Summer 9-1-2018

Assembling of NiOx/MWCNTs-GC Anodic Nanocatalyst for Water Electrolysis Applications

Yaser M. Asal Mr.
The British University in Egypt, yasser.mohamed@bue.edu.eg

Islam M. Al-Akraa Dr
The British University in Egypt

Saher D. Khamis Eng
The British University in Egypt

Recommended Citation

Asal, Yaser M. Mr.; Al-Akraa, Islam M. Dr; and Khamis, Saher D. Eng, "Assembling of NiOx/MWCNTs-GC Anodic Nanocatalyst for Water Electrolysis Applications" (2018). *Chemical Engineering*. 90.
https://buescholar.bue.edu.eg/chem_eng/90

Int. J. Electrochem. Sci., 13 **(2018)** 9712 – 9720, doi: 10.20964/2018.10.01

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Assembling of NiOx/MWCNTs-GC Anodic Nanocatalyst for Water Electrolysis Applications

Islam M. Al-Akraa[*], *Yaser M. Asal, Saher D. Khamis*

Department of Chemical Engineering, Faculty of Engineering, The British University in Egypt, Cairo 11837, Egypt
[*]E-mail: islam.ahmed@bue.edu.eg; islam0886@yahoo.com

Received: 14 May 2018 / *Accepted:* 3 June 2018 / *Published:* 1 September 2018

Glassy carbon (GC) electrode is intended to be modified with nickel oxide (NiOx) and multiwalled carbon nanotubes (MWCNTs) in the anodic reaction of water electrolysis. NiOx deposition time is optimized and a 5 min was enough to attain the maximum activity. A further modification of the catalyst with MWCNTs could greatly enhance its stability during continuous electrolysis. As an outcome, an energy amount of 21.7 kWh/KgO_2 is minimized. Several electrochemical and materials characterization setups will be utilized to test the catalyst activity and to know its geometry and structure.

Keywords: Catalysis; Water splitting; Nickel; MWCNTs.

1. INTRODUCTION

Due to the huge population growth, increased demand on energy, and the uncleanliness of traditional energy sources, we should think about alternative, available, and clean energy technologies [1-4]. Of these technologies, electrochemical water splitting is considered one of the most non-traditional clean methods for hydrogen production [3, 5]. It involves the hydrogen evolution reaction (HER, $2H^+/2e^-$) and oxygen evolution reaction (OER, $4H^+/4e^-$) [6]. Unfortunately, the efficiency of electrochemical water splitting is hindered by OER, in which molecular oxygen is obtained from the water oxidation [6]. It is a vital reaction in several energy conversion systems as well as many industrial applications [6, 7].

From kinetics point of view, OER involves a transfer of four electrons that results in a high overpotentials and very slow kinetics [8]. That makes research directed to develop an efficient catalyst capable of crossing these two great obstacles. In several previous investigations, RuO_2 and IrO_2

showed a very high activity toward OER [9, 10]. However, their usgae has been limited because they are expensive and their supply for large-scale applications is inadequate [6, 11, 12].

Nickel oxide (NiOx) is one of the most intersting electrocatalysts incorporated in electrochemical systems because of its high activity and conductance [13, 14]. It has been used in catalysis [15], sensors [16], batteries [17, 18], and solar cells [19]. Most of the recent research focused on NiOx usage as an electrocatalyst for the hydrogen evolution [20, 21], few have explored its potential toward OER [22, 23], this prompts the research into improving an efficient, catalytically active, and stable NiOx-based anodes for OER.

Herein, we report on fabricating a NiOx-modified glassy carbon (GC) electrode for OER by a simple electrochemical route. The NiOx deposition will be optimized seeking the highest efficiency. Moreover, the influence of incorporating multiwalled carbon nanotubes (MWCNTs) on the catalyst stability will be monitored.

2. EXPERIMENTAL

A cleaned, polished with aqueous slurries of alumina powder (down to 0.06 μm) then washed thoroughly with second distilled water, GC electrode (*d* = 5.0 mm) was used as the working electrode. A spiral Pt wire and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively.

The electrode's modification with NiOx was attained in two successive steps. The first one involved assembling of metallic nickel on the GC electrode from an aqueous solution of 0.1 M acetate buffer solution (ABS, pH = 4.0) containing 0.1 M $Ni(NO_3)_2$ by a constant potential electrolysis at −1 V. Next, the metallic Ni was oxidized in 0.1 M phosphate buffer solution (PBS, pH = 7) by scanning the potential between −0.5 and 1 V for 10 cycles at 100 mV s^{-1} [24].

Modifying the GC electrode with MWCNTs was carried out by dispersion of 10 mg MWCNTs in 1 ml aliquots of 5% Nafion/ethanol and sonication for 1 h. Then, 10 µL of the suspension is applied evenly at the GC electrode and the ethanol was evaporated for 1 h at room temperature. Finally, the electrode was washed with double distilled water.

The electrochemical investigations were performed at room temperature (25±1 ^{o}C) in a solution of 0.1 M NaOH in a three-electrode glass cell using a Bio-Logic SAS potentiostat (model SP-150) operated with EC-Lab software.

A field emission scanning electron microscope (FE-SEM, QUANTA FEG 250) joined to an energy dispersive X-ray spectrometer (EDS) unit was engaged to determine the electrode surface shape and structure.

3. RESULTS AND DISCUSSION

3.1. Electrochemical and Material characterization

Figure 1 displays CVs obtained at (a-e) NiOx/GC with NiOx loading time interval and (f) NiOx (5 min)/MWCNTs-GC modified electrodes The measurements are carried out in an basic solutions to probe the oxidation/reduction behavior of the electrodeposited NiOx at the GC surface [5]. A redox couple is observed in all cases which systematically getting higher in current with increasing loading time (due to increasing the amount of deposited Ni and therefore the amount of NiOx at the electrode surface) which is attributed to the redox transformation between lower and higher oxidation states of Ni [25].

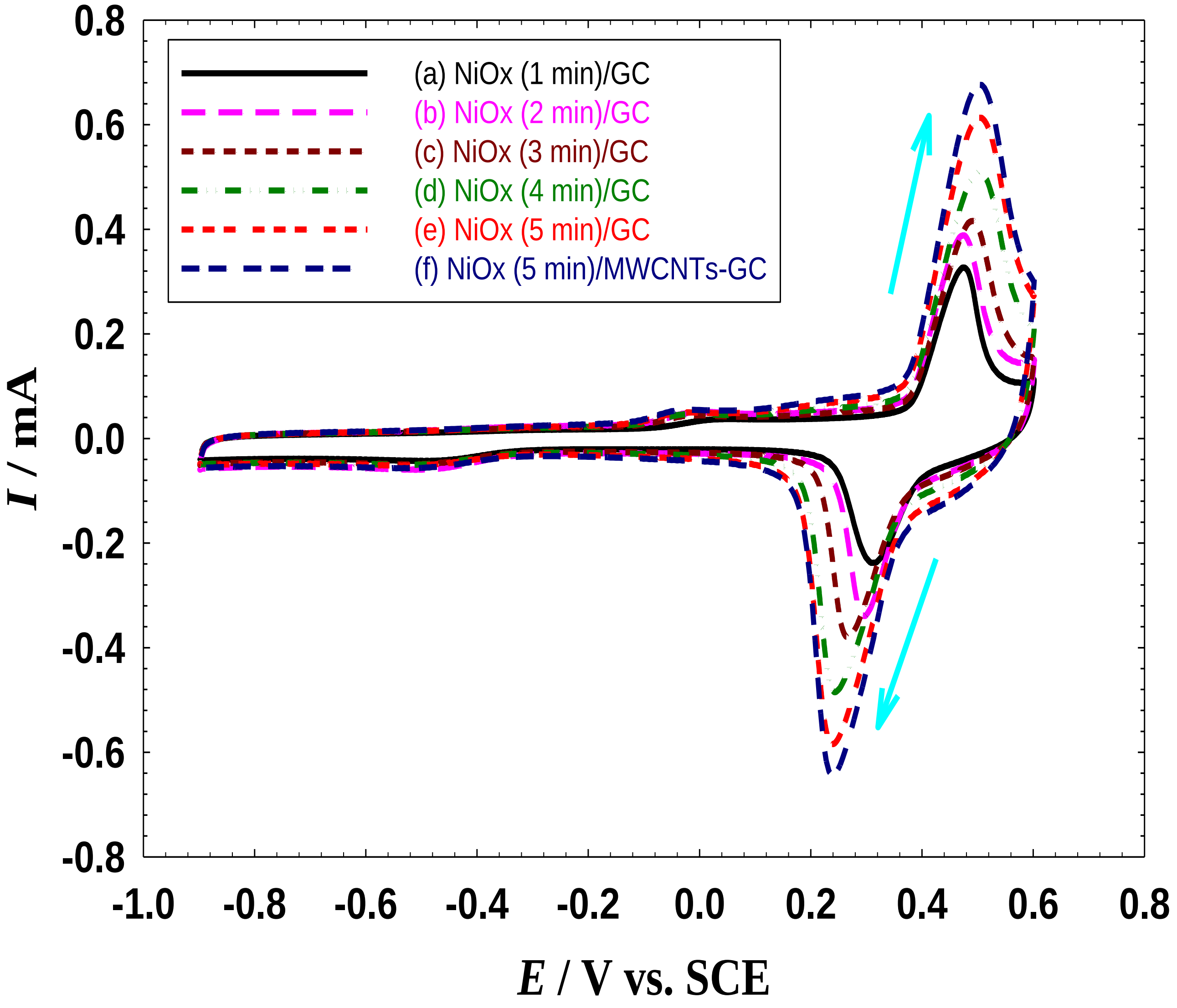


Figure 1. CVs obtained at (a-e) NiOx/GC with several NiOx loading times and (f) NiOx (5 min)/ MWCNTs-GC modified electrodes measured in 0.1 M NaOH at a potential scan rate of 100 mVs^{-1}.

Structurally, Fig. 2A and B shows FE-SEM micrographs of the NiOx (5 min)/GC and NiOx (5 min)/MWCNTs-GC modified electrodes, respectively. It gives a clear picture about assembling the NiOx onto the GC and the MWCNTs-GC electrodes in cauliflower-like structures with ca. 95 nm particle diameter.

The EDS analysis in Fig. 3 inferred about the successful deposition of the catalyst ingredients and aided to calculate its comparative ratios. The peaks of C, O, and Ni appeared on their assigned positions and their relative ratios summarized in the table inserted as inset of Fig. 3.

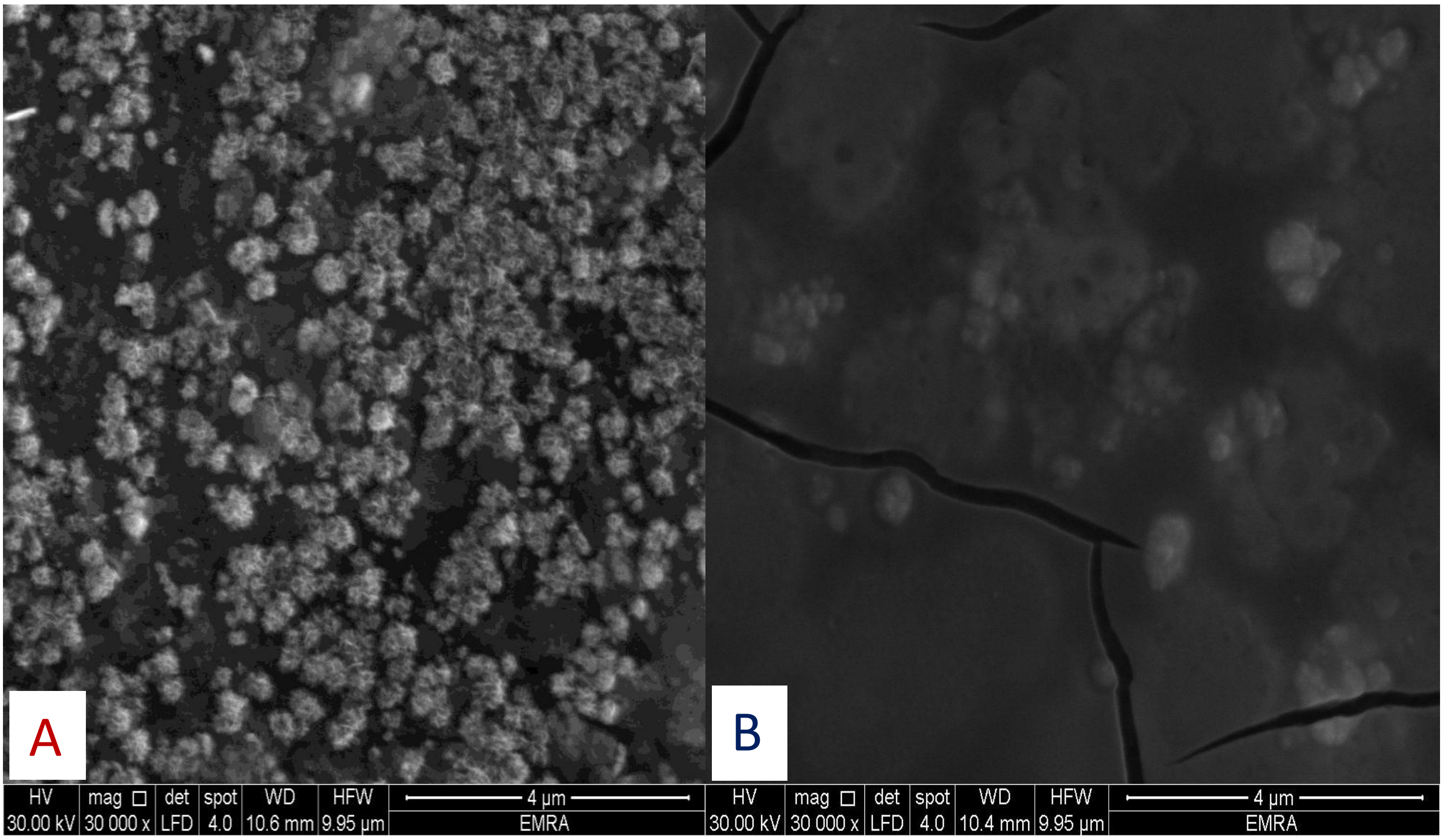
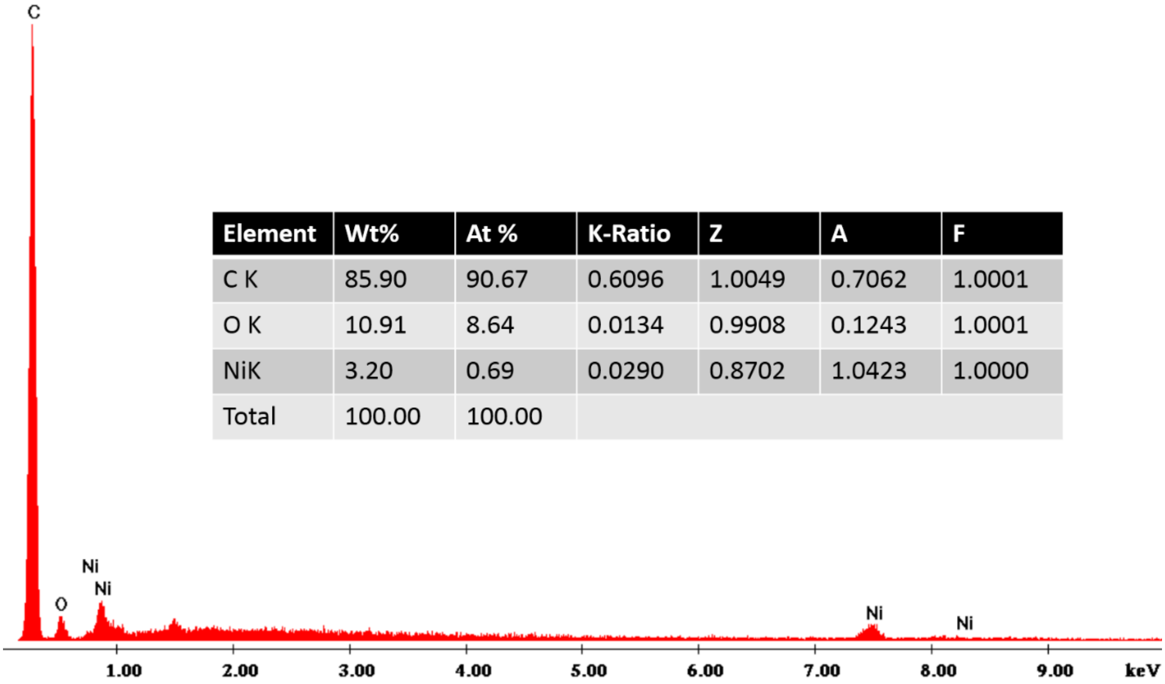


Figure 2. FE-SEM micrographs of the NiOx (5 min)/GC (A) and NiOx (5 min)/MWCNTs-GC (B) electrodes.



Element	Wt%	At %	K-Ratio	Z	A	F
C K	85.90	90.67	0.6096	1.0049	0.7062	1.0001
O K	10.91	8.64	0.0134	0.9908	0.1243	1.0001
NiK	3.20	0.69	0.0290	0.8702	1.0423	1.0000
Total	100.00	100.00				

Figure 3. EDS analysis of the NiOx (5 min)/GC modified electrode.

3.2. Electrocatalytic activity toward OER

Figure 4 shows the linear sweep voltammograms (LSVs) of the NiOx/GC and NiOx/MWCNTs-GC modified electrodes measured in 0.1 M NaOH solution at a potential scan rate of 50 mV s^{-1}.

In case of OER, the lower the onset potential, at which the reaction starts (E_{onset}), the electrode acquired, the higher activity the electrode shows. The reason behind that comes from that this negative shift will directly be translated to a power saving which is the main concern that industry face in the long run. Actually, the E_{onset} for OER at the bare GC electrode appeared at ca. 1.5 V (Fig. 4g). Fascinatingly, as NiOx was successively electrodeposited (starting with 1 min deposition) at the GC and MWCNTs-GC electrodes, the E_{onset} could be observed to decrease also in a systematic mode until reaching 5 min which was the ideal deposition time (Fig.4 a-f). The shift in the E_{onset} related compared with that of the bare GC electrode ($|E_{onset} - E_{onset\ (bare\ GC)}|$) at 0.4 mA, and the equivalent energy saving values could be obtained based on the equation referenced previously [3]. Table 1 summarizes all these values.

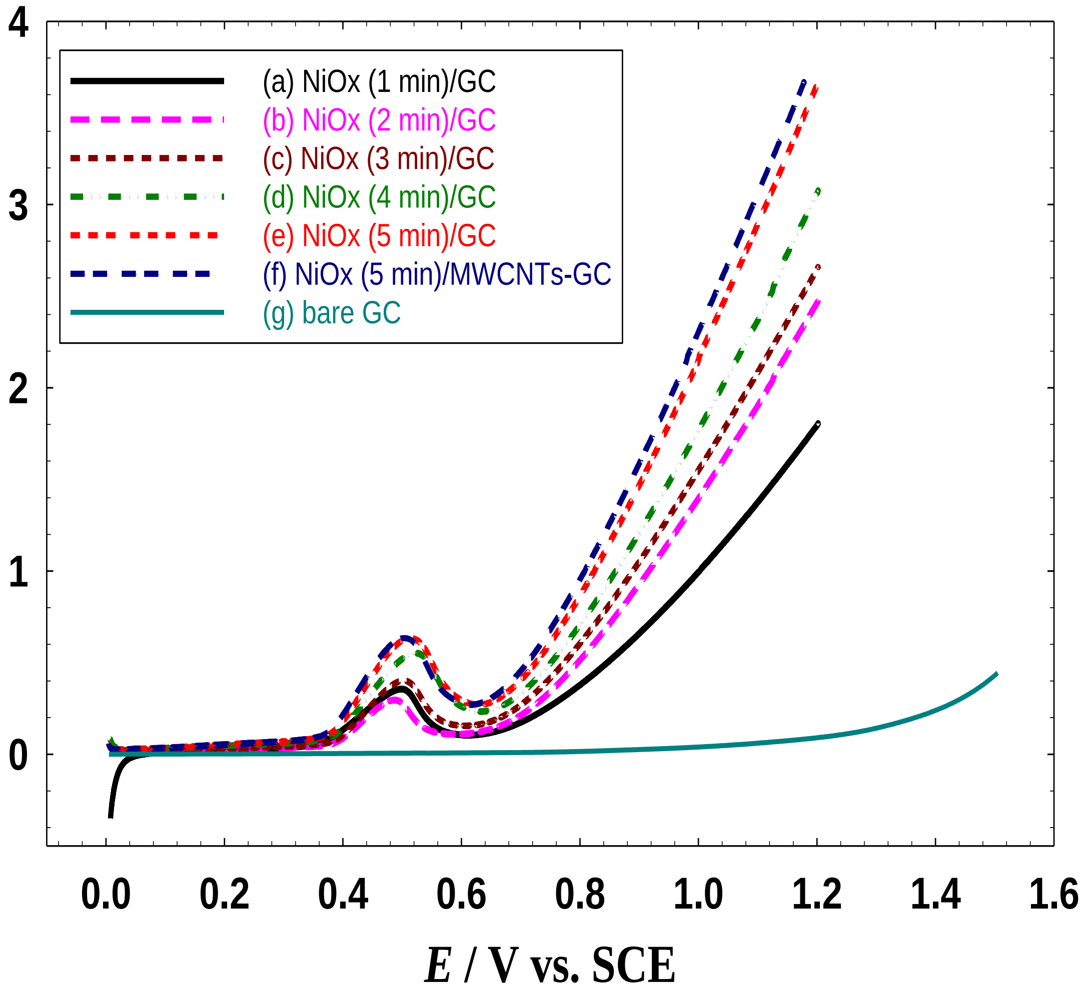


Figure 4. LSVs obtained at (a-e) NiOx/GC with several NiOx loading times, (h) NiOx (5 min)/ MWCNTs-GC, and (i) bare GC electrodes measured in 0.1 M NaOH. Potential scan rate: 50 mVs^{-1}.

Table 1. A summary of the E_{onset}, negative shift in the E_{onset} compared to that of the bare GC electrode ($|E_{onset} - E_{onset\ (bare\ GC)}|$) at 0.4 mA, and the corresponding energy saving values.

Electrode	E_{onset}, V	$\vert E_{onset} - E_{onset\ (bare\ GC)}\vert$, V	Power saving, kWh/Kg O_2
bare GC	1.50	---	---
NiOx (1 min)/GC	0.81	0.69	18.5
NiOx (2 min)/GC	0.77	0.73	19.6
NiOx (3 min)/GC	0.75	0.75	20.1
NiOx (4 min)/GC	0.73	0.77	20.6
NiOx (5 min)/GC	0.70	0.80	21.4
NiOx (5 min)/MWCNTs-GC	0.69	0.81	21.7

The distinctive activity showed at the modified electrodes toward OER can be described in view of the general mechanism for the OER that has been considered in basic media [26-28] :

$$M + OH^- \rightarrow MOH + e^- \quad (1)$$
$$MOH + OH^- \rightarrow MO^- + H_2O \quad (2)$$
$$MO^- \rightarrow MO + e^- \quad (3)$$
$$2\,MO \rightarrow 2M + O_2 \quad (4)$$

Where M refers to metal active surface site. The step at which the rate is depending on is frequently assigned to the adsorption and the initial charge transfer, i.e., Reaction 1 [3, 29]. Here, the catalytic enhancement is believed to derive from the redox mediation by NiOx [30]. This can, definitely, makes the charge transfer easier and will so catalyze OER.

A comparison between the E_{onset} value of the NiOx (5 min)/ MWCNTs-GC electrode catalyst and other catalyst reported in literature are summarized in table 2. Herein, it is valuable to mention that although the E_{onset} value is somehow close but our proposed catalyst, NiOx (5 min)/ MWCNTs-GC, is still acquire a higher stability.

Table 1. A summary of the E_{onset}, negative shift in the E_{onset} compared to that of the bare GC electrode ($|E_{onset} - E_{onset\ (bare\ GC)}|$) at 0.4 mA, and the corresponding energy saving values.

Electrode	E_{onset}, V (ca.)	Reference electrode	Reference
AuNPs-NH_2/GC	1.7	RHE	[3]
nano-MnOx/Au	1.7	Ag/AgCl/KCl(sat)	[29]
nano-NiOx/GC	1.7	Ag/AgCl/KCl(sat)	[30]
FeCoN-Gs	1.5	Ag/AgCl/KCl(sat)	[31]
MWCNT/CuO-400	1.65	RHE	[32]
Mn-Fe oxide	1.7	RHE	[33]

3.3. Stability toward OER

Durability of the NiOx (5 min)/GC and NiOx (5 min)/MWCNTs-GC modified electrodes has been tracked through recording the current as a function of time at 0.8 V, *i-t*, and the potential as a function of time at 0.2 mA, *E-t*.

Figure 5 shows the *i-t* curves for the NiOx (5 min)/GC (Fig. 5a) and NiOx (5 min)/MWCNTs-GC modified electrodes (Fig. 5b). The stability of the NiOx (5 min)/GC electrode was not good enough although it acquired a high activity toward OER. This could be indicated from the fast decay of current during continuous electrolysis because of the buildup of the produced oxygen gas bubbles at the electrode surface. This can either decrease the effective surface area of the modified electrode and/or reduce the mechanical stability of the NiOx and thus lowers the overall catalytic performance of the modified electrode [3]. Interestingly, the addition of MWCNTs, in case of the NiOx (5 min)/MWCNTs-GC electrode could greatly enhance the stability where the current was twice that of the NiOx (5 min)/GC electrode.

From other side, Fig. 6 shows the *E-t* curves for the NiOx (5 min)/GC (Fig. 6a) and NiOx (5 min)/MWCNTs-GC modified electrodes (Fig. 6b). Again, the NiOx (5 min)/MWCNTs-GC had a lower overpotential. The OER overpotential at the NiOx (5 min)/MWCNTs-GC modified electrode reduced by a value of ca. 150 mV compared with that of the unmodified NiOx (5 min)/GC electrode for the 1800 s of continuous electrolysis. This strongly supports the data in Fig. 5 and it is believed that the nature of MWCNTs is beyond this enhancement in the catalyst stability.

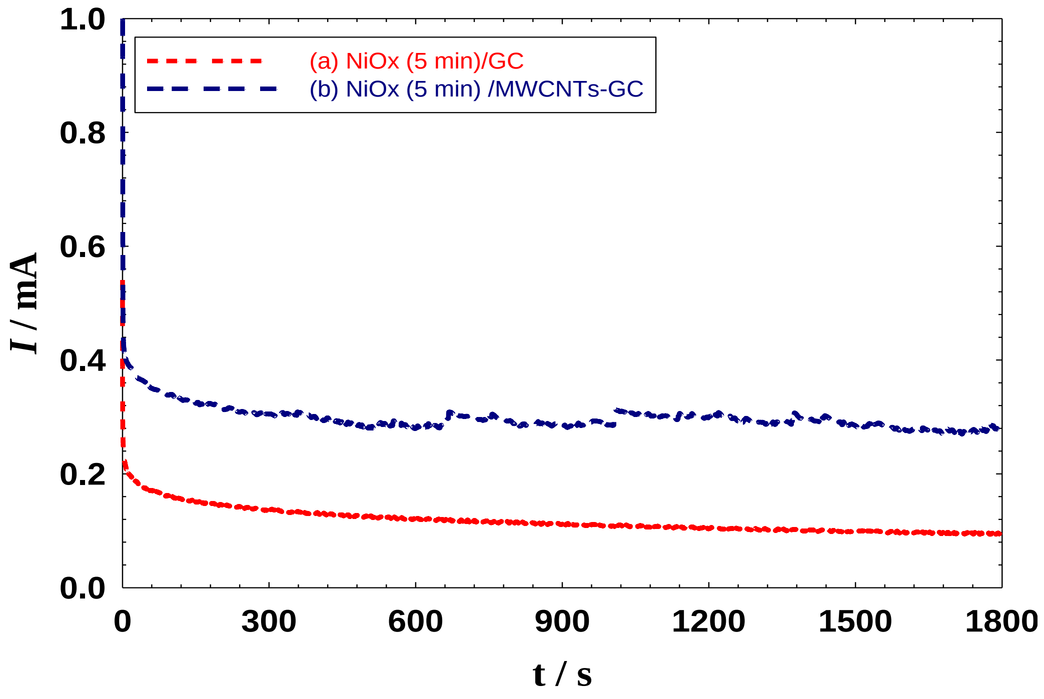


Figure 5. *i-t* curves of the NiOx (5 min)/GC and NiOx (5 min)/MWCNTs-GC modified electrodes measured in 0.1 M NaOH at 0.8 V.

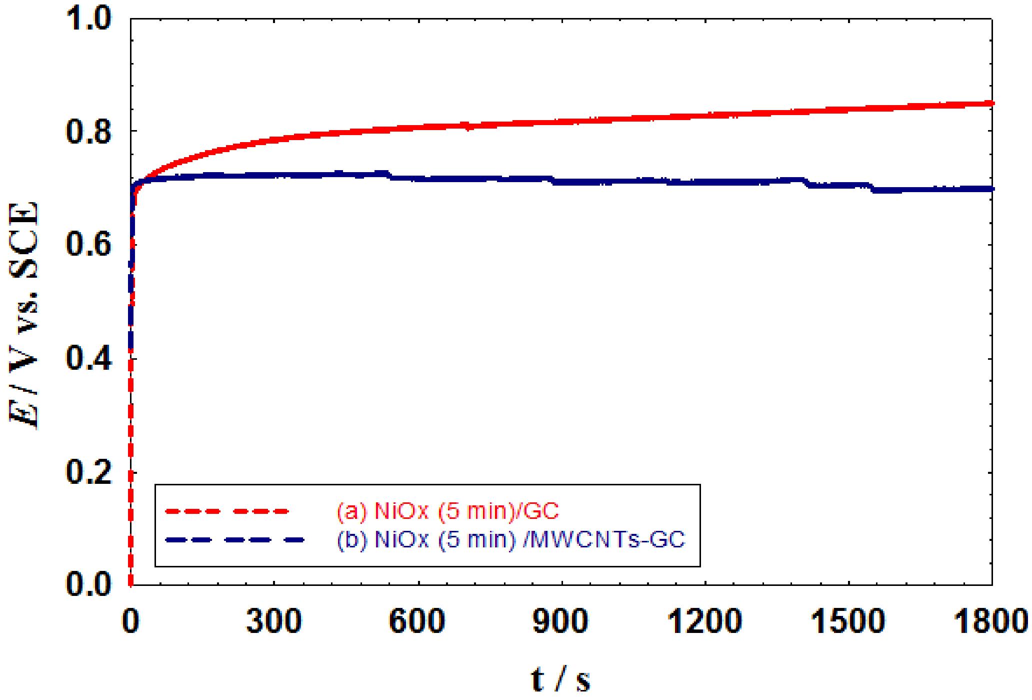


Figure 6. *E-t* curves of the NiOx (5 min)/GC and NiOx (5 min)/MWCNTs-GC modified electrodes measured in 0.1 M NaOH at 0.2 mA.

4. CONCLUSION

A simple adjustment for the GC electrode with MWCNTs and NiOx is proposed for OER. Optimization of the NiOx deposition has been carried out where 5 min was adequate to achieve the highest catalytic performance, lowest E_{onset} and highest power saving. The NiOx (5 min)/MWCNTs-GC modified electrode acquired a negative shift in the E_{onset} with a value of 0.81 V compared with the bare GC electrode. This comes from the easiness of the charge transfer mediated by NiOx. The corresponding energy usage is minimized by a value of 21.7 kWh/Kg of O_2. Moreover, its stability was good in terms of high current and low potential during continuous electrolysis.

References

1. I.M. Al-Akraa, *Int. J. Hydrogen Energy*, 42 (2017) 4660.
2. I.M. Al-Akraa, A.M. Mohammad, M.S. El-Deab and B.E. El-Anadouli, *Int. J. Hydrogen Energy*, 40 (2015) 1789.
3. I.M. Al-Akraa, A.M. Mohammad, M.S. El-Deab and B.E. El-Anadouli, *Arabian J. Chem.*, 10 (2017) 877.
4. A.M. Mohammad, I.M. Al-Akraa and M.S. El-Deab, *Int. J. Hydrogen Energy*, 43 (2018) 139.
5. I.M. Sadiek, A.M. Mohammad, M.E. El-Shakre, M.I. Awad, M.S. El-Deab and B.E. El-Anadouli, *Int. J. Electrochem. Sci.*, 7 (2012) 3350.
6. E. Arciga-Duran, Y. Meas, J.J. Pérez-Bueno, J.C. Ballesteros and G. Trejo, *Electrochim. Acta*, 268 (2018) 49.
7. S. Trasatti, Encyclopedia of Electrochemical Power Sources, Elsevier, Amsterdam, 2009, p. 49.
8. T.J. Meyer, Nature, 451 (2008) 778.

9. J. Rossmeisl, Z.W. Qu, H. Zhu, G.J. Kroes and J.K. Nørskov, *J. Electroanal. Chem.*, 607 (2007) 83.
10. V. Pfeifer, T.E. Jones, J.J.V. Vélez, M.T. C. Massué, R.A. Greiner, D. Teschner, F. Girgsdies, M. Scherzer, J. Allan, M. Hashagen, G. Weinberg, S. Piccinin, M. Hävecker, A. Knop-Gericke and R. Schlögl, *Phys. Chem. Chem. Phys.*, 18 (2016) 2292.
11. M. Gong, Y. Li, H. Wang, Y. Liang, J.Z. Wu, J. Zhou, J. Wang, T. Regier, F. Wei and H. Dai, *J. Am. Chem. Soc.*, 135 (2013) 8452.
12. L. Jia, K. Harbauer, P. Bogdanoff, I. Herrmann-Geppert, A. Ramírez, R.v.d. Krol and S. Fiechter, *J. Mater. Chem.*, 2 (2014) 20196.
13. E.L. Miller and R.E. Rocheleau, *J. Electrochem. Soc.*, 144 (1997) 3072.
14. V. Gowthami, P. Perumal, R. Sivakumar and C. Sanjeeviraja, Physica B: *Condensed Matter*, 452 (2014) 1.
15. D. Levin and J.Y. Ying, in R.K. Grasselli, S.T. Oyama, A.M. Gaffney and J.E. Lyons (Editors), Studies in Surface Science and Catalysis, Vol. 110, Elsevier, 1997, p. 367.
16. Y.-L.T. Ngo, L.T. Hoa, J.S. Chung and S.H. Hur, *J. Alloys Compd.*, 712 (2017) 742.
17. C.-C. Hu and C.-Y. Cheng, *J. Power Sources*, 111 (2002) 137.
18. X. Huang, J. Wu, R. Guo, Y. Lin and P. Zhang, *Int. J. Hydrogen Energy*, 39 (2014) 21399.
19. P. Qin, M. Linder, T. Brinck, G. Boschloo, A. Hagfeldt and L. Sun, *Adv. Mater.*, 21 (2009) 2993.
20. X. Yan, L. Tian and X. Chen, *J. Power Sources*, 300 (2015) 336.
21. M. Wu, L. Fan, R. Ma, J. Zhu, S. Gu, T. Wang, D. Gong, Z. Xu and B. Lu, *Mater. Lett.*, 182 (2016) 15.
22. J. Liang, Y.-Z. Wang, C. Wang and S. Lu, *J. Mater. Chem.*, 4 (2016) 9797.
23. F. Basharat, U.a. Rana, M. Shahid and M. Serwar, *RSC Adv.*, 5 (2015) 86713.
24. A.M. Mohammad, G.A. El-Nagar, I.M. Al-Akraa, M.S. El-Deab and B.E. El-Anadouli, *Int. J. Hydrogen Energy*, 40 (2015) 7808.
25. I.M. Al-Akraa, A.M. Mohammad, M.S. El-Deab and B.E. El-Anadouli, *J. Electrochem. Soc.*, 162 (2015) F1114.
26. A.C. Ferreria, E.R. Gonzalez, E.A. ticianelli, L.A. Avaca and B. Matvienko, *J. Appl. Electrochem.*, 18 (1988) 894.
27. P. Rasiyah, A.C.C. tseung and D.B. Hibbert, *J. Electrochem. Soc.*, 129 (1982) 1724.
28. Y. Matsumoto, S. Yamada, T. Nishida and E. Sato, *J. Electrochem. Soc.*, 127 (1980) 2360.
29. A.M. Mohammad, M.I. Awad, M.S. El-Deab, T. Okajima and T. Ohsaka, *Electrochim. Acta*, 53 (2008) 4351.
30. I.M. Sadiek, A.M. Mohammad, M.E. El-Shakre and M.S. El-Deab, *Int. J. Hydrogen Energy*, 37 (2012) 68.
31. W. Wang, D.D. Babu, Y. Huang, J. Lv, Y. Wang and M. Wu, *Int. J. Hydrogen Energy*, 43 (2018) 10351.
32. A. Chinnappan, D. Ji, C. Baskar, X. Qin and S. Ramakrishna, *J. Alloys Comp.*, 735 (2018) 2311.
33. N. Bhandary, P.P. Ingole and S. Basu, *Int. J. Hydrogen Energy*, 43 (2018) 3165.