{0.2}O_2$ were evaluated for their electrochemical performance.

2. Spray-drying process

In this work, spray-drying process was introduced to the existing sol-gel process as an intermediate step for the continuous mass production of the pre-calcination precursor materials. In this process, the solvent of the solution containing starting materials is instantly eliminated by hot air, so that spray-dried powders (xerogel) can retain the homogeneity of the solution state, while the continuous production of the precursors is possible. Spray-dryers are commonly used to make homogeneous powder substances, whose particles are usually spherical in shape with a size 10~140 μm.[11-13] The schematic diagram describing the main parts of spray-dryer is shown in Fig. 1. The spray drying process begins as a preheated solution is pumped into the atomizing nozzle. The nozzle increases the surface area of the starting solution by creating a fine mist.
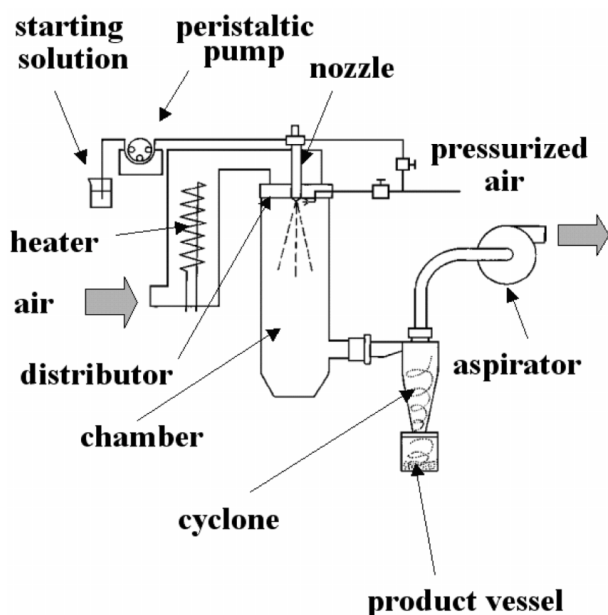
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Fig. 1. Schematic diagram describing the major parts of lab-scale spray dryer.

Then the mist is sprayed into a chamber where air has been heated to the temperature above the vaporization temperature of the solvent. The rate of solvent vaporization is dependent on many process conditions such as a flow rate of the solution, a temperature of the starting solution, airflow rate, inlet air temperature, mist droplet's size, and total concentration of the starting materials in the solution. The droplets are dried by hot air as they are separated centrifugally within the cyclone from the humid air, which is expelled to the atmosphere by the aspirator.

Sol-gel process combined with spray drying has some advantages over the conventional process. As mentioned earlier, using spray-drying, sol-gel process can be a continuous process, such that mass production of precursor materials can be possible, and this process requires shorter drying time than the conventional sol-gel process. Because spray-drying occurs instantaneously when the precursor solution is sprayed into the drying chamber, segregation of the precursor materials in the product can be effectively blocked. But in case of rotary evaporation process, segregation can occur due to the difference in the specific gravity or the solubility of the various materials in the starting solution during the solvent elimination. The main disadvantage of adopting this process is that the powders prepared by this method are easy to take hollowed structures.[14] When the sprayed mist is exposed to the hot air, the vaporization of solvent starts from the surface of the droplets, which makes an inherent shell structure, as is commonly observed in the ultrasonic spray pyrolysis. Because hollow structured materials tend to have low material density generally, which means the low energy density when it is used for cathode materials, formation of shell structures should be suppressed as much as possible. However, in this application during the initial heat-treatment of precursors,

organic function groups existing in the precursor will burn and several precursor powders will combine together to be a ceramic powder of large size and hollowed space inside the precursor disappears.
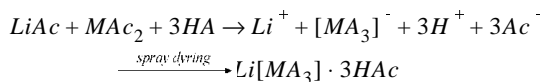
3. Experimental procedure

The typical cathode materials of the layered structure, $LiCoO_2$ and $Li\ Ni_{0.8}Co_{0.2}O_2$ were prepared by sol-gel process combined with spray drying using acetate source materials as following schemes. The stoichiometric amount of metal acetate starting materials, $LiCH_3COO \cdot 2H_2O$, $Co(CH_3COO)_2 \cdot 4H_2O$ and in case of $LiCo_{0.2}Ni_{0.8}O_2$, $Ni(CH_3COO)_2 \cdot 4H_2O$, was weighed and dissolved to make a complete solution in distilled water. Proper amount of acrylic acid ($CH_2CHCOOH$, pKa^*=4.25 at 25°C)[15] considering acid to metal ion ratio R between 0.5~3, was also dissolved in water and the individual solutions were mixed under constant stirring. The pH of the solution was measured around 2.0. The mixture was then stirred at the elevated temperature (80~90°C) for 1~3 hrs until proper viscosity is obtained, where numbers of unit chelate are thought to experience polymerization reaction to be a large molecule. This solution is then, transported to the Büch 190 mini spray dryer with peristaltic pump and spray-dried into the drying chamber through the atomizing nozzle by pressurized air, maintaining inlet temperature of the hot air around 190~220°C and outlet temperature around 80~120°C by adjusting mainly proper aspiration rate and solution feed rate. The xerogel inside the product vessel was, then, collected and subjected to further heat treatment at 500°C for 6 hrs in air and subsequently, at 800°C for 12~24 hrs in air for $LiCoO_2$ and in oxygen atmosphere in case of $LiNi_{0.8}Co_{0.2}O_2$

Structural properties of the compounds synthesized at different condition were studied by the X-ray diffraction (XRD) technique. Chemical analysis of the synthesized materials was carried out with an atomic absorption spectroscopy (AAS). The surface and particle morphology of the synthesized materials were analyzed using scanning electron microscope (SEM). The electrochemical performance of the materials was studied by assembling 2 cm×2 cm pouch cells and the cells were galvanostatically cycled at a 0.2 C rate(1C=140 mAh/g) for 3 cycles and 0.5 C thereafter between 3.0 and 4.2 V in a multi-channel battery tester. The synthesized cathode materials were mixed with 8% carbon black and 5% PVdF as binder, and made into a slurry using NMP as a solvent and coated onto aluminum foil which was used as a current collector. The coated aluminum foil was allowed to dry overnight at room temperature and then it was roller pressed to better adhere the materials to the current collector. The cathodes were cut as 2 cm×2 cm from the foil. The cells were assembled inside drying room using lithium metal as an anode, polypropylene film as a separator and a 1 M $LiPF_6$ in 1:1:1(v/v/v) EC-EMC-DMC co-solvent as an electrolyte.

$^*pK_a$=-logK_a where K_a is the equilibrium constant for HA$\longleftrightarrow$H$^+$+A$^-$

4. Results

The spray-drying of the starting solution, heated at 80°C was performed with atomizing nozzle pressure about 5 bar, maintaining inlet temperature of the hot air around 190~220°C by electric heater and outlet temperature around 80~120°C by adjusting mainly aspiration rate and solution feed rate. The SEM image of the spray-dried xerogel for $LiNi_{0.8}Co_{0.2}O_2$ is shown in Fig. 2. As can be seen from Fig. 2, the xerogel assumes various shapes of diverse sizes, such as dimpled sphere, hollowed sphere, and cracked sphere. The size and distribution of the spray-dried powders are mainly dependent on the atomizing nozzle type. It has been well known that the spray-dried powders are liable to take the hollowed and dimpled structures, mainly because the evaporation of the solvent starts from the surface of the droplets. And when the drying is completed and the temperature of the xerogel cools down, the pressure inside the shell becomes lower than the atmospheric pressure, then the xerogel is crumpled to have a dimpled structure. Because the starting solution continues to transform into the xerogel precursor through spray-drying method, the mass production of precursor is possible. Transition metal atom (M^-) usually meets with three acrylate ions ($CH_2=CHCOO^-; A^-$) in the water to be complex ions $[MA_3]^-$, and through spray-drying there occurs instant evaporation of water as well as polymerization of complex ions $[MA_3]^-$ using the $C=C$ double bond in acrylate ions with adjacent neighbors to form a xerogel.

$$LiAc + MAc_2 + 3HA \rightarrow Li^+ + [MA_3]^- + 3H^+ + 3Ac^-$$
$$\xrightarrow{\text{spray dyring}} Li[MA_3] \cdot 3HAc$$

The XRD patterns for the $LiCoO_2$ and $LiNi_{0.8}Co_{0.2}O_2$ synthesized with different calcination time are shown in Fig. 3 and corresponding lattice parameters are tabulated in Table 1. All the diffraction patterns indicate good crystallinity and a single phase with peaks indexed in the $R\bar{3}m$ space group. For $LiCoO_2$, the lattice parameters and their ratio increase with calcination time. The splitting of the 006/102 and 108/110
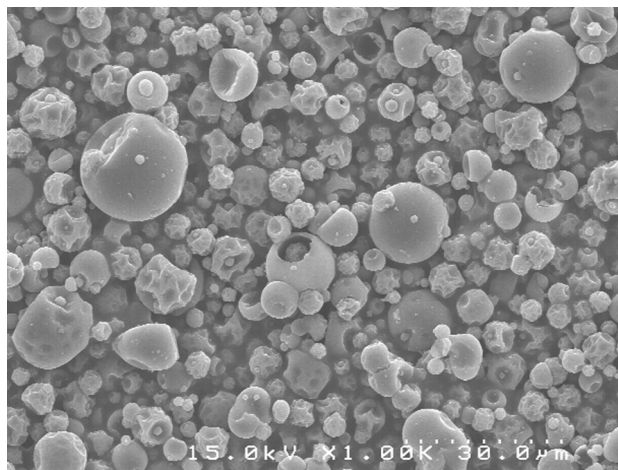
peaks are prominent, indicating good hexagonal ordering for all the compounds synthesized. The splitting is more distinct in case of $LiCoO_2$. The intensity ratio, I_{003}/I_{104}, is generally regarded as the degree of hexagonal ordering. The ratio was greater when the calcination time was 12 h for $LiCoO_2$. For $LiNi_{0.8}Co_{0.2}O_2$, R factor, defined by Reimer et al.,[16] was calculated to be smaller when the calcination time was 12 h. Because R factor is regarded as an indicator for cation mixing in lithium nickel oxide,(i.e. the smaller R is, the severer the degree of cation mixing) powders with small R factor will show better electrochemical performance.
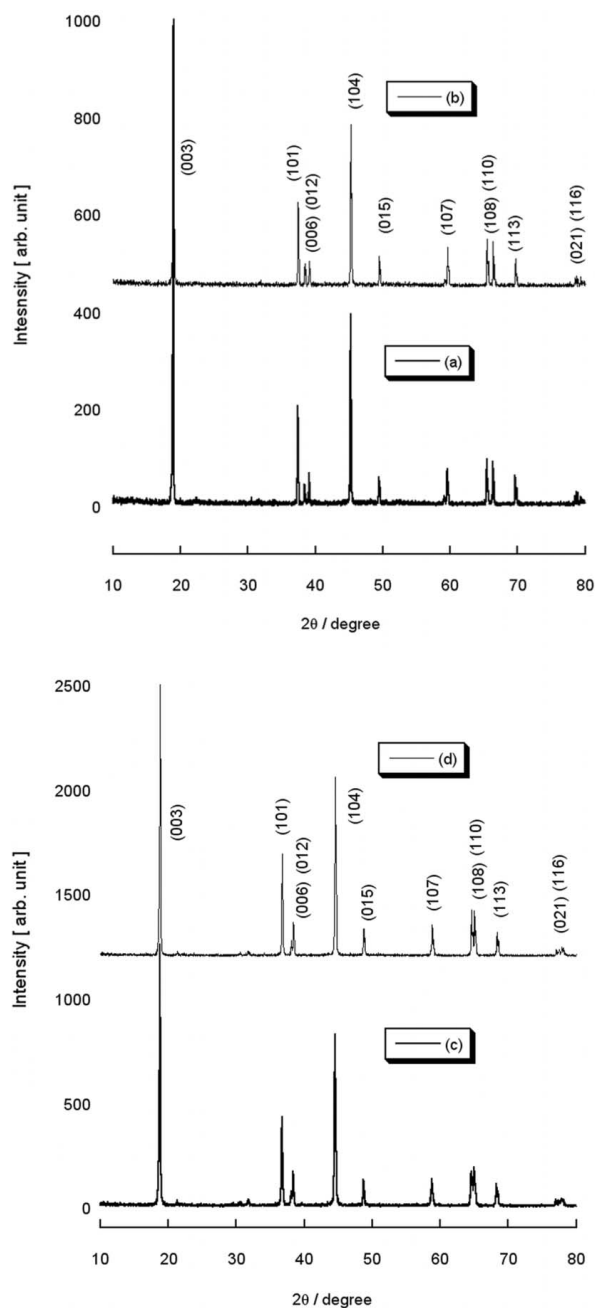

Fig. 3. XRD patterns of the synthesized powders depending on calcination time (a) $LiCoO_2$, 12 h (b) $LiCoO_2$, 24 h (c) Li $Ni_{0.8}Co_{0.2}O_2$, 12 h (d) Li $Ni_{0.8}Co_{0.2}O_2$, 24 h.

Fig. 2. SEM image of spray-dried xerogel for $LiNi_{0.8}Co_{0.2}O_2$.

Table 1. Lattice parameters from XRD data (a) LiCoO$_2$, 12 h (f) LiCoO$_2$, 24 h (c) Li Ni$_{0.8}$Co$_{0.2}$O$_2$, 12 h (d) Li Ni$_{0.8}$Co$_{0.2}$O$_2$, 24 h (calculated by least square method using 10 diffraction peaks)

Process	a (Å)	c (Å)	c/a	I_{003}/I_{104}	R factor	Unit Cell Volume (Å^3)
(a)	2.8199	14.0706	4.9898	3.88		96.89
(b)	2.8214	14.0828	4.9914	2.63		97.08
(c)	2.8617	14.1855	4.9570	1.67	0.475	100.60
(d)	2.8684	14.1805	4.9437	1.74	0.482	101.04

R factor : R=$(I_{006}+I_{102})/I_{001}$
Unit cell volume : Cell Vol.=$(\sqrt{3}/2)a^2c$

The SEM images of synthesized powders calcined at 800°C for 12 h and 24 h are shown in Fig. 4(a) and (b). For LiCoO$_2$, particles are usually in angular, elongated shape with a size of 1~2 mm for 12 h and 2~3 mm for 24 h. There was no distinct agglomeration for this powder. In case of LiNi$_{0.8}$Co$_{0.2}$O$_2$, particles of submicron irregular size and shape are agglomerated to be larger size particles of micro-size as shown in Fig. 4(c) and (d).

Table 2 shows the results of the elemental analyses for the synthesized powders and they agree well with targeted compositions. A small difference in lithium content from the initial stoichiometry represents the lithium loss during the calcination

treatment, and longer calcination time brings about more lithium loss in the synthesized powders.

Cycling performance of LiCoO$_2$ and LiNi$_{0.8}$Co$_{0.2}$O$_2$ synthesized at different condition is shown at Fig. 5. For LiCoO$_2$, the compounds synthesized with different calcination time showed an almost identical behavior with an initial capacity of about 135 mAh/g, which implies that calcination time over 12 h has little effect on cycling performance of LiCoO$_2$. For LiNi$_{0.8}$Co$_{0.2}$O$_2$, the compound synthesized at 24 h showed a higher initial capacity than calcined for 12 h but as far as the capacity retention is concerned, the compound for 12 h exhibited far better cyclic performance.
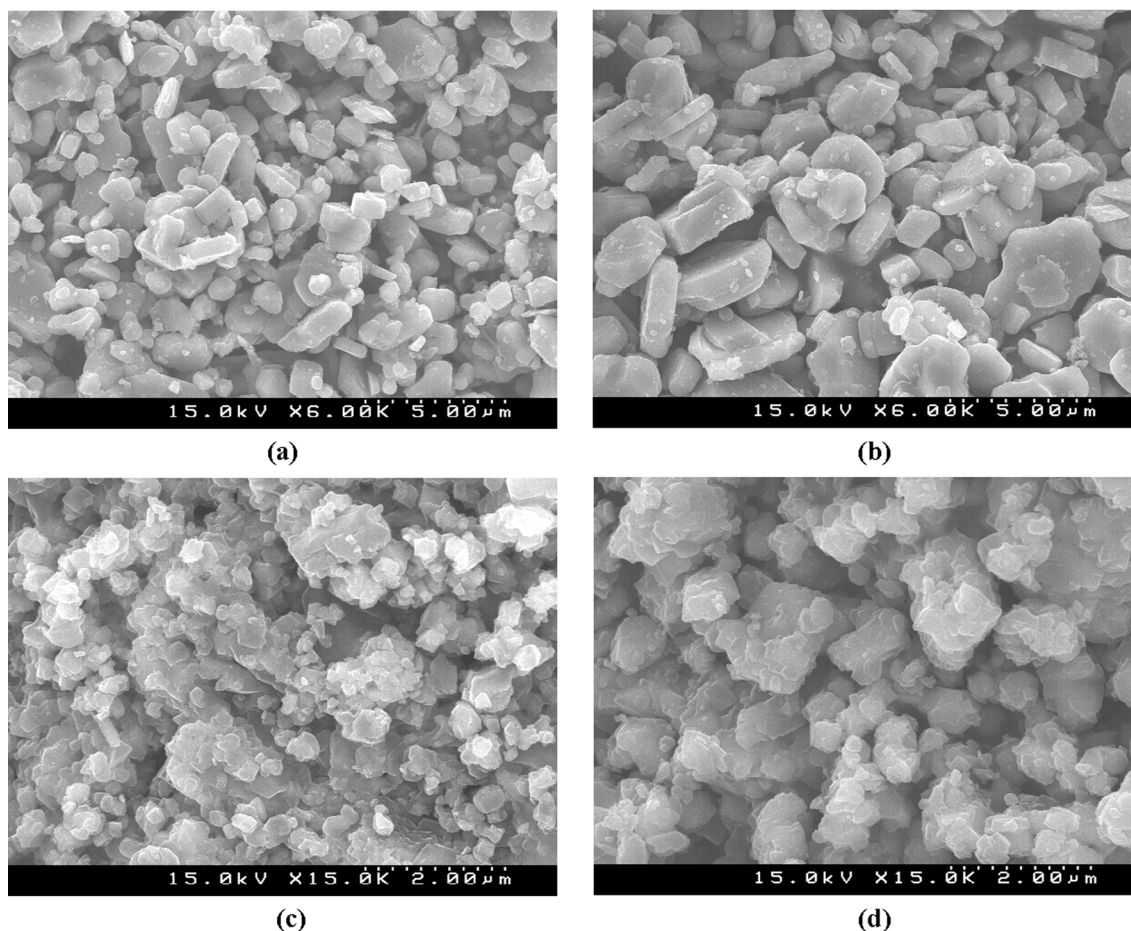

(a)

(b)

(c)

(d)

Fig. 4. SEM images of the synthesized powders prepared at various calcination time (a) LiCoO$_2$, 12 h (b) LiCoO$_2$, 24 h (c) Li Ni$_{0.8}$Co$_{0.2}$O$_2$, 12 h (d) Li Ni$_{0.8}$Co$_{0.2}$O$_2$, 24 h .

Table 2. AAS composition analysis of the synthesized materials

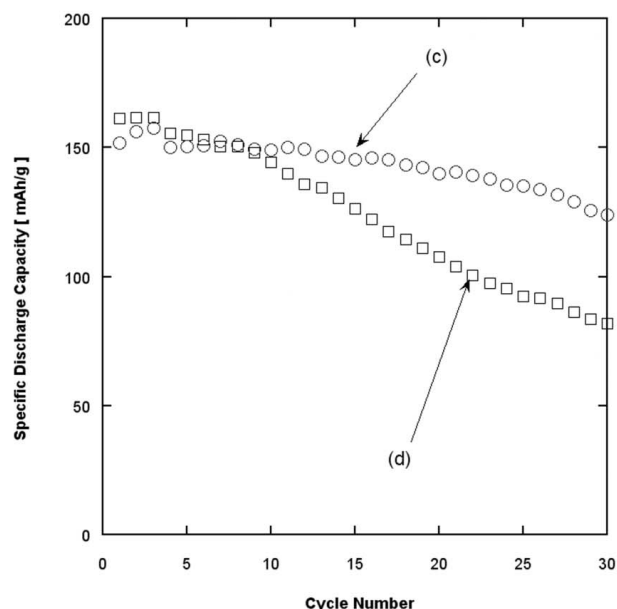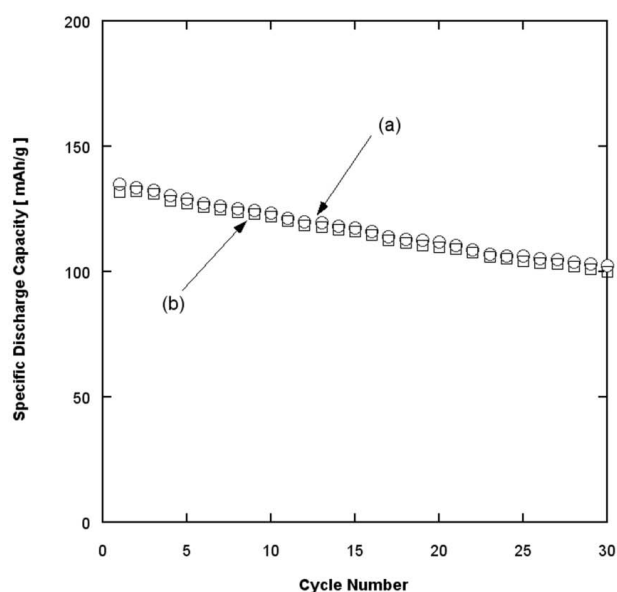| Target composition (calcination time)	AAS composition analysis (mol %)			Li/(Co+Ni) molar ratio
	Li	Co	Ni	
$LiCoO_2$, (12 h)	0.974	0.991		0.983
$LiCoO_2$, (24 h)	0.980	1.01		0.974
$Li\ Ni_{0.8}Co_{0.2}O_2$, (12 h)	0.924	0.185	0.743	0.996
$Li\ Ni_{0.8}Co_{0.2}O_2$, (24 h)	0.952	0.199	0.780	0.973

Fig. 5. Cycling performance of the synthesized powders prepared at various calcination time (a) $LiCoO_2$, 12 h (b) $LiCoO_2$, 24 h (c)Li $Ni_{0.8}Co_{0.2}O_2$, 12 h (d) Li $Ni_{0.8}Co_{0.2}O_2$, 24 h.

5. Conclusion

An acrylic acid assisted sol-gel method combined with spray drying was successfully employed to prepare polycrys-

talline $LiCoO_2$, and $LiNi_{0.8}Co_{0.2}O_2$ cathode materials and their crystalline, structural, and electrochemical properties of the compounds synthesized at different calcination period are investigated. The precursors of $LiCoO_2$ and $Li\ Ni_{0.8}Co_{0.2}O_2$ were continuously produced through spray drying from the solution containing molecularly homogeneous chelating unit. The process variables, such as pH of the starting solution, spray drying conditions, and calcination conditions were optimized. The XRD pattern for the synthesized material indicated a good crystallinity with a layered structure.

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