



Nickel Oxide Thin Films for Oxygen Evolution Reaction

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Abstract: Active and cheaper catalysts is the essential element in electrochemical water splitting. In this work, we have synthesized nickel oxide (NiO) thin films on the conductive stainless steel substrate by both chemical bath deposition and electrode position methods. Structural study of the prepared thin films of nickel oxide done by using XRD technique. Further, obtained (NiO) thin films prepared using both synthesis techniques are used for Oxygen evolution reaction (OER) by LSV in 1 M KOH electrolyte. The chemically bath deposited and electro deposited (NiO) thin films exhibited over potential of 324.3 mV and 331.8 mV respectively at a current density of 10 mA cm⁻² and corresponding tafel slopes of 75.33 and 87.17 mV dec⁻¹. Hence chemically bath deposited nickel oxide (NiO) thin film electro catalyst showed good catalytic behavior.

Keywords: Thin film, catalyst, OER, Oxide, Alkaline.

I. INTRODUCTION

Nowadays, lifestyle of peoples creates large energy demand and therefore it is necessary to develop capable energy conversion devices and discovery of substitute energy sources to fulfill these needs. [1-10]. To overcome this challenge alternative energy sources can be used as substitute. Irrespective of additional energy sources like solar energy, wind energy sustains limited energy due to its irregularity [11]. Accordingly, the dependency on fossil fuels reduced by converting energy from renewable sources [12]. Hydrogen (H₂) is a best alternative energy source due to its high energy density [13-15]. Production of hydrogen by using electrochemical water splitting is the best way for making hydrogen as a clean chemical fuel [5, 9, 16]. Today, noble electro catalysts are the best and active electro catalysts due to their requirement of low over potential for water splitting. But their price and shortage limits use of noble catalysts [17, 18]. Hence, it is necessary to develop highly efficient and stable electro catalysts towards OER by using cheap non-noble elements. Recently the transition metal based OER electro catalysts are best alternatives due to abundance and low-cost in comparison to precious metals [19-23]. From last decades nickel (Ni) and Ni-based materials shown the good catalytic nature regarding OER and economically abundant in earth crust [24-26]. The various catalytic properties of nickel oxides included in several useful devices [27-29]. These outcomes inspire the progress of simplistic production methods of the NiO metal electrodes as OER catalyst.

Herein, we report the synthesis of nickel oxide thin films on a stainless steel substrate by chemical bath deposition and electro deposition method. The prepared (NiO) thin films can be directly used for further structural and electrochemical characterizations. The stable and efficient electro catalyst can be used in the large extent production of hydrogen via electrochemical water splitting.

II. EXPERIMENTAL

Nickel oxide thin films synthesized by following two methods:

a) Chemical Bath Deposition

Prior the deposition, stainless steel substrates polished by zero grade polish paper. Then cleaned with detergent, double distilled water and then ultrasonically cleaned with the mixture of ethanol and double distilled water for 15 minutes. Finally substrates were dried and then cleaned with acetone directly used for deposition. In CBD method, precursor solution prepared in the double distilled water (DDW) and then immersing the suitable substrate in the bath solution for

the deposition. Here, the 0.2 M Nickel Chloride [Ni (Cl)₂ 6H₂O] and Ammonia solution [NH₄OH] are the starting materials for making the bath solution. As prepared NiOH thin films annealed at 350 °C to form the NiO by removing OH content.

b) Electro Deposition

In electro deposition method, the precursor solution was formed using 0.05 M Nickel nitrate [Ni (NO₃)₂.6H₂O] and double distilled water (DDW). The electro deposition experiment was performed in a potentiostat in which Pt, saturated calomel electrode (SCE) and stainless-steel substrates used as counter, reference and working electrode respectively. NiOH films deposited on the (SS) substrate via potentiostatic mode at a fixed potential -0.9 V/SCE. After deposition films were annealed at 350 °C to form oxide phase.

Structural and electrochemical study of prepared catalyst was done by X-ray diffractometer and Electrochemical workstation CHI (6002E) instruments with NiO thin film, Pt and Ag/AgCl electrode as working electrode, counter electrode and reference electrode respectively in 1M KOH solution at room temperature. All measured potentials were converted to the reversible hydrogen electrode (RHE) using following Nernst equation [30]:

$$E_{RHE} = E_{Ag/AgCl} + (0.059 \times pH) + 0.197$$

To determine the OER activity of prepared thin films determined by Linear Sweep Voltammetry (LSV). Tafel slope was obtained by polarization curve.

III. RESULTS AND DISCUSSION

The structural analysis of chemically bath deposited and electrodeposited NiO electrocatalyst was investigated using XRD. Fig.1 shows the XRD graphs of NiO catalysts by CBD and ED method and it shows that the NiO has cubic crystal structure. The diffraction peaks of CBDNiO film were indexed at 37.28°, 43.6°, and 62.9° corresponding to planes (111), (200) and (220) respectively and EDNiO film were indexed at 37.28°, 43.6°, 62.9° and 75.44° corresponding to planes (111), (200), (220) and (311) respectively. This result is matched with the pattern of NiO cubic structure (JCPDS card no. 47-1049) [31]. (#) symbols represents the peaks for stainless steel substrates.

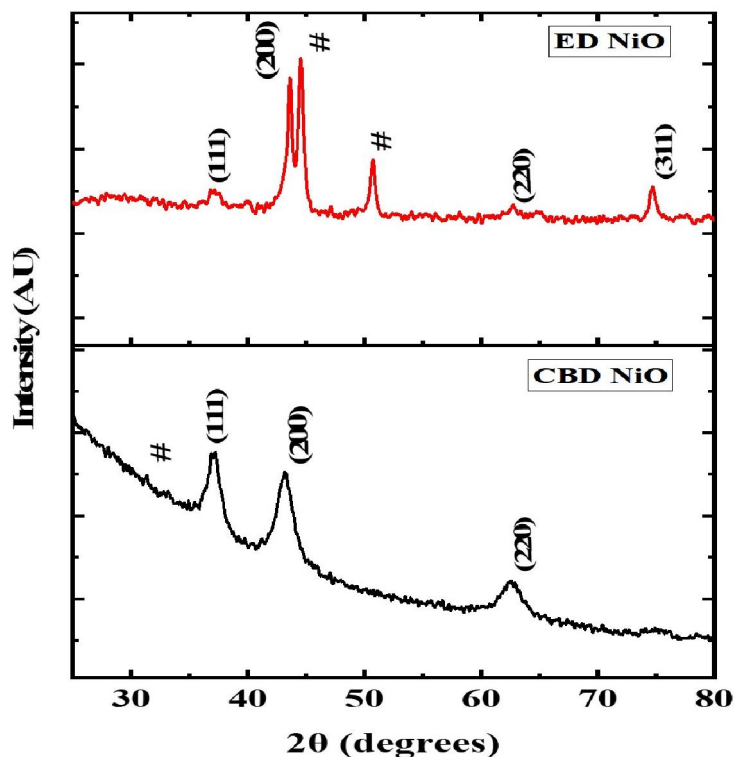


Fig.1 XRD pattern of CBD and ED NiO

OER activity was monitored by (LSV) in 1M KOH. Fig. 2 (a) represents the LSV curves of CBD NiO and ED NiO thin film catalysts. From these polarization curves it was clearly seen that onset potential 1.55V vs. (RHE) and over potential 324.3 mV of CBD NiO to reach the current density of 10 mA cm⁻². ED NiO shows the onset potential 1.56 V vs. (RHE) and over potential 331.8 mV at a current density of 10 mA cm⁻². Fig. 2 (b) represents the Tafel plots of CBD NiO and ED NiO thin films. It shows the Tafel slope of 75.33 and 87.17 mV dec⁻¹ for CBD NiO and ED NiO respectively. Small value of the over potential and Tafel slope shows its better catalytic behavior for OER in water splitting.

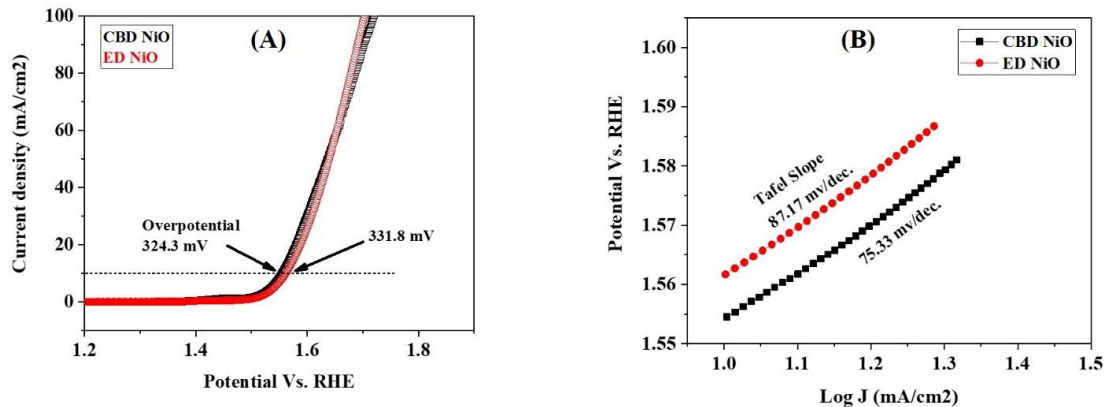


Fig. 2 (a) LSV and (b) Tafel plots of CBD and ED NiO

Electro catalyst	Synthesis Process	Electrolyte	OER (over potential) (mV)	Tafelslope (mV dec ⁻¹)	Reference
NiO	Electro deposition	1M NaOH	450	120	[32]
NiO/NiNDs@NF	Electro deposition	1M KOH	360	90	[33]
NiO	Chemical Bath Deposition	1M KOH	345	48	[34]
NiO@SS	Chemical Bath Deposition	1M KOH	324.3	75.33	This work
NiO@SS	Electrodeposition	1M KOH	331.8	87.17	This work

Table 1: A comparison of OER activity with other published results

A comparability of OER activity in this work with other published literature NiO electrocatalyst is given in Table 1. Hence chemically bath deposited NiO thin film electrocatalyst exhibits the excellent OER kinetics in the electrochemical water splitting.

IV. CONCLUSION

We have reported chemically bath deposited and electrodeposited NiO thin films for OER electro catalysts in the catalytic water splitting. The CBD NiO thin film electro catalyst demonstrated excellent OER performance and required very small over potential of 324.3 mV to hold the current density of 10 mAcm⁻² and small tafel slope of 75.33 mV dec⁻¹ in 1M KOH solution. ED NiO shows an over potential of 331.8 mV and tafel slope of 87.17 mV/dec. This OER performance enhanced due to high active surface area of catalyst. Hence the NiO electro catalyst with excellent catalytic behavior acts as a promising material for water splitting application.

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REFERENCES

- [1]. M.I. Jamesh, A.S. Prakash, "Advancement of technology towards developing Na-ion batteries". *Journal of Power Sources*, 2018, 378: 268–300.
- [2]. S.B. Lai, M.I. Jamesh, Y.L. Dong, J.H. Wang, Y.-P. Li, J.-F. Liu, X.-C. Wu, X. M. Sun, "A promising energy storage system: rechargeable Ni–Zn battery Rare Metals". 2017, 36: 381–396.
- [3]. M. Sathiya, K. Hemalath, K. Ramesh, J.M. Tarascon, A.S. Prakash, "Synthesis, Structure, and Electrochemical Properties of the Layered Sodium Insertion Cathode Material: $\text{NaNi}^{1/3}\text{Mn}^{1/3}\text{Co}^{1/3}\text{O}_2$ ". *Chemistry of Materials*, 2012, 24: 1846–1853.
- [4]. T.R. Cook, D.K. Dogutan, S.Y. Reece, Y. Surendranath, T.S. Teets, D.G. Nocera, "Solar energy supply and storage for the legacy and nonlegacy worlds". *Chemical Review*, 2010, 110: 6474–6502.
- [5]. Jamesh M.I., "Recent progress on earth abundant hydrogen evolution reaction and oxygen evolution reaction bifunctional electro catalyst for overall water splitting in alkaline media". *Journal of Power Sources*, 2016, 333: 213-236.
- [6]. H. Wang, H. Dai, "Strongly coupled inorganic–nano-carbon hybrid materials for energy storage". *Chemical Society Reviews*, 2013, 42: 3088–3113.
- [7]. S. Chu, A. Majumdar, "Opportunities and challenges for a sustainable energy future". *Nature*, 2012, 488: 294–303.
- [8]. M.D. Symes, L. Cronin, "Decoupling hydrogen and oxygen evolution during electrolytic water splitting using an electron-coupled-proton buffer". *Nature Chemistry*, 2013, 5: 403–409.
- [9]. J.A. Turner, "Sustainable Hydrogen Production". *Science*, 2004, 305: 972–974.
- [10]. Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier, H. Dai, " Co_3O_4 nanocrystals on graphene as a synergistic catalyst for oxygen reduction reaction". *Nature Materials*, 2011, 10: 780–786.
- [11]. N.S. Lewis, D.G. Nocera, "Powering the planet: Chemical challenges in solar energy utilization". *Proceedings of the National Academy of Sciences*, 2006, 103: 15729–15735.
- [12]. Z.L. Wang, D. Xu, J.J. Xu, X.B. Zhang, "Oxygen electrocatalysts in metal–air batteries: from aqueous to nonaqueous electrolytes". *Chemical Society Reviews*, 2014, 43: 7746-7786.
- [13]. Dresselhaus, M. S., Thomas, I. L., "Alternative energy technologies". *Nature*, 2001, 414: 332-337.
- [14]. Crabtree, G. W., Dresselhaus, M. S., Buchanan, M. V., "The Hydrogen Economy". *Physics Today*, 2004, 57: 39-44.
- [15]. Choi, C. L., Feng, J., Li, Y., Wu, J.; Zak, A., Tenne, R.; Dai, H., "WS₂ nanoflakes from nanotubes for electrocatalysis". *Nano Research*, 2013, 6: 921-928.
- [16]. K. Zeng, D. Zhang, "Recent progress in alkaline water electrolysis for hydrogen production and applications". *Progress in Energy and Combustion Science*, 2010, 36: 307–326.
- [17]. Qirong Shi, Chengzhou Zhu, Dan Du and Yuehe Lin, "Robust noble metal-based electrocatalysts for oxygen evolution reaction". *Chem. Soc. Rev.*, 2019, 48: 3181-3192.
- [18]. Oh, N.K., Seo, J., Lee, S. et al. "Highly efficient and robust noble-metal free bifunctional water electrolysis catalyst achieved via complementary charge transfer". *Nat Commun* 2021, 12: 4606.
- [19]. P.T. Babar, A.C. Lokhande, B.S. Pawar, M.G. Gang, Eunjin Jo, Changsik Go, M.P. Suryawanshi, S.M. Pawar, JinHyeok Kim, "Electrocatalytic performance evaluation of cobalt hydroxide and cobalt oxide thin films for oxygen evolution reaction". *Applied Surface Science*, 2018, 427: 253-259
- [20]. H. Osgood, S.V. Devaguptapu, H. Xu, J. Cho, G. Wu, "Transition metal (Fe, Co, Ni, and Mn) oxides for oxygen reduction and evolution bifunctional catalysts in alkaline media". *Nano Today*, 2016, 11: 601-625.
- [21]. S.M. Pawar, B.S. Pawar, B. Hou, J. Kim, A. Ahmed, H.S. Chavan, Y. Jo, S. Cho, A.I. Inamdar, J.L. Gunjekar, H. Kim, S. Cha, H. Im, "Self-assembled two-dimensional copper oxide nanosheet bundles as an efficient oxygen evolution reaction (OER) electrocatalyst for water splitting applications". *Journal of Material Chemistry A*, 2017, 5: 12747-12751.
- [22]. P.T. Babar, B.S. Pawar, A.C. Lokhande, M.G. Gang, J.S. Jang, M.P. Suryawanshi, S. M. Pawar, JinHyeok Kim, "Annealing temperature dependent catalytic water oxidation activity of iron oxyhydroxide thin films". *Journal of Energy Chemistry*, 2017, 26: 757-761

- [23]. R. J. Deokate, S. H. Mujawar, H. S. Chavan, S. S. Mali, C. K. Hong, H. Im, A. I. Inamdar, "Chalcogenide nanocomposite electrodes grown by chemical etching of Ni-foam as electrocatalyst for efficient oxygen evolution reaction". *International Journal of Energy Research*, 2020, 44 (2): 1233-1243.
- [24]. Varun Vij, Siraj Sultan, Ahmad M. Harzandi, Abhishek Meena, Jitendra N. Tiwari, Wang-Geun Lee, Taeseung Yoon, and Kwang S. Kim, "Nickel-Based Electrocatalysts for Energy-Related Applications: Oxygen Reduction, Oxygen Evolution, and Hydrogen Evolution Reactions". *ACS Catalysis* 2017, 7 (10): 7196-7225
- [25]. Gong, M., Wang, DY., Chen, CC. et al. "A mini review on nickel-based electrocatalysts for alkaline hydrogen evolution reaction". *Nano Res.*, 2016, 9: 28-46.
- [26]. Xingxing Yu, Tianyi Hua, Xiang Liu, Zhiping Yan, Peng Xu, and Pingwu Du, "Nickel-Based Thin Film on Multiwalled Carbon Nanotubes as an Efficient Bifunctional Electrocatalyst for Water Splitting". *ACS Applied Materials & Interfaces*, 2014, 6 (17): 15395-15402
- [27]. L. Han, S. Dong, E. Wang, "Transition-Metal (Co, Ni, and Fe)-Based Electrocatalysts for the Water Oxidation Reaction". *Advanced Materials*, 2016, 28: 9266-9291.
- [28]. H.G. El-Shobaky, "Surface and catalytic properties of Co, Ni and Cu binary oxide systems". *Applied Catalysis A: General*, 2004, 278 (1): 1-9
- [29]. Zhou Dishan, Yan Aifeng, Wu Ying, Wu Tinghua, "A facile synthetic route to flower-like NiO and its catalytic properties". *Indian Journal of Chemistry*, 2013, 52A: 51-56
- [30]. Lu, X., Zhao, C. "Electrodeposition of hierarchically structured three-dimensional nickel-iron electrodes for efficient oxygen evolution at high current densities". *Nat Commun*, 2015, 6: 6616
- [31]. Dhole, I.A., Navale, Y.H., Pawar, C.S. et al. "Physicochemical and supercapacitive properties of electroplated nickel oxide electrode: effect of solution molarity". *J Mater Sci: Mater Electron*, 2018, 29: 5675-5687
- [32]. E. Arciga-Duran, Y. Meas, J.J. Pérez-Bueno, J.C. Ballesteros, G. Trejo, "Effect of oxygen vacancies in electrodeposited NiO towards the oxygen evolution reaction: Role of Ni-Glycine complexes". *Electrochimica Acta*, 2018, 268: 49-58
- [33]. Yu, H., Quan, T., Mei, S. et al. "Prompt Electrodeposition of Ni Nanodots on Ni Foam to Construct a High-Performance Water-Splitting Electrode: Efficient, Scalable, and Recyclable". *Nano-Micro Lett.*, 2019, 11: 41
- [34]. Cosentino, Salvatore, et al. "High intrinsic activity of the oxygen evolution reaction in low-cost NiO nano-walled electro catalysts." *Materials Advances*, 2020, 1: 1971-1979.