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Nickel hydroxide deposited indium tin oxide electrodes as electrocatalysts for direct oxidation of carbohydrates in alkaline medium

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ABSTRACT

In this work, the direct electrochemical oxidation of carbohydrates using nickel hydroxide modified indium tin oxide (ITO) electrodes in alkaline medium is demonstrated; suggesting the feasibility of using carbohydrates as a novel fuel in alkaline fuel cells applications. The chosen monosaccharides are namely glucose and fructose; disaccharides such as sucrose and lactose; and sugar acid like ascorbic acid for this study. ITO electrodes are chemically modified using a hexagonal lyotropic liquid crystalline phase template electrodeposition of nickel. Structural morphology, growth, orientation and electrochemical behaviour of Ni deposits are characterized using SEM, XRD, XPS and cyclic voltammetry (CV), respectively. Further electrochemical potential cycling process in alkaline medium is employed to convert these Ni deposits into corresponding nickel hydroxide modified electrodes. These electrodes are used as novel platform to perform the electrocatalytic oxidation of various carbohydrates in alkaline medium. It was found that bare and Ni coated ITO electrodes are inactive towards carbohydrates oxidation. The heterogeneous rate constant values are determined and calculated to be two orders of magnitude higher in the case of template method when compared to non-template technique. The observed effect is attributed to the synergistic effect of higher surface area of these deposits and catalytic ability of Ni(II)/Ni(III) redox couple.

1. Introduction

Direct electrochemical oxidation of sugars is of a very high interest from several points of view ranging from biomedical applications involving blood sugar analysis, fuel cells applications to ecological approaches like waste water treatment in food industries [1–5]. The particular interest lays in the alkaline fuel cells applications where the focus was on developing new electrocatalytic materials as platform to carry out the oxidation of fuels, in this case carbohydrates in order to obtain a very high current density. The key point for this purpose is to oxidize sugars at relatively a negative potential compared to the oxygen reduction [6,7]. Some of the electrodes such as gold, platinum, glassy carbon, copper, nickel, mercury, bismuth, silver, nickel oxide, ruthenium and metal complexes were explored to investigate the direct electrochemical oxidation of sugars in alkaline medium [8–17]. As for as the electrocatalytic materials are concerned, there is an intense study aiming to track down the suitable catalysts for the desired applications. Among the various possible electrocatalysts, nickel hydroxide attracts much investigation, specifically as a fuel cell catalyst, secondary batteries and electrocatalyst for organic synthesis [18–20]. Owing to its unique electrocatalytic effect arising from the unpaired 'd' electrons and vacant 'd' orbitals associated with the oxidized form of nickel oxy-hydroxide (Ni^{3+}) that are readily available to bind any adsorbed species, nickel hydroxide has been extensively employed in many electrocatalytic processes [21,22]. It is also well-known that nickel and nickel hydroxide exhibit excellent electrocatalytic behaviour in alkaline medium [23–25]. In addition, preparation of these materials involves a simple procedure; it forms a stable redox species in alkaline medium and cost-effective.

In the case of fuel cells, there are several types namely proton exchange membrane fuel cells (PEMFC), direct methanol fuel cells (DMFC), alkaline fuel cells (AFC), phosphoric acid fuel cells, molten carbonate fuel cells, solid oxide fuel cells (SOFC), microbial fuel cells (MFC), etc. were developed [26,27] and shown to have potential applications from small power requirements to an industrial facility. Primarily they are classified by the kind of electrolyte materials employed. Most of the fuel cells mentioned above use chemicals such as methanol, ethanol, hydrocarbons, phosphoric acid, carbonate and solid oxide materials as fuels that undergo chemical reaction to produce energy [26]. In contrast, MFC use sugars, mainly

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glucose, as a fuel substrate along with electrochemically active redox enzymes to generate current [26]. However, as per literature, the usage of carbohydrates as a fuel in chemical fuel cells especially in the case of alkaline fuel cells is scarcely reported [28–32]. In fact, even before the arrival of lithium batteries, direct carbohydrates oxidation fuel cells were used as a promising source of autonomous energy supply for medical implants [30]. Some nanostructured electrodes having high electrocatalytic activity towards glucose oxidation in alkaline medium were developed [31,32]. These electrodes were shown to have several problems mainly arising out of technological and engineering approaches adopted for the fuel cell assemblies [28,33,34]. Most of these experimental works were focused on evaluating the performance of cell assembly by measuring the power density values. More detailed investigation on the fundamental aspect of electrochemical oxidation process is completely ignored. A systematic study on understanding the kinetics and determining the kinetic parameters of direct electrochemical oxidation of carbohydrates is absolutely essential. These data may be useful to assess the performance and fabrication of direct carbohydrate oxidation fuel cells. Based on these points, a novel platform for the direct electrochemical oxidation of carbohydrates using nickel hydroxide modified ITO electrodes that have potential applications in alkaline fuel cells as an electrocatalytic material (nickel hydroxide) and as a fuel (carbohydrates) was proposed.

In this work, a direct electrochemical oxidation of carbohydrates in alkaline medium using nickel hydroxide modified ITO electrodes was shown. Several carbohydrates such as monosaccharides (glucose and fructose), disaccharides (sucrose and lactose) and sugar acid (ascorbic acid) were used for the investigation. Chemical modification of ITO electrode was performed using a simple template electrodeposition of nickel followed by electrochemical potential cycling in alkaline medium, as shown in Scheme 1. Structural morphology, growth and orientation of these Ni deposits were characterized using scanning electron microscope (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Redox properties and electron transfer behaviour of these modified electrodes were investigated using the most popular electrochemical technique namely cyclic voltammetry (CV). Direct electrochemical oxidation of carbohydrates in alkaline medium was investigated using CV. Rate constant values for the electrocatalytic oxidation reactions were determined from the corresponding cyclic voltammograms.

2. Materials and methods

2.1. Chemicals

Nickel chloride (Riedel-deHaen), boric acid (Sisco), nickel sulphamate (Grauer & Wheel India Ltd.), Triton X-100 (SD Fine chemicals), sodium hydroxide (Merck), hydrochloric acid (Fischer Scientific), acetone (Fischer Scientific), hydrogen peroxide (Ranbaxy), glucose (Sigma Aldrich), fructose (Ranbaxy), sucrose (Ranbaxy), lactose (Ranbaxy), ascorbic acid (Merck) and liquid ammonia (Merck) were used in this study. All these chemicals were used as received unless otherwise stated. All the aqueous solutions were prepared using millipore water obtained from a quartz distillation unit having a resistivity of 18 MΩ cm. ITO substrates were purchased from Delta Technologies Limited, Stillwater, MN, USA. This plate (25 mm × 75 mm × 0.7 mm) is a single-side polished, SiO_2 passivated float glass coated with ITO film of 200–500 nm thickness and with a sheet resistance of $R_s = 4–8\ \Omega$. For electrochemical studies, this big plate was cut into small pieces of pre-defined geometric area and was used as strips.

2.2. Electrochemical cell and electrode pre-treatment

An electrochemical cell with a three-electrode configuration was used in this study. A platinum rod and a saturated calomel electrode (SCE) were employed as counter and reference electrodes, respectively. Bare and nickel electrodeposited ITO substrates were used as working electrodes. Initially ITO pieces were cleaned ultrasonically using acetone and water for 10 min, respectively. After that it was immersed in 5 ml of an aqueous solution consisting of hydrogen peroxide, liquid ammonia (ammonium hydroxide) and water in the ratio of 1:3:4 for about an hour. Later on it was washed thoroughly with water; rinsed with millipore water and immediately used for the analysis. Fabrication of a working electrode was carried out by connecting the pre-cleaned ITO plates with copper rod; then covered by parafilm and teflon, respectively. Prior to use, the counter electrode, platinum rod was dipped in 1:1 ratio of water and concentrated nitric acid solution for a couple of minutes and the reference, saturated calomel electrode was rinsed thoroughly with millipore water.

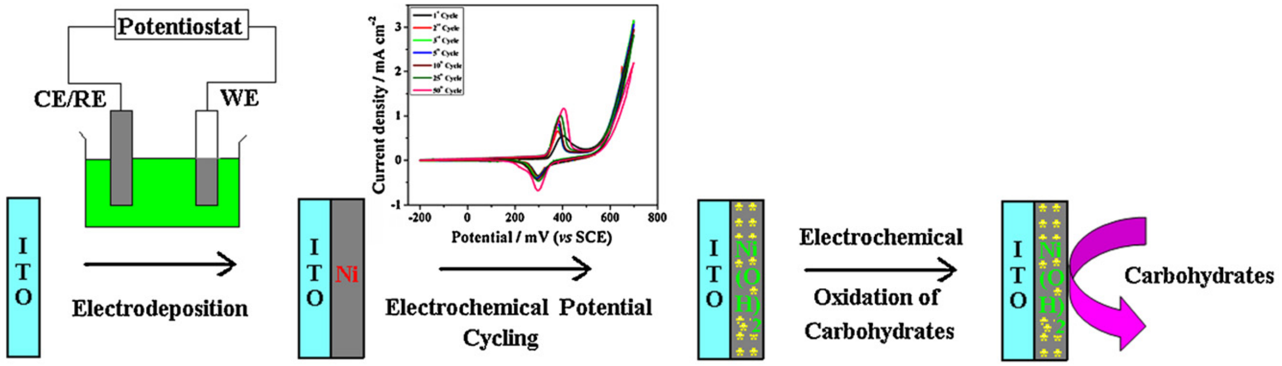
2.3. Electrodeposition of nickel on ITO electrodes

ITO electrodes were chemically modified by a simple method involving electrodeposition of nickel (Scheme 1). Two types of nickel electroplating bath for the deposition were used. One comprises of nickel sulphamate bath (non-template) consisting of $6\ g\ l^{-1}$ nickel chloride, $30\ g\ l^{-1}$ boric acid and $300\ g\ l^{-1}$ nickel sulphamate in water and the other includes a template as electrolytes during the process of electrodeposition. The template is a two component system comprises of Triton X-100 (58 wt%) and water (42 wt%), which exhibits a hexagonal lyotropic liquid crystalline phase at room temperature [35,36]. During template electrodeposition of nickel, the aqueous phase in the above mentioned compositions was replaced by nickel sulphamate bath. The template was prepared by adding 10 ml of Triton X-100 to 15 ml of nickel sulphamate bath and stirred for 1 h at a temperature of ∼40 °C. Then the mixture was cooled down to room temperature to obtain a green coloured thick gel solution. This template maintains the liquid crystalline nature up to 29 °C and above which it goes to the isotropic phase [35,36].

A pre-cleaned ITO substrate was used as a cathode and a sulphurized nickel bar was used as an anode. Two different solutions namely nickel sulphamate bath (without template) and a hexagonal lyotropic liquid crystalline phase (template) as mentioned earlier were used as electrolytic solutions. Electrodeposition of nickel was performed at a constant potential of −1.5 V vs. SCE (potentiostatic) for a fixed amount of time (60 s and 120 s) and the process was monitored using chronoamperometry. After the deposition, Ni deposited ITO plates were taken out washed thoroughly with enormous amount of water in order to remove the physically adsorbed surfactants; rinsed with millipore water and used immediately for further characterization and analysis.

2.4. Surface characterization of Ni deposited ITO electrodes

Structural morphology, growth, orientation and nature of nickel deposits on ITO electrodes were characterized using surface analytical techniques such as scanning electron microscope (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). SEM analysis was performed using Hitachi model S3000-H. XRD measurements were carried out in XPERT-PRO multipurpose X-ray diffractometer from The Netherlands using Cu Kα radiation with a wavelength of 1.540 Å. The 2θ value was varied from 20° to 80°. X-ray photoelectron spectroscopic studies were carried out using Multilab 2000 model, Thermo Scientific, UK. A source of Al Kα having a binding energy of 1486.4 eV was used for the study.



Scheme 1. Schematic representation of the methodology followed in this work to fabricate a novel platform to perform electrocatalytic oxidation of carbohydrates in alkaline medium.

Initially a full scan from −10 to 1100 eV was performed and later on individual scans of 30–50 eV having a step energy of 0.5 eV were carried out in order to analyze the presence of specific elements and their corresponding oxidation states.

2.5. *Electrochemical characterization*

Electrochemical technique namely cyclic voltammetry (CV) was used to study the redox properties and electron transfer mechanism of Ni deposits on ITO electrodes. CV experiments were performed in the potential range between −0.2 V and 0.7 V vs. SCE at a potential sweep rate of 50 mV s^{-1} in 0.5 M NaOH aqueous solution. A peak formation in CV suggesting the redox behaviour of Ni deposits in alkaline medium was observed. Scan rate dependence of this redox behaviour was also investigated. A wide range of scan rates starting from 2, 5, 10, 20, 50, 100, 200 and 500 mV s^{-1} were used for the study. Subsequently the surface structure of Ni deposits on ITO electrodes was altered and chemically converted into nickel hydroxide films using electrochemical potential cycling process by performing CV in alkaline solution. The Ni electrodeposited ITO electrodes were subjected to various numbers of potential cycling starting from 2, 5, 10, 25, 50 and 100 cycles in 0.5 M NaOH aqueous solution at a sweep rate of 50 mV s^{-1}.

2.6. *Electrocatalytic oxidation of carbohydrates using nickel hydroxide modified ITO electrodes*

Electrocatalytic behaviour of these chemically (nickel hydroxide) modified ITO electrodes towards direct electrochemical oxidation of various carbohydrates was investigated using CV experiments. Monosaccharides namely glucose (blood sugar) and fructose (fruit sugar); disaccharides such as sucrose (table sugar) and lactose (milk sugar); and sugar acids like ascorbic acid were used as model systems for the study. CV experiments were carried out in a 0.5 M NaOH aqueous solution between a potential range of −0.2 V and 0.7 V vs. SCE at a potential scan rate of 50 mV s^{-1}. A stock solution of 250 mM sugars was used for the analysis. An incremental addition of carbohydrates starting from micromolar concentration was carried out. After each addition the corresponding cyclic voltammogram was recorded. For comparison, the direct electrochemical oxidation of carbohydrates was also performed using both the bare (unmodified) and Ni coated ITO electrodes in alkaline medium.

2.7. *Instrumentation*

Electrochemical methods such as cyclic voltammetry and potentiostatic electrodeposition experiments were performed using Electrochemical Impedance Analyzer model 6310, EG&G Instruments from Princeton Applied Research, USA. Electrochemical experiments and their analysis of data were carried out using *echem* software provided by EG&G.

3. Results and discussion

3.1. *Characterization of Ni electrodeposits on ITO electrodes*

SEM, XRD and XPS were used for the analysis of structural morphology, growth, orientation and chemical nature of nickel electrodeposits on ITO electrodes. These electrodes were obtained by a simple process of electrodeposition. On contrast to bare ITO, which is colourless, nickel deposited ITO electrodes produced using the template and non-template methods display a grey or black colour coating results from the electrodeposition of nickel.

3.1.1. *SEM analysis*

Fig. 1 shows the SEM pictures of bare ITO and Ni electrodeposited ITO electrodes. It can be seen from the figure that bare ITO exhibits no structural features (Fig. 1a), while the Ni deposited electrodes show distinguishable structural changes. The morphology of an individual deposit depends upon the electrolyte used for deposition. For example, Ni coated electrode obtained using nickel sulphamate bath shows a dense array of nickel particles eventually leading to a film formation (Fig. 1b) having cracks and defects. At higher resolution, SEM pictures of Ni electrode obtained from non-template method show the formation of dense nickel nanoparticles. On the other hand Ni deposit produced using the lyotropic hexagonal liquid crystalline phase as a template exhibits a porous structure (Fig. 1c). These pores are deep, uniform and spread across the homogeneous film. The depth of these pores is in the range of tens of micron in size. The formations of fine Ni particles and the pores are further evident from their corresponding higher resolution SEM images. These morphological changes essentially arise from the structure of template used for the electrodeposition process. The formation of pores and cracks indicates that the surface area of these materials is higher suggesting the possibility of excellent electro-catalytic behaviour. The efficiency of these electrode materials depends upon the accessibility of electrolyte or species through these pores and cracks.

3.1.2. *X-ray diffraction (XRD) studies*

The crystal structure and orientation of as deposited Ni film on ITO electrodes were studied by XRD analysis. Fig. 2a–c shows the thin film XRD of bare ITO electrode, template deposited Ni film on ITO electrodes with and without template, respectively. It can

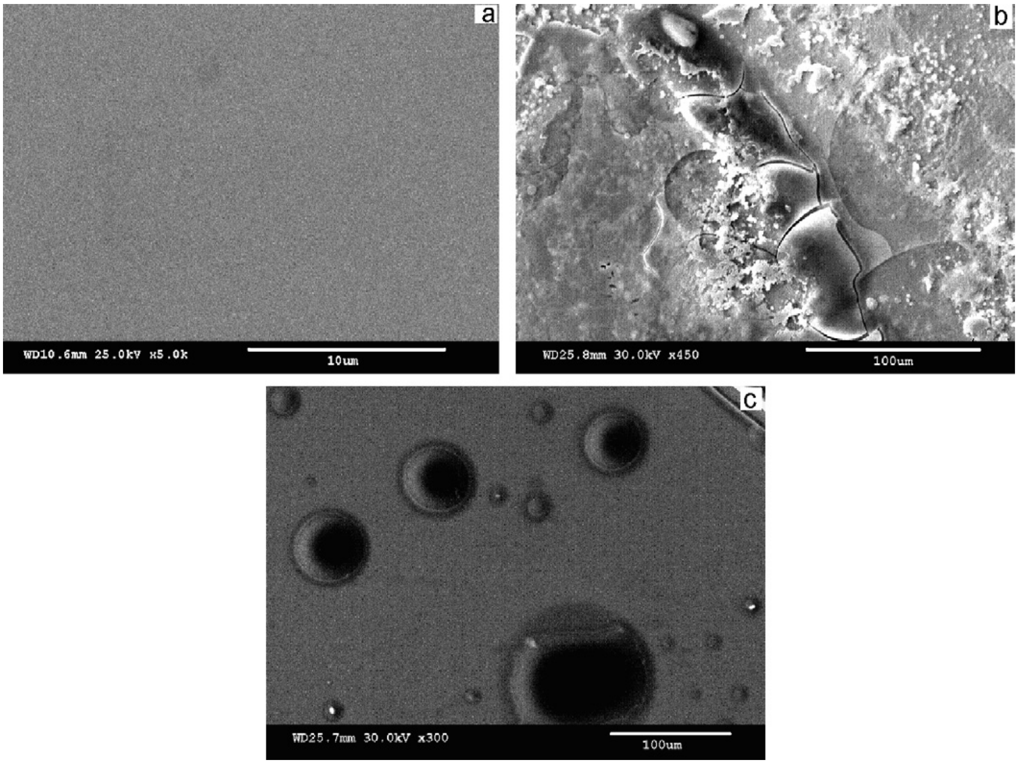


Fig. 1. SEM pictures of (a) bare ITO electrode, (b and c) Ni deposited ITO electrodes obtained using a non-template and the template methods, respectively. The other parameters were shown in the respective diagram.

be noticed from the figure that XRD pattern of Ni deposited electrodes clearly reveal the characteristic peaks expected for nickel with face centered cubic (fcc) structure [37,38] in addition to the reflections observed for bare ITO electrode. Ni deposited electrodes show the peaks at 44.3° and 51.8° corresponding to 1 1 1 and 2 0 0 planes respectively and are indicated by the asterisk mark in the figure. This also reveals that the resultant Ni films were of pure fcc nickel. The ratio of intensities of 1 1 1 and 2 0 0 planes associated with these Ni electrodes with and without template suggests that there is a preferential growth and orientation of Ni film along 2 0 0 direction in the case of template electrodeposition. On the contrary non-template method exhibits a preferential growth along 1 1 1 plane.

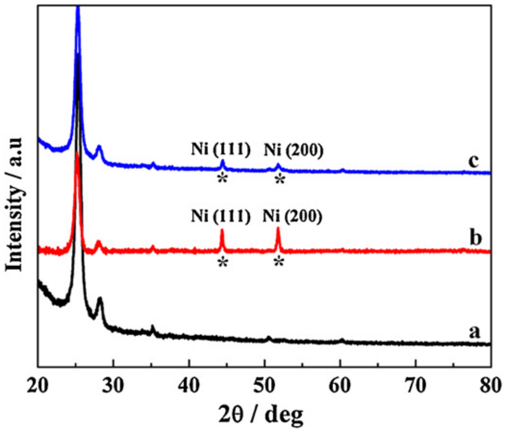


Fig. 2. XRD spectra of (a) bare ITO, (b and c) Ni deposited ITO electrodes produced using the template and non-template methods, respectively. Here "*" denotes the peaks corresponding to Ni deposits.

3.1.3. X-ray photoelectron spectroscopic (XPS) analysis

XPS was used to identify the composition of elements and chemical nature of the adsorbed films present on the modified ITO electrodes. Ni electrodeposited ITO electrodes were dried properly and used as strips for the analysis. Initially these electrodes were scanned over a broad range of −10 to 1100 eV (binding energy) and later on for individual elements, especially for Ni over a scan range of 30–50 eV. For comparison the XPS spectrum of a bare ITO electrode is also analyzed. It shows the peaks formation corresponding to indium at 444.2 eV ($3d_{5/2}$) and 451.8 eV ($3d_{3/2}$) and for tin at 486.3 eV ($3d_{5/2}$) and 494.7 eV ($3d_{3/2}$), respectively, in addition to the usual carbon and oxygen peaks. Fig. 3 shows the XPS spectra of electrodeposited Ni on ITO electrodes obtained using both the template (Fig. 3B) and non-template (Fig. 3A) methods. The formation of peaks at 853.4 eV and 871.7 eV suggest the presence of Ni 2p electrons having spins 3/2 and 1/2 respectively indicating the formation of Ni film during the process of electrodeposition [2,25].

3.2. Electrochemical characterization

The electron transfer properties and redox behaviour of Ni deposited ITO electrodes were investigated using CV studies in alkaline medium. On contrary to bare ITO electrode, which do not show any peaks, Ni coated ITO electrodes show a redox peak formation. A potential range of −0.2 V to 0.7 V vs. SCE was used for the study at a potential scan rate of 50 mV s^{-1}. An anodic peak potential of 0.38 V vs. SCE and the cathodic peak potential of 0.31 V vs. SCE were formed when template deposited Ni on ITO electrodes were investigated in 0.5 M NaOH aqueous solution. This redox peak indicates the formation of a single electron reversible redox process corresponding to nickel hydroxide–oxy-hydroxide redox couple [$Ni(OH)_2$–Ni(OOH)] on Ni coated electrodes [2,25,39–41]. By integrating the area (charge) under this redox peak, one can determine

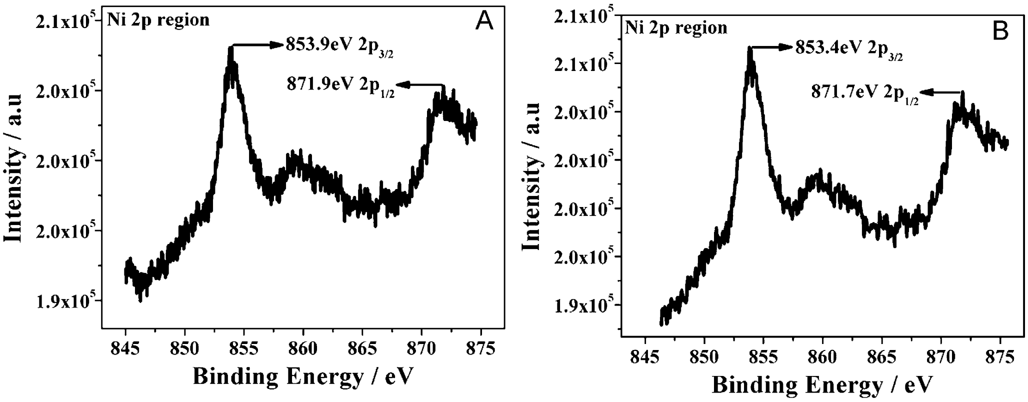


Fig. 3. XPS spectra of Ni 2p region from the Ni electrodeposits on ITO electrodes obtained using a non-template (A) and the template (B) methods, respectively.

the surface coverage of modified films using the following equation [42].

$$\Gamma = \frac{q}{nFA} \tag{1}$$

where Γ is the surface coverage on the electrode, q is the charge measured by integrating the area under the redox peak, n is the number of electrons, F is the Faraday's constant and A is the geometric area of electrode used for the analysis. The charge values of 68.95 μC and 16.4 mC are measured for the Ni deposits obtained using the non-template and the template methods, respectively. Using Eq. (1), the surface coverage values of 3.57×10^{-9} mol cm^{-2} (2.15×10^{15} molecules cm^{-2}) and 8.50×10^{-7} mol cm^{-2} (5.12×10^{17} molecules cm^{-2}) were determined for the Ni deposits produced from the non-template and the template methods, respectively. It can be observed that the template method results in the formation of higher amount of Ni deposits and these values suggest the formation of thick layers of nickel deposits on ITO electrodes [25,42].

The electro-active surface area (true area) of these nickel deposits on ITO electrodes has been determined by measuring the anodic charge associated with the formation of nickel hydroxide during CV experiments carried out in 0.5 M NaOH aqueous solution [35,43,44]. An estimation of area under the anodic peak

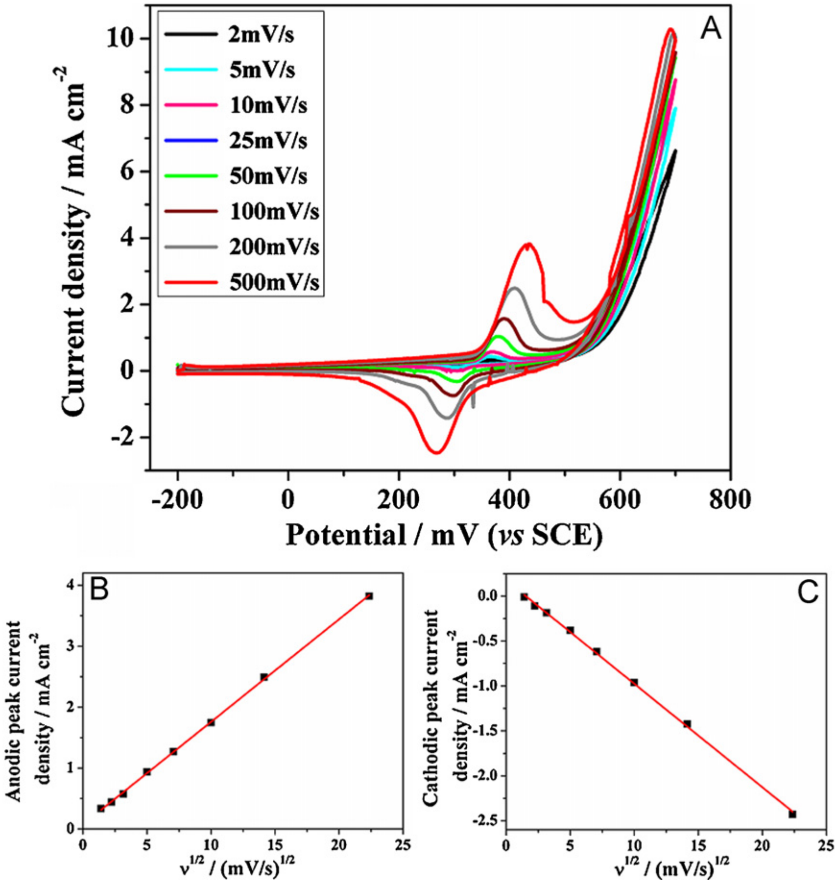


Fig. 4. Cyclic voltammograms of a template deposited Ni electrode in 0.5 M NaOH aqueous solution for various scan rates ranging from 2 to 500 mV s^{-1} were displayed in (A). Plots of peak currents (both anodic and cathodic) vs. square root of scan rate were shown in (B) and (C).

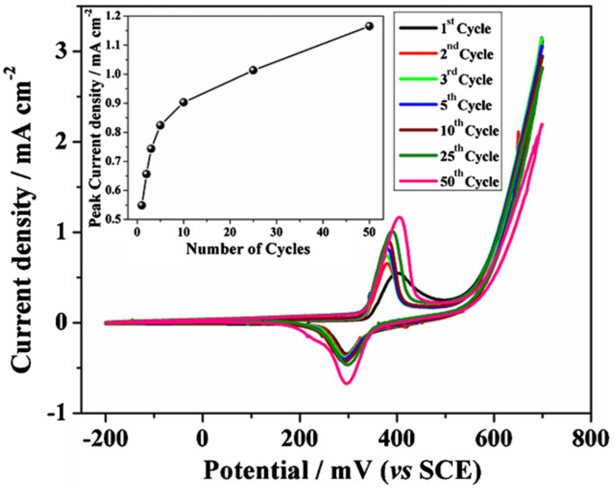


Fig. 5. CVs of a template deposited Ni on ITO electrodes in 0.5 M NaOH aqueous solution for various numbers of cycles (1–50) at a potential scan rate of 50 mV s^{-1}. Inset shows the peak current calculated from the respective CV vs. the number of cycles employed.

provides an electro-active area of 86.45 cm^2 for the Ni deposit obtained using the template method. This corresponds to a surface roughness factor of 480 in comparison to the roughness factor of 4 obtained for smooth nickel electrode without the template. The roughness factor values determined in this work is higher than the sintered nickel and porous nickel obtained using high internal phase emulsion (HIPE) as a template [43,44] and lower than the Raney nickel [45]. Nevertheless the roughness factor values obtained in the present work suggest the higher surface area of the Ni deposits produced using the template.

The effect of scan rate on the redox behaviour of Ni deposited ITO electrodes is also investigated. A wide range of scan rate starting from 2 mV s^{-1} to 500 mV s^{-1} was employed and the corresponding cyclic voltammograms were shown in Fig. 4. Here CVs of template deposited Ni electrodes are shown and it is worth mentioning that similar results are observed for Ni coated electrodes obtained using non-template method. It can be observed from the figure that the redox current increases with the increasing scan rate. Analysis of the peak current relationship with the scan rate shows that the corresponding peak currents (both anodic and cathodic) are linear with respect to square root of scan rate suggests that the redox process is surface confined and diffusion controlled. The respective plots were displayed in Fig. 4B and C.

Ni electroplated ITO electrodes were chemically converted into nickel hydroxide electrodes by a process of electrochemical potential cycling in alkaline medium using CV. As coated Ni electrodes were subjected to potential cycling in 0.5 M NaOH aqueous solution at a potential scan rate of 50 mV s^{-1} within a potential ranging from −0.2 V to 0.7 V vs. SCE. Several numbers of cycles from 2, 3, 5, 10, 25, and 50 were carried out in alkaline medium. The corresponding CVs were displayed in Fig. 5. During this process an increase was observed in the current indicating the enhancement of $Ni(OH)_2$–Ni(OOH) redox current, eventually resulting in the formation of nickel hydroxide films on ITO electrodes. Inset shows the plot of peak current vs. the number of cycles employed during CV studies. It is clear from the inset that the redox current increases with the cycles and this attains saturation for higher number of cycles.

3.3. SEM and XPS characterization of nickel hydroxide modified ITO electrodes

Structural and morphological analyses of nickel hydroxide modified electrodes obtained using an electrochemical potential cycling process were carried out using SEM and XPS studies. Fig. 6a and b shows the SEM pictures of nickel hydroxide electrodes produced from the respective non-template and template methods. It can be noted from the figure that the electrochemical cycling process in an alkaline medium results in the formation of crystalline dendritic growth in the case of non-template technique where a simple nickel electroplating bath was employed. And in the case of template it still retains the porous structure but leads to the formation of tiny pits and rough structures resulting in high surface area for such electrodes. Another interesting point observed in this case is the filling up of pores suggesting the conversion to nickel hydroxide films arising from the aggregation of particles present inside the pores. Similarly XPS is also used to confirm the conversion to nickel hydroxide by electrochemical methods and the corresponding spectra of Ni 2p region of such modified electrodes were shown in Fig. 7. Compared to nickel coated ITO electrodes (Fig. 3), these nickel hydroxide electrodes display a positive shift in binding energy. The formation of peaks at 854.8 eV and 872.8 eV indicate the presence of respective Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ electrons having higher binding energy compared to Ni 2p electrons obtained from Ni deposits on ITO electrodes. These binding energy values agree very well with the reported values of nickel hydroxide [25,46,47].

3.4. Electrocatalytic oxidation of carbohydrates

Nickel hydroxide modified electrodes were investigated towards the direct electrochemical oxidation of carbohydrates in alkaline medium in order to evaluate the potential of this electrode as an alternative, new electrocatalytic material for alkaline fuel cells applications. A variety of sugars are used namely glucose, fructose, sucrose, lactose and a sugar acid like ascorbic acid in these studies using both the Ni deposited and nickel hydroxide modified ITO electrodes. For comparison the carbohydrates oxidation using bare ITO electrode is also studied. Initial experiments were performed with glucose, as an example of a carbohydrate in order to determine the suitable electrode to be used as a catalytic material for investigating the oxidation of sugars. Fig. 8A and B shows the CVs of nickel hydroxide modified electrodes obtained by electrochemical potential cycling of nickel produced from the respective non-template (A) and template (B) methods tested for the oxidation of glucose in 0.5 M NaOH aqueous solution at a potential scan rate of 50 mV s^{-1}. Inset shows the same CV plots for bare ITO electrode. In all these figures ‘a’ denotes the CVs performed in the absence of glucose and ‘b’ represents the CVs carried out in the presence of 4 mM glucose. Bare ITO electrode was found to be ineffective towards the oxidation of any carbohydrates as it is evident from the absence of peaks and very little change in the oxidation current on adding sugars observed from the corresponding CV (Fig. 8A inset). Upon adding 4 mM of glucose, on contrary to bare ITO electrode, nickel hydroxide electrodes show a dramatic increase in the current due to oxidation of glucose. The oxidation of glucose occurs at 0.48 V vs. SCE. The template deposited electrodes (Fig. 8B) show a 2.5fold increase in the oxidation current on comparison to non-template coated electrodes (Fig. 8A), suggesting the potential use of these modified electrodes as novel electrocatalytic materials. It is also observed that the plated Ni electrodes (before electrochemical potential cycling) provide a very weak signal enhancement for the addition of glucose implying that the electrochemical potential cycling and its conversion into nickel hydroxide are essential for the electrocatalytic oxidation of glucose.

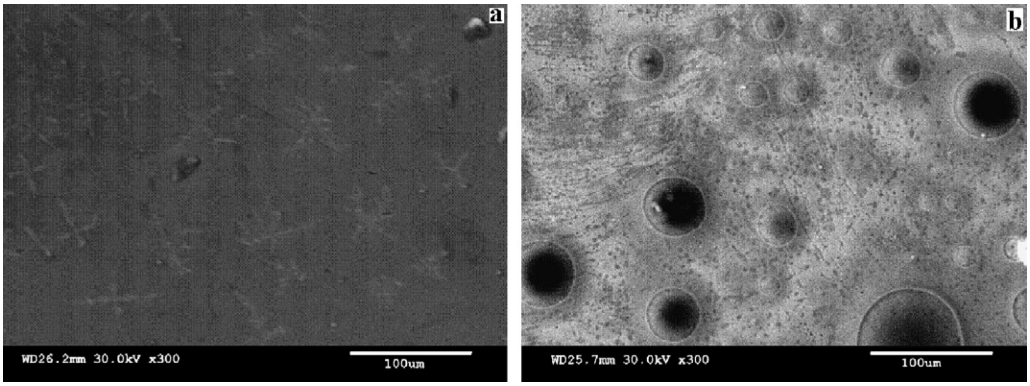


Fig. 6. SEM pictures of nickel hydroxide modified electrodes produced by electrochemical potential cycling process in an alkaline medium using the nickel electrodes obtained from (a) the non-template and (b) the template methods, respectively. The other parameters were displayed in the respective images.

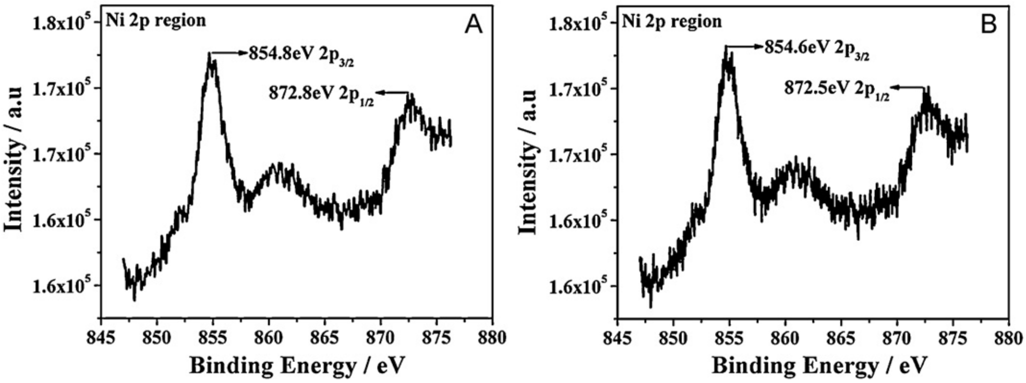


Fig. 7. XPS spectra of Ni 2p region from the nickel hydroxide modified electrodes obtained using a non-template (A) and the template (B) methods, respectively.

Similarly, the direct electrochemical oxidation of other carbohydrates namely fructose, sucrose, lactose and ascorbic acid using nickel hydroxide electrode in alkaline medium is also investigated. Fig. 9A and B displays the corresponding CVs in 0.5 M NaOH aqueous solution performed at a potential scan rate of 50 mV s^{-1} using nickel hydroxide electrode obtained from non-template and template methods, respectively. For comparison, the CV recorded is also provided before adding any carbohydrates. It can be observed from these figures that the oxidation current increases significantly by 4fold on adding carbohydrates and the effect is much more pronounced (10fold) in the case of nickel hydroxide electrode prepared using the template. Interestingly, the oxidation potential of ascorbic acid is shifted by ~0.15 V more positive when compared to the oxidation potential of other carbohydrates and the oxidation current was also observed to be a minimum. In the case of template method, the oxidation of all the carbohydrates yielded a very similar current density and this is found to be 2.5fold more than the nickel hydroxide electrode produced using non-template method.

The electro-catalytic behaviour of nickel hydroxide electrode was further investigated by varying the concentration of carbohydrates and the change in oxidation current density was measured using CV. A stock solution of 250 mM carbohydrates was used for the study. Successive addition of carbohydrates to 0.5 M NaOH solution was carried out and the corresponding CV was recorded

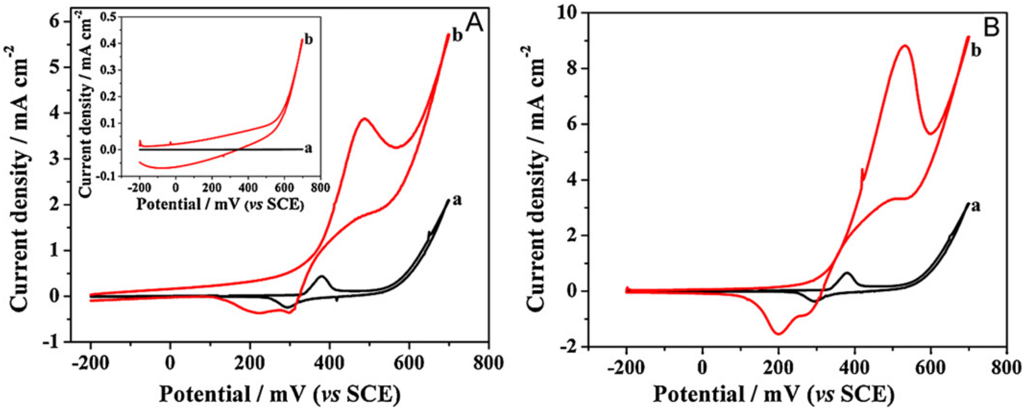


Fig. 8. Cyclic voltammograms in 0.5 M NaOH aqueous solution at a sweep rate of 50 mV s^{-1} for nickel hydroxide electrodes obtained by the process of electrochemical potential cycling of nickel electrodes produced from the non-template (A) and the template methods (B), respectively. Inset shows the same plots for bare ITO electrodes. In all these figures 'a' denotes the CVs performed in the absence of glucose and 'b' represents the CVs carried out in presence of 4 mM glucose.

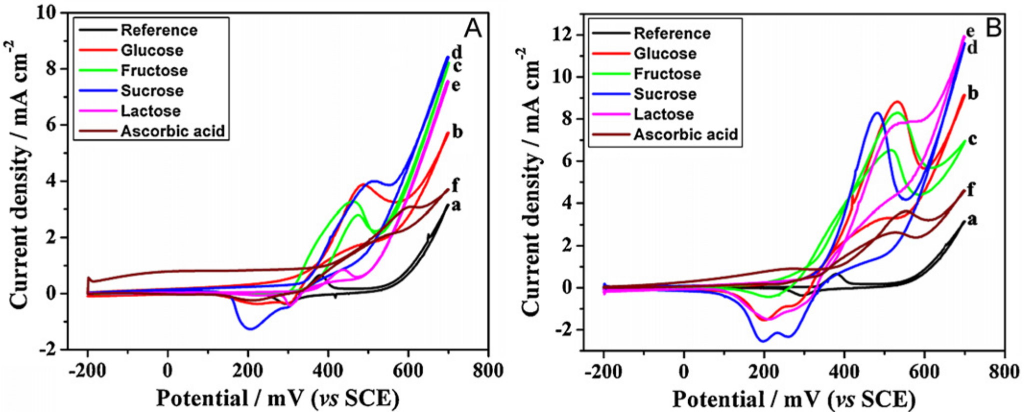


Fig. 9. CVs of nickel hydroxide modified electrodes obtained from the non-template (A) and the template (B) methods respectively in 0.5 M NaOH aqueous solution at a potential scan rate of 50 mV s^{-1} for the addition of a fixed concentration of various carbohydrates. Here 'a' denotes the corresponding CV of nickel hydroxide electrodes before adding any carbohydrates and (b) glucose, (c) fructose, (d) sucrose, (e) lactose and (f) ascorbic acid additions.

for each addition. Fig. 10 displays the change in oxidation current density with respect to the added concentrations of all the carbohydrates using nickel hydroxide electrode obtained using non-template (A) and template (B) methods. The oxidation current density was measured form the peak potential resulting from each and every addition of carbohydrates. It can be seen from these figures that the incremental addition of carbohydrates from 0.5 mM to 28 mM results in the systematic enhancement of oxidation current density. In the case of nickel hydroxide prepared using a non-template method, both glucose and sucrose provided similar higher current density in contrast to lactose and ascorbic acid which yielded lower oxidation current density values. On contrary, all the sugars except ascorbic acid resulted in higher (3fold enhancement) oxidation current density values when nickel hydroxide electrodes produced using a template method were employed. It is also evident from these figures that the initial addition of carbohydrates results in the linear increase of oxidation current density and at higher concentrations it attains saturation.

The heterogeneous electron transfer rate constants (k) for the direct electrochemical oxidation of various carbohydrates on nickel hydroxide electrodes were calculated using the following equation [42] and were given in Table 1.

$$I = nFAkC \tag{2}$$

where I is the current density measured during oxidation process, n is the number electrons involved, F is the Faradays constant, A is the geometric area of electrode, k is the rate constant and C is the concentration of carbohydrates. The rate constant values given in Table 1 reveal that nickel hydroxide electrode is catalytically active towards carbohydrates oxidation. Using a template results in two order of magnitude change in the rate constant values when compared to the same electrode obtained using a non-template method. These values are 100fold higher than the similar rate constant values reported for the oxidation of carbohydrates on other modified electrodes [11,13,15–17,23,48,49]. The difference observed in the present work is attributed to the higher surface area resulting from the use of a template during deposition and catalytic effect of Ni$^{2+/3+}$ redox couple.

3.5. Reproducibility and stability of nickel hydroxide electrodes

The reproducibility of these electrodes was examined by fabricating several nickel hydroxide modified ITO electrodes and monitoring the oxidation current response in 0.5 M NaOH solution having a fixed concentration of 5 mM carbohydrates using CV. The variation in the carbohydrates oxidation current density among these electrodes was calculated to be less than 2% which suggests the fabrication method employed in this work is highly reproducible. These electrodes were stored at room temperature (27 ± 2 °C) when not in use. The long term stability of these electrodes was evaluated for every 7 days over a period of 45 days by measuring the current response for the oxidation of carbohydrates in 0.5 M NaOH solution. From these experiments it was found that the current response was decreased to 97.5% of its original value

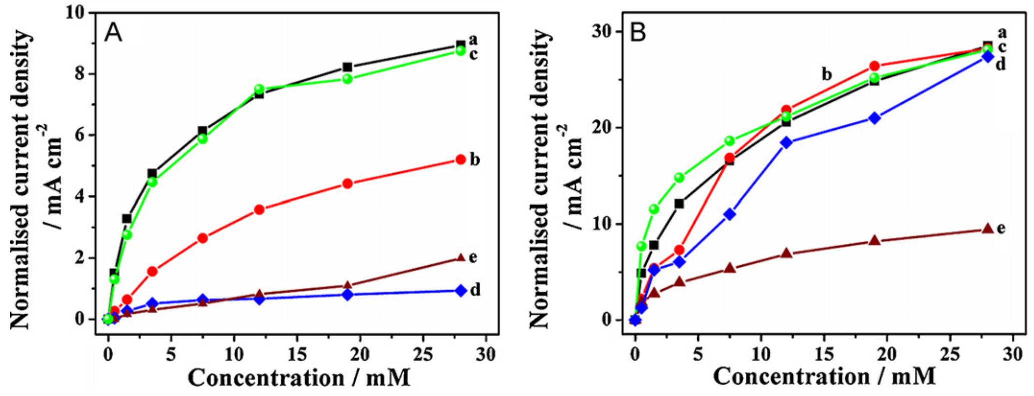


Fig. 10. Plots of normalized current density vs. concentration corresponding to nickel hydroxide electrodes obtained using the non-template (A) and the template (B) methods respectively for the successive incremental additions of (a) glucose, (b) fructose, (c) sucrose, (d) lactose and (e) ascorbic acid. The current density values were determined at the peak potential resulted from the respective CVs recorded for each addition.

Table 1
Normalized peak current density and heterogeneous electron transfer rate constants (k) determined from the CVs corresponding to the direct electrochemical oxidation of various carbohydrates (at a fixed concentration of 4 mM) on nickel hydroxide electrodes obtained using both the non-template and template methods.

Sample	Normalized peak current density		Heterogeneous electron transfer rate constant (k)	
	Non-template ($mA\,cm^{-2}$)	Template ($mA\,cm^{-2}$)	Non-template $10^6\ k\ (cm\,s^{-1})$	Template $10^4\ k\ (cm\,s^{-1})$
Glucose	4.7450	12.0746	43.903	11.117
Fructose	1.5606	7.2885	14.440	67.436
Sucrose	4.4667	14.7828	41.328	13.677
Lactose	0.5110	6.0604	04.728	05.607
Ascorbic acid	0.3073	3.8810	02.843	03.591

and even after 45 days its response comes down to 95%. Also there was no obvious potential shift observed for the electro-catalytic oxidation of carbohydrates. These results have convincingly proved that the electrode material prepared in the present work is highly stable; reproducible and possess long term electrocatalytic activity.

3.6. Mechanism of carbohydrates oxidation

A possible mechanism for the direct electrochemical oxidation of carbohydrates on nickel hydroxide modified ITO electrodes is proposed. In order to establish the catalytic activity of these modified electrodes, CVs were recorded in the absence and presence of several carbohydrates in 0.5 M NaOH aqueous solution. The electrochemical redox behaviour observed in absence of any sugar for these electrodes is attributed to Ni(II)/Ni(III) redox couple and the governing process is expressed as follows:

$$\mathrm{Ni(OH)_2 + OH^- \leftrightarrow Ni(OOH) + H_2O + e^-} \tag{3}$$

$$\text{(or)}\quad \text{simply, } \mathrm{Ni(II) \leftrightarrow Ni(III) + e^-} \tag{4}$$

On adding carbohydrates, it was observed that the oxidation current increases significantly and the reduction current decreases with increasing concentrations of sugar. The oxidation of carbohydrates on these modified nickel hydroxide surfaces could be expressed as a direct electro-oxidation process and is controlled by the Ni(II)/Ni(III) redox couple according to the following reaction.

$$\mathrm{Ni(OOH)} + \text{carbohydrates} \rightarrow \mathrm{Ni(OH)_2} + \text{Product} \tag{5}$$

Initially added sugar moiety gets adsorbed onto nickel hydroxide surface and this step is a kind of dehydration step. Then the Ni(III) species produced by the oxidation of Ni(II) rapidly oxidizes the dehydrated intermediate at anodic potentials. During this process Ni(II) species are produced by sacrificing Ni(III) [2,41,50]. As a result, change in concentrations of Ni(II) and Ni(III) species causes the increase of anodic and decrease of cathodic peak currents. From these experiments, it is concluded that nickel hydroxide modified ITO electrodes obtained from the template deposition exhibit higher current density values for the oxidation of carbohydrates at a lower positive potential. These electrodes also show excellent stability and reproducibility. These salient features can be attributed to two important factors viz., (i) the electrocatalytic activity of Ni(II)–Ni(III) redox couple and (ii) the surface roughness and porous nature of the catalyst.

4. Conclusions

All the results clearly demonstrate the possibility of preparing a novel electrocatalyst for the direct electrochemical oxidation of carbohydrates in alkaline medium using nickel hydroxide modified ITO electrodes. In this work, the possible way is shown to use carbohydrates as a fuel in the alkaline fuel cells. ITO electrodes are chemically modified with Ni electrodeposits using the template and non-template methods. A two component mixture consists of Triton X-100 and water containing the nickel salt exhibiting a lyotropic hexagonal liquid crystalline phase is used as a template. In the case of non-template technique, a simple nickel electroplating bath is used. Ni coated ITO electrodes are chemically converted into nickel hydroxide electrodes by the process of electrochemical potential cycling in alkaline medium. Structural morphology, growth and nature of these deposits are investigated using SEM, XRD and XPS. These nickel hydroxide modified ITO electrodes show an excellent catalytic behaviour towards the direct electrochemical oxidation of carbohydrates. A variety of sugars namely glucose, fructose, sucrose, lactose and ascorbic acid is investigated. For comparison similar studies are also carried out using bare ITO and Ni deposited ITO electrodes and found to be catalytically inactive towards carbohydrates oxidation. The heterogeneous electron transfer rate constant values determined from CVs indicate a minimum of two order of enhancement in the rate of reaction for the template method. These results clearly reveal nickel hydroxide modified ITO electrodes act as a good electrocatalyst with higher stability and reproducibility towards the carbohydrates oxidation.

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References

[1] E. Shoji, M.S. Freund, J. Am. Chem. Soc. 123 (2001) 3383.
[2] T. You, O. Niwa, Z. Chen, K. Hayashi, M. Tomita, S. Hirono, Anal. Chem. 75 (2003) 5191.
[3] L. Wu, X. Zhang, H. Ju, Biosens. Bioelectron. 19 (2007) 141.
[4] L. Meng, J. Jin, G. Yang, T. Lu, H. Zhang, C. Cai, Anal. Chem. 81 (2009) 7271.
[5] J.D. Newman, A.P.F. Turner, Biosens. Bioelectron. 20 (2005) 2435.
[6] S.B. Aoun, G.S. Bang, T. Koga, Y. Nonaka, T. Sotomura, I. Taniguchi, Electrochem. Commun. 5 (2003) 317.
[7] S. Mho, D.C. Johnson, J. Electroanal. Chem. 500 (2001) 524.
[8] S. Yamazaki, N. Fujiwara, S. Takeda, K. Yasuda, Chem. Commun. 46 (2010) 3607.
[9] S. Arimori, S. Ushiroda, L.M. Peter, A.T.A. Jenkins, T.D. James, Chem. Commun. (2002) 2368.
[10] H.J. Schafer, R. Schneider, Tetrahedron 47 (1991) 715.
[11] R. Ojani, J.B. Raoof, S. Fathi, Electroanalysis 20 (2008) 1825.
[12] P. Parpot, N. Nunes, A.P. Bettencourt, J. Electroanal. Chem. 596 (2006) 65.
[13] K. Sugawara, F. Yamamoto, S. Tanaka, H. Nakamura, J. Electroanal. Chem. 394 (1995) 263.
[14] P. Parpot, K. Servat, A.P. Bettencourt, H. Huser, K.B. Kokoh, Cellulose 17 (2010) 815.
[15] S. Berchmans, H. Gomathi, G. Prabhakara Rao, J. Electroanal. Chem. 394 (1995) 267.
[16] D. Das, P.K. Sen, K. Das, J. Appl. Electrochem. 36 (2006) 685.
[17] D. Das, P.K. Sen, K. Das, J. Electroanal. Chem. 611 (2007) 19.
[18] M.C. Daniel, D. Astruc, Chem. Rev. 104 (2004) 293.
[19] C. Burda, X. Chen, R. Narayan, M.A. El-Sayed, Chem. Rev. 105 (2005) 1025.
[20] J. Chen, D.H. Bradhurst, S.X. Dou, H.K. Liu, J. Electrochem. Soc. 146 (1999) 3606.
[21] L.X. Lo, B.J. Hwang, J. Electrochem. Soc. 142 (1995) 445.

[22] L.A. Hutton, M. Vidotti, A.N. Patel, M.E. Newton, P.R. Unwin, J.V. Macpherson, J. Phys. Chem. C 115 (2011) 1649.
[23] S. Berchmans, H. Gomathi, G. Prabhakara Rao, Sens. Actuators B 50 (1998) 156.
[24] M. Vidotti, C.D. Cerri, R.F. Carvalhal, J.C. Dias, R.K. Mendes, S.I.C. Torresi, L.T. Kubota, J. Electroanal. Chem. 636 (2009) 18.
[25] V. Ganesh, D. Latha Maheswari, S. Berchmans, Electrochim. Acta 56 (2011) 1197.
[26] A.K. Shukla, P. Suresh, S. Berchmans, A. Rajendran, Curr. Sci. 87 (2004) 455.
[27] B.D. McNicol, D.A.J. Rand, K.R. Williams, J. Power Sources 83 (1999) 15.
[28] M. Pasta, F.L. Mantia, R. Ruffo, F. Peri, C.D. Pina, C.M. Mari, J. Power Sources 196 (2011) 1273.
[29] J.O.M. Bockris, B.J. Piersma, E. Gileadi, Electrochim. Acta 9 (1964) 1329.
[30] S. Kerzenmacher, J. Ducree, R. Zengerle, F. Von Stetten, J. Power Sources 182 (2008) 1.
[31] C. Jin, I. Taniguchi, Mater. Lett. 61 (2007) 2365.
[32] P. Schechner, E. Kroll, E. Bubis, S. Chervinsky, E. Zussman, J. Electrochem. Soc. 154 (2007) B942.
[33] P. Schechner, L. Mor, S. Kimchie, H. Tarabeah, C. Dosoretz, K. Hemmes, Proceedings of 2nd International Conference on Fuel Cell Science, Engineering and Technology, Rochester, United States, NY, June, 2004, p. 491.
[34] P. Schechner, E. Bubis, L. Mor, Proceedings of 3rd International Conference on Fuel Cell Science Engineering and Technology, Ypsilanti, MI, United States, May, 2005, p. 661.
[35] V. Ganesh, V. Lakshminarayanan, Electrochim. Acta 49 (2004) 3561.
[36] A.N. Galatanu, I.S. Chronakis, D.F. Anghel, A. Khan, Langmuir 16 (2000) 4922.
[37] C. Hammond, The Basics of Crystallography and Diffraction, Oxford University Press, Oxford, 1997.
[38] V. Ganesh, D. Vijayaraghavan, V. Lakshminarayanan, Appl. Surf. Sci. 240 (2005) 286.
[39] S. Park, H. Boo, T.D. Cheng, Anal. Chim. Acta 556 (2006) 46.
[40] C. Wang, L. Yin, L. Zhang, R. Gao, J. Phys. Chem. C 114 (2010) 4408.
[41] A. Salimi, M. Roushani, Electrochem. Commun. 7 (2005) 879.
[42] A.J. Bard, L.R. Faulkner (Eds.), Electrochemical Methods: Fundamentals and Applications, second ed., John Wiley & Sons, New York, 2002.
[43] I.J. Brown, S. Sotiropoulos, Electrochim. Acta 46 (2001) 2711.
[44] I.J. Brown, S. Sotiropoulos, J. Appl. Electrochem. 30 (2000) 107.
[45] S. Rausch, H. Wendt, J. Electrochem. Soc. 143 (1996) 2852.
[46] K.S. Kim, N. Winograd, Surf. Sci. 43 (1974) 625.
[47] J.C.D. Jesus, J. Carrazza, P. Pereira, F. Zaera, Surf. Sci. 397 (1998) 34.
[48] M. Jafarian, F. Forouzandeh, I. Danaee, F. Gobal, M.G. Mahjani, J. Solid State Electrochem. 13 (2009) 1171.
[49] I. Danaee, M. Jafarian, F. Forouzandeh, F. Gopal, M.G. Mahjani, Electrochim. Acta 53 (2008) 6602.
[50] L.M. Lu, L. Zhang, F.L. Qu, H.X. Lu, X.B. Zhang, Z.S. Wu, S.Y. Huan, Q.A. Wang, G.L. Shen, R.Q. Yu, Biosens. Bioelectron. 25 (2009) 218.