

# A Basic Study On Nano-Li<sub>2</sub>NiO<sub>2</sub> Highly Porous Spheres For Lithium Ion Battery Applications

<sup>1</sup> M. ANILKUMAR, <sup>2</sup> V. RAJANESH, <sup>3</sup> K. PRABHU, Dr. CS. SUNANDANA\*

1.M.Anilkumar,(Electronics and communication engineering,UOH,Hyderabad,500046)

2.V.Rajanesh,( Electronics and communication engineering,Jntuhces,Sulthanpur,502273)

3.K.Prabhu( Electronics and communication engineering,Jntuhces,Sulthanpur,502273)

E-mail: anilhcu1990@gmail.com , rajaneshv@gmail.com kprabhu2003@gmail.com,

**Abstract** :Nano-Li<sub>2</sub>NiO<sub>2</sub> porous microsphere were synthesized by hydrothermal and subsequent calcinations methods using Li<sub>2</sub>SO<sub>4</sub>.H<sub>2</sub>O and Ni (NO<sub>3</sub>).6H<sub>2</sub>O as raw materials. The reasonable property could be attributed to the unique porous nanostructure with large volume for fast transportation of Li ions in hollow porous Li<sub>2</sub>NiO<sub>2</sub> spheres is beneficial to the high reversible capacity.

**Key words**:Porous materials, Microstructure, FTIR

(\*corresponding author: [sunandana@gmail.com](mailto:sunandana@gmail.com); C S Sunandana; Tel: +91-40-3010-500 ext, 4324;  
fax: +91-40-3010-120)

## I. Introduction

During the last two decades, there have been tremendous efforts in developing rechargeable lithium-ion battery with high energy density and long cycle life to meet the ever increasing demands of portable electronics, implanted medical device, and electric vehicles. One of the most promising future generation candidates for safe, low-cost and long-lasting high energy density rechargeable energy storage systems is without any doubt the porous materials.

In recent years, porous materials have received much attention because of their high specific surface areas and pore volumes, applicable in gas storage, catalysis, and photovoltaics. A porous structure can provide voids to cushion electrode materials from pulverization in lithium ion batteries [1–4]. Recently, many mesoporous structured materials have been developed as electrode materials for lithium ion batteries, including cathode materials such as LiCoO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, LiFePO<sub>4</sub> and LiTiO<sub>2</sub> [5–9]. Each of these materials demonstrates typical pore sizes, different wall thicknesses and a specific pore arrangement. Accurate control of the morphology of these materials is one of the major issues for many applications. Since nanoporous materials possess unique, beneficial chemical, physical, and mechanical properties, they can be used for a wide variety of applications which include catalysis, adsorption and separation, biological molecular isolation and purifications, environmental pollution control, chemical sensors, etc. In particular, nanoporous materials have attracted the attention of the scientific community, especially in

the field of semiconductors, microelectronics, electrode materials for batteries, fuel cells, super capacitors, and optical devices. This has been motivated the design and development of nanoporous materials. However, synthesis and modification of nanoporous materials are more challenging than commercial ceramics. The properties of materials can be tuned by their components, size and morphology, it is important to realize the controlled synthesis of a material [10, 11]. Recently, porous micro-nanostructures have attracted increasing interest owing to their large surface areas and wide applications in many fields [12–15]. The two-dimensional anisotropic structure of Li<sub>2</sub>NiO<sub>2</sub> possesses great structural flexibility against the volume variation during the charge-discharge process of a battery. However, unlike their hollow and mesoporous counterparts, the Li<sub>2</sub>NiO<sub>2</sub> have been less studied. We developed a novel approach to synthesize hierarchical flower-like spheres assembled from Li<sub>2</sub>NiO<sub>2</sub>.

Here we report a facile synthesis of high-quality, crystalline, mesoporous Li<sub>2</sub>NiO<sub>2</sub> spheres by a hydrothermal method. We strongly believe this basic study of Li<sub>2</sub>NiO<sub>2</sub> mesoporous nanostructures could exhibit superior electrochemical performance for reversible lithium storage in lithium-ion batteries and high charge-storage performance in super capacitors.

## 2. Experimental Section

The synthesis of  $\text{Li}_2\text{NiO}_2$  has been carried out in six steps described below

Step-1: Lithium sulfate ( $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ) and Nickel Nitrate  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  mixed in the ratio 1:2.

$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O} = 1.28 \text{ gm}$  (10 mM of Lithium sulfate)

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} = 5.816 \text{ gm}$  (20 mM of nickel nitrate)

Water ( $\text{H}_2\text{O}$ ) = 150 ml (double distilled Water)

Step-2: Both Lithium sulfate and Nickel nitrate mixed with 150 ml doubled distilled water and stirred 48 h to get uniform solution.

Step-3: Add 6 gm of NaOH to the solution, it is easily precipitating and the supernatant solution and precipitate solutions are separated.

Step-4: That precipitate solution contains unwanted chemicals such as  $\text{SO}_4$ ,  $(\text{NO}_3)_2$  and Na (sulphate Nitrate and sodium) are removed by washing and centrifuge 4-5 times with centrifuge spinning machine. The supernatant solution separated. The remaining precipitate solution is  $\text{Li}_2\text{NiO}_2$ , which is confirmed by XRD.

Step5: The solid solution is transferred to the Oven, which is at  $1000^\circ\text{C}$  for 24 h, after that taking out grinding 1h for making the  $\text{Li}_2\text{NiO}_2$  nano-powder.

Step6: The final reaction as follows and structure of  $\text{Li}_2\text{NiO}_2$  is confirmed with JCPDF card number 26-1175.



### Characterization techniques

The structure of the porous  $\text{Li}_2\text{NiO}_2$  was identified by X-ray diffraction (XRD) pattern using PHILIPS X-ray diffractometer with  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.54060 \text{ \AA}$ ) for diffraction angles  $2\theta$  between  $10-90^\circ$ . FTIR spectra of the samples were recorded on a Bruker Tensor 27 IR spectrometer by using KBr as dispersant. The morphology and crystal structure were analyzed by high-resolution FESEM (Zeiss, Model Ultra 55) coupled with energy dispersive spectrum.

## 3. Results and Discussion

Figure 1 shows the XRD patterns of the prepared porous spheres of  $\text{Li}_2\text{NiO}_2$  nanoparticles. All diffraction peaks can be completely indexed to orthorhombic structure crystalline  $\text{Li}_2\text{NiO}_2$ , indicating that there is no impurity in the  $\text{Li}_2\text{NiO}_2$  powder. The diffraction peaks at  $19.665^\circ$ ,  $33.7163^\circ$ ,  $38.984^\circ$ ,

$52.44^\circ$ ,  $59.44^\circ$ ,  $59.364^\circ$ ,  $62.987^\circ$ ,  $70.6244^\circ$ ,  $73.3005^\circ$  can be assigned to (002), (011), (103), (202), (114), and (204) (022), (121) and (017) planes of orthorhombic  $\text{Li}_2\text{NiO}_2$  (JCPDF no 26-1175). The Bragg peaks of the spherical clusters of  $\text{Li}_2\text{NiO}_2$  are markedly broadened, suggesting that very fine grain sizes and defects in the spherical clusters of  $\text{Li}_2\text{NiO}_2$  were produced in the synthesizing process.

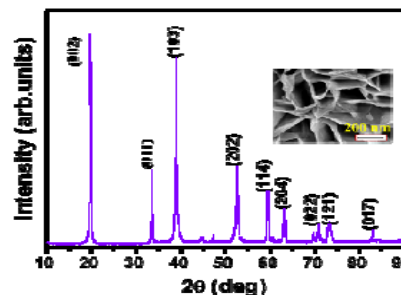


Figure 1. XRD pattern of  $\text{Li}_2\text{NiO}_2$  powder.

The crystallite size of  $\text{Li}_2\text{NiO}_2$  was calculated using the Scherrer equation, and the calculated crystallite sizes of  $\text{Li}_2\text{NiO}_2$  in the as-prepared spherical clusters of  $\text{Li}_2\text{NiO}_2$  are 20nm.

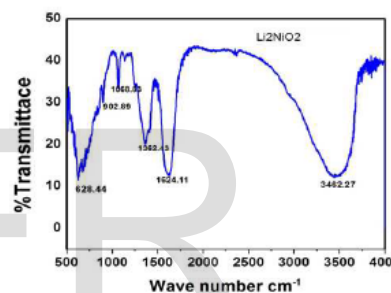


Figure 2. FTIR spectrum of  $\text{Li}_2\text{NiO}_2$

The molecular structural features and different vibrational modes of  $\text{Li}_2\text{NiO}_2$  have been extensively studied by infrared spectroscopy. The infrared (IR) spectrum of  $\text{Li}_2\text{NiO}_2$  was recorded in the wave number range  $500$  to  $4000 \text{ cm}^{-1}$  using FTIR spectrometer (Bruker Tensor 27 IR) as shown in figure 2. The vibrational motions in  $\text{Li}_2\text{NiO}_2$  can be divided into two classes; those that originate from the intra molecular vibrations of the  $\text{NiO}_2$  oxo – anion and the external optical modes of  $\text{NiO}_2$ . The IR spectra of  $\text{Li}_2\text{NiO}_2$  sample in the low wave number region ( $500-700 \text{ cm}^{-1}$ ) involves bending modes of  $\text{NiO}_2$  and in the high wave number region ( $700-1300 \text{ cm}^{-1}$ ) involves stretching vibrations. In  $\text{Li}_2\text{NiO}_2$ , the  $\text{NiO}_2$  and  $\text{NiO}_2$  are part of a ‘train’ a molecular ions train providing a framework for the structure. In the low wave number region, the bands at  $628 \text{ cm}^{-1}$  and  $902 \text{ cm}^{-1}$  are observed due to active symmetric and asymmetric bending modes of Ni-O bonds. These low frequency modes are thus particularly sensitive to the local environment and structure of the olivine lattice. In the high wave number region the band observed at  $1068 \text{ cm}^{-1}$  is assigned to the anti-symmetric stretching mode. The vibrations of the phosphate units are split into many components due to

the correlation effect induced by the coupling with of Ni-O units in the materials. A big peak at 3462 cm<sup>-1</sup> is observed in the spectrum corresponding to O-H stretching & deformation vibrations. It is identified as impurity peak of -OH group due to NiO<sub>2</sub>·2H<sub>2</sub>O. This rich spectrum thus gives the evidence that this sample is well crystallized.

The phase purity of the product was confirmed by x-ray diffraction (XRD) and energy dispersive spectrum, and it can be seen from the field-emission scanning electron microscope (FESEM) image that the sample contains uniform spheres of ~2 μm in diameter (fig. 3a). Under a higher magnification, the spheres are shown to have subunits pointing radially outward (fig. 3b). It was found that the concentration of NaOH in the system has an important effect on the assembly of the porous spheres building blocks into the hierarchical structure. Figure 3.c image taken in few micron scale for EDS analysis, the EDS spectrum in figure 3.d showing the good stoichiometry of our product. No other impurities was not detected.

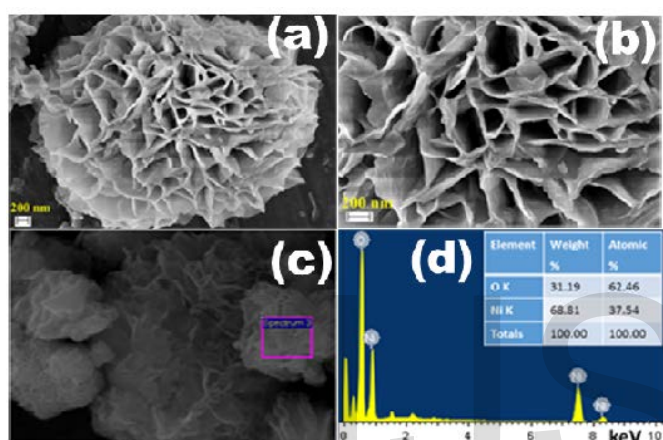


Figure 3. FESEM images of (a) Li<sub>2</sub>NiO<sub>2</sub> (b) High magnification of Li<sub>2</sub>NiO<sub>2</sub> (c) Large scale image for EDS analysis (d) EDS spectrum of Li<sub>2</sub>NiO<sub>2</sub>

#### 4. Conclusion

In summary, highly porous Li<sub>2</sub>NiO<sub>2</sub> microstructures have been successfully synthesized via a hydrothermal method. After heat treatment at 400 °C for 4 h the precursor was converted into the flower like porous sphere of Li<sub>2</sub>NiO<sub>2</sub>. The material has been characterized extensively by XRD for crystal structure, FTIR and FESEM for microstructure, EDS for elemental analysis. Sub-micron sized particles of Li<sub>2</sub>NiO<sub>2</sub> film with average crystallite size of 24 nm and the observed FTIR spectrum was assigned to stretching and bending modes of the Nickel Oxide group.

#### 5. References

1. D.L. Li, H. S. Zhou, I. Honma, Nat. Mater. 3 (2004) 65.
2. K.M. Shaju, P.G. Bruce, Adv. Mater. 18 (2006) 2330.
3. F. Jiao, P.G. Bruce, Adv. Mater. 19 (2007) 657.

4. K.X. Wang, M.D. Wei, M.A. Morris, H.S. Zhou, J.D. Holmes, Adv. Mater. 19 (2007) 3016.
5. F. Jiao, K.M. Shaju, P.G. Bruce, Angew. Chem. Int. Ed. 44 (2005) 6550.
6. J.Y. Luo, Y.G. Wang, H.M. Xiong, Y.Y. Xia, Chem. Mater. 19 (2007) 4791.
7. X.X. Li, F.Y. Cheng, B. Guo, J. Chen, J. Phys. Chem. B 109 (2005) 14017.
8. G.X. Wang, H. Liu, J. Liu, S.Z. Qiao, G.M. Lu, P. Munro, H. Ahn, Adv. Mater. 22 (2010) 4944.
9. Y. Ren, L.J. Hardwick, P.G. Bruce, Angew. Chem. 122 (2010) 2624.
10. D.S. Zhang, X. Du, L.Y. Shi and R. Gao, Dalton Trans., 41 (2012) 14455.
11. Y.H. Ni, Y. Zhu, X. Ma, Dalton Trans., 40 (2011) 3689.
12. H. Li, D.S. Zhang, P. Maitarad, L.Y. Shi, R. Gao, J. Zhang, W. Cao, Chem. Comm. 48 (2012) 10645.
13. D.S. Zhang, Y. Qian, L.Y. Shi, H. Mai, R. Gao, J. Zhang, W. Yu, W. Cao, Catal. Comm. 26 (2012) 164.
14. X. Du, D.S. Zhang, L.Y. Shi, R. Gao and J. Zhang, Nanoscale 5 (2013) 2659.
15. D.S. Zhang, T. Yan, H. Li and L.Y. Shi, Microporous Mesoporous Mater. 141 (2011) 110.