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Synthesis and Electrochemistry of Nanostructured Nickel Oxide for Energy Storage Ultracapacitor Applications

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Abstract

Nano nickel oxide (NiO) is synthesized facially and hydrothermally. XRD confirms FCC as NiO crystal structure. FT-IR proves functional groups and purity levels. NiO electrochemistry is fully revealed using CV, GCD and EIS, in 1M KOH electrolyte. CV identifies the PC behavior of NiO, via observing redox peaks. Furthermore, the GCD curve exhibits the specific capacitance 185F/g, at a current density 0.3A/g, with superior cyclic stability of 93%, up to 1500cycles. Research results confirm the Nano NiO is suitable for ultra-capacitive applications. Nanosheet array performs better than nanoparticle coat.

Keywords: *Hydrothermal, electrode, nanoscience, nanomaterial, nanosheet, nickel oxide, supercapacitor, ultracapacitor*

INTRODUCTION

Batteries or capacitors are conventional energy storage devices. Ultracapacitor or supercapacitor is the latest and best way to store energy. It provides high power and energy density. It exhibits long cycle life, low internal resistance, fast charging, fast discharging, harmless, and low cost [1, 2]. Furthermore, it is possible to interface with batteries and fuel cells in hybrid electric vehicles. It aids hybrid vehicles due to high power and energy [3−8]. Ultracapacitors are 2 types: EDLC and PC. Carbon-based materials such as fullerene, graphene, graphite, SWCNT, MWCNT, and activated carbons, are used in EDLC. On the other hand, metal oxides, conducing polymers and composite are widely used in PC. PC shows superior rate capability with high specific capacitance and virtuous life cycles. PC is better than EDLC. Device performance depends on the electrode materials (morphology, size, porosity, surface area and etc.), electrolytes, and interaction between electrode and electrolytes. Currently, RuO_2 is widely used in energy storage >1580F/g. RuO_2 is endowed with other good features such as charge-discharge characteristics and electrical conductivity. High price and lethal nature of RuO_2 restricts its commercialization. So, researchers have developed another class of materials, such as manganese oxide, nickel oxide, cobalt oxide, copper oxide, etc., as electrode materials for supercapacitor applications. Each and every material has its own merits and demerits. Current research focuses on the development of NiO as an electrode material due to its fabulous properties of high charge transfer rate, well distinct redox performance, low cost, p-type semiconductor, and good chemical and thermal stability with environmental friendly [2−8]. There are numerous synthesis approaches exist to synthesis nanostructured NiO with different shapes and sizes such as microwave, wet-chemical, hydrothermal, sonochemical, precipitation, pulsed laser deposition and micro-emulsion process, etc.

Hydro-thermal is applied with facile synthesis on Ni-form [2−8]. Crystallinity,

surface purity and surface morphologies are examined by XRD, FT-IR and FE-SEM respectively. Further, the electrochemical performances are inspected using CV, EIS and GCD. EIS and GCD is done in presence of 1M KOH electrolyte [2].

NANOSYNTHESIS

In this review article, hydrolysis plus thermal process method is explained to synthesis NiO, without any surfactants, and complex process [2−8]. Reagent chemicals used are: nickel chloride hexahydrate ($NiCl_2.6H_2O$) and potassium hydroxide (KOH).Synthetic process involves: mixing 1M $NiCl_2$ and 2M KOH, stirring for 30min, heating whole mix in 50 ml Teflon-coated stainless steel at 130°C for 5h, washing products with deionized water, and drying at 90ºC.Characterisationof: nano NiO product is done for its crystallinity, surface purity and surface morphology. XRD measures crystallinity. XRD analysis is done by using X-ray diffractometer with CuKα radiation (λ=1.5406Å). FT-IR spectroscopy is done to identify the presence of functional groups, and to obtain surface purities. Microstructures and particle sizes are studied via FE-SEM. Fig.1 shows the XRD diffraction peaks @ 2θ = 37.2º, 43.2º and 63.0º correspond to the (111), (200) and (220) planes respectively. Observation is well indexed with the standard FCC structure of NiO with Fm3m space group. There are no other peaks observed in XRD, which is confirmed the purity of material. Fig. 2 shows the FT-IR spectrum of nano NiO. The strong band at 445cm^{-1}corresponds to the vibration of Ni–O bond. Moreover, the broad absorption band centered at 3445$cm^{-1}$is attributable to the band O–H stretching vibrations, due to the fact that the NiO may tend to physically adsorb water molecule. This result is further evidence to confirm the purity of nickel oxide [2].

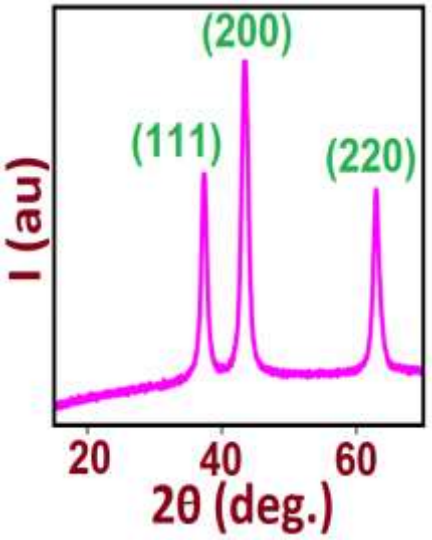


Figure 1: *XRD of Nanostructured NiO.*

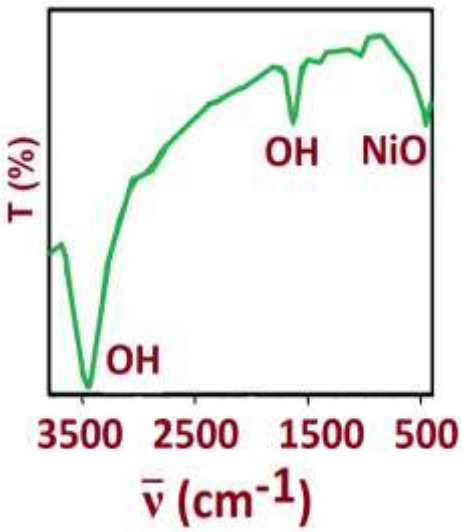


Figure 2: *FT-IR of Nanostructured NiO.*

Fig. 3 shows the FE-SEM images of NiO samples. The surface morphology reveals the hexagonal structure of NiO. The figure also reveals the homogeneous surface with lesser particle aggregation [2].

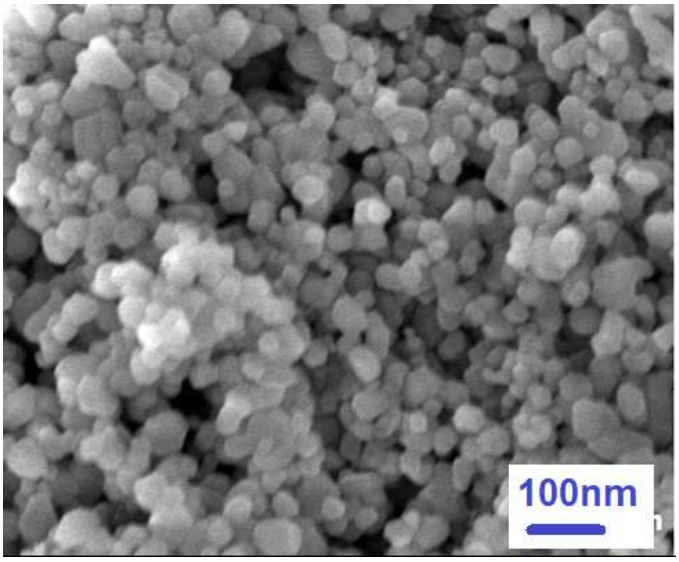


Figure 3: *FE-SEM of Nanoparticle NiO.*

ULTRACAPACITOR

Electrochemical performances are inspected using CV, EIS and GCD. EIS and GCD is done in presence of electrolyte 1M KOH. Electrochemical analysis is carried out via a modern electrochemical workstation coated Ni-foam (Sponge), Ag/AgCl, and Pt are designated as a working, reference and counter electrodes in three electrode cell system [2−8]. Electrode characterization in done in electrochemical workstation, using 1M KOH as electrolyte. Working Nano NiO is prepared a slurry mass obtained from 75% NiO, 15% acetylene black, and 10% PVDF, using solvent N-Methi-2-Pyrrolidone, and using ultrasonic stirring. An adequate amount (~5µL) of slurry was used to deposit on Ni foam with coating area: $1\times1cm^2$. Before the process, Ni foam was washed with acid, detergent, ethanol and deionized water to remove all surface impurities. Nanostructured NiO is examined via electrochemical measurements. Fig. 4 displays CV curves of NiO electrode at different scan rates (5, 10, 20, 30 and 40 mV/s) in 1M KOH electrolyte. The electrode reveals two strong peaks at anodic and cathodic sides, suggesting the typical pseudo capacitance behavior with respect to Faradaic Redox reaction of NiO. Oxidation peak is: at anodic side due to the conversion of NiO into NiOOH. Reduction peaks is: at cathodic side with respect to reverse reaction. Charge storage (energy storage) mechanism of NiO electrode follow the below equations (Eqns. 1 and 2).

$$NiO + OH^{-} = NiOOH + e^{-} \quad \ldots. (1)$$

$$Ni\ (OH)_2 + OH^{-} = NiOOH + H_2O + e^{-} \quad .... (2)$$

In CV curve, the current of redox process increases with increasing scan rates. Furthermore, the oxidation and reduction peaks shift towards the positive and negative regions; these are same in many literatures. Fig. 5 reveals the galvanostatic discharge curves of NiO electrode with respect to different current densities in 1M KOH electrolyte. The discharge time decreased, while increasing current densities. The observed semi-symmetric discharge curves confirmed the pseudo-capacitance behavior of NiO electrodes, suggesting the existence of redox reaction at the electrode/electrolyte interface. Specific capacitance of NiO electrode is calculated from the following equation (Eqn.3).

$$C_s = \frac{I\,\Delta t}{m\,\Delta V} \quad \ldots. \quad (3)$$

Where, Cs is the specific capacitance of the working electrode (F/g), I is the current (A), m is the mass of working electrode material (g), ΔV is the potential window, and Δt is the discharge time (s).The calculated specific capacitance value is 1850F/g at 0.3A/g. Fig. 6 shows Cs versus Id plot. At low Id, OH- contains enough time to diffuse and interact with NiO, showing high Cs. But, at high Id, OH- does not contain enough time to diffuse and so shows low Cs.

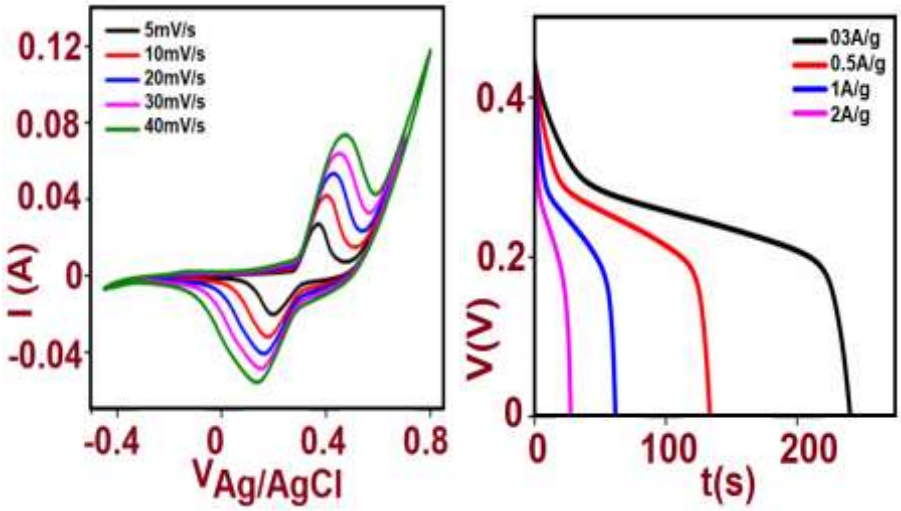
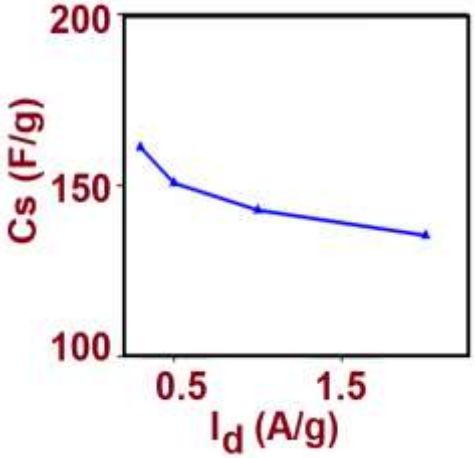


Figure 4: *CV curve of NiO electrode.* ***Figure 5:*** *GCD curve of NiO electrode.*

Moreover, the working electrode stability is more important in energy storage applications. NiO is employed in cyclic stability test at current density of 6A/g up to 1500cycles (Fig. 7). The life cycle revealed that the synthesized NiO electrode exhibited nearly 93 % stability for 1500 cycles. This stability result confirmed the absence of material leaching from electrode surface. However, the superior specific capacitance is not observed, which may due to the effect of electrode resistance (internal resistance of the electrode material, electrolyte resistance and contact resistance between the electrode and current collector). When EIS is applied, Nyquist plot is as shown in Fig. 8, for frequency range 0.01-100Hz. The solution resistance (Rs) and charge-transfer resistance (Rct) are calculated from the high frequency region of the impedance plot. The Rs and Rct values of NiO corresponds to 1.98 Ω and 4.02 Ω respectively. The straight-line slop at low frequency region represents the Warburg impedance, W of the electrolyte ions into the pore structure of electrode surface. The solution resistance and charge transfer resistance are confirmed the movement of faster or slower ion diffusion of between electrolyte and working electrode. Hence, the above results are clearly confirmed the nickel oxide electrode will perform an important role in energy storage application. Fig. 9 shows EIS of NiO nanosheet array on NiO foam for various cycles (high quality nanocrystalline NiO sheet on NiO foam). Fig.10 shows SEM image of NiO nanosheet array on NiO foam. Nanosheet array on Ni form is better than nanoparticle layer on NiO form [2].



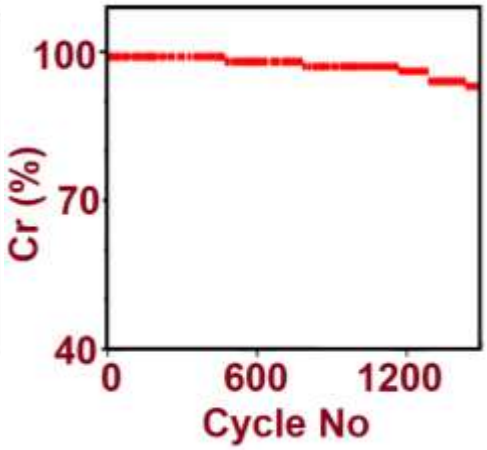
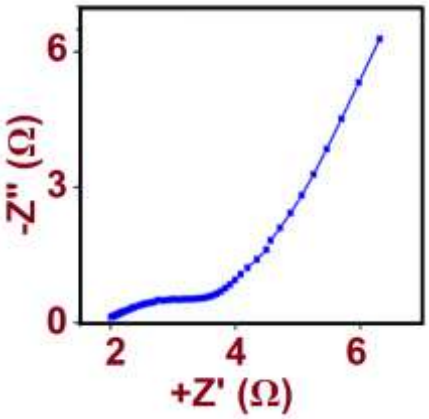


Figure 6: *Cs versus current density.* ***Figure 7:*** *Cyclic stability test.*



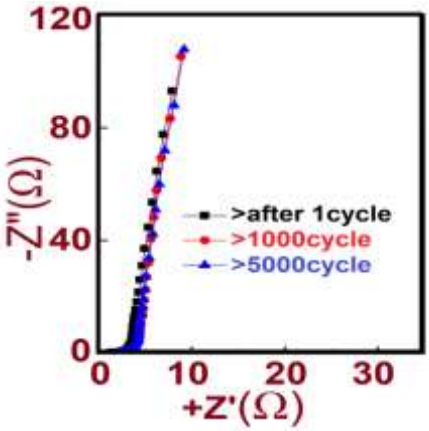


Figure 8: *Nyquist plot for NiO electrode.* ***Figure 9:*** *Nyquist of NiO nanosheet.*

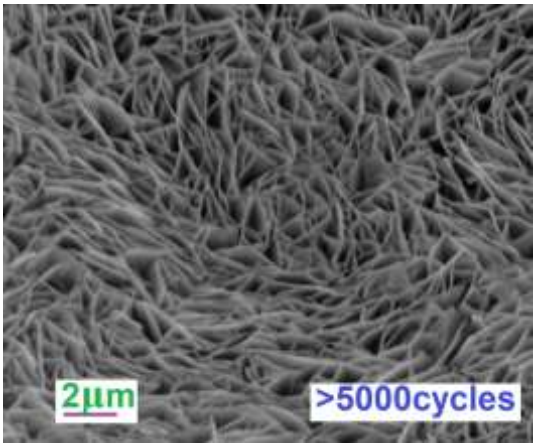


Figure 10: *SEM of NiO nanosheet.*

CONCLUSION

Facile synthetic nano NiO contains FCC vide XRD. Presence of functional groups NiOOH has been revealed by FT-IR. Electrochemistry exhibits maximum Cs 185 F/g, at a I_d 0.3 A/g, with cyclic stability of 93%, up to 1500cycles. Impedance measurement reveals solution resistance and charge transfer resistance, which are the clear evidence for adhesion of NiO on electrode surface and also the interaction of electrode and electrolytes.

Nanosheet array performs better than nanoparticle coat.

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