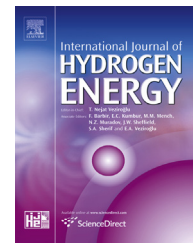




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Electrocatalytic oxidation of ethylene glycol and glycerol on nickel ion implanted-modified indium tin oxide electrode

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ABSTRACT

The electrochemical behaviour of direct ethylene glycol and glycerol oxidation on a novel nickel ion implanted-modified indium tin oxide electrode (NiNPs/ITO) was investigated. The investigation is used to verify the feasibility of using the NiNPs/ITO electrode in the ethylene glycol and glycerol fuel cells. The size and morphology of nickel nanoparticles (NiNPs) on the substrate surface was determined by scanning electron microscopy (SEM). The cyclic voltammetry (CV) technique was utilized to characterize the typical electrochemical behaviours of the NiNPs/ITO electrode. In alkaline medium (0.2 M NaOH), a good redox behaviour of Ni(III)/Ni(II) coupled at the surface of modified electrodes can be observed. Electrochemical performances were measured by current–time curve technology. We find that the NiNPs/ITO electrode exhibits a satisfactory electrocatalytic activity toward ethylene glycol and glycerol with good stability, making it a prime candidate for use in ethylene glycol and glycerol fuel cells.

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Introduction

It is well-known that fossil fuel reserves are rapidly depleted, with the world facing energy shock as a result. At the same time, the use of fossil fuels is well recognized for its detrimental effects that may drive an environmental and social crisis [1]. Under these circumstances, it is necessary to search for a viable alternative fuel and develop new energy conversion devices to solve the energy generation problems. In the past few decades, direct fuel cells based on small organic molecules have attracted dramatic attention as possible

power devices, particularly for hand-held electronic devices and electric vehicles because of their high energy density, efficiency, low environmental pollution and low operating temperature [2,3]. In previous reports [4–10], the electrocatalytic oxidations of various small organic molecules such as methanol, ethanol and formaldehyde on different modified electrodes have been investigated for application in fuel cells. As appealing candidates, ethylene glycol and glycerol are good potential source in fuel cells owing to its high reactivity in electro-oxidation, inflammability, lower toxicity and high boiling point that enables easy handling and storage [11]. The theoretical energy density of ethylene glycol and glycerol are

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close to that of alcohols (5.2, 5.0, 6.1 and 8.6 kWh/kg for ethylene glycol, glycerol, methanol and ethanol, respectively) making them attractive oxidation fuels for direct fuel cells [12]. Furthermore, many studies have shown that ethylene glycol can be directly produced from the catalytic conversion of biomass-related cellulose and glycerol is also easily available from the biodiesel manufacture [13,14]. Thus ethylene glycol and glycerol are recognized as renewable fuels [15–18]. Considering all these advantages, ethylene glycol and glycerol are promising alternative fuels for direct fuel cells.

Noble metals such as Ag, Pd and Pt, well known for their excellent electrocatalytic ability, are easily poisoned by strong adsorbed CO_{ads} species formed during the oxidation of organics which can slow down the kinetics of the oxidation reaction [4]. Furthermore, a number of challenges such as the high cost and limited world supply hinder their practical applications in commercialization of direct fuel cell. Nickel nanoparticles used as modification material are of great interest in fuel cell research thanks to the low cost, relatively high natural abundance and good corrosion resistance ability [19,20]. Additionally, Ni exhibits superior electrocatalytic activity towards oxidation of small organic compounds in alkaline media [21,22]. Therefore, nanosized nickel based materials are widely used as electro-catalyst for both anodic and cathodic reactions in organic synthesis and aqueous electrolysis [23–26]. One instance, Ferdowsi et al. prepared a modified electrode with Ni nanoparticles deposited on the graphite electrode. Compared to the graphite electrode, the modified electrode exhibits a lower onset potential with a higher anodic current density for methanol oxidation [27]. In another example, Ojani et al. [15] demonstrated a Ni/SDS-POAP/CPE electrode fabricated by open circuit accumulation of Ni(II) on the surface of SDS-POAP/CPE that was prepared by the electro-polymerization of o-aminophenol on a carbon paste electrode in the presence of sodium dodecyl sulphate (SDS). The modified electrode showed a high catalytic performance for the electrocatalytic oxidation of methanol and ethylene glycol. Despite the obvious advantages of the use of nickel nanoparticles in electrochemical applications, exploration of advanced methods is still necessary to increase the electrocatalytic ability of Ni particle-based electrodes dramatically.

Ion implantation is a versatile and powerful material surface modification technique that can be used to embed nanometre-scale clusters and crystals in the near surface region providing practical and excellent electrode materials with long-term stability, catalytic activity and reproducibility [28,29]. Specifically, in this facile, low cost and eco-friendly technique, a selected host material is directly injected with the desired ions the size of which can be easily controlled by changing the implantation conditions [30]. Indium tin oxide (ITO) was chosen as the electrode substrate because it has the advantages of excellent optical transparency, high electrical conductivity, wide electrochemical working window, low capacitive current, stable electrochemical and physical properties [31–33]. In the present paper, our group selected ITO as the substrate and we have successfully fabricated the NiNPs/ITO electrode by ion implantation. The NiNPs/ITO electrode exhibited an enhanced electrocatalytic activity and good long-

term stability for the electrocatalytic oxidation of ethylene glycol and glycerol. The results shows that it is an ideal anode for ethylene glycol and glycerol fuel cells.

Experimental

Reagents and materials

ITO glass was obtained from Beijing Tsinghua Engineering Research Centre of Liquid Crystal Technology. All chemicals were of analytical grade and were used as purchased without any further purification. Triply distilled water was used in this study as the solvent. All measurements were carried out at room temperature.

Fabrication of the NiNPs/ITO electrode

A sheet of ITO glass was cleaned ultrasonically in triply distilled water, ethanol and then again with triply distilled water for 5 min, respectively. Ion implantation was performed using a Beijing Normal University (BNU) metal vapour vacuum arc (MEVVA) implanter. Nickel ions with 10 keV at the fluences of 1.0×10^{17} ions/cm² were implanted onto the pretreated ITO surface to form the NiNPs/ITO electrode. The electrode was washed with distilled water and ethanol for several times prior to use.

Instrumentation

All electrochemical experiments were carried out using a CHI660D electrochemical workstation (CH instrument Inc, USA). A standard three-electrode system was employed consisting of a platinum wire as the auxiliary electrode, an Ag/AgCl electrode as the reference electrode and a bare or modified ITO electrode ($A = 50 \text{ mm}^2$) as the working electrode. Scanning electron microscope (SEM) (Hitachi X650, Japan) was performed to characterize the structure and morphology of the NiNPs/ITO electrode. A SEM was also equipped with an energy-dispersive X-ray spectrometer (EDS) detector for elemental analysis. X-ray photoelectron spectroscopy (XPS) measurement was performed on an AXIS Ultra spectrometer (Shimadzu, Japan).

Results and conclusions

Characterization of NiNPs/ITO electrode

SEM images of NiNPs/ITO electrode

SEM was employed to show the surface morphologies of the bare ITO and NiNPs/ITO electrodes. Fig. 1-A shows the structure of the bare ITO electrode surface, with some rugged grains apparent on the surface. Following implantation, a remarkable change of the surface morphology was observed. As shown in Fig. 1-B, we can clearly see that most of the spherical-shaped grains disappeared and a large number of NiNPs were distributed on the surface of this electrode. The particle size histograms present a wide distribution of

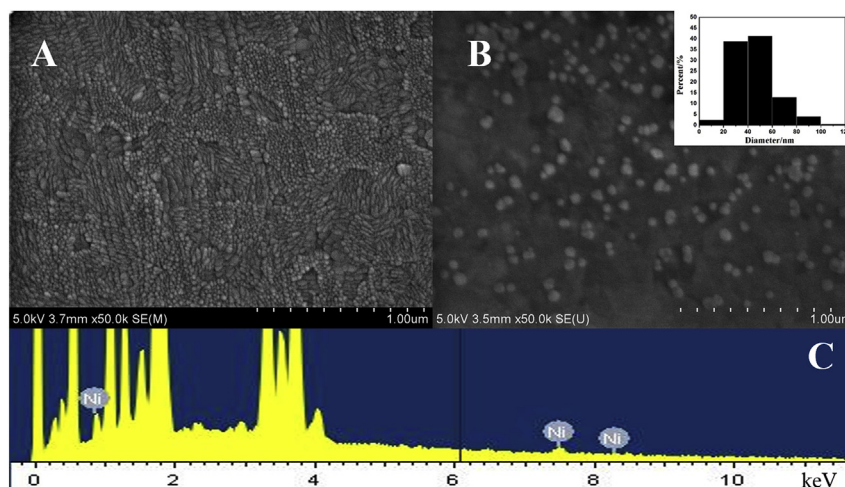


Fig. 1 – SEM images of bare ITO (A) and NiNPs/ITO (B). Inset of plot (B): the particle size statistics. EDS image of NiNPs/ITO (C).

18–110 nm of NiNPs (Fig. 1-B insert), averaging 46 nm. Furthermore, three peaks corresponding to Ni are clearly detected by EDS (Fig. 1-C), indicating the successful implantation of NiNPs onto the ITO film. The above results are in good agreement with the SEM finding.

XPS images of NiNPs/ITO electrode

The Ni 2p XPS spectrum of NiNPs/ITO precursor is presented in Fig. 2. None of any nickel peaks is observed on ITO electrode (curve a). Fig. 2 curve b shows the XPS survey spectrum of the NiNPs/ITO electrode. One strong satellite peaks at 852.2 eV correspond to Ni (2p_{3/2}) were observed. It can be concluded that the implanted Ni is in the zero valent metallic state by comparing the binding [34–36]. This result indicates that we have successfully implanted NiNPs onto the ITO electrode surface.

Electrochemical behaviours of NiNPs/ITO electrode with CV

After scanning the modified electrode for 30 cycles in 0.2 M NaOH solution from –1.0 V to 1.5 V, the electrochemical behaviour of the bare ITO (a) and the NiNPs/ITO (b) were examined using cyclic voltammetry (Fig. 3). As shown by curve

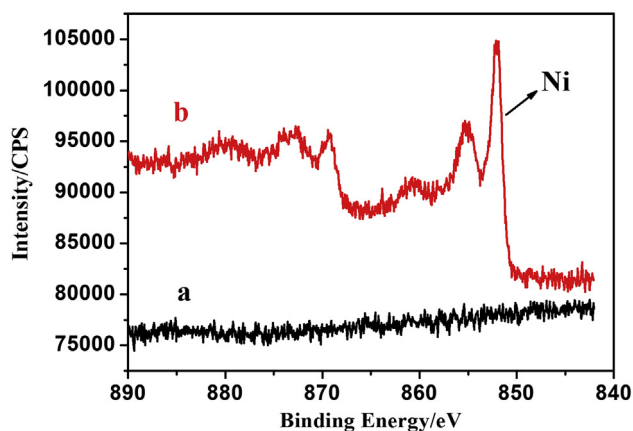


Fig. 2 – XPS spectra of bare ITO (a) and NiNPs/ITO (b).

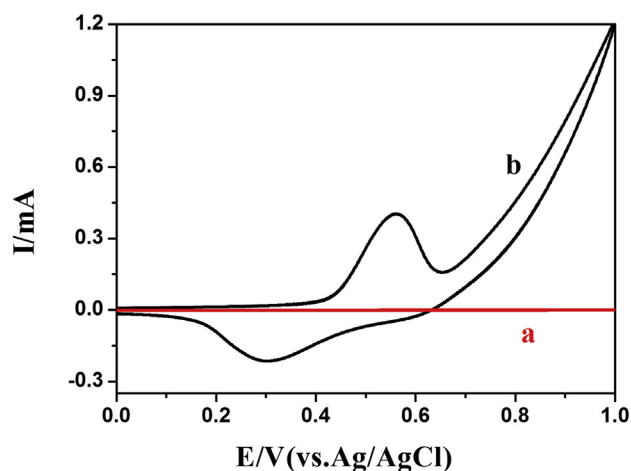
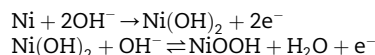


Fig. 3 – CV of bare ITO (a) and NiNPs/ITO (b) in 0.2 M NaOH at a scan rate of 100 mV s⁻¹.

a, no reaction current was observed on the bare ITO, indicating that ITO is non-electroactive in the selected potential range. However, two well-defined redox peaks corresponding to Ni(II)/Ni(III) redox couple appeared in curve b in 0.2 M NaOH from 0.0 to 1.0 V. As can be clearly observed, the peak in the anodic direction at 0.562 V arises from the oxidation of Ni(OH)₂ to NiOOH at the electrode surface and the peak in the cathodic direction at 0.293 V is attributed to the reduction of NiOOH to Ni(OH)₂ [37,38]. This can be described by the following mechanisms:



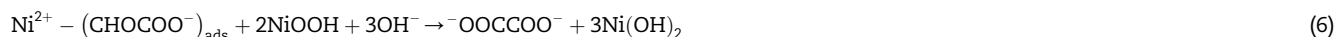
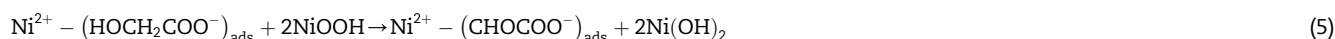
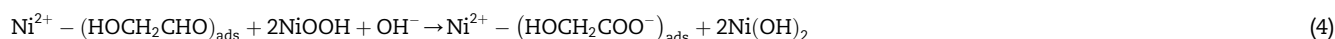
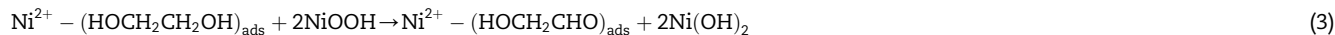
Using the Randles–Ševčík equation, the electrochemically active area was found using the relationship between the peak currents and the scan rates:

$$i_p = 2.69 \times 10^5 n^{3/2} A D_0^{1/2} \nu^{1/2} C_0$$

where n is the number of electrons transferred, A is the effective area of the NiNPs/ITO electrode, D_0 is the diffusion coefficient of the rate-limiting proton, v is the scan rate and C_0 is the concentration of $[\text{Fe}(\text{CN})_6]^{3-/4-}$. The average slope of i_p against $v^{1/2}$ is not shown. The area A is thus calculated to be $1.25 \times 10^5 \text{ cm}^2$.

Fig. 4-A shows CV data for the NiNPs/ITO electrode in the presence of various concentrations of NaOH solution with concentration in the 0.1 M–0.5 M range. As shown in Fig. 4-B, the peak currents increased with NaOH solution concentrations increasing from 0.1 M to 0.3 M, however, we can clearly see that the currents declined when the NaOH solution concentration is increased from 0.3 M to 0.5 M. By contrast, when the NaOH solution concentration is increased, the peak potentials first declined with NaOH concentrations increasing from 0.1 M to 0.2 M then increased, as shown in Fig. 4-C. Thus, we can conclude that OH^- participates in the electrode reaction and its concentration affects the peak current and potential. And NaOH concentration of 0.2 M was chosen as the optimal condition for carrying out the electrochemical experiments.

0.03 M ethylene glycol. It is obvious that no peaks are present in curve a and curve b. However, as can be observed from curve d, the oxidation current of ethylene glycol corresponds to the oxidation of Ni(II) to Ni(III) (according to Eq. (1)) and the reduction current in the negative sweep of potential corresponds to the reduction of Ni(III) to Ni(II). Upon the addition of 0.03 M ethylene glycol, curve d shows a rapidly increased current in the anodic direction due to the adsorption of ethylene glycol by the NiNPs/ITO electrode and the oxidation of ethylene glycol to glycollate which is the intermediate product (according to Eqs. (1)–(4)). Besides, the oxidation peak in the reversed direction at 0.640 V for the further oxidation of glycollate to oxalate (according to Eqs. (5) and (6)). Based on the CV results obtained above and the hypotheses proposed in previous reports [39–44], a possible mechanism for the ethylene glycol oxidation on the surface of the NiNPs/ITO electrode can be written as follows, which can demonstrate the favourable electrocatalytic activity for ethylene glycol oxidation on the NiNPs/ITO:



We examined the effect of the scan rate in the range of 50–800 mV s^{-1} (Fig. 5). It is observed that as potential scan rate is increased, the anodic peak potentials shift to more positive implying that this electrode reaction is quasi-reversible. Furthermore, the inset of Fig. 5 suggests that both the anodic and cathodic peak currents are linearly proportional to the square root of the potential scan rate with the correlation coefficients of 0.9968 and 0.9957, indicating that the electro-oxidation on the NiNPs/ITO is a diffusion-controlled process.

The electrocatalytic oxidation of ethylene glycol by NiNPs/ITO

The electrocatalytic properties of NiNPs/ITO in alkaline media were characterized with CV. Fig. 6 displays CV responses of the bare ITO and the NiNPs/ITO in the absence (curve a and curve c) and presence (curve b and curve d) of

To evaluate the electrocatalytic activity of NiNPs/ITO electrode toward ethylene glycol oxidation, the results obtained by this study were compared with those of other research works in the literature. As revealed in Table 1, this modified electrode in our study has exhibited higher electrocatalytic activity for oxidation of ethylene glycol.

Furthermore, we investigated the effect of ethylene glycol concentration. Fig. 7 depicts CV of the NiNPs/ITO electrode in the presence of various concentrations of ethylene glycol in the range of 0.01–0.06 M. We can clearly observe that the increase in the concentration was followed by an increase in the oxidation peak currents and potentials. As presented in the inset of Fig. 7, the oxidation peak currents are linearly depended on the concentrations and the correlation coefficient is 0.9881. It is supposed that this phenomenon is due to the presence of a diffusion-controlled process that appears to

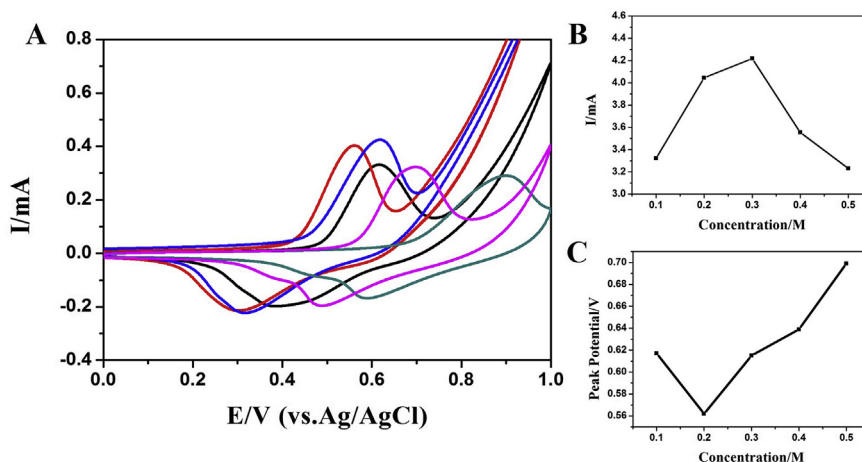


Fig. 4 – (A) CV for 0.1, 0.2, 0.3, 0.4, 0.5 M of NaOH solution concentrations (volume: 10 mL) on NiNPs/ITO electrode. (B) Peak currents versus concentration. (C) Peak potentials versus concentration. Scan rate: 100 mV s^{-1} .

play an important role at ethylene glycol concentrations from 0.01 M to 0.06 M [28,37] Undoubtedly, the data presented in the figure show that ethylene glycol can be efficiently catalysed at the surface of the NiNPs/ITO electrode.

From the standpoint of practical use, high catalytic stability is another attractive characteristic of the fabricated metal nanoparticles modified electrode. The stability of the NiNPs/ITO electrode was investigated by current–time curve technique with a long time window at a constant potential of 0.74 V versus Ag/AgCl in 0.2 M NaOH containing 0.03M ethylene glycol (Fig. 8 A). It is important to note that firstly the current decreased slowly and then reached a relatively stable value after 500 s. This observation implies that NiNPs/ITO electrode exhibits an excellent stability for the oxidation of ethylene glycol. Fig. 8-B shows that the anodic peak currents

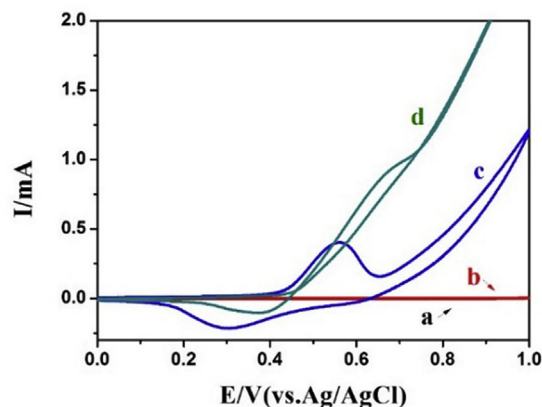


Fig. 6 – CV of bare ITO and NiNPs/ITO in the absence (curve a and curve c) and presence (curve b & curve d) of 0.03 M ethylene glycol in 0.2 M NaOH. Scan rate: 100 mV s^{-1} .

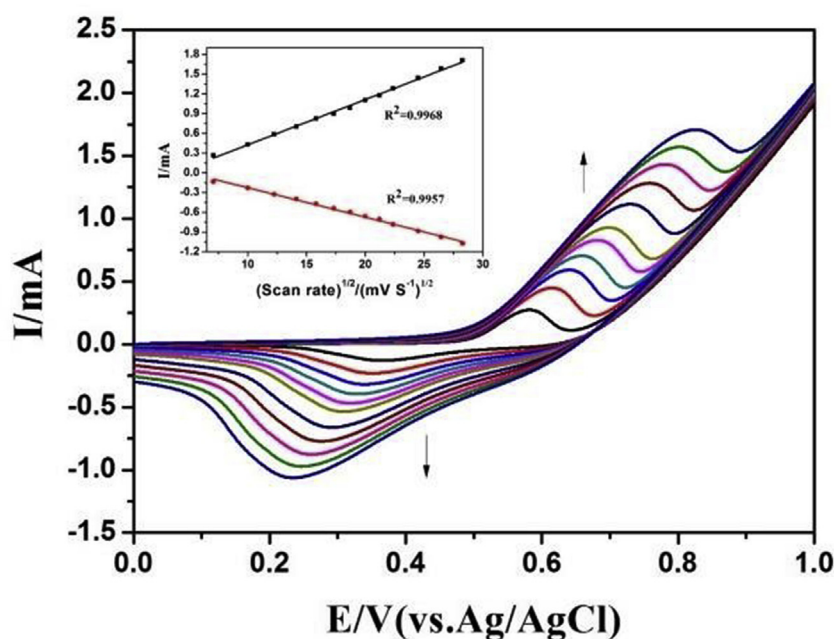


Fig. 5 – CV of the NiNPs/ITO in 0.2 M NaOH solution, scan rates from inner to outer are 50, 100, 150, 200, 250, 300, 350, 400, 450, 500, 600, 700 and 800 mV s^{-1} , respectively. Inset of Fig. 4: plot of anodic and cathodic peak currents versus the square root of scan rates.

Table 1 – Comparison for electrocatalytic activity of NiNPs/ITO electrode with other modified electrodes for ethylene glycol oxidation reaction.

Modified electrode	Alcohol solution	E_p/V	I_p/mA	Ref. No.
Ni/SDS-PPAA/CPE	0.1 M NaOH/0.02 M EG	0.60 (vs. Ag/AgCl)	0.45	[28]
Ni/SDS-POAP/CPE	0.1 M NaOH/0.28 M EG	0.80 (vs. Ag/AgCl)	1.00	[45]
PolyNiTSPc/Au/Q	pH 11 buffer electrolyte/1 M EG	0.52 (vs. Ag/AgCl)	0.60	[46]
Ni/PMT(TX-100)/MCPE	0.1 M NaOH/0.06 M EG	0.67 (vs. Ag/AgCl)	1.70	[15]
NiNPs/ITO	0.2 M NaOH/0.03 M EG	0.64 (vs. Ag/AgCl)	0.80	This work

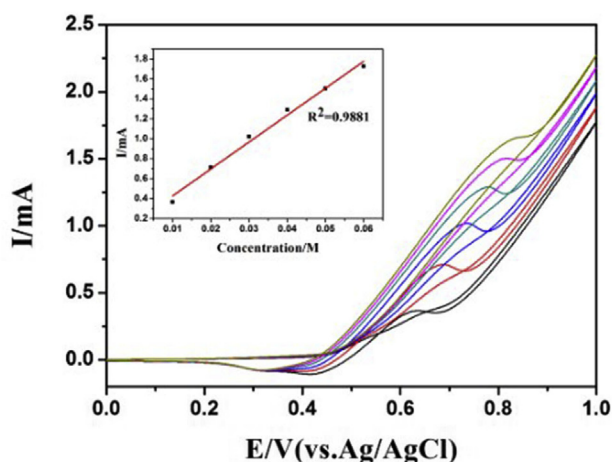


Fig. 7 – CV of NiNPs/ITO electrode with different concentrations of ethylene glycol: 0.01, 0.02, 0.03, 0.04, 0.05 and 0.06 M in 0.2 M NaOH. Inset of plot: peak currents versus concentrations of ethylene glycol. Scan rate: 100 mV s⁻¹.

of ethylene glycol oxidation increased slightly with increasing cycle number. After scanning for 300 cycles using CV, the peak current was 1.520 mA, equal to 105% of that (1.450 mA) at the first cycle. Based on the above, we can draw a conclusion that

ion implanted NiNPs display favourable stability making them a viable and promising alternative catalyst for oxidation of small organic molecules in fuel cells.

The electrocatalytic oxidation of glycerol by NiNPs/ITO

As shown in Figs. 9 (A) and Fig.10, it is obvious that there are many similarities between the graphs for ethylene glycol and glycerol. We could found that the anodic peak current of ethylene glycol oxidation was slightly higher than that of glycerol, indicating that nickel nanoparticles show higher catalytic activity toward ethylene glycol oxidation on the NiNPs/ITO electrode. According to the reported previously results [47–50], glycerol oxidation shared the similar mechanism with ethylene glycol. Fig. 9-B shows the current–time curve of the NiNPs/ITO electrode in the 0.2 M NaOH toward 0.02 M glycerol at a constant potential of 0.70 V versus Ag/AgCl for 3000 s. Inspection of the figure shows the current decreased slowly during the first 500 s, however, the current still decreased slightly after 500 s, which is different from the current–time curve of 0.03 M ethylene glycol. This implies that the NiNPs/ITO electrode also has a high stability toward glycerol oxidation. Furthermore, we also studied the relationship between the anodic peak current and the number of cycles in 0.02 M glycerol. After scanning through 300 cycles by CV, the peak current was 0.459 mA, equals 97% of that (0.473 mA) at the first cycle.

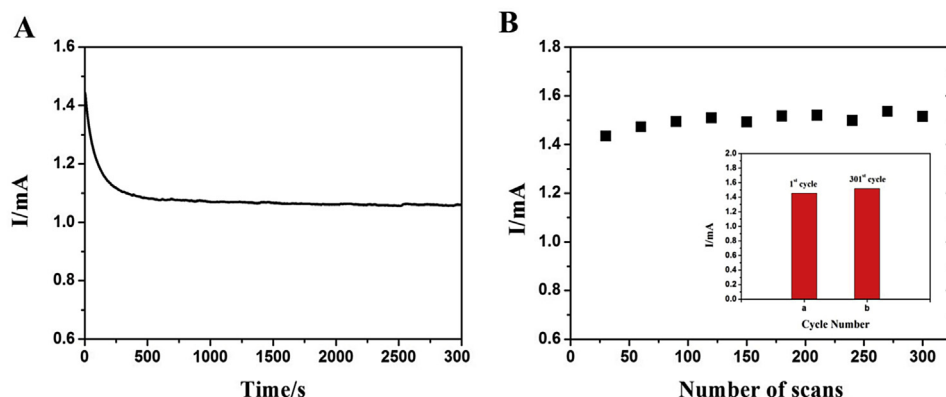


Fig. 8 – (A) I–t relations for ethylene glycol oxidation on NiNPs/ITO electrode in 0.2 M NaOH containing 0.03 M ethylene glycol. (B) Relationship between the peak current obtained by CV and the cycle number in 0.03M ethylene glycol in 0.2 M NaOH. Inset of plot (B): Peak currents of the NiNPs/ITO electrode of the first cycle and 301st cycle in prepared solution. Scan rate: 100 mV s⁻¹.

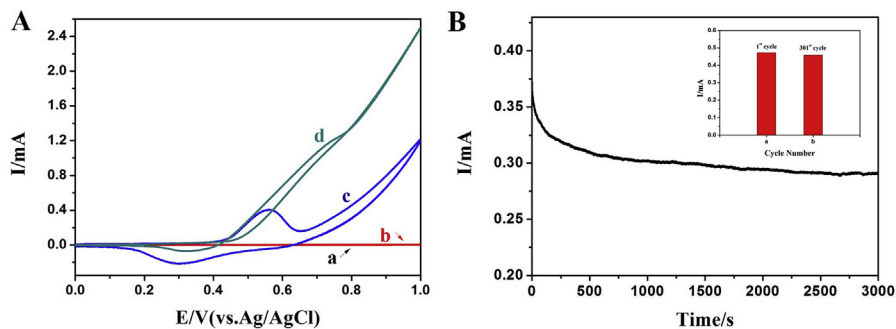


Fig. 9 – (A) CV of bare ITO and NiNPs/ITO in the absence (curve a and curve c) and presence (curve b and curve d) of 0.02M glycerol in 0.2 M NaOH. (B) I–t relations for glycerol oxidation of the NiNPs/ITO electrode in 0.2 M NaOH containing 0.02 M glycerol. Insert of plot (B): Peak currents of NiNPs/ITO electrode of the first cycle and 301st cycle in prepared solution. Scan rate: 100 mV s^{-1} .

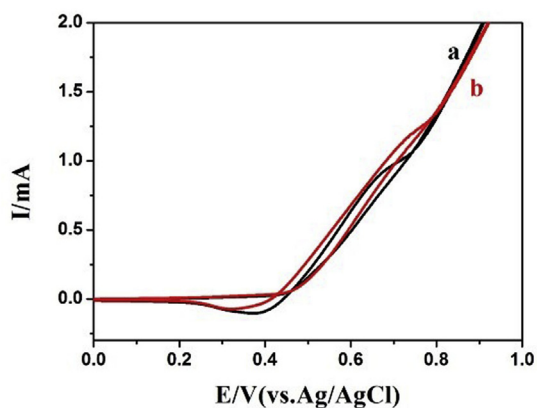


Fig. 10 – CV of NiNPs/ITO in 0.03M ethylene glycol (curve a) and 0.02 M glycerol (curve b) in 0.02 M NaOH. Scan rate: 100 mV s^{-1} .

Conclusions

In this work, NiNPs have been modified onto ITO electrode by ion implantation to prepare a novel functional electrode and the electro-oxidation of organics was catalysed by Ni(III) on the surface of this modified electrode. With nickel ions at the fluences of 1.0×10^{17} ions/cm², the NiNPs/ITO electrode exhibited good catalytic performance for the electrocatalytic oxidation of ethylene glycol and glycerol in alkaline solution. Moreover, the proposed electrode shows satisfactory stability when continued cycling by CV. All these results suggested that the NiNPs/ITO can act promising catalysts for fuel cells.

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REFERENCES

- [1] Stradiotto NR, Toghiani KE, Xiao L, Moshar A, Compton RG. The fabrication and characterization of a nickel nanoparticle modified boron doped diamond electrode for electrocatalysis of primary alcohol oxidation. *Electroanalysis* 2009;21:2627–33.
- [2] Tarrús X, Montiel M, Vallés E, Gómez E. Electrocatalytic oxidation of methanol on CoNi electrodeposited materials. *Int J Hydrogen Energy* 2014;39:6705–13.
- [3] Kannan P, Yoon C-S, Yi S-C, Lee SY, Kim D-H. Shape-controlled synthesis of gold–nickel bimetallic nanoparticles and their electrocatalytic properties. *Mater Chem Phys* 2015;156:1–8.
- [4] Yu Y, Wang T, Fu Y, Su W, Hu J. Platinum nanoparticles ion-implanted-modified indium tin oxide electrode for electrocatalytic oxidation of formaldehyde. *Int J Hydrogen Energy* 2014;39:17617–21.
- [5] Yu Y, Jia M, Tian H, Hu J. The fabrication of silver ion implantation-modified electrode and its application in electrocatalytic oxidation of formaldehyde. *J Power Sources* 2014;267:123–7.
- [6] Joo J, Uchida T, Cuesta A, Koper MT, Osawa M. Importance of acid-base equilibrium in electrocatalytic oxidation of formic acid on platinum. *J Am Chem Soc* 2013;135:9991–4.
- [7] Lamy C, Belgsir E, Leger J. Electrocatalytic oxidation of aliphatic alcohols: application to the direct alcohol fuel cell (DAFC). *J Appl Electrochem* 2001;31:799–809.
- [8] Macak JM, Barczuk PJ, Tsuchiya H, Nowakowska MZ, Ghicov A, Chojak M, et al. Self-organized nanotubular TiO₂ matrix as support for dispersed Pt/Ru nanoparticles: enhancement of the electrocatalytic oxidation of methanol. *Electrochem Commun* 2005;7:1417–22.
- [9] Gao G-Y, Guo D-J, Li H-L. Electrocatalytic oxidation of formaldehyde on palladium nanoparticles supported on multi-walled carbon nanotubes. *J Power Sources* 2006;162:1094–8.
- [10] Cao H, Fan Z, Hou G, Tang Y, Zheng G. Ball-flower-shaped Ni nanoparticles on Cu modified TiO₂ nanotube arrays for electrocatalytic oxidation of methanol. *Electrochimica Acta* 2014;125:275–81.
- [11] Ramulifho T, Ozoemena KI, Modibedi RM, Jafta CJ, Mathe MK. Electrocatalytic oxidation of ethylene glycol at palladium-bimetallic nanocatalysts (PdSn and PdNi) supported on sulfonate-functionalised multi-walled carbon nanotubes. *J Electroanal Chem* 2013;692:26–30.

- [12] Xin L, Zhang Z, Qi J, Chadderdon D, Li W. Electrocatalytic oxidation of ethylene glycol (EG) on supported Pt and Au catalysts in alkaline media: reaction pathway investigation in three-electrode cell and fuel cell reactors. *Appl Catal B Environ* 2012;125:85–94.
- [13] Lam BTX, Chiku M, Higuchi E, Inoue H. Preparation of PdAg and PdAu nanoparticle-loaded carbon black catalysts and their electrocatalytic activity for the glycerol oxidation reaction in alkaline medium. *J Power Sources* 2015;297:149–57.
- [14] Qi J, Xin L, Chadderdon DJ, Qiu Y, Jiang Y, Benipal N, et al. Electrocatalytic selective oxidation of glycerol to tartrate on Au/C anode catalysts in anion exchange membrane fuel cells with electricity cogeneration. *Appl Catal B Environ* 2014;154–155:360–8.
- [15] Ojani R, Raof J-B, Goli M, Alinezhad A. High electrocatalysis of ethylene glycol oxidation based on nickel particles electrodeposited into poly (m-toluidine)/Triton X-100 composite. *J Appl Electrochem* 2013;43:927–37.
- [16] Coutanceau C, Demarconnay L, Lamy C, Léger JM. Development of electrocatalysts for solid alkaline fuel cell (SAFC). *J Power Sources* 2006;156:14–9.
- [17] Livshits V, Peled E. Progress in the development of a high-power, direct ethylene glycol fuel cell (DEGFC). *J Power Sources* 2006;161:1187–91.
- [18] Tehrani RMA, Ab Ghani S. Electrocatalysis of free glycerol at a nanonickel modified graphite electrode and its determination in biodiesel. *Electrochimica Acta* 2012;70:153–7.
- [19] Fan X, Burton R, Zhou Y. Glycerol (byproduct of biodiesel production) as a source for fuels and chemicals—mini review. *Open Fuels Energy Sci J* 2010;3:17–22.
- [20] Scott K, Taama W, Argyropoulos P, Sundmacher K. The impact of mass transport and methanol crossover on the direct methanol fuel cell. *J Power Sources* 1999;83:204–16.
- [21] Habibi B, Delnavaz N. Electrocatalytic oxidation of formic acid and formaldehyde on platinum nanoparticles decorated carbon-ceramic substrate. *Int J Hydrogen Energy* 2010;35:8831–40.
- [22] Yi Q, Niu F, Yu W. Pd-modified TiO₂ electrode for electrochemical oxidation of hydrazine, formaldehyde and glucose. *Thin Solid Films* 2011;519:3155–61.
- [23] Pan D, Wang X, Li J, Wang L, Li Z, Liu Y, et al. Radiolysis route to Pt nanodendrites with enhanced comprehensive electrocatalytic performances for methanol oxidation. *Catal Commun* 2015;62:14–8.
- [24] Fan C, Piron D, Sleba A, Paradis P. Study of electrodeposited nickel-molybdenum, nickel-tungsten, cobalt-molybdenum, and cobalt-tungsten as hydrogen electrodes in alkaline water electrolysis. *J Electrochem Soc* 1994;141:382–7.
- [25] Raj IA, Vasu K. Transition metal-based hydrogen electrodes in alkaline solution—electrocatalysis on nickel based binary alloy coatings. *J Appl Electrochem* 1990;20:32–8.
- [26] Casadei MA, Pletcher D. The influence of conditions on the electrocatalytic hydrogenation of organic molecules. *Electrochimica Acta* 1988;33:117–20.
- [27] Ferdowsi GS, Seyedsadjadi SA, Ghaffarinejad A. Ni nanoparticle modified graphite electrode for methanol electrocatalytic oxidation in alkaline media. *J Nanostructure Chem* 2014;5:17–23.
- [28] Ojani R, Raof J-B, Rahemi V. Evaluation of sodium dodecyl sulfate effect on electrocatalytic properties of poly (4-aminoacetanilide)/nickel modified carbon paste electrode as an efficient electrode toward oxidation of ethylene glycol. *Int J Hydrogen Energy* 2011;36:13288–94.
- [29] Townsend P. Optical effects of ion implantation. *Rep Prog Phys* 1987;50:501.
- [30] Liu C, Chen Q, Jiao J, Li S, Hu J, Li Q. Surface modification of indium tin oxide films with Au ions implantation: characterization and application in bioelectrochemistry. *Surf Coatings Technol* 2011;205:3639–43.
- [31] Booth MA, Leveneur J, Costa AS, Kennedy J, Travas-Sejdic J. Tailoring the conductivity of polypyrrole films using low-energy platinum ion implantation. *J Phys Chem C* 2012;116:8236–42.
- [32] Muntele CI, Ichou R, Muntele IC, Sarkisov S, Ila D. Surface characterization of silicon carbide following shallow implantation of platinum ions. *Surf Coatings Technol* 2007;201:8339–42.
- [33] Song Y, Ma Y, Wang Y, Di J, Tu Y. Electrochemical deposition of gold–platinum alloy nanoparticles on an indium tin oxide electrode and their electrocatalytic applications. *Electrochimica Acta* 2010;55:4909–14.
- [34] Ali-Löytty H, Louie MW, Singh MR, Li L, Sanchez Casalongue HG, Ogasawara H, et al. Ambient-pressure XPS study of a Ni–Fe electrocatalyst for the oxygen evolution reaction. *J Phys Chem C* 2016;120:2247–53.
- [35] Kaviani R, Choi S-I, Park J, Liu T, Peng H-C, Lu N, et al. Pt–Ni octahedral nanocrystals as a class of highly active electrocatalysts toward the hydrogen evolution reaction in an alkaline electrolyte. *J Mater Chem A* 2016;4:12392–7.
- [36] Dündar-Tekkaya E, Yürüm Y. Effect of loading bimetallic mixture of Ni and Pd on hydrogen storage capacity of MCM-41. *Int J Hydrogen Energy* 2015;40:7636–43.
- [37] Golikand AN, Asgari M, Maragheh MG, Shahrokhian S. Methanol electrooxidation on a nickel electrode modified by nickel–dimethylglyoxime complex formed by electrochemical synthesis. *J Electroanal Chem* 2006;588:155–60.
- [38] Mac Aodha D. Development of mediated enzymatic fuel cells for operation in blood. 2013.
- [39] Tammam RH, Fekry AM, Saleh MM. Electrocatalytic oxidation of methanol on ordered binary catalyst of manganese and nickel oxide nanoparticles. *Int J Hydrogen Energy* 2015;40:275–83.
- [40] Chang SC, Ho Y, Weaver MJ. Applications of real-time FTIR spectroscopy to the elucidation of complex electroorganic pathways: electrooxidation of ethylene glycol on gold, platinum, and nickel in alkaline solution. *J Am Chem Soc* 1991;113:9506–13.
- [41] Serov A, Kwak C. Recent achievements in direct ethylene glycol fuel cells (DEGFC). *Appl Catal B Environ* 2010;97:1–12.
- [42] Marchionni A, Bevilacqua M, Bianchini C, Chen YX, Filippi J, Fornasiero P, et al. Electrooxidation of ethylene glycol and glycerol on Pd-(Ni-Zn)/C anodes in direct alcohol fuel cells. *ChemSusChem* 2013;6:518–28.
- [43] de Lima RB, Paganin V, Iwasita T, Vielstich W. On the electrocatalysis of ethylene glycol oxidation. *Electrochimica Acta* 2003;49:85–91.
- [44] Casella IG, Cataldi TRI, Salvi AM, Desimoni E. Electrocatalytic oxidation and liquid chromatographic detection of aliphatic alcohols at a nickel-based glassy carbon modified electrode. *Anal Chem* 1993;65:3143–50.
- [45] Ojani R, Raof J-B, Fathi S. Poly(o-aminophenol) film prepared in the presence of sodium dodecyl sulfate: application for nickel ion dispersion and the electrocatalytic oxidation of methanol and ethylene glycol. *Electrochimica Acta* 2009;54:2190–6.
- [46] Ureta-Zañartu MS, Alarcón A, Muñoz G, Gutiérrez C. Electrooxidation of methanol and ethylene glycol on gold and on gold modified with an electrodeposited polyNiTSPc film. *Electrochimica Acta* 2007;52:7857–64.
- [47] Behr A, Eilting J, Irawadi K, Leschinski J, Lindner F. Improved utilisation of renewable resources: new important derivatives of glycerol. *Green Chem* 2008;10:13–30.

- [48] Schouten KJP, Kwon Y, van der Ham CJM, Qin Z, Koper MTM. A new mechanism for the selectivity to C1 and C2 species in the electrochemical reduction of carbon dioxide on copper electrodes. *Chem Sci* 2011;2:1902.
- [49] Simões M, Baranton S, Coutanceau C. Electro-oxidation of glycerol at Pd based nano-catalysts for an application in alkaline fuel cells for chemicals and energy cogeneration. *Appl Catal B Environ* 2010;93:354–62.
- [50] Oliveira VL, Morais C, Servat K, Napporn TW, Tremiliosi-Filho G, Kokoh KB. Glycerol oxidation on nickel based nanocatalysts in alkaline medium – identification of the reaction products. *J Electroanal Chem* 2013;703:56–62.