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 of ammonia complex with nickel ions at temperature 623 K. As-prepared films were used for structural, surface morphological and optical characterizations. 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°, so the film behaves in hydrophilic nature. The capacitive characteristics of the films deposited on FTO substrate were investigated using cyclic voltammetry. The maximum interfacial and specific capacitance of 23 mF/cm² 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 energy storage devices for application involving high power and energy density as well as high cycle capacity requirements [1, 2]. Supercapacitors have been investigated worldwide as the next generation Electric double-layer capacitor (EDLCs). The EDLCs, which are based on high surface area carbon materials, mainly utilize the capacitance arising from purely non-faradaic charge separation at an electrode/electrolyte interface. Electrochemical supercapacitors may utilize the charge-transfer pseudocapacitance stemming from reversible faradaic reaction occurring at the electrode surface. For EDLCs, porous carbon materials with high surface area, e.g., active carbon, carbon fiber, carbon gel, etc., are commonly used as the electrode materials [3–8].

Interest in nickel oxide (NiO) thin films is growing fast due to their importance in many applications such as, electrochromic device [9], solar thermal absorber [10], Tandem dye-sensitized solarcells (TDSSC) [11], battery cathode [12] and gas sensors [13]. The most attracting features of NiO are excellent durability, chemical stability and large span optical density [9]. The electrochemistry of nickel oxide has been well investigated. Liu and Anderson [14] develop electrochemical capacitor using porous NiO derived by sol–gel method with specific capacitance 200–250 F/g. Specific capacitance 240 F/g for nickel oxide films prepared by relatively inexpensive and controllable electrochemical precipitation method followed by heat treatment reported by Shrinivasan and Weidner[15]. Cheng et al. [16] reported the maximum specific capacitance 696 F/g for sol–gel-derived NiO xeroxogels. Different techniques have been currently used in order to produce nickel oxide thin films; Spray pyrolysis method [17]; RF sputtering [18], electron beam evaporation [19], dc magnetron sputtering [20], anodic electrodeposition [21], cathodic electrodeposition [6], chemical vapour deposition [22].

In this work, nickel oxide thin film was prepared from nickel chloride (NiCl₂·6H₂O) 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 wettability, respectively. The capacitive properties of the nickel oxide thin film were investigated by cyclic voltammetry.

II. Experimental

The substrates were initially boiled in chromic acid for 10 min, washed with double distilled water and dipped in labogent detergent and again washed with double distilled water. These substrates were further treated with ultrasonic waves for 15 min, prior to the deposition. 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 and fluorine-doped tin oxide (FTO) coated glass substrates (10 V/cm²) kept at 623 K. The spray rate of 4 cm³/min was maintained by using air as a carrier gas. The temperature was controlled with an electronically temperature controller. Evolved hazardous fumes were expelled out from deposition chamber using an exhaust system attached to the spray pyrolysis unit. The nozzle to substrate distance...
was 28 cm. The thickness of the NiO film was determined by weight difference method using a sensitive microbalance and found to be 0.7 mm were used for further characterization. To study the structural properties of the films, X-ray diffraction (XRD) analysis was performed on a Philips (PW-3710) diffractometer with chromium target (λ = 2.2896 Å). The surface morphological study of the nickel oxide films was carried out by scanning electron micrograph (SEM). The electrochemical analysis of the nickel oxide films deposited on FTO coated glass substrate was studied by cyclic voltammetry (CV) using the 273 A EG&G Princeton Applied Research Potentiostat and forming an electrochemical cell comprising platinum as a counter electrode, saturated calomel electrode (SCE) as a reference electrode 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:

\[
Ni(\text{Cl}_2) + 2\text{NH}_4\text{OH} \xrightarrow{\Delta} Ni(\text{OH})_2 + 2\text{NH}_4\text{Cl} \rightarrow \text{NiO} \tag{1}
\]

3.2. Film characterization

3.2.1. Structural studies

Structural analysis of nickel oxide films was carried out on a Philips PW-3710 diffractometer with chromium target by varying diffraction angle 2θ from 20° to 80°. Fig. 1(a,b) shows a typical XRD pattern of as-deposited 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 pattern exhibits a major XRD peak reflection along (1 1 1) plane. Another peak corresponding to (2 0 0) plane is observed with lower scattering intensity. It is noteworthy onto amorphous glass substrate using the spray pyrolysis technique. The oriented growth might be due to the more roughness on FTO substrates during deposition. The observed 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 polycrystalline NiO films by spray pyrolysis technique. Eze [12] has observed the appearance of some XRD peak reflections corresponding to NiO after annealing of chemically deposited nickel oxide film.

![Fig. 1 (a) X-ray diffraction pattern of nickel oxide thin film onto glass substrate](image)
3.2.2. Surface morphological studies

The surface morphology of the spray-deposited NiO thin film was investigated by scanning electron micrographs. Fig. 2(a, b) shows the SEM images of spray-deposited NiO thin film on glass and FTO substrate, respectively. From SEM one can see the smaller grains with some overgrown clusters. This overgrowth can be explained on the basis of nucleation and coalescence process. On FTO grown nanograins may have increased their size and elongated shape of particles. Thus, the larger grains appear to grow by coalescence of smaller ones. The average grain size of nickel oxide was found to be 120 nm from the micrograph. The film surface is well-covered without any pinholes and cracks. Such surface morphology with nanosized grains may offer increased surface area, feasible for supercapacitor properties.
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° means complete wetting and contact angle of 180° 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°. 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.](image)

3.2.4. Electrochemical supercapacitor properties

In order to study the application of NiO in electrochemical supercapacitors, the supercapacitor properties of NiO electrode were studied from CV curves in aqueous KOH electrolyte. Fig. 4 shows the typical cyclic voltammogram of spray-deposited NiO thin film electrode in 1 M KOH solution at scan rate of 20 mV/s. The capacitance in NiO capacitor arises from the charging or discharging of the Faradaic redox reactions (pseudocapacitance). The electrode was stable for >1000cycles. From these data, capacitance was calculated for NiO electrode using following relation:

\[ C = \frac{I}{\text{dV/dt}} \]

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

The NiO electrode exhibited interfacial capacitance of 23 mF/cm² and the specific capacitance of 187 F/g. Lin et al. [24] have obtained the specific capacitance of 291 F/g using NiO electrode prepared by sol–gel method. The relatively low capacitance may be attributed to the anhydrous nature of NiO electrode; due to high temperature preparation technique and the resistance of current collector, i.e., FTO-coated glass substrate. The capacitance values can be increased by the use of highly conductive substrate, which are stable at high temperature, since highly conducting substrate is necessary for the supercapacitor [25].
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IV. Conclusions

The oriented nickel oxide thin films were prepared onto glass and FTO substrate by spray pyrolysis technique from an aqueous bath. As-prepared films were polycrystalline with (1 1 1) and (2 0 0) planes of nickel oxide. The surface morphology and contact angle measurement revealed the total coverage of substrates with elongated nanosized grains over the surface and hydrophilic nature of thin film electrode, respectively. The interfacial capacitance and specific capacitance of spray-deposited NiO electrode was 23 mF/cm² and 187 F/g, respectively.

References