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Preparation and characterization of spray deposited nickel oxide(NiO) thin film electrode for supercapacitor

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Abstract: *In the present work, we report a spray pyrolysis route for preparation of nickel oxide (NiO) thin films on the glass and FTO substrate from solution of nickel chloride and ammonia. The deposition process based on the thermal decomposition ofammonia complex with nickel ions at temperature 623 K. As-prepared films were used for structural, surface morphological and opticalcharacterizations. Deposited NiO thin films were crystalline nature, SEM study of the film revealed elongated grains over the surface. The water contact angle of NiO film on glass substrate is less than 90^0, so the film behaves in hydrophilic nature. Thecapacitive characteristics of the films deposited on FTO substrate wereinvestigated using cyclic voltammetry. The maximum interfacial and specific capacitance of23 mF/cm^2 and 187 F/g was obtained in 1 M KOH electrolyte.*

Keywords: *NiO thin films; Spray pyrolysis; Contact angle; Supercapacitor*

I. Introduction

Electrochemical supercapacitors are becoming attractive energystorage devices for application involving high power and energydensity as well as high cycle capacity requirements [1, 2]. Supercapacitorshave been investigatedworldwide as the next generation Electric double-layer capacitor (EDLCs). TheEDLCs,which are basedon high-surface area carbon materials, mainly utilize the capacitancearising from purely nonfaradaic charge separation at anelectrode/electrolyte interface. Electrochemical supercapacitorsmay utilize the charge-transfer pesudocapacitance stemming fromreversible faradaic reaction occurring at the electrode surface. ForEDLCs, porous carbon materials with high-surface area, e.g. activecarbon, carbon fiber, carbon gel, etc., are commonly used as theelectrode materials [3–8].

Interest in nickel oxide (NiO) thin films is growing fast due totheir importance in many applications such as, electrochromicdevice [9], solar thermal absorber [10], Tandemdye-sensitized solarcells (TDSSC) [11], battery cathode [12] and gas sensors [13]. Themost attracting features of NiO are excellent durability, chemicalstability and large span optical density [9]. The electrochemistry ofnickel oxide has been well investigated. Liu and Anderson [14]develop electrochemical capacitor using porousNiOderivedbysol–gel method with specific capacitance 200–250 F /gA specificcapacitance 240 F/g for nickel oxide films prepared by relativelyinexpensive and controllable electrochemical precipitation methodfollowed by heat treatment reported by Shrinivasan and Weidner[15]. Cheng et al. [16] reported the maximum specific capacitance696 F/g for sol–gel-derived NiOxxerogels.Different techniques have been currently used in order toproduce nickel oxide thin films; Spray pyrolysis method [17]; RF sputtering [18], electron beam evaporation [19], dc magnetronsputtering [20], anodic electrodeposition[21], cathodicelectrodeposition[6], chemical vapour deposition [22],

In this work, nickel oxide thin film was prepared from nickel chloride ($NiCl_2$-$6H_2O$) precursor by successive ionic layer adsorption and reaction (SILAR) method on copper substrate. The structural and surface morphology was studied by X-ray diffraction(XRD), scanning electron microscopy (SEM) and surface wettabibilty, respectively. The capacitive properties of the nickel oxide thin film were investigated by cyclic voltammetry.

II. Experimental

The substrates were initially boiled in chromic acidfor 10 min, washed with double distilled water anddipped in labogent detergent and again washed withdouble distilled water. These substrates were furthertreated with ultrasonic waves for 15 min, prior to thedeposition. For the deposition of nickel oxide thin films, 0.05 M nickel chloride was prepared in doubledistilled water. The solution was sprayed through aglass nozzle onto ultrasonically cleaned hot glass andfluorine-doped tin oxide (FTO) coated glass substrates(10 V/cm2) kept at 623 K. The spray rate of 4 cm3/minwas maintained by using air as a carrier gas. Thetemperature was controlled with an electronictemperature controller. Evolved hazardous fumeswere expelled out from deposition chamber usingan exhaust system attached to the spray pyrolysis unit.The nozzle to substrate distance was 28 cm. Thethickness of the NiO film was determined by weightdifference method using a sensitive microbalance andfound to be 0.7 mm were used for further characterization. Tostudy the structural properties of the films, X-raydiffraction (XRD) analysis was performed on a Philips(PW-3710) diffractometer with chromium target(l = 2.2896 A °). The surface morphological study ofthe nickel oxide films was carried out by scanningelectron micrograph (SEM). The electrochemical analysisof the nickel oxide films deposited on FTO coatedglass substrate was studied by cyclic voltammetry(CV) using the 273 A EG&G Princeton AppliedResearch Potentiostat and forming an electrochemicalcell comprising platinum as a counter electrode,saturated calomel electrode (SCE) as a referenceelectrode in 1 M KOH electrolyte.

III. Results and discussion

3.1. Film formation

Aqueous solution of nickel chloride, when sprayed over the hot substrates, fine droplets of solution thermally decompose after falling over the hot surface of substrates. This results in the formation of well adherent and uniform nickel oxide film. The possible
chemical reaction that takes place is as follows:

$$Ni(Cl_2) + 2NH_4OH \xrightarrow{\Delta} Ni(OH)_2 + 2NH_4Cl_2 \rightarrow NiO \qquad (1)$$

3.2. Film characterization

3.2.1. Structural studies

Structural analysis of nickel oxide films was carriedout on a Philips PW-3710 diffractometer withchromium target by varying diffraction angle 2θ from20^0 to 80^0Fig. 1(a,b)shows a typical XRD pattern of asdeposited nickel oxide thin films onto glass and FTO substrate, respectively. The XRD pattern on glass substrate shows amorphous nature while on FTO showed the polycrystalline structure. It is seen that XRD patternexhibits a major XRD peak reflection along (1 1 1)plane. Another peak corresponding to (2 0 0) plane isobserved with lower scattering intensity. It is noteworthy onto amorphous glass substrate using the spraypyrolysis technique. The oriented growth might bedue to the more roughness on FTO substrates during deposition. Theobserved d values and standard d values [ASTM datafile No. 78-0423] of NiO are in good agreement. Thenickel oxide is formed in a single-phase, i.e. NiO.Kadam and Patil[2] have obtained polycrystallineNiO films by spray pyrolysis technique. Eze[12]has observed the appearance of some XRD peakreflections corresponding toNiOafter annealing of chemically deposited nickel oxide film.

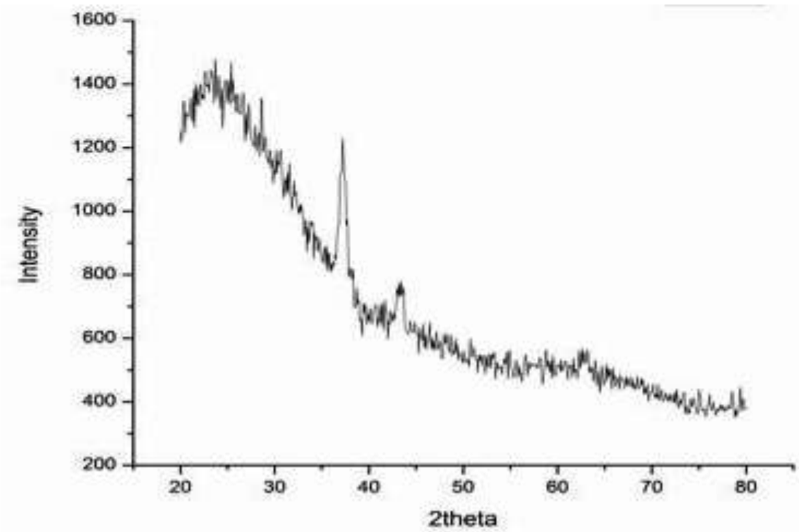

Fig. 1 (a) X-ray diffraction pattern of nickel oxide thin film onto glass substrate

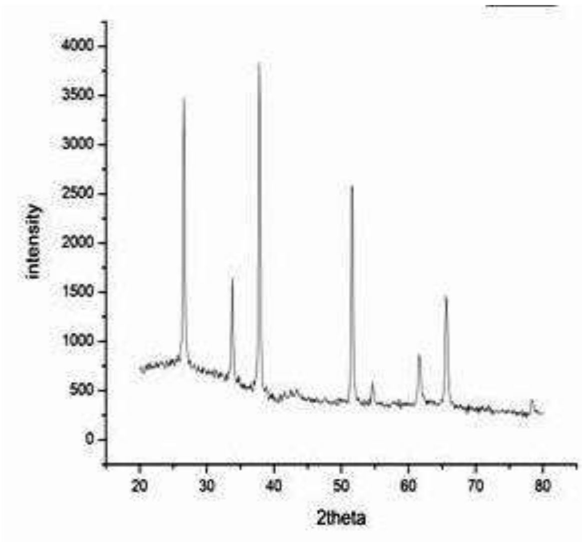

Fig. 1 (b) X-ray diffraction pattern of nickel oxide thin film onto FTO substrate

3.2.2. Surface morphological studies

The surface morphology of the spray-depositedNiO thin film was investigated by scanning electronmicrographs. Fig. 2(a, b)shows the SEM images of spraydepositedNiO thin film on glass and FTO substrate, respectively. From SEM one can see thesmaller grains with some overgrown clusters.This overgrowth can be explained on the basis ofnucleation and coalescence process. On FTO grownnanograins may have increased their size and elongated shape of particles. Thus, thelarger grains appear to grow by coalescence of smallerones. The average grain size of nickel oxide was foundto be 120 nm from the micrograph. The film surface iswell-covered without any pinholes and cracks. Such surface morphology with nanosized grains may offerincreased surface area, feasible for supercapacitor properties.

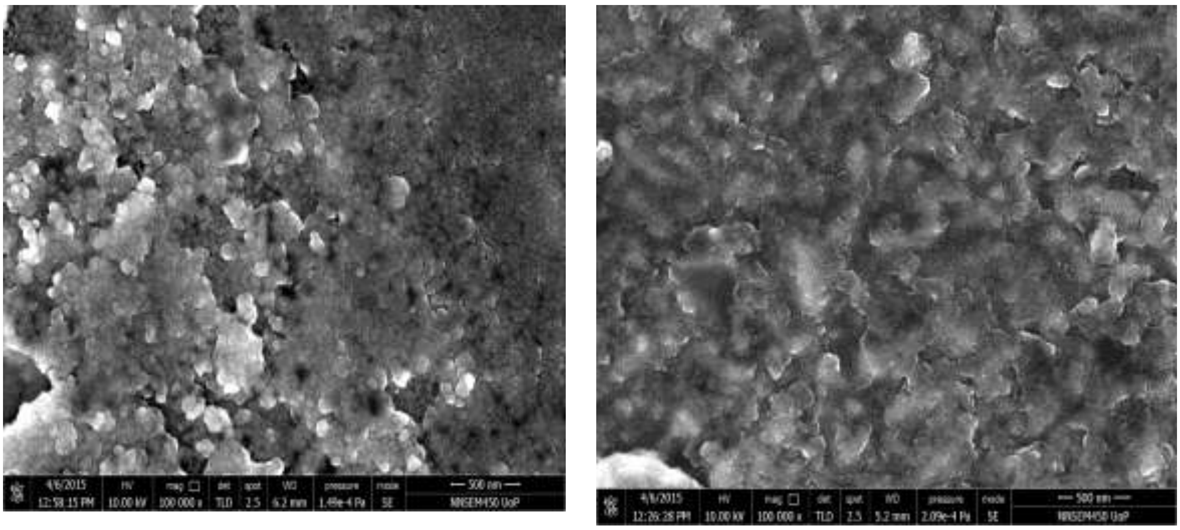

Fig. 2 Scanning electron micrographs of nickel oxide thin film onto (a) glass and (b) FTO substrates

3.3.3: Contact Angle Measurement:-

The wetting of solid with water, where air is the surrounding medium, is dependent on the relation between the interfacial tension (water/air, water/solid) the ratio between these tensions determines the contact angle (θ) between a water droplet on a given surface. Contact angle of 0^0 means complete wetting and contact angle of 180^0 correspond to complete non-wetting. Both super-hydrophilic and super-hydrophobic surfaces are important for practical applications. From the images, it is observed that, the water contact angles of as deposited film on FTO was 67^0. High wettability gives rise to small water contact angle which has direct surface tension relation. For supercapacitor application thin film electrode should be hydrophilic nature

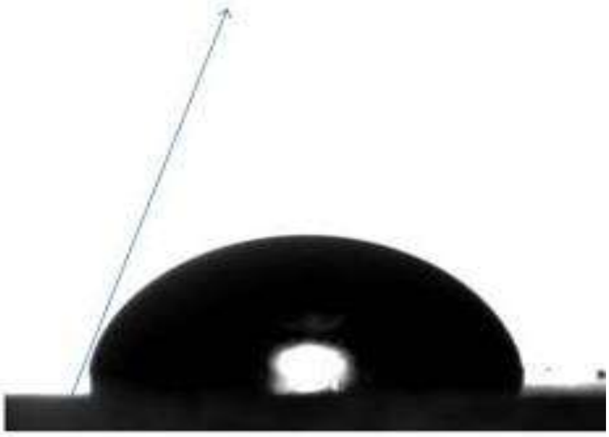

Fig. 3 Measurement of water contact angles of nickel oxide thin film onto FTO substrates.

3.2.4. Electrochemical supercapacitor properties

In order to study the application of NiO inelectrochemical supercapacitors, the supercapacitorproperties of NiO electrode were studied from CVcurves in aqueous KOH electrolyte.Fig. 4shows the typical cyclic voltammogram ofspray-deposited NiOthin film electrode in 1 MKOH solution at scan rate of 20 mV/s. The capacitancein NiO capacitor arises from the charging ordischarging of the Faradaic redox reactions (pseudocapacitance).The electrode was stable for >1000cycles. From these data, capacitance was calculated for NiO electrode using following relation:

$$C = I / dv / dt$$

Where, I is the average current in ampere and dV/dt isthe voltage scanning rate (20 mV/s). The specific capacitance(F/g) of NiO electrode was obtained bydividing its respective weight.

The NiO electrode exhibited interfacial capacitanceof 23 mF/cm2 and the specific capacitance of187 F/g. Lin et al. [24] have obtained the specificcapacitance of 291 F/g using NiO electrodeprepared by sol–gel method. The relatively lowcapacitance may be attributed to the anhydrous natureof NiO electrode; due to high temperature preparationtechnique and the resistance of current collector,i.e. FTO-coated glass substrate. The capacitancevalues can be increased by the use of highlyconductive substrate, which are stable at hightemperature, since highly conducting substrate isnecessary for the supercapacitor[25].

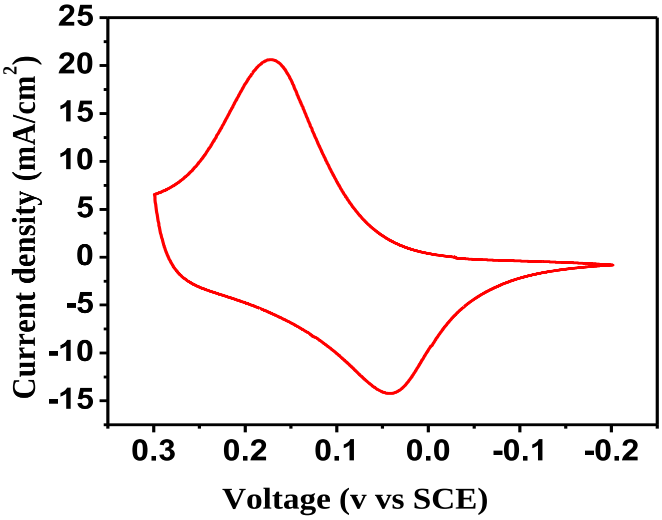

Fig. 4 The CV curves of NiO electrode at 1M concentrations of KOH electrolyte at scanning rate of 20 mV/s.

IV. Conclusions

The oriented nickel oxide thin films were preparedonto glass and FTO substrate by spray pyrolysis technique froman aqueous bath. As-prepared films were polycrystalline with(1 1 1) and (2 0 0) planes of nickel oxide.The surface morphologyand contact angle measurement revealed the totalcoverage of substrates with elongated nanosized grains over the surfaceand hydrophilic nature of thin film electrode, respectively. The interfacial capacitance and specific capacitance ofspray-deposited NiO electrode was 23 mF/cm^2 and 187 F/g, respectively.

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