CHAPTER 1

Electrical impedance analysis for nano crystalline NiO prepared by combustion method

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Abstract

Nanocrystalline NiO material has been synthesized using a tartaric acid based sol-gel combustion method. The obtained XRD peaks for various calcinating temperatures have been analyzed and reported. The XRD particle size is determined by using the Scherrer formula and it is found to be ~27nm at 600 °C. The structural identification of NiO has been done using Fourier transform infrared spectroscopy (FTIR). The spherical shaped agglomerated NiO particles are characterized by using the SEM technique and the atomic percentages are verified by EDX techniques. The electrical conductivities of sintered NiO are evaluated through an impedance analysis and the activation energy is found to be 0.21 eV.

Keywords

Nanocrystalline, XRD, SEM, Impedance, Electrical Conductivity, Cathode Materials

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1. Introduction

Nickel oxide is one of the most interesting transition metal oxides and it has enormous attention due to its usage in different applications such as magnetic devices [1], electrochromic films [2], gas sensors [3,4], dye sensitized photo cathodes [5,6], catalysis [7], etc. Nano crystalline nickel oxide has more enhanced properties than the micro sized particles because of the quantum size effect, surface effect, macroscopic quantum tunneling effect and volume effect [8]. The reduction of the grain size in nano sized NiO material is better for the capacitive enhancement and has proven more advantages for enhancing electrochemical energy storage properties including power and energy density [9, 10]. It has a high ion and electron transport because of the large surface to volume ratio and also the formation of a short diffusion pathway between the nano grains [11,12]. Nano materials are easily adopted in materials science because of their novel properties due to their size and shape. Also, new synthetic approaches are available for getting nano samples and to enhance their growth mechanisms, etc. Thus, several synthesis methods are attempted to prepare the nano particles in different forms such as nano grain, nano rod, nano sheet, etc. Dual fuel based combustion is one of the methods to prepare nano crystalline materials [13]. Citric acid and tartaric acid are used as a fuel and capping agent to make very fine nano sized metal oxide particles. In this study, an attempt has been made to synthesize nano crystalline NiO materials by a citric acid and tartaric acid based combustion process.

2. Material synthesis

Analytical grade nickel nitrate was used as a precursor material and citric acid and tartaric acid are used as fuels of the tartaric acid based sol-gel combustion method. Fig 1. shows the preparation of nano crystalline NiO powder by the combustion method. Stoichiometric amount of nickel nitrate was added with distilled water and the solution was marked as label A. The citric acid and tartaric acid were weighed as per 1:1 metal ion ratio and they were dissolved with distilled water. The solution was named as B. Solution B was added drop wise to solution A and the final mixture was stirred continuously under heating resulting in a transparent resin. The sticky resin was dried at 150° C at a heating rate of 1°/min. Then, it was calcined at different temperatures and characterized by

various techniques such as XRD, FTIR, SEM-EDX. Electrical conductivity of the sample was analyzed using the experimentally measured impedance parameters. The powder X-ray diffraction (XRD) patterns were obtained using Bruker made X-ray diffractometer (D8 advanced ECO XRD systems with SSD160 1 D Detector) with monochromatic Cu K α radiation ($\lambda = 1.5418\text{\AA}$) at diffraction angle between 5° to 120° . Infrared spectroscopic analysis was carried out with a Shimadzu FTIR-8700 Fourier transform infrared spectrometer in the wavelength range 800 to 350 cm^{-1} . For electrical conductivity analysis, the nano crystalline NiO sample was pelletized and sintered at 600°C and the sintered pellets were painted with silver paste and annealed at 300°C . The electrical impedance was measured using Hioki made impedance analyzer in the frequency range 40 Hz to 1MHz .

Figure. 1 Preparation of nano crystalline NiO powder by the sol-gel combustion method

3. Results and discussion

3.1 X-ray diffraction studies

Figure. 2 XRD patterns for NiO sample, calcined at various temperatures and Rietveld refinement profile, calcined at 600° C.

The observed diffraction patterns and Rietveld refined diffraction patterns are shown in fig.2. The observed broad lines signify that the crystallite size is small. Additional X-ray diffraction peaks other than allowed for the system are not observed in the X-ray patterns, this fact indicates the high degree of phase purity in the synthesized NiO materials. The

observed X-ray peaks indicate the formation of cubic phase NiO nano particles and this is verified through the JCPDS data (#00-047-1049) [14]. All the observed peaks were indexed as face centered cubic structure of NiO crystalline material. The lattice parameter of NiO is found to be $a = 4.2154^\circ$. The observed peaks confirm that the precursors and fuels have no role to play in the crystal structure. The crystallite size is also evaluated using the Scherrer formula and it is found to be $\sim 27\text{nm}$ for the sample calcined at 600°C .

3.2 FTIR studies

Figure. 3 FTIR Spectra for NiO sample, calcined at various temperatures.

Fig. 3. shows the FTIR spectra for NiO materials, calcined at different temperatures within the frequency range of 800 cm^{-1} to 350 cm^{-1} . The observed broad FTIR peak at 450 cm^{-1} , indicates the formation of a NiO band [15]. At increased temperatures, the broadening of the FTIR peaks also increases, which confirms the growth of NiO particles.

3.3 SEM-EDX analysis

SEM images of the NiO samples, calcined at 250° , 400° and 600° and the STEM image of NiO sample, calcined at 600° are shown in figs.4a-d. The SEM images show spherical shaped particles, having size $\sim 50\text{nm}$. With increasing sintering temperature, the particle

size also increases. STEM image also show a particle size of around $\sim 50\text{nm}$. EDX spectrum confirmed the existence of Ni and O in the NiO sample, calcined at 600° as shown in fig. 5. Table 1 of EDX data shows the individual atomic percentage of NiO sample, which confirms the stoichiometry of the synthesized nano crystalline NiO sample.

Table 1: Atomic weight percentage of elements obtained from EDX spectra.

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (3 Sigma) [wt.%]
Oxygen	K-series	17.38	85.30	95.51	7.24
Nickel	K-series	3.00	14.70	4.49	0.51
Total		20.37	100.00	100.00

Figure. 4 a,b,c,d SEM images for NiO samples, calcined at 250°C , 400°C and 600°C and STEM image of the NiO sample at 600°C .

Figure. 5 EDX spectrum for NiO samples, calcined at 600 °C.

3.4 Electrical impedance studies

Fig.6 shows the electrical impedance plot for the NiO sample, heat treated at different temperatures. The value of the impedance decreases while the sintering temperature increases. The complex impedance data is fitted using Z- data software.

Figure. 6 Electrical impedance plot for NiO samples, sintered at 600 °C and Figure. 7 Electrical impedance plot with Equivalent circuit for NiO samples, heat treated at 70°C.

Fig 7. shows that the fitted electrical impedance plot of the NiO sample, heat treated at 70°. The impedance plot shows a semicircle which is equivalent to parallel combination of a resistance and a capacitance. The bulk impedance is measured by extension of the semicircle on the x-axis [16]. Bulk impedances of the sample are measured for NiO nano materials, heated at various temperatures. The bulk conductivity is also calculated using

the relation $\sigma = 1/RA$. Fig.8. shows $\log(\sigma T)$ vs $1000/T$ plot for the NiO sample, sintered at 600° . Using the plot of conductivity vs temperature, the activation energy is evaluated and is found to be 0.213eV.

Figure. 8 $\log(\sigma T)$ vs $1000/T$ plot for nano crystalline NiO sample, sintered at 600° C and Figure. 9 $\log(\sigma)$ vs $\log(\omega)$ plot for nano crystalline NiO sample, sintered at 600° C.

Fig 9. shows the plot of ac conductivity for various frequencies of NiO nano materials. The DC conductivity at lower frequencies increases with rising temperature. Fig.10. shows the plot of frequency dependent ac electrical conductivity. It is seen that the peak frequencies are shifted towards higher frequencies with rising temperature.

Figure. 10 $\log \sigma$, $\log(-Z'')$ vs $\log \omega$ plot for sintered nano crystalline NiO sample, heat treated at difference temperatures.

3.5 Transference number studies

Figure 11. Polarization current as a function of time for nano crystalline NiO sample at RT.

The ionic and electronic transference numbers have been evaluated for nano crystalline NiO sample pellet, sintered at 600° C using the DC polarization technique by applying an voltage of 1V. Fig. 11 shows the polarization current as a function of time for nano crystalline NiO sample. The decreasing polarization current can be attributed to migration of ions due to the applied field and balanced by the diffusion due to the concentration gradient [17]. Thus, the resulting current is only due to the electrons and holes. The ionic and electronic transference numbers are calculated by DC polarization techniques using the relation $t_i = (I_f - I_e)/I_t$ and $t_e = (I_f/I_e)$. The ion transference number is found to be 0.93 and electron transference number 0.07.

4. Conclusions

Nano crystalline NiO material has been synthesized by the tataric acid based combustion method. The recorded XRD pattern confirms that the obtained peaks correspond to NiO with cubical structure. FTIR peaks confirm the NiO band structure. SEM images show agglomerated nano sized spherical particles. EDX spectrum has confirmed the presence of stoichiometric Ni and O elements in the NiO sample. Bulk impedance and conductivities have been analyzed and the activation energy is found to be 0.21eV. The transference numbers have been evaluated through DC polarization techniques. It indicates the possibility of ionic and electronic motion in the NiO samples. These results can be applied to cathode materials in a solid state battery.

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