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Research Article

GREEN SYNTHESIS OF SPHERICAL-SHAPED $Ni_{1/3}Co_{1/3}Mn_{1/3}CO_3$ PARTICLES

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Keywords

Nanoparticle,
Hydrothermal Treatment
Ni-Co-Mn Carbonate,
$Ni_{1/3}Co_{1/3}Mn_{1/3}CO_3$

Abstract

In this study, we reported a simple and green manufacturing of a uniform, sphere-shaped $[Ni_{1/3}Co_{1/3}Mn_{1/3}]CO_3$ nanoparticles, which can be considered as a precursor for $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$. Ni-Co-Mn carbonate particle was prepared via three steps, (1), the mixing metal sulfate salts with Na_2CO_3 which, formed the primary precipitation, (2) the addition of $(NH_4)_2CO_3$, responsible for the increasing conversion rate, (3) the hydrothermal treatment lead to existing of recrystallization and spherical shape of $[Ni_{1/3}Co_{1/3}Mn_{1/3}]CO_3$ particles. The morphology and crystalline structure of the present material is characterized by Energy-dispersive X-ray Spectroscopy (EDS), Scanning Electron Microscopic (SEM) and X-ray diffraction (XRD). Analysis outcomes indicated that the particle's growth mechanism of spherical composition is depend on a dissolution-recrystallization process of metal salts and $(NH_4)_2CO_3$ dissociation process. This study opens a green avenue to prepare cathode materials in the lithium-ion battery application.

YEŞİL YÖNTEM İLE KÜRESEL $Ni_{1/3}Co_{1/3}Mn_{1/3}CO_3$ PARÇACIKLARIN SENTEZİ

Anahtar Kelimeler

Nanopartikül,
Hidrotermal,
Ni-Co-Mn karbonat,
$Ni_{1/3}Co_{1/3}Mn_{1/3}CO_3$

Öz

Bu çalışmada, tek tip, küre şeklinde bir $[Ni_{1/3}Co_{1/3}Mn_{1/3}]CO_3$ nanopartiküllerinin basit ve çevreye duyarlı sentez yöntemiyle üretilmesini çalışılmıştır. Ni-Co-Mn karbonat partikülü üç aşamada hazırlandı, (1), birincil sülfat oluşturan Na_2CO_3 ile metal sülfat tuzlarının karıştırılması, (2) ekstra $(NH_4)_2CO_3$ ilave edilmesi reaksiyonun gerçekleşmesine neden olan kimyasal, (3) hidrotermal metodu ile $[Ni_{1/3}Co_{1/3}Mn_{1/3}]CO_3$ partiküllerinin kristallenmesi ve küresel şeklinin oluşması. Mevcut malzemenin morfolojisi ve kristalin yapısı, Enerji-dağıtıcı X-ışını Spektroskopisi (EDS), Taramalı Elektron Mikroskopik (SEM) ve X-ışını kırınımı (XRD) ve ile karakterize edildi. Analiz sonuçları, parçacığın küresel yapı mekanizmasının, metal tuzlarının bir çözünme-yeniden kristalizasyon işlemine ve $(NH_4)_2CO_3$ ayrışma işlemine dayandığını göstermiştir. Bu makelde yapılan araştırmalar ile, lityum iyon pilleri için katot materyalleri hazırlamanmasında çevreye duyarlı hidrotermal yönteminin kullanılması bu konuda yeni yaklaşımlar açacaktır.

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1. Introduction

In the last decade, there is an increasing request for renewable and sustainable energy due to the the depletion of usage of fossil fuel source and consequent growth of environmental worries. Thus, the energy storage technology especially Li-ion batteries and supercapacitors have drawn a great deal of attention (Altinci and Demir 2020); (Demir, Tessema et al. 2018); (Demir, Ashourirad et al. 2018) (Ashourirad, Demir et al. 2018) (Demir, Farghaly et al. 2018) (Demir, Saraswat et al. 2017). $LiCoO_2$ is the broadly applied active cathode electrode material for Li-ion

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batteries (LIBs) thanks to its high capacity, high output voltage, and extraordinary cycling stability. (Kalluri, Yoon et al. 2017), (Kwak, Lim et al. 2020), (Park, Kim et al. 2010); (Li, Zhu et al. 2019) On the other hand, cobalt-oxide based cathode electrodes suffer from environmental issues and the costly market price of cobalt. (Gong and Yang 2011); (Shi, Xiao et al. 2018) These drawbacks have been urged to discover alternative cathode materials in replacement of $LiCoO_2$ for Li-ion batteries such as layered rock salt structured $LiCoO_2$ (Nayaka, Zhang et al. 2018), spinel structured $LiMn_2O_4$, (Yan, Lin et al. 2020) layered $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$, (Jo, Ku et al. 2018) and olivine structured $LiFePO_4$, (Gong, Xue et al. 2016)etc. Among these materials, layered $Li[Ni_xCo_yMn_{1-x-y}]O_2$ is the most fascinating replacements of $LiCoO_2$ due to high discharge capacity, operating voltage, high rate capability, proper structural and thermal resistivity, cycle-ability.. The high electrochemical performance of $Li[Ni_xCo_yMn_{1-x-y}]O_2$ is caused by the synergic effect of nickel, cobalt, and manganese elements. (Jo, Ku et al. 2018) Taking account of electrochemical activity, each element plays a crucial role in making important to balance the as-prepared composition. In detail, increasing the amount cobalt atoms suppress the cation mixing and enhances the stability of the structure while excess cobalt atoms result in capacity loss; introducing nickel atoms give an advantage of rising the capacity of the material, on contrary, excess of nickel limits proper cation mixing, cause to decrease the cycling stability; manganese in the composition improve the safety, but an excess of it leads to the structural deterioration. (Kim, Park et al. 2019)

Commonly, $Li[Ni_xCo_yMn_{1-x-y}]O_2$ is prepared from either $[Ni_xCo_yMn_{1-x-y}](OH)_2$ or $[Ni_xCo_yMn_{1-x-y}](CO_3)$ precursors. (Liu, Tan et al. 2019) Not only the electrochemical performance but also phase purity, the crystallinity, particle morphology, textural properties, and cation distribution of $Li[Ni_xCo_yMn_{1-x-y}]O_2$ material extremely depends on the synthesis procedure of precursor. The conventional synthesis methods such as co-precipitation (Hou, Zhang et al. 2017), solid-state(Wang, Yin et al. 2017), sol-gel synthesis, (Zhu, Yang et al. 2019) etc., were usually applied in the synthesis of Ni-Mn-Co based materials. Unfortunately, each method has advantages and disadvantages due to the difficulties of controlling homogeneously and impurity of as-prepared materials through the synthesis pathway. For instance, the sol-gel synthesis method requires a high calcination temperature for a pure phase, which leads to undesirable particle growth. Considering this aspect, the co-precipitation approach has been reported to synthesize metal hydroxide precursor, which is a novel method to manufacture materials under milder conditions. Sol-gel synthesis offers easy controlling and various morphologies processes while the condition of such reaction is hardly controlled and too much reaction time is required. (Nayak, Erickson et al. 2018) Thus, it is urgent to find out a simple and controlled preparation method to obtain the materials with proper electrochemical activity, high crystallinity, and pure phase. Hydrothermal treatment is a promising method to increase material crystallinity and well-distributed cation into a composite (Shi, Zhang et al. 2018). This is because the hydrothermal reaction is performed at relatively a low temperature while maintaining high pressure in a closed container.

In the present paper, we synthesized $[Ni_{1/3}Co_{1/3}Mn_{1/3}]CO_3$ precursor via hydrothermal treatment assisted co-precipitation process under relatively mild reaction conditions. Hydrothermal treatment was applied by converting primary precipitates into the spherical-like shape $[Ni_{1/3}Co_{1/3}Mn_{1/3}]CO_3$ along with the presence of ammonium carbonate. Taking into account of exploring the synthesis procedure and mechanism, it was successfully controlled tuning of precursors with different morphological and physical properties.

3. Material and Method

3.1. Experimental part

Materials and Method

All chemicals including nickel sulfate hexahydrate ($NiSO_4·6H_2O$, 99.1%), cobalt sulfate heptahydrate ($CoSO_4·7H_2O$, 99.4%), manganese sulfate monohydrate ($MnSO_4·H_2O$, 99%), ethanol, sodium carbonate, ammonium carbonate chemicals were used as an analytic grade. The deionized water (DI) as a solvent was used to prepare solutions throughout the hydrothermal process. In the typical experimental procedures for preparing $[Ni_{1/3}Co_{1/3}Mn_{1/3}]CO_3$ as followed: first, 0.1M $NiSO_4$, 0.1M $CoSO_4$, and 0.1M $MnSO_4$ salt solutions were dissolved separately in 2 ml water with magnetic stirring to keep the molar ratio of Ni:Co:Mn to 1:1:1 and mixed. These ratios are based on the reference Luo at all. (Tang, Lu et al. 2016). Then, as-prepared solutions were well-mixed with the 2 mL of 0.4M Na_2CO_3 under 15 minutes magnetic stirring. Afterward, the primary nanoprecipitate $[Ni_{1/3}Co_{1/3}Mn_{1/3}]CO_3$ in a slurry phase was obtained and quickly transferred into a 20 mL autoclave made of Teflon-lined stainless steel. Then, 4 ml 0.3 M $(NH_4)_2CO_3$ was poured into the same autoclave and sealed to protect oxidation from air. The hydrothermal treatment condition is set to 180 °C for 24 hours in the oven. After the hydrothermal process, materials were allowed spontaneous cooing until reaching room temperature. Finally, the precipitates were extracted from the aqueous dispersed solution via the centrifugation process, subsequently, washed with DI water, acetone and ethanol up to 5 times. The as-obtained solid material was dried in an oven at 90 °C 24 hours.

Characterization

Scanning electron microscopy (SEM) images were analyzed by a Hitachi SU-70 instrumentation. The sample was processed by dispersing each specimen onto a sticky carbon surface, which attached to a flat sample holder. Then the sample was coated with platinum to increase conductivity at a pressure of 10^{-5} mbar in an N_2 atmosphere for 60 s before SEM imaging. Energy-dispersive X-ray spectroscopy (EDS) elemental mapping of Co, Mn and Ni was performed using the (SEM; EDAX HITACHI) with an acceleration voltage of 200 kV to probe the elemental distribution of the sample. The degree of crystallization was determined by collecting Powder X-ray diffraction patterns Siemens D5000 instrument operating at 40 kV and 40 mA, using Cu Kα radiation (k = 0.15406 nm) by scanning 2θ ranging 10–80° in X-ray diffraction spectra.

5. Result and Discussion

In this paper, we are predominantly aimed to explore the effectiveness of hydrothermal method for manufactiring spherical Ni-Co-Mn carbonate nanoparticles. Figure 1 shows synthesis pathway of spherical Ni-Co-Mn carbonates nanoparticles. The production yield was found to be 85 % wt. based on the starting materials. To understand the evolution of morphology and degree of crystallization, SEM, X-ray diffraction (XRD), as well as EDS analysis, were conducted. Figure 2 depicts variable SEM images of $[Ni_{1/3}Co_{1/3}Mn_{1/3}]CO_3$ subsequently the hydrothermal treatment. It is seen that the hydrothermal treatment results in change surface morphology of present material. As it seen, an average size of 2–3 µm uniform spherical particles was existed after hydrothermal treatment. It is important to note that egg-like particles around 600 nm size stick to main spherical particles were found to see the high-resolution SEM image.

Figure 1. Synthesis pathway of spherical Ni-Co-Mn carbonates nanoparticles

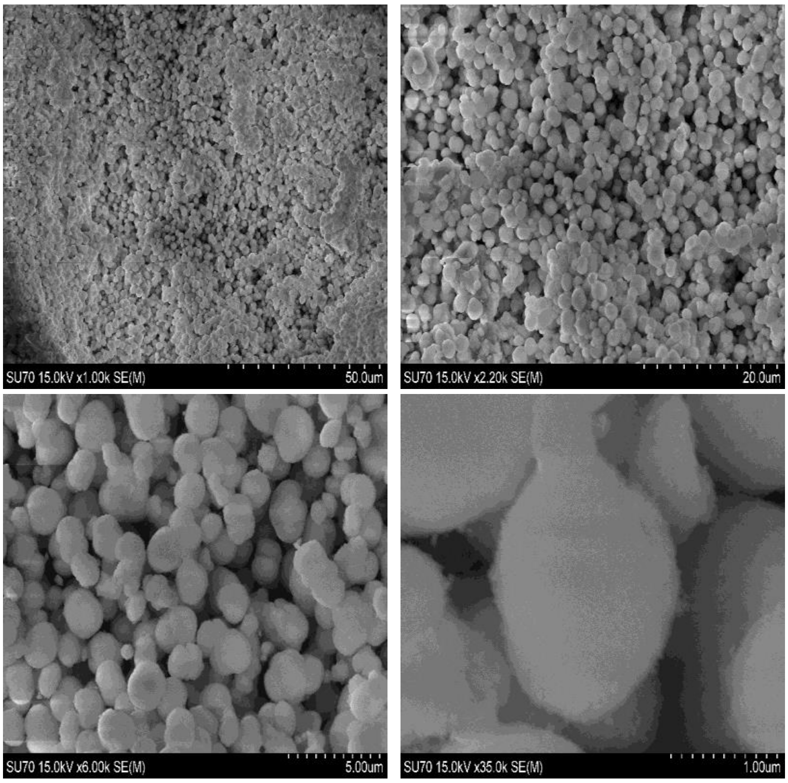

Figure 2. SEM images of $[Ni_{1/3}Co_{1/3}Mn_{1/3}]CO_3$ particles

The elemental distribution profile of Ni, Co, and Mn elements on $[Ni_{1/3}Co_{1/3}Mn_{1/3}]CO_3$ particles are presented in Figure 3. The blue, brown and purple dots show the elemental mapping of cobalt, nickel and manganese, respectively. The brightness scale of each color implies the intensity of the element signal. Moreover, uniform distribution reveals a successful uniform distribution of composition onto the spherical precipitates. Based on the EDS results, it is possible to manufacture uniform and well-distributed spherical Ni-Mn-Co carbonate particles at a size of micron along with the identical element ratio as the precursors via the hydrothermal treatment.

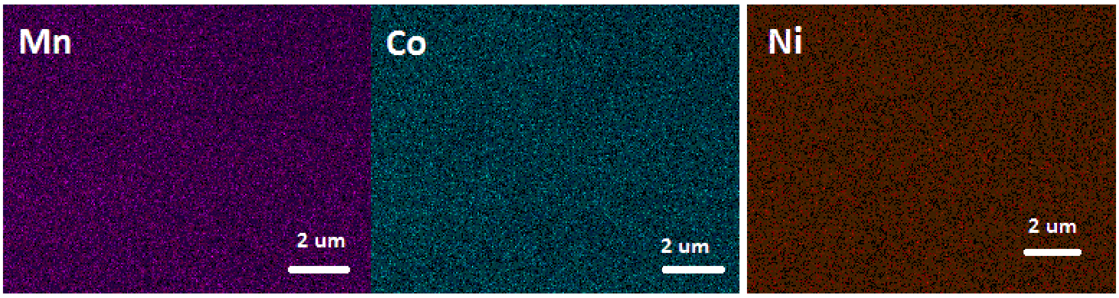

Figure 3. EDS mapping of $[Ni_{1/3}Co_{1/3}Mn_{1/3}]CO_3$ particles

The energy dispersive spectroscopic EDS analysis reflects the elemental molar ratio of the composite approximately is Ni:Co:Mn = 0.30:0.29:0.27, which is close to the ratio of the starting materials presented in Table 1. The Ni:Co:Mn molar ratio is close to 1:1:1, which is agreed with XRD data.

Table 1. Elemental compotion of $[Ni_{1/3}Co_{1/3}Mn_{1/3}]CO_3$

The starting ratio of Materials	Expected Formula	Ni	Co	Mn	C	O
Ni:Co:Mn = 1:1:1	$Ni_{1/3}Co_{1/3}Mn_{1/3}CO_3$	0.3015	0.2929	0.2680	2.65	11.12

Recently, core-shell structures for cathode materials have been gaining more attention, since the core-shell structure not only limits the existing of solid electrolyte interphase (SEI) but also hinder volume expansion. To explore the phase evolution of Ni-Mn-Co nanoparticles with hydrothermal treatment, the as-prepared sample was collected and subjected to XRD analysis. The crystalline peaks of identified using the $MnCO_3$ standard JCPDS file number 83-1763 (Ryu, Lim et al. 2014). Figure 4 displays the XRD plot of $[Ni_{1/3}Co_{1/3}Mn_{1/3}]CO_3$. Although the different identified carbonate peaks were exist in the XRD characterization, the atomic distribution of Co, Ni and Mn and in the carbonate composite appears to be uniform in Figure 3 (the EDS mapping). Subsequently hydrothermal treatment, a well-crystalline structure has existed. As seen, variable crystalline phases were detected. Moreover, the XRD plot of $[Ni_{1/3}Co_{1/3}Mn_{1/3}]CO_3$ is pretty accord with identical $MnCO_3$ plot and presents comprehensive integrated lines that assign to the mixing of $CoCO_3$, $NiCO_3$, and $MnCO_3$. (Tang, Lu et al. 2016).

Based on the experimental results, we proposed a schematic synthesis mechanism of $[Ni_{1/3}Co_{1/3}Mn_{1/3}]CO_3$ nanoparticle. It was found that three facts govern spherical shape formation. First, the former nano-particles existed when mixing of Na_2CO_3 with Ni, Mn and Co sulfate solution, where CO_3 substituted with SO_4^{-2} molecules, it is important to bear in mind that former particles are not formed fully crystalline structure, second, the spherical nano-compostis are consist of nano-crystals as the latter precipitates along with crystalline structure distinguished from the former nano-particles; third, $(NH_4)_2CO_3$ is responsible again developing for not only the dissolution and but also recrystallization processes. This mechanism is in accord with the previous proposal. (Tang, Lu et al. 2016) It was previously reported that the thermodynamics stability of the nanocrystals is better than the primary precipitates. (Tang, Lu et al. 2016), (Lee, Kang et al. 2004), Also, the $(NH_4)_2CO_3$ in solution may lead to dissociation for discharging NH_3 to increase the conversion rate. (Myung, Lee et al. 2005)Moreover, four steps govern the conversion process: (1) metal sulfates dissolve in the solution to grow up to primary nano-precipitates; (2) the nuclei of secondary precipitates form and generate crystals (nano size) in aqueous solution; (3) the nanocrystals gradually aggregate to development of spherical particles in solution; finally (4) (Lee, Kang et al. 2004) while the primary precipitates are consuming, in solution, metal contents will decrease until the recrystallization process terminates because of restriction on thermodynamics equilibrium. It is important to note that, the addition of $(NH_4)_2CO_3$ would raise the relative amount of metals in solution, along with the conversion rate from the latter nano-crystal to crystal nanoparticles. Meanwhile, the $(NH_4)_2CO_3$ inhibits the development and aggregation of nano-size crystals to an extensive increasing of nanocrystal size and the size of their aggregation. It should be kept in mind that the conversion rate is essential for controlling the growth and aggregation of as-prepared nanoparticles to form a fully crystalline structure, and it extends the size distribution of the as-prepared material. Nonetheless, further investigation is required to control the growth and aggregation of nanocrystals (Tang, Lu et al. 2016).

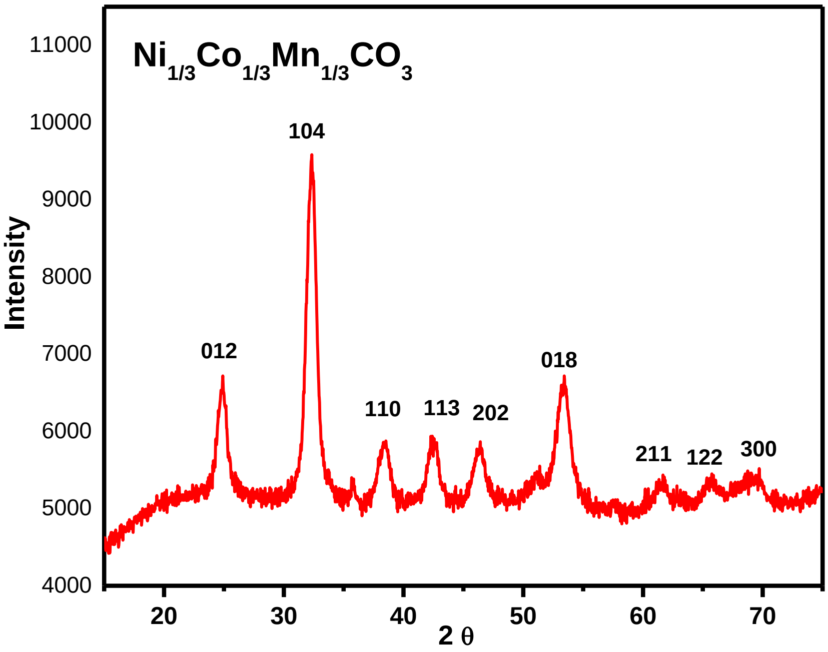

Figure 4. XRD patterns of $[Ni_{1/3}Co_{1/3}Mn_{1/3}]CO_3$ powders.

Conclusions

In this paper, we reported a simple and green approach to synthesize well-distributed and spherical-like particles of $[Ni_{1/3}Co_{1/3}Mn_{1/3}]CO_3$, which is an essential precursor for preparing $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$. The controllable hydrothermal treatment method was applied to convert Ni-Co-Mn sulfate salt to Ni-Co-Mn carbonate nanoparticles. Notably, the simple hydrothermal treatment along with the co-precipitated process led to the existence of spherical nano crystal $[Ni_{1/3}Co_{1/3}Mn_{1/3}]CO_3$ powder. Upon the characterization techniques, it was suggested that the mechanism of crystal particle formation is based on a dissolution-recrystallization process. As a result, a present study can enlighten away for the preparation of cathode electrode materials by engaging this strategy and it would be applied in next-generation Li-ion battery technology.

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Conflict of Interest

No conflict of interest was declared by the author.

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