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Title	Deposition and characterization of NiOx coatings by magnetron sputtering for application in dye-sensitized solar cells
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Publication date	2010-05
Publication information	Awais, Muhammad, Mahfujur Rahman, J. M. Don MacElroy, Nadia Coburn, Danilo Dini, Johannes G. Vos, and Denis P. Dowling. "Deposition and Characterization of NiOx Coatings by Magnetron Sputtering for Application in Dye-Sensitized Solar Cells" 204, no. 16–17 (May, 2010).
Publisher	Elsevier
Item record/more information	http://hdl.handle.net/10197/2454
Publisher's version (DOI)	10.1016/j.surfcoat.2010.02.027

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**Deposition and characterization of NiO_x coatings by magnetron sputtering for
application in dye-sensitized solar cells**

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Abstract

Nickel oxide (NiO_x) due to its *p*-type nature has considerable potential as a photocathodic material in energy conversion devices such as dye-sensitized solar cells (DSSCs). However, NiO_x has not been extensively used for this application mainly because of low light harvesting efficiency due to limited dye loading on the coatings. In this study NiO_x coatings were deposited using the dc- magnetron sputtering technique from a nickel target in an argon/oxygen plasma. One of the advantages of magnetron sputtering is the ability to control

coating properties such as mechanical performance and chemical stoichiometry. It is anticipated that by enhancing the interconnectivity between NiO_x particles and by optimizing surface roughness, it may be possible to enhance dye adsorption and increase its ability to absorb visible light. NiO_x coatings were deposited onto both silicon wafer and indium tin oxide (ITO) covered glass substrates. The influence of deposition parameters such as pressure, nickel target current and substrate bias voltage were correlated with the coating properties of surface roughness, thickness, crystallographic structure and surface energy. This evaluation was carried out using optical profilometry, spectroscopic ellipsometry, XRD and contact angle measurements respectively. It was observed that deposited coating morphology and roughness were significantly influenced by the deposition parameters. For example increasing the deposition pressure from 0.20 to 0.40 Pa led to an increase in surface roughness (Ra) from 1.6 to 3 nm. Associated with this increase in roughness the surface energy increased from 36 to 61 mN/mm. The NiO_x coatings were spectrally sensitized with Ru-complex dye containing -COOH groups as anchoring moieties. The dye adsorptions on NiO_x coatings, deposited on ITO substrates, were investigated in transmission mode using UV-vis spectroscopy in the range of 400 – 800 nm. It was observed that for the coatings with the highest surface energy, there was an increase of up to 60 % in the level of dye adsorption. The electroactivity of the NiO_x thin films deposited on Ni substrate at 0.4 Pa has been verified through the occurrence of redox processes of reduction and lithium intercalation within the oxide film.

Keywords: Dye-sensitized solar cell; Nickel oxide; Sputtering; Surface roughness; Dye adsorption

PACS codes: 84.60.Jt; 68.47.Gh; 81.15.Cd; 68.43.-h

1. Introduction

Dye-sensitized solar cells (DSSCs) [1] are being developed in applications ranging from photovoltaics to consumer electronics [2]. DSSCs are photovoltaic devices that present the advantage of being fabricated through low-cost processes and do not require photoactive materials with a high degree of purity [1]. However, their efficiency is generally lower than the best-performing thin film solar cells based on IV-VI semiconductors (CdTe~16 %, CIGS~19 % lab efficiency) [3] and crystalline silicon (~23 % lab efficiency) [4]. In the case of conventional DSSCs, dye sensitization involves solely the semiconductor anode made of *n*-type TiO₂ nanoparticles [1,5]. The counterelectrode is generally a metallic cathode with no photoelectrochemical activity [1,6,7]. Such a DSSC configuration can exhibit efficiencies up to 11.1 % [8]. A method of further enhancing the efficiency was suggested by He et al. is to substitute the cathode with a dye-sensitized photoactive *p*-type metal oxide. This tandem dye-sensitized solar cell designs utilize more of the solar spectrum [9]. The efficiency, however of *p*-type metal oxides is still very low, which limits their effectiveness in tandem DSSCs [10]. Amongst the potential reasons highlighted for the poor conversion efficiency of the cathode within tandem DSSC, is inefficient light absorption capability, poor charge injection efficiency and charge transport rate, along with inner resistance [11,12]. One method of improving this efficiency would be to produce a *p*-type metal oxide surface with a surface exhibiting high roughness and porosity. This surface morphology ensures higher light absorption by the monolayer of adsorbed dye. However, the re-reduction of oxidized dye, in other words, the injection of a hole into the *p*-type material is dependent on whether an intimate contact between the *p*-type material and the dye molecules is formed or not. For the efficient re-reduction of the oxidized dye molecules, a significant issue is, the incomplete pore filling of *p*-type materials which restricts the thickness of porous films used in DSSCs [11,13].

The focus of this research is on NiO_x which has a considerable potential for use as a cathode in tandem cells. This is due to its *p*-type nature [14] its excellent chemical stability, in addition to well defined optical and electrical properties [15]. Moreover, NiO_x is considered as a model semiconductor substrate due to its wide band-gap energy range from 3.6 to 4.0 eV [14]. NiO_x films have been fabricated by various techniques which include spray pyrolysis [16], plasma enhanced chemical vapor deposition [17], pulsed laser deposition [18], chemical bath deposition [19], sol-gel [9,20] and magnetron sputtering [14,21,22]. From these methods the sol-gel technique has been used mainly to prepare NiO_x coatings for the application in tandem dye-sensitized solar cells. In a previous study [9] it was demonstrated that for an optimized tandem dye-sensitized solar cell the photocurrents from the two electrodes should be matched. This can be achieved by adjusting the amounts of dye and/or electrodes film thicknesses. In this work, the potential of magnetron sputtering as a technique for depositing NiO_x coatings is investigated, in order to improve the performance of tandem DSSCs. The magnetron sputtering technique has an advantage in terms of controlling the film thickness, morphology and chemical stoichiometry compared with the alternative sol-gel deposition process. The potential of magnetron sputtering for the deposition of metal oxide coatings was successfully demonstrated in the case of TiO_2 coatings for the use in DSSCs [23]. Recently, Hossain et al. [24] concluded that DSSC with TiO_2 electrode deposited at higher sputtering pressure exhibited an increase in photoelectron conversion efficiency. These findings led us to consider magnetron sputtering as a feasible technique for the preparation of NiO_x coatings. The objective of this study is to control the properties of the NiO_x coatings in order to enhance the level of dye adsorption. This was carried out by adjusting the coating deposition parameters of pressure, target current and substrate bias voltage. To our knowledge, this is the first report on the application of magnetron sputtering for the deposition of NiO_x coatings for the use in dye-sensitized solar cells.

2. Experimental

2.1. *Sample preparations and deposition of NiO_x coatings*

Silicon wafer, glass, Ni plate (0.3 mm) and Indium Tin Oxide (ITO) were utilized as the substrates for the NiO_x coating deposition studies. The substrates were ultrasonically cleaned in methanol followed by acetone, each for 5 min prior to coating deposition. The deposition study was performed using a Teer Coatings UDP450 magnetron deposition system, in a closed-field arrangement, in argon plasma with 28 % of oxygen using transition model. The substrates were sputtered clean in argon plasma with a treatment pressure and voltage of 0.20 Pa and -400 V respectively, for 20 min prior to coating deposition. A Ni target with dimensions of 300 mm × 100 mm × 2 mm was used for the deposition and three dummy targets were utilized to complete the closed magnetic field. The substrates were fixed to a rotating substrate holder (1-fold rotation), and were rotated at a speed of 3 rpm with a target-to-substrate distance of approximately 10 cm. The deposition parameters are listed in Table I.

2.2. *Characterization equipments*

The film thickness and band gap of NiO_x coatings were measured using a J.A. Woollam's spectroscopic ellipsometer. The ellipsometric data was recorded at incident angles of 70° and 75°. The Triple Tauc-Lorentz (T-L) dispersion model was applied to fit the measured ellipsometric data to obtain the coating thicknesses [25]. The surface roughness was measured using a WYKO NT1100 optical profilometer. A CP- II (Veeco) Atomic Force Microscope (AFM) scanner was used for surface examinations. The AFM images were recorded in non-contact mode with silicon (phosphorous doped) cantilevers (Veeco, nominal spring constant = 40 N m⁻¹, tip radius < 10 nm). The surface morphology of the deposited coatings was examined using a FEI dual ion beam SEM system. X-ray Diffraction (XRD) measurement were carried out using a Philips glancing angle system operating at 40 kV and 35 mA with Cu K α radiation in normal diffraction mode. The detector was a PW 1711 (thin film measurement configuration) with a PW 3020 goniometer and a scan rate of 0.6°/min was used. Surface energy measurements were obtained using the sessile drop contact angle technique. These

measurements were obtained at room temperature with a video capture apparatus (OCA 20 from Dataphysics Instruments). Surface energy calculations were carried out using three test liquids: Deionised water, Ethylene glycol and Diiodomethane. The polar and dispersive surface energies were calculated by OWRK method [26]. The X-ray Photoelectron Spectroscopy (XPS) were recorded using a Kratos AXIS 165 spectrometer with a monochromatic X-ray source (Al K_{α} 1486.58 eV) and XPS survey spectra were collected in the binding energy range of 0 – 1400 eV.

2.3. *Dye sensitization and UV-vis spectroscopy*

NiO_x coatings were sensitized with 0.3 mM Ru-complex dye [Ru(bpy)₂dcB](PF₆)₂ (bpy: 2,2'-bipyridine; dcB: 4,4'-dicarboxy-2,2'-bipyridine) [27], containing appropriate anchoring moieties (carboxylic group), in a 99.8 % ethanol solution for 24 h. This immersion was carried out in darkness because the absorption of ambient light might lead to photo-degradation of the molecules dissolved in ethanol. The dye adsorption was investigated in transmission mode using Varian Cary 5 UV-vis spectrophotometer in the range of 400 – 800 nm.

2.4. *Electrochemical cell preparation*

The electrochemical cell had a three-electrode configuration with Ni/NiO_x as working electrode and Li rods (from Sigma-Aldrich) as reference and counter electrodes, respectively. The electrolyte was 0.5 M LiClO₄ in anhydrous propylene carbonate (from Fisher). In the following the reported potential values of the electrochemical determinations are referred to the Li⁺/Li couple. Cells were assembled under Ar atmosphere inside a glove-box from Innovative Technology (Newbury Port, Massachusetts, USA), with oxygen content below 10 ppm and water content below 5 ppm. The open circuit voltage (OCV) of the cell was 2.9 V.

2.5. *Electrochemical experiments*

In the present work two types of electrochemical experiments have been carried out: cyclic voltammetry [28] and the determination of electrochemical impedance spectra [29]. Both

experiments have been conducted with an electrochemical analyzer (model 604C) from CH Instruments (Austin, Texas, USA).

3. Results and discussion

The objective of the study is to evaluate how the properties of NiO_x coatings such as thickness, roughness, chemical structure and surface energy influencing the level of dye adsorption. These properties were systematically varied by adjusting the following deposition parameters: deposition time, pressure, target current and substrate bias voltage.

3.1. Thickness of the coatings

Fig. 1a, b and c demonstrates the effect on NiO_x coatings thickness of altering deposition pressure, target current and substrate bias voltage, respectively. An increase in the thickness of the coating was observed from ~175 to ~360 nm, by increasing the deposition pressure from 0.20 to 0.46 Pa as shown in Fig. 1a. An increase in the deposition pressure allows that more argon atoms come into the chamber (resulting in an increased bombardment of target). This in turn results in a higher deposition rate [24]. Fig. 1b demonstrates the effect of target current on thickness, with the increase in the target current from 1 to 2.5 A, an increase in the thickness of the coating was observed from ~90 to ~352 nm. This can be explained by the ejection of more nickel atoms from the Ni target at higher target current, with consequent increase in the deposition rate [15]. With the increase in the bias voltage, a decrease in the coating thickness was observed from ~175 to ~142 nm as shown in Fig. 1c. This decrease may be due to a combination of two effects: (i) with the increase in bias voltage, the level of ion bombardment of the coating increases and (ii) an increased level of self sputtering of the deposited coating may occur [30].

3.2. Band gap energy (E_g) of NiO_x coatings

From the ellipsometric data, the refractive index (n) and extinction coefficient (k) of the NiO_x coatings were extracted and the absorption coefficient (α) of the coatings was obtained via the

relationship $\alpha = 4\pi k/\lambda$, where λ is the wavelength of the incident light. The optical band gap E_g was calculated using the Eq. (1) [25]:

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \quad (1)$$

Where A is a constant and $h\nu$ is the incident photon energy. The variation of $(\alpha h\nu)^2$ versus $h\nu$ for the ~75 nm thick NiO_x coating deposited at 0.2 and 0.4 Pa (deposition conditions are listed in Table II) is shown in Fig. 2. The E_g value is determined from the intercept on the x-axis of the linear portion of $(\alpha h\nu)^2$ versus $h\nu$ in correspondence of $\alpha = 0$ (Fig. 2). The band gap (E_g) for the NiO_x coatings deposited at two different pressures was estimated to be 3.7 eV, which is in good agreement with the results reported by Sato et al. (3.6 – 4.0 eV) for NiO_x coatings deposited by magnetron sputtering [14].

3.3. Coating surface roughness

The surface roughness of the NiO_x coatings was analyzed using both optical profilometry and AFM. In order to achieve a higher surface roughness the influence of deposition pressure, target current and bias voltage were investigated.

Surface roughness (Ra) was found to increase with pressure in the range of 0.20 to 0.46 Pa as shown in Fig. 3a. This increase may be associated with the increase of ionic flux on the deposited surfaces [31,32]. The effect of the target current on the surface roughness is shown in the Fig. 3b. This is similar to a report in the literature which has correlated an increase in Ra with increased grain size for coatings deposited at higher target current [33]. Surface roughness was found to decrease with an increase in bias voltage from 0 to -100 V as shown in Fig. 3c. As outlined earlier, this may be due to an increase in the level of ion bombardment leading to an increase in coating density with an associated decrease in coating thickness [30]. The effect of the deposition pressure on the surface roughness of the NiO_x coatings was also examined by AFM (Fig. 4). A similar trend of increased surface roughness with pressure was observed as for optical profilometry. The coatings exhibited a uniform granular structure at

low pressure (0.20 Pa), whereas a needle-like structure is observed for the coatings deposited at higher pressure (0.40 Pa).

An XPS study was carried out to investigate the effect of deposition pressure on the chemical composition of NiO_x coatings deposited at pressures of 0.20 to 0.40 Pa (Fig. 5). The Ni 2p_{3/2} spectra of NiO_x coatings are presented in Fig. 5a. They are composed of two peaks at 853.9 eV and 855.5 eV which have been assigned to Ni⁺² (NiO) and Ni⁺³ (Ni₂O₃) respectively [34,35]. This is in addition to the very broad peak at ~861 eV, which is the shake up satellite peak of Ni⁺² and Ni⁺³. The complex peak structure makes it difficult to deconvolute the peaks. However, the O 1s spectra shown in Fig. 5b indicates two peaks at 529.4 eV and 531.4 eV, these are assigned to the oxides of NiO and Ni₂O₃ respectively [34,35]. The similarities between the XPS spectra confirm that the increase in the deposition pressure does not affect the chemical composition of the NiO_x coatings. This conclusion is supported by the lack of change in XRD spectra peak positions with the change in deposition pressure (Fig. 6). A change in texture is clearly visible however when comparing the peak intensities of the preferred orientations of the NiO_x coatings with the change in deposition pressure. Based on the XRD data and using the Scherrer formula, a reduction in grain size from 9.8 nm to 6.9 nm was observed with the increase in deposition pressure from 0.2 to 0.4 Pa. The SEM images of the NiO_x coatings confirmed this decrease with increase in deposition pressure as illustrated in Fig 7.

3.4. *Surface energy measurements*

The purpose of the study was to determine how enhanced surface energy could be achieved by modifying the deposition parameters. It is anticipated that a higher surface energy should lead to enhanced level of dye adsorption. With the change in deposition pressure, target current and substrate bias voltage, there was a change in the surface roughness and an associated variation in the water contact angle and surface energy as shown in Fig. 8a, b and c. A similar finding was reported by Stüber et al. who observed a linear change in the surface

energy of the sputtered coatings with increasing surface roughness [36]. From this study it was concluded that of the deposition parameters investigated the deposition pressure had the most significant influence on enhancing both surface roughness and energy of the NiO_x coatings.

3.5. *Dye adsorption and UV-vis spectroscopic studies*

A dye adsorption study was carried out on NiO_x coatings deposited on ITO substrates at pressures in the range of 0.20 to 0.40 Pa. In order to investigate only the effect of surface roughness on the level of dye adsorption the coating thickness was maintained at ~75 nm by controlling the deposition time. The deposition parameters used in this study are listed in Table II. The absorption spectra of the dye-sensitized NiO_x coatings resemble the UV-vis spectra of the Ru-complex dye in liquid solution as illustrated in Fig. 9 [37]. These UV-vis absorption spectra were normalized by assigning 1 to the maximum level of absorption obtained for the coating deposited at the highest deposition pressure (0.4 Pa). There is no substantial difference between the spectrum shape of the dye dissolved in an organic solvent with that of the dye adsorbed onto the NiO_x coatings (Fig. 9). This indicates that there are no significant modifications in dye properties when adsorbed onto the metal oxide surfaces. A gradual increase of dye absorbance with increasing deposition pressure was observed for the dye-sensitized NiO_x coatings within the spectral range of 400 – 800 nm (Fig. 9). This increase was associated with an increase in surface roughness and surface energy with the deposition pressure (Fig. 10). Since the optical absorbance is directly related to the amount of the light absorbing species [38], it was concluded that higher level of dye adsorption is achieved for the NiO_x coatings deposited at higher deposition pressures.

3.6. *Electrochemical activity of NiO_x coatings*

Due to their enhanced surface roughness and energy, the NiO_x coatings deposited at 0.4 Pa (~75 nm thick) were selected for cyclic voltammetry studies. This study was carried out in the potential window 1.4 – 3.0 V vs Li⁺/Li in 0.5M LiClO₄ propylene carbonate [39] (Fig. 11).

Within this range the redox process that occurs is the reversible reduction of NiO_x according to the Eq. (2) [40]:

In this equation, the value of y indicates the extent of lithium electrochemical intercalation in NiO_x coatings and this is usually below 0.5 [40]. As demonstrated in Fig. 11, the onset of NiO_x thin film reduction is shown to be below 1.9 V, whereas the reverse process of NiO_x re-oxidation takes place in the range of 2.2 – 2.6 V. In the absence of the oxide layer there is no electrochemical response of the bare nickel substrate within the same potential range. The relatively large separation between the peaks of reduction and oxidation of the NiO_x thin films is indicative of the occurrence of a redox process in the solid state [28]. This was further confirmed using the electrochemical impedance spectroscopy (EIS), which was determined at different levels of NiO_x reduction (Fig. 12). In this figure the amplitude of the electrical stimulus was 0.01 V, an electrolyte was 0.5 M LiClO_4 in propylene carbonate and frequency (ω) range of 10^{-1} - 10^5 Hz was employed.

In the pristine state, i.e. in absence of lithium (applied potential: 2.5 V), fully oxidized NiO_x displays a quasi vertical electrochemical impedance spectrum (Fig. 12). This response is typical of a poor electronic conductor that approaches the behaviour of a capacitance [40]. The electrochemical process involving NiO_x in the pristine state is controlled by ionic diffusion following lithium intercalation reaction [41]. When Li_yNiO_x is formed (applied potential: 1.6 V) the corresponding electrochemical impedance spectrum is characterized by a semicircular region at higher frequencies. This is followed by a Warburg-type line with a 45° slope [40], which evolves in a quasi vertical line as a consequence of the finite thickness of the sample [41]. A transition from diffusion controlled regime to charge-transfer controlled kinetics occurs as the amount of lithium increases in the NiO_x film [41]. This evolution indicates that the electroactivity of the sputtered NiO_x thin coating is dependent on ionic diffusion within the pristine film (low frequency range). It is partially dependent on ion

transfer at the film/electrolyte interface and on electron transfer at the Ni/NiO_x interface (high frequency range) in the lithiated film [41].

4. Conclusions

The objective of this study was to enhance the dye adsorption onto NiO_x coatings and therefore potentially to enhance its efficiency for use in tandem dye-sensitized solar cells. In order to achieve this objective the sputter deposition conditions varied were pressure, target current and substrate bias voltage. The study revealed that deposition pressure had the most significant influence on the properties of the NiO_x coatings. As the pressure was increased from 0.20 to 0.40 Pa there was a broadly linear increase in NiO_x coatings surface roughness (Ra) and a corresponding increase in surface energy. The enhanced Ra is likely to be associated with the increase in ionic bombardment at higher deposition pressures. There was no associated crystal structure change as demonstrated by XRD examination with the increase in deposition pressure. There was however a reduction in grain size for coatings deposited at higher pressure as demonstrated using XRD and SEM analyses.

The effect of deposition pressure increase on the level of Ru-complex dye sensitization of the NiO_x coatings was monitored using UV-vis spectroscopy. It was demonstrated for the rougher NiO_x coatings deposited at higher pressure, that a 60 % increase in the level of dye adsorption was achieved. It was also shown by electrochemical impedance spectroscopy measurements that the kinetics of NiO_x reduction is controlled by ionic diffusion within the pristine film. In conclusion, this study demonstrated that the light harvesting potential of dye-sensitized NiO_x coatings can be significantly enhanced by adjusting the magnetron sputtering deposition conditions. In addition to modifying the sputtering conditions it may be possible to further enhance coating surface area through the roughening of the substrate prior to the application of the NiO_x coatings.

Acknowledgements

The authors wish to acknowledge the financial support from Science Foundation Ireland (Project No. 07/SRC/B1160). Prof. Declan Gilheany of Celtic Catalysts is acknowledged for the use of his laboratory equipment.

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Tables

Table I. NiO_x deposition process conditions with changing deposition pressure from 0.20 to 0.46 Pa, target current from 1 to 2.5 A and substrate bias voltage from 0 to -100 V.

	Cleaning	Deposition conditions for the variation of pressure	Deposition conditions for the variation of target current	Deposition conditions for the variation of substrate bias voltage
Working pressure (Pa)	0.20	0.20 – 0.46	0.20	0.20
% of O ₂ in plasma	–	28	28	28
Target current (A)	0.3	1.5	1 – 2.5	1.5
Substrate bias voltage (V)	-400	-50	-50	0 – -100
Target to substrate distance (cm)	10	10	10	10
Speed of rotation (rpm)	–	3	3	3
Process time (min)	20	40	40	40

Table II. Deposition process conditions used for NiO_x dye-sensitization experiments

	Deposition
Working pressure (Pa)	0.20 – 0.40
% of O ₂ in plasma	28
Target current (A)	2.0
Substrate bias voltage (V)	-40
Target to substrate distance (cm)	10
Speed of rotation (rpm)	3
Deposition time (minutes)	8 – 12

Figure captions

Fig. 1: Effect of (a) deposition pressure, (b) target current and (c) substrate bias voltage on the thickness of the deposited NiO_x coatings.

Fig. 2: Plot of $(ah\nu)^2$ versus $h\nu$ for the NiO_x coatings deposited at 0.20 and 0.40 Pa deposition pressure, the E_g value (3.7 eV) is determined from the intercept on the x-axis.

Fig. 3: Effect of (a) deposition pressure, (b) target current and (c) substrate bias voltage on coating surface roughness (Ra).

Fig. 4: AFM examination of the surface morphology of the NiO_x coating deposited at the two deposition pressures shown.

Fig. 5: XPS spectra of (a) Ni 2p and (b) O 1s of NiO_x coatings deposited at the three deposition pressures shown.

Fig. 6: X-ray diffraction pattern of NiO_x coatings deposited at the three deposition pressures shown.

Fig. 7: The SEM images of NiO_x coatings deposited at different deposition pressures (a) 0.2 Pa and (b) 0.4 Pa.

Fig. 8: Effect of (a) deposition pressure, (b) target current and (c) substrate bias voltage on NiO_x coatings surface energy and water contact angle.

Fig. 9: Normalized absorption spectra of Ru-complex dye on NiO_x coatings deposited at the deposition pressures shown. The orange curve gives the molar extinction coefficient (ϵ) of Ru-complex in acetonitrile.

Fig. 10: Effect of deposition pressure on (a) surface roughness and (b) contact angle and surface energy of the NiO_x coatings with the thickness of ~75 nm.

Fig. 11: Cyclic voltammetry of a thin film of NiO_x (thickness: ~75 nm) deposited by magnetron sputtering on 0.3 mm thick Ni plate. Electrolyte: 0.5 M LiClO₄ in propylene carbonate; scan rate: 40 mV s⁻¹. Blue arrows indicate the direction of scan.

Fig. 12: Impedance spectra of a pristine (lithium-free) NiO_x thin film electrode (thickness: ~ 75 nm) on Ni plate at 2.5 V (full grey circles), and partially lithiated NiO_x thin film electrode (thickness: ~ 75 nm) on Ni plate at 1.6 V (empty red circles). Z' and Z'' represent the real and imaginary components of the complex impedance of the cell, respectively. The arrows indicate the direction of increasing frequency.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Fig. 12