SYNTHESIS AND CHARACTERIZATION OF $Ni(OH)_2$ NANOPOWDERS AND NiO:8YSZ COMPOSITES

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By

Anurag Kumar

(Roll No. 110CR0623)

Under the guidance of

Prof. Bibhuti B. Nayak

Department of Ceramic Engineering
National Institute of Technology
Rourkela, Odisha - 769008

CERTIFICATE

This is to certify that the thesis entitled, "SYNTHESIS AND CHARACTERIZATION OF $Ni(OH)_2$ NANOPOWDERS AND NiO:8YSZ COMPOSITES" submitted by Anurag Kumar in partial fulfillment of the requirement for the award of Bachelor of Technology Degree in Ceramic Engineering at National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any Degree or Diploma.

Date:

Prof. Bibhuti B. Nayak

Dept. of Ceramic Engineering
National Institute of Technology Rourkela

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Anurag Kumar

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LIST OF ABBREVIATIONS

Sl. No.	*Abbreviation*	Full Form
1.	$Ni(OH)_2$	Nickel Hydroxide
2.	SEM	Scanning Electron Microscope
3.	XRD	X-Ray Diffraction
4.	NiO	Nickel Oxide

ABSTRACT

In the current work nickel hydroxide powder was synthesized through the precipitation method by using 0.5 molar sodium hydroxide solution, 1 molar nickel chloride hexahydrate solution and hydrazine hydrate solution. Three different powders were prepared by varying the amount of hydrazine hydrate solution (5 ml, 10 ml and 20 ml). XRD analysis of the as synthesis powders shows that on increasing the amount of hydrazine hydrate solution the powder becomes more crystalline and to get the amorphous nickel hydroxide synthesis requires small amount of hydrazine solution. Amorphous nickel hydroxide has smaller particle size and higher surface area of 132.87 m^2/g. Morphology of as-synthesised powders indicated that the lower amount of hydrazine results in particle size of nanometre range. The DSC-TG curve shows that there is maximum percentage of mass loss at around 300^0C which is due to conversion of nickel hydroxide into nickel oxide. The calcined powders of $Ni(OH)_2$ and 8 wt.% YSZ was used for preparing NiO: 8YSZ composites. Microstructure and EDS mapping was performed to understand the NiO distribution in 8YSZ matrix.

Keywords: Nickel hydroxide; Nickel oxide; YSZ; Anode; Microstructure, X-ray diffraction

1.1 Introduction:

Nickel hydroxide is widely used as the positive electrode material in nickel- based batteries because of its higher electrochemical performance. The electrochemical performance of amorphous nickel hydroxide is higher than that of high crystallization nickel hydroxide because of an ideal disordered structure. Nickel hydroxide is used as the positive electrode active material in the alkaline secondary batteries such as Ni/MH, Ni/Zn, Ni/Cd and Ni/Fe. On addition of nanoscale $Ni(OH)_2$ to the conventional spherical nickel hydroxide, the discharge specific capacity of electrode increases.

With the rapid progress of research and development of hydrogen storage alloy materials and nickel/metal hydride batteries (Ni/MH) in recent years, the preparation of high-performance nickel hydroxide electrode materials has become a critical issue. The practical importance of nickel hydroxide structure and its electrochemical properties is not only limited to battery application, nickel hydroxide or nickel oxide electrodes also find applications in fuel cells, electrochemical capacitors, electrolyzers, electrosynthetic cells, catalysts and electrochromic devices.

1.2 Polymorphic forms of Nickel Hydroxide:

There are two polymorphic forms of nickel hydroxide namely α- $Ni(OH)_2$ and β- $Ni(OH)_2$. During the charging- discharging process, α-$Ni(OH)_2$ and β-$Ni(OH)_2$ are transformed into γ- NiOOH and β- NiOOH respectively. It has been found that the electrochemical properties of α- $Ni(OH)_2$ is better than that of β- $Ni(OH)_2$. α- $Ni(OH)_2$ can be transformed to γ-NiOOH in a lower potential than that required for β- $Ni(OH)_2$ to β- NiOOH transformation. The α/γ system has a higher discharge capacity than that of β/β system [1].

Moreover the α/γ system can be transformed reversibly without any mechanical deformation and swelling of the electrode during the cycling process unlike the β/β system [2]. However, α- $Ni(OH)_2$ is unstable in strong alkali solutions and is converted to β- $Ni(OH)_2$. To stabilize α- $Ni(OH)_2$ has drawn attention a considerable attention from scientists and many efforts have been made in this field.

Ni:8YSZ composite is used as an anode material in SOFC (Solid Oxide Fuel Cell). A SOFC is an electrochemical device that converts chemical energy of a fuel and an oxidant gas directly into electricity. It has high operating temperature of about 600^0C-1000^0C. Main components of SOFC are electrolyte, cathode, anode and interconnect. Fuel such as H_2 is brought into the anode side. The oxygen gas is reduced to the oxide ion and migrates through

the electrolyte via ionic conduction to the anode. At the anode these oxide ions combine with the hydrogen and produce water and electrons. SOFC has many advantages over other fuel cells such as high energy conversion efficiency, low emission of pollutants and fuel flexibility which make it a suitable alternative of non-renewable energy resources.

Different materials used for anode are CeO_2, $SrTiO_3$, Ni:8YSZ, etc. but Ni:8YSZ is still the most preferred material. An anode must have high electrical conductivity, high electrochemical or catalytic activity and high porosity. Ni:8YSZ cernet satisfies these conditions. Nickel acts as an electron conductor and the catalyst for the anode reacrions. The functions of YSZ are to support the nickel metal particles and to provide an anode the thermal expansion coefficient matching to those of other cell components. It is reported that the volume % of nickel must be in the ratio between 40%-60% to achieve hogh conductivity, good porosity and mechanical strength.

The finer microstructure of Ni:8YSZ consisting of uniformly arranged Ni, YSZ and pore phases would result in increase in three phase boundary and better electrochemical performance.Among different methods of preparation of NiO:8YSZ nanocomposites, the combustion synthesis is a low cost and simple technique.

1.3 Applications of Nickel Hydroxide nanopowders and NiO: 8YSZ composites:

Nickel Hydroxide nanopowders:

(i) For the storage of electrochemical energy.

(ii) As an electrode material in electrochemical cell.

(iii) For chromosomal DNA quantification assay.

NiO: 8YSZ composites:

(i) As an anode material in SOFC.

2.1 Literature review

Guan Xiao-Yan *et al.* prepared and studied electrochemical performance of nano-scale nickel hydroxide with different shapes. They prepared nano-scale $Ni(OH)_2$ composite electrodes by mixing 10 wt.% samples with spherical $Ni(OH)_2$ to carry out charge–discharge test. The results showed that the nano-scale $Ni(OH)_2$ composite electrodes have higher discharge specific capacity and the nickel hydroxide nanoneedles show a better performance than the others. The elementary charge–discharge experiments revealed that the discharge specific capacity of $Ni(OH)_2$ electrodes with the obtained nano-sized $Ni(OH)_2$ addition is distinctly higher than that of microsized $Ni(OH)_2$ electrode, so the obtained β-Ni(OH)2 nanocrystals is expected to be a promising additive material for Ni/MH battery[3]. Changjiu Liu *et al*. studied the Structure and electrochemical performance of Y(III) and Al(III) codoped amorphous nickel hydroxide. The electrochemical performance of the sample was characterized by the charge/discharge test and cyclic voltametry. Their results showed that the amorphous nickel hydroxide codoped with Y(III) and Al(III) has many structural defects and therefore results in a relatively high specific capacity (351.83mAh/g at a charge/discharge rate of 0.2C)and good electrochemical reversibility[4]. Quansheng Song *et al.* studied the structural characteristics of nickel hydroxide synthesized by a chemical precipitation route under different pH values. The structural characteristics of the synthesized β-$Ni(OH)_2$, such as degree of crystallinity, crystalline lattice disorders, crystallite size and crystal growth orientation were strongly related to the pH values of the chemical precipitation reaction. The amounts of sulphate, carbonate and water species adsorbed in crystals, and the thermal stability of the β-$Ni(OH)_2$ also depended on the pH. Under relatively high pH values, the synthesized nickel hydroxide materials possessed a reduced crystallite size and lower thermal stability, more crystalline defects and a higher Ni composition. All these characteristics were likely to be advantageous for the improvement of electrochemical activity of nickel hydroxide [5]. Wei-Kang Hu *et al.* performed the evaluation of nanocrystal sized α- $Ni(OH)_2$ as an electrode material for alkaline rechargeable cells. The results showed that α-phase nickel hydroxide with nano-sized, well-crystallized particles exhibit not only a high electrochemical capacity up to 380–400 mAh/g, but also an excellent rate-capacity performance and long-time stability during electrochemical cycling with up to 100% overcharge as well as under a long-term float charge. In contrast, the β-phase nickel hydroxide showed a lower specific capacity and poorer cycling stability under similar overcharge cycling [6]. Xijiang Han *et al.* studied the morphology and electrochemical performance of nano-scale nickel hydroxide prepared by supersonic

coordination– precipitation method. They prepared nano-phase nickel hydroxide samples by a method combining supersonic and coordination-precipitation methods. The samples exhibit β-phase $Ni(OH)_2$ through X-ray diffraction analysis. It was shown that the grain size with the irregular grain shape is about 40 nm and ranges from 20 to 50 nm through transmission electron microscopy. Clustering phenomena were observed. The positive electrode discharge test made of a mixture of micrometre sized spherical $Ni(OH)_2$ and nano-phase $Ni(OH)_2$ was carried out. The results showed that the capacity of the electrode can be increased by about 14% when the nano-phase $Ni(OH)_2$ doped concentration is 8 wt.% [7]. Changjiu Liu *et al.* performed synthesis and characterization of amorphous α-nickel hydroxide. Amorphous α-nickel hydroxide was successfully synthesized by rapid freezing micro-emulsion precipitation method. The structure and property of the amorphous α-nickel hydroxide were characterized by XRD, TEM, IR, Raman spectra, and thermal gravimetric analysis. The results of the IR spectroscopy and thermal gravimetric analysis indicated that the amorphous α-nickel hydroxide contains water molecules and anions. Raman spectrum displayed more peaks indicating the highly disordered feature of the amorphous α-nickel hydroxide. Cyclic voltammogram and charge/discharge tests showed that the amorphous α-nickel hydroxide in alkaline media has a relatively high discharge capacity (350mAh/g) and good structural stability which indicates its potential application as an electrode material for secondary alkaline batteries [8]. Li ZHAO *et al.* prepared and studied the electrochemical performance of nano-scale $Ni(OH)_2$ doped with zinc. They prepared Nano-scale $Ni(OH)_2$ doped with Zn by precipitation transformation method and characterized by XRD and TEM. The electrochemical performance was investigated by cyclic voltammetry and constant current technology. The measurement results indicated that the lattice parameters of nano-scale $Ni(OH)_2$ were changed and the agglomeration of particles became obvious with the increased Zn-doped content. Compared with undoped one, the discharge specific capacities of nanoscale $Ni(OH)_2$ doped with 10% Zn are enhanced by 8% and 6%, respectively, at the discharge rate of 0.2*C* and 3*C*[9]. Jeerapan Tientong *et al.* synthesized Nickel and Nickel Hydroxide Nanopowders by Simplified Chemical Reduction. Nickel nanopowders were synthesized by a chemical reduction of nickel ions with hydrazine hydrate at pH ~12.5. Sonication of the solutions created a temperature of 54–65°C to activate the reduction reaction of nickel nanoparticles. The solution pH affected the composition of the resulting nanoparticles. Nickel hydroxide nanoparticles were formed from an alkaline solution (pH~10) of nickel-hydrazine complexed by dropwise titration. X-ray diffraction of the powder and the analysis of the resulting Williamson-Hall plots revealed that the particle size of the powders ranged from 12 to 14 nm. Addition of polyvinylpyrrolidone

into the synthesis decreased the nickel nanoparticle size to approximately 7 nm. Dynamic light scattering and scanning electron microscopy confirmed that the particles were in the nanometer range [10]. H. B. Li *et al.* prepared amorphous nickel hydroxide nanospheres with ultrahigh capacitance and energy density as electrochemical pseudocapacitor materials. The amorphous nickel hydroxide electrode exhibited high capacitance (2,188 F/g), and the asymmetric pseudocapacitors of the amorphous nickel hydroxide exhibited high capacitance (153 F/g),high energy density (35.7Wh/kg at a power density of 490W/kg) and super-long cycle life (97% and 81% charge retentions after 5,000 and 10,000 cycles, respectively). The integrated electrochemical performance of the amorphous nickel hydroxide was commensurate with crystalline materials in supercapacitors. These findings promoted the application of amorphous nanostructures as advanced electrochemical pseudocapacitor materials [11]. Takehisa Fukui *et al.* Synthesised NiO:YSZ composite particles for an electrode of solid oxide fuel cells by spray pyrolysis. The NiO:YSZ composite particle that has NiO grains uniformly covered with fine YSZ grains was formed after the final sintering stage up to 1000°C[12]. Swadesh K. Pratihar *et al.* Prepared nickel coated YSZ powder for application as an anode for solid oxide fuel cell. Nickel-yttria stabilized zirconia (Ni-YSZ) cermet is widely used as an anode material for solid oxide fuel cells (SOFCs). While the nickel-to-nickel chain maintains the electrical conductivity path, the YSZ contributes to lowering the thermal expansion and inhibits nickel coarsening during high temperature (1000 ◦C) operation. An electroless technique is employed to prepare a uniform nickel coating on the YSZ powder [13]. Kazuyoshi Sato *et al.* synthesized NiO/YSZ nanocomposite particles via co-precipitation method for electrochemically active Ni/YSZ anode. They investigated the effect of pH on the morphology of the composite particles, as well as on the microstructure and the electrochemical property of the Ni/YSZ anode. The particles synthesized at pH 10 involved aggregated composites and large NiO.

EXPERIMENTAL WORK

3.1 Synthesis of Nickel Hydroxide powder:

Nickel hydroxide was synthesized by precipitation method using molar solution of nickel chloride hexahydrate ($NiCl_2.6H_2O$), semi molar solution of sodium hydroxide (NaOH) and varying concentration (5ml, 10ml, and 20ml) of hydrazine hydrate (N_2H_5OH). After synthesis, the precipitate of nickel hydroxide was formed. The precipitate powder was washed several times with hot DI water. The solution was filtered using Whatmann filter paper. The filtrate was dried for 4 hours at 100^0C. The dried mass was grinded properly using an agate mortar. In this way fine powder of nickel hydroxide was obtained.

The above process was repeated two more times with different stated amounts of hydrazine. Finally three different types of nickel hydroxide powders were obtained. These powders were calcined at 500^0C and 650^0C in pit furnace with soaking time of 1 hour.

3.2 Preparation of NiO:YSZ composite:

Two composites were prepared using the nickel hydroxide powders calcined at 650^0C (powders prepared with 5 ml and 20 ml hydrazine hydrate). For preparation of composites equal amounts of calcined nickel hydroxide powder and YSZ (Yttria Stabilized Zirconia) powder were taken. Powders were mixed properly in an agate mortar. 3% PVA (Poly Vinyl Alcohol) solution was added dropwise and the content was mixed properly.

The final content was pressed using a hydraulic press at a pressure of 5.1 tonnes and dual time of 120 sec. The pressed mass was dried in a drying oven at 100^0C for 1 hour. The dried mass was sintered at 1300^0C for 1 hour. In this way composites were ready for their characterisations.

3.3 General Characterization:

3.3.1 Bulk Density (BD) and Apparent Porosity (AP):

The bulk density (BD) and apparent porosity (AP) of the composites were calculated by Archimedes principle using vacuum method in water medium.

The apparent porosity and bulk density were calculated as follows:

W_d =Dry weight of the sample,
W_s = Soaked weight of the sample,
W_a =Suspended weight of the sample

$$\text{Apparent porosity} = [(W_s-W_d)/(W_s - W_a)]\times 100$$

$$\text{Bulk density} = W_d/(W_s - W_a)$$

3.3.2 Thermal Analysis:

Thermal decomposition of $Ni(OH)_2$ powder to NiO powder was studied using thermogravimetric and differential scanning calorimetry DSC/TG by heating the sample at 100°C/min in N_2 atmosphere in a thermal analyser (Model Netzsch, STA 449C). Alpha alumina was used as reference material.

3.3.3 X-ray Diffraction:

Phase analysis was studied using the X-ray diffraction (Rigaku, Japan) at room temperature with filtered 0.154056 nm Cu-Kα radiation. Samples were scanned in a continuous mode from 20^0-80^0 at a scanning rate of $20^{0/min}$.

3.3.4 Microstructural analysis:

Microstructural features were studied using Felid Emission Scanning Electron Microscope (NOVA, NanoSEM). For preparation of sample, the powder was dispersed in isopropyl alcohol in an ultra-sonication bath (20 kHz, 500 W) for half an hour for removing the debris. One pinch of the well-grinded sample powder was deposited on to the carbon tape pasted on the brass plate. This brass plate was coated for 1 minute and then used for microscopy.

3.3.4 Brunauer–Emmett–Teller (BET) Analysis:

Surface area of the powder was measured by BET analysis (Quantachrome). The sample powder was degased at a degasing temperature of 150^0C for 2 hours.

RESULTS AND DISCUSSION

4.1 Thermal Analysis (DSC-TG):

Figure 1 shows the DSC-TG curves of as synthesized nickel hydroxide powders synthesized using 5 ml hydrazine. Two endothermic peaks were observed in the DSC curve, in which the first endothermic peak is at around 150^0C due to the removal of adsorbed water molecules and the second peak at around 300^0C corresponds to the decomposition of nickel hydroxide into nickel oxide. These endothermic peaks are also supported by weight loss in TG curve in which a mass loss of about 5% occurs at around 150^0C which is due to removal of water molecules and mass loss of about 20% occurs at around 300^0C which is due to conversion of nickel hydroxide into nickel oxide.

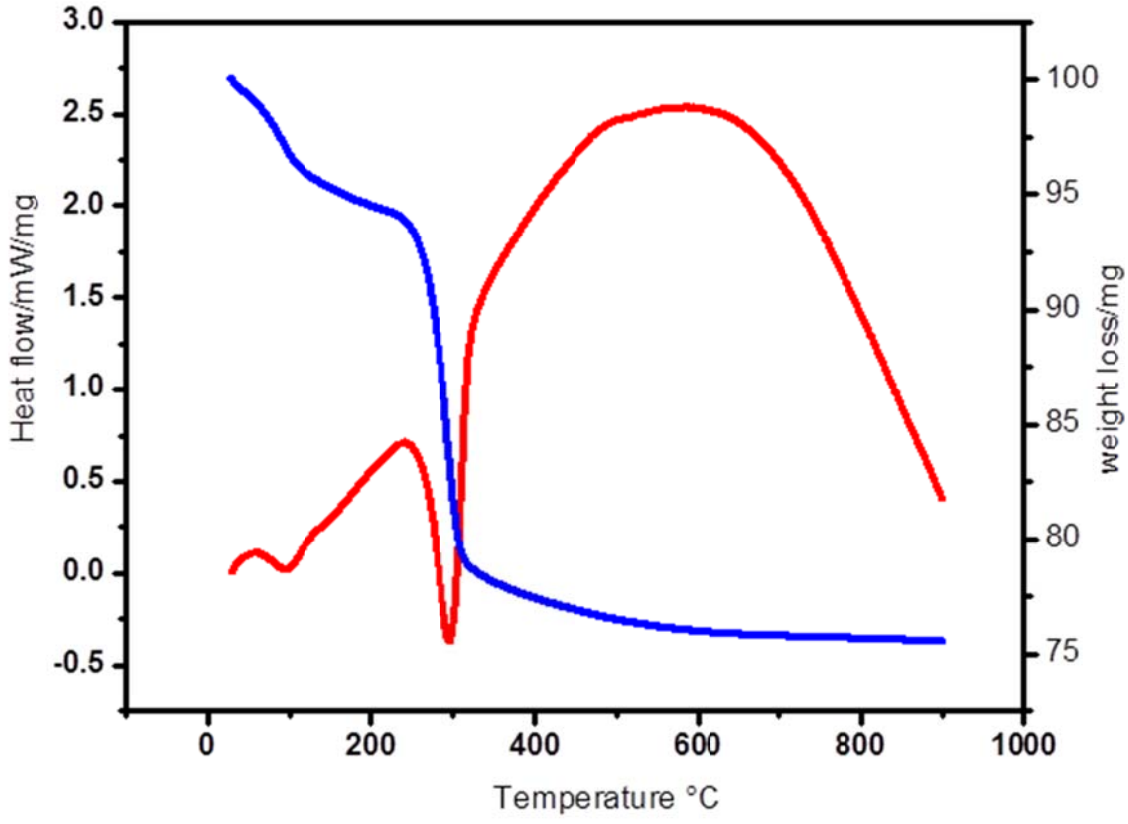
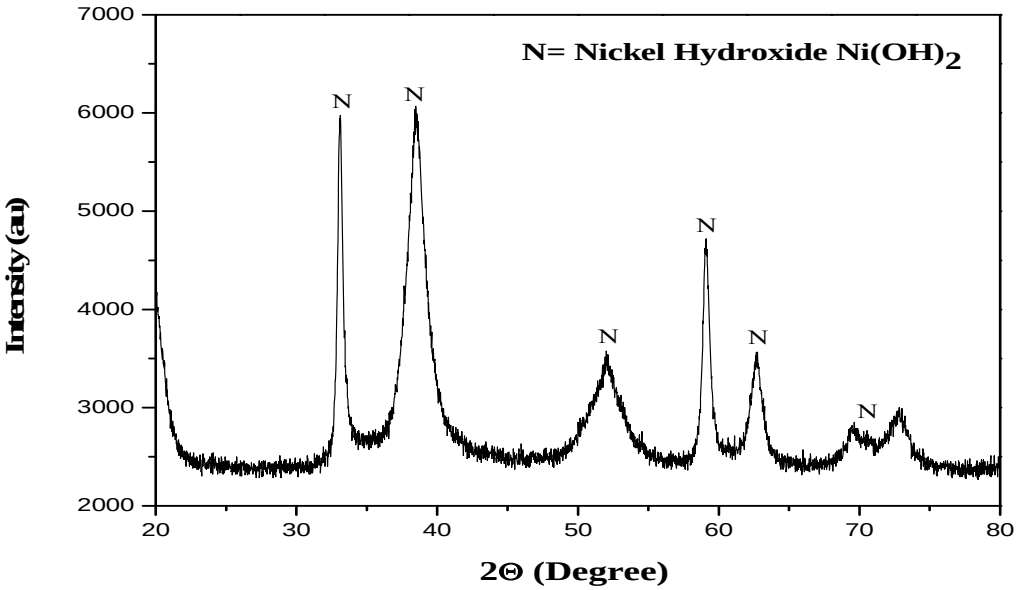


Fig 2: DSC-TG curve of as synthesized $Ni(OH)_2$ powder

4.2 Structural Analysis (XRD):

The results of XRD analysis are shown in Figures 2, in which Figure 2 (a) and (b) shows the XRD patterns of as synthesized $Ni(OH)_2$ powders prepared using 5 ml and 20 ml HH, respectively. All the peaks correspond to crystalline $Ni(OH)_2$, which matches with the JCPDS file no. 01-1047. It is observed that the crystallilnity of these $Ni(OH)_2$ powders increase with increase in amount of HH.



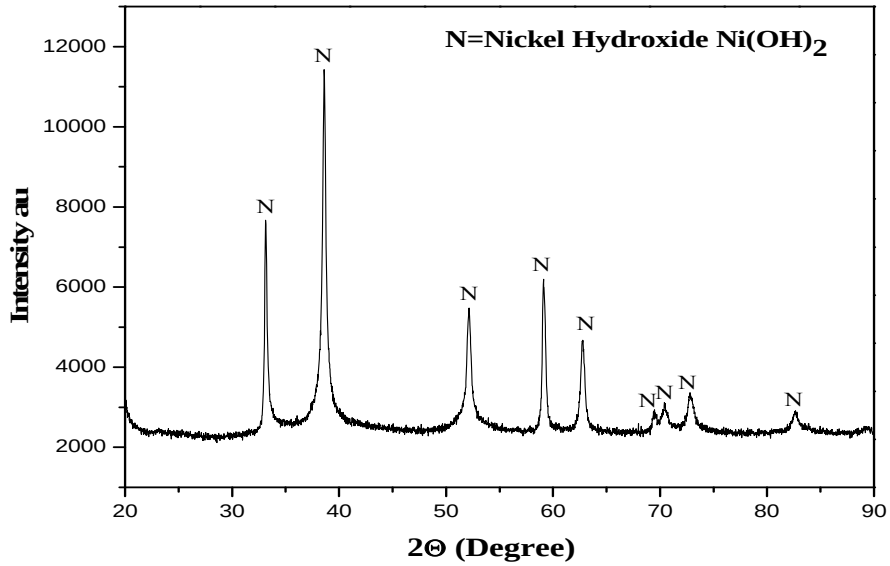


Fig 2(b): XRD pattern of as synthesized nickel hydroxide powder prepared using 5 ml HH (a) and 20 ml HH (b)

The crystallite sizes of these $Ni(OH)_2$ powders were found to be 6 and 35 nm synthesized using 5 ml and 20 ml HH, respectively.

After calcination at 650°C, the $Ni(OH)_2$ gets converted into crystalline NiO, the XRD pattern of which is shown in figures 3(a) and (b). The XRD patterns match with the JCPDS file no. 73-1523. These XRD patterns further confirms that above 300°C, the crystalline $Ni(OH)_2$ decomposes to give crystalline NiO. Also, there is no as such difference between these patterns, which proves that after calcination both the powders with different amount of HH, gives NiO.

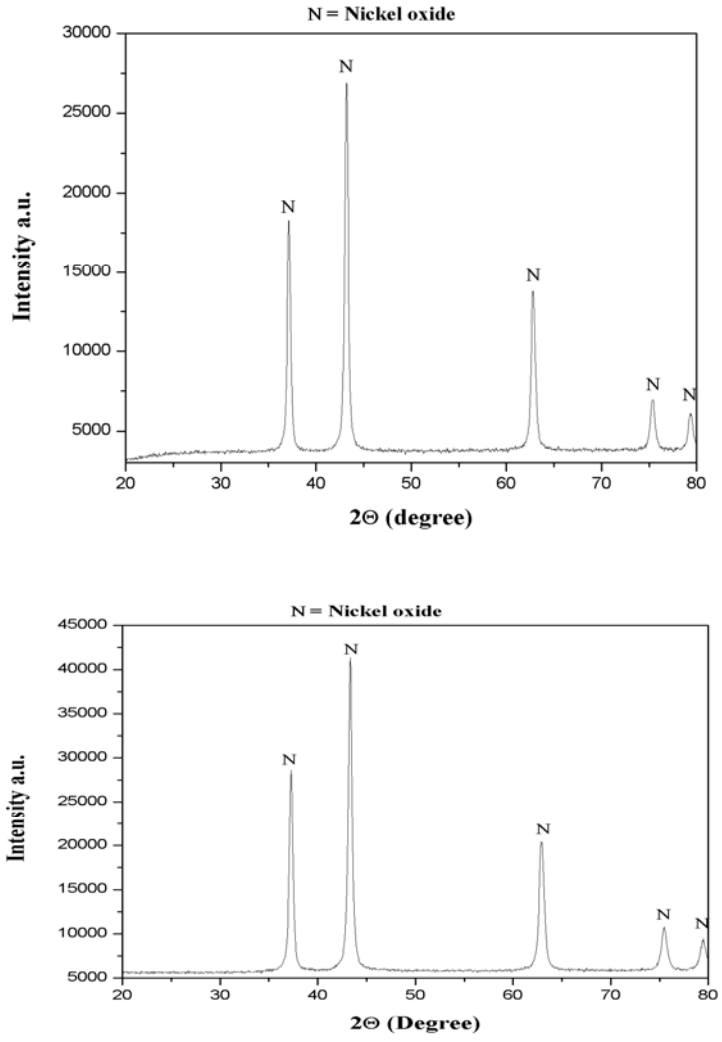


Fig 3: XRD patterns of calcined (650°C) nickel hydroxide powders synthesized using 5 ml (a) and 20 ml (b) HH.

4.3 Surface area analysis (BET):

The BET surface area of the as synthesized $Ni(OH)_2$ powder was found to be 132.87 m^2/g. The average particle size can be estimated by assuming all the particles to have the same spherical shape and size. The average particle diameter, D, is given by:

$$D = 6 / (S_{sp}.d_a)$$

where S_{sp} is the specific surface area per unit mass of the sample and d_a is the true density.

$$d_a = 4.10 g/cc \text{ for } Ni(OH)_2$$

Therefore, the average particle size of the powder is found to be approximately 11 nm.

4.4 Field Emission Scanning Electron Microscopy:

FESEM images (Fig. 4) give the microstructure of as synthesized nickel hydroxide powders. Both the nickel hydroxide powders synthesized using 5 ml and 20 ml HH are found to be agglomerates of very fine particles less than 100 nm.

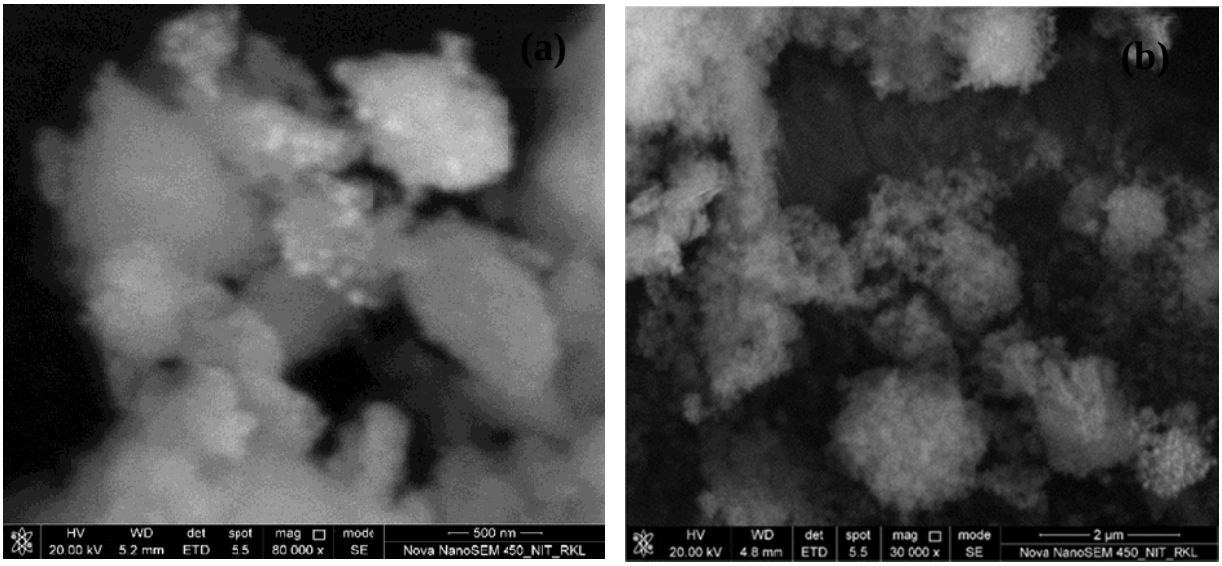


Fig 4: (a) Morphology of nickel hydroxide powders synthesized using 5ml (a) and 20 ml (b) HH.

4.5 Density Measurement:

The density of the composites was measured by Archimedes principle. The percentage bulk density and percentage apparent porosity of both the composites are shown in table 1.

Sample name	%BD	%AP
Composite 1 (5 ml HH)	88.97	11.03
Composite 2 (20ml HH)	96.37	3.63

4.6 Microstructural Analysis:

Microstructure of composite 1 and composite 2 shows that the zirconia particles and nickel oxide particles are densely packed. Secondary images of composites show that nickel oxide particles are uniformly distributed among the zirconia particles. Nickel oxide particles are also present on the surface of the zirconia particles.

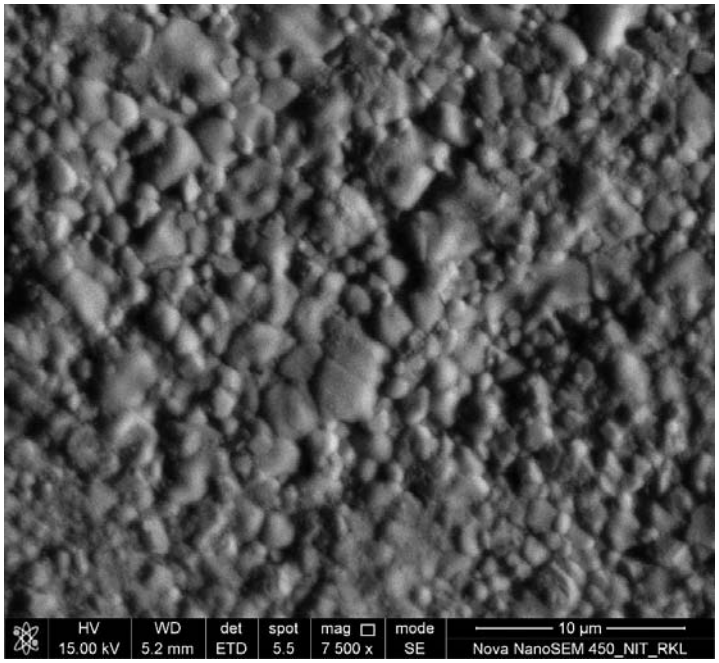


Fig 6(a):Microstructure of composite 1

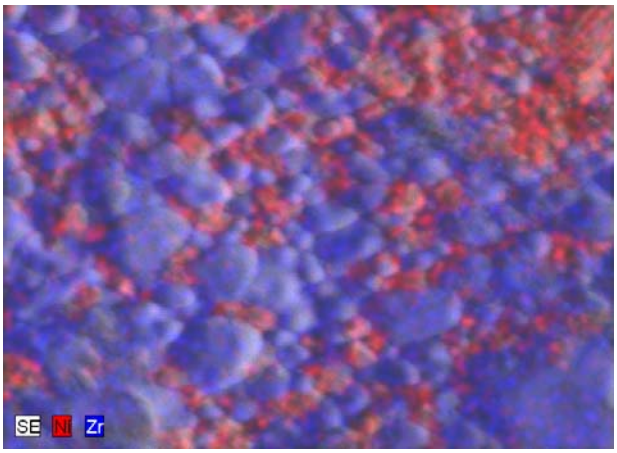


Fig 6(b): EDS mapping image of composite 1

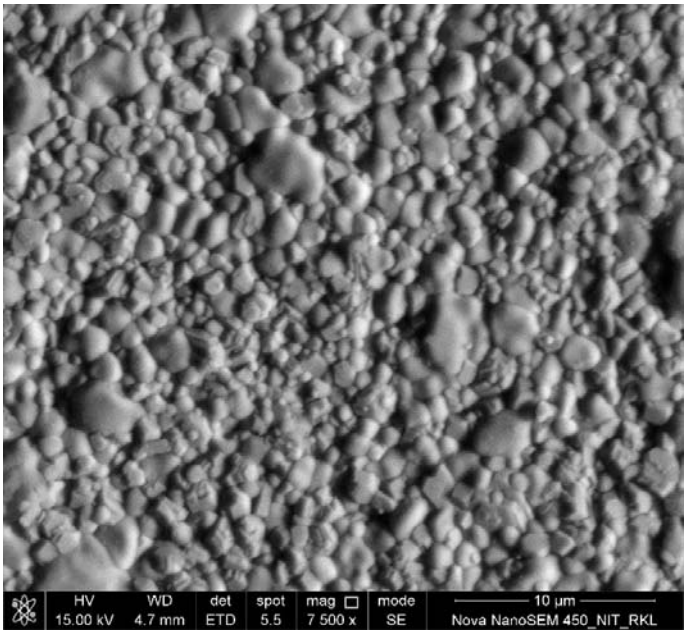


Fig 7(a): Microstructure of composite 2

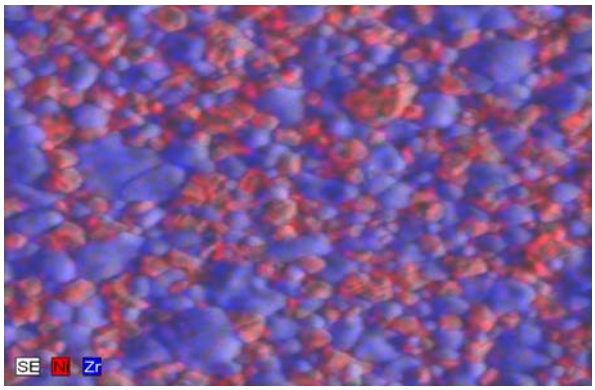


Fig 7(b): EDS mapping image of composite 2

CONCLUSIONS

Different amount of HH results in different crystallite size of as synthesized $Ni(OH)_2$ powder. 5 ml hydrazine hydrate prepared sample shows smaller crystallite size than 10 or 20 ml prepared samples. The crystallite size of 5ml HH powder is 6 nm whereas that of 20 ml HH powder is 35mm. This shows that on increasing the amount of HH the crystallite size of powder increases. The BET surface area of 5ml HH as synthesized powder is 132.87m^2/g. This makes it suitable for electrode material in electrochemical cell. The composite prepared using the calcined nickel hydroxide and YSZ shows the uniform distribution of zirconia and nickel oxide particles. The nickel oxide particles are also present on the surface of zirconia particles. The process of making NiO: 8YSZ via $Ni(OH)_2$ powder may also help to make Ni:8YSZ composite, which may be used as an anode material in solid oxide fuel cell.

Future work

To prepare Ni: 8YSZ cermet using $Ni(OH)_2$ nanopowders and 8YSZ powders through various methods such as solid state route, co-precipitation route for suitability as anode material for IT-SOFC applications. Different characterization such as microstructure, EDS mapping, electrical conductivity and TEC may be evaluated for different samples prepared by different methods.

References:

1. R. Barnard, C.F. Randell and F.L. Tye, J. Appl. Electrochem**.,** 10, 109 (1980)
2. P. V. Kamath, M. Dixit, L. Indira, A. K. Shukla, V. G. Lumar and N. Munichandraiah, J. Electrochem. Soc., 141, 2956 (1994)
3. Guan Xiao-yan and Deng Jian-cheng. 61 (2007) 621–625
4. Changjiu Liu, HuabinWu and YanweiLi, Journal of Physics and Chemistry of Solids 70 (2009) 723–726
5. Quansheng Song, Zhiyuan Tang, Hetong Guo and S.L.I. Chan, Journal of Power Sources 112 (2002) 428–434
6. Wei-Kang Hua, Xue-Ping Gao, Dag Noreus , Trygve Burchardt and Nils K. Nakstad, Journal of Power Sources 160 (2006) 704–710
7. Xijiang Han, Xiaomei Xie, Chongquan Xu, Derui Zhou and Yongli Ma, Optical Materials 23 (2003) 465–470
8. Changjiu Liu and Yanwei Li, Journal of Alloys and Compounds 478 (2009) 415–418
9. Li ZHAO, Zhi-hao LIU and Lei JIN, Trans. Nonferrous Met. Soc. China 23(2013) 1033−1038
10. Jeerapan Tientong, Stephanie Garcia, Casey R. Thurber and Teresa D. Golden, Journal of Nanotechnology, Volume 2014, Article ID 193162
11. H. B. Li, M. H. Yu, F. X. Wang, P. Liu, Y. Liang, J. Xiao, C. X. Wang, Y. X. Tong & G. W. Yang, DOI: 10.1038/NCOMMS2932
12. Takehisa Fukuia, Satoshi Oharaa, Makio Naitoa, Kiyoshi Nogi, Powder Technology 132 (2003) 52– 56
13. Swadesh K. Pratihar, A. Das Sharma, R.N. Basu, H.S. Maiti, Journal of Power Sources 129 (2004) 138–142
14. Kazuyoshi Sato, Go Okamoto, Makio Naito, Hiroya Abe, Journal of Power Sources 193 (2009) 185–188.