



## Research Article

# A New Concept for the Electrosynthesis of Nanosized Nickel Oxyhydroxide Alloys for Alkaline Oxygen Evolution

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**Abstract:** The objective of this concept article is to develop a new method for synthesizing nickel hydroxides, with a special interest in nickel oxyhydroxide (NiOx), which is extensively studied as an electrocatalyst for the alkaline oxygen evolution reaction (OER) in water electrolysis for hydrogen generation. The adoption of hydrogen economy faces several challenges, but effective OER catalysts can help to generate hydrogen cost-effectively for energy. We propose using the electrodeposition of NiOx from a redox surfactant microemulsion to create nanoscale NiOx particles that enhance the material's electronic and geometric properties, leading to maximum energy efficiency for the OER. The microemulsion approach is a bottom-up technique that can be performed at low temperatures, making it a low-cost method. This technique can be used to synthesize other nanoscale materials.

**Keywords:** nanosized nickel hydroxide, nanosized nickel oxyhydroxide, redox microemulsion, redox surfactant, nanosized nickel oxyhydroxide alloys

## 1. Introduction

A recent literature review on nickel hydroxide and related materials [1] shows different methods of synthesizing nickel hydroxide, with six being the most commonly used. These techniques include chemical precipitation, electrochemical precipitation, sol-gel synthesis, chemical aging, hydro- and solvothermal synthesis, and surface layers on nickel. Three key variables in selecting the synthesis method of Ni(OH)<sub>2</sub> are phase ( $\alpha$ ,  $\gamma$ ,  $\beta$ ), crystallinity, and product morphology (porosity, nanostructured, etc.). Of all these synthesis methods, the most popular for the oxygen evolution reaction (OER) in water electrolysis are the electrochemical-derived methods, such as electrodeposition and electrochemical aging, as these methods allow certain control of the phases  $\gamma$  and  $\beta$ . These phases are associated with the electroactivity of nickel oxyhydroxide (NiOx)-based catalysts for the OER [2–7].

NiOx is a widely researched material for alkaline OER due to its excellent catalytic activity and earth abundance. The addition of iron dopant to NiOx resulted in an excellent catalyst for the OER [8–11], making this a promising area for further research. Most of the published literature [9–18] focuses on bulk electrodeposited alloys of NiOx, including iron. However, this concept paper aims to improve the geometric factor in addition to the electronic factor. Developing nanosized particles of NiOx alloys can enhance the geometric factor, but there is currently no literature on synthesizing nanosized nickel oxyhydroxide alloys. We believe that electrochemical-derived methods to synthesize nanoparticles of NiOx alloys can produce highly active catalysts for the OER.

Although our main focus is the OER, this material/method can be tested for fuel cells and batteries. In addition, this technique can be used to synthesize other chemicals for nanoapplications.

We have developed a derived Watts bath to electrodeposit thin films of FeNiOx (iron as a doping material) and found highly active combinations for alkaline OER [19–22]. We believe that using a redox surfactant – for example, the one used by Rosslee [23]. (i.e. used to electrolytically recover chemicals in solution) – as a microemulsion of a Watts bath in oil can be achieved (i.e. reverse micelles), as shown in Fig. 1. Making nanosized NiOx alloys with such a microemulsion can make better NiOx-based catalysts. We have worked with Raney NiOx in the past and proven that a porous substrate [20], such as Raney Ni, enhances the geometric factor of NiOx. It should be noted that Rosslee also mentions light-activated surfactants [23], and we will consider developing alternative methods of NiOx synthesis involving such a surfactant in the future.

## 2. Rationale

### 2.1 Redox surfactant-based microemulsion

Fig. 1 shows the difference between emulsion and microemulsion. Immiscible liquids, like water and oil, can make a microemulsion when a surfactant is added, as Fig. 1 illustrates. A surfactant is a long organic molecule with one end that is hydrophilic and the other hydrophobic, and it acts as an emulsifying agent by reducing the interfacial tension ( $\gamma$ ) between two immiscible liquids. A redox surfactant – for instance, 11-(ferrocenylundecyl)trimethylammonium bromide [23] – can be used to make a Watts bath soluble in oil via microemulsion. Nanosized aqueous core (refer to Fig. 1) micelles can be coulombically attracted to a charged electrode for a reaction to occur.

### 2.2 Redox microemulsion-assisted electrodeposition

Fig. 2 shows a three-electrode setup for electrodeposition (top left), pulse and continuous electrodeposition regimes (top right), and the role that the redox surfactant plays during the electrodeposition of nanosized particles of NiOx alloys (bottom). A Watts-derived media and oil microemulsion are employed as the solution for the electrodeposition of nanosized NiOx alloys. A few technical considerations must be highlighted: a pulse voltage or continuous current as the method of electrodeposition is determined empirically, and the oil background electrolyte for the electrodeposition requires an inert supporting salt to make it conductive.

### 2.3 OER mechanism on NiOx-based electrocatalysts

Fig. 3 shows typical cyclic voltammograms (CVs) of NiOx electrocatalysts for the OER [9–18]. The oxidation and reduction peaks of the  $\square/\square$  system are shown (i.e. Ni (III/II)), including the oxygen evolution region. Three CVs are drawn: the common or typical CV found in most literature, a highly efficient CV found in a few publications, and a poorly efficient CV, which is also found in some publications and interpreted as highly efficient occasionally. We have developed a method to synthesize NiOx-based catalysts [19] that exhibit a CV similar to that found in highly efficient OER electrocatalysts, and we use this method in combination with redox surfactants to synthesize better OER catalysts (refer to Fig. 2).

There is a debate in the electrochemical community about the suitable mechanism for the OER on NiOx, with some publications claiming that the  $\square$ -NiOx phase is active while others argue in favor of the  $\square$ -NiOx phase [2–7]. We recognize the importance of describing the OER mechanism and know these conflicts in the literature. The similarity in properties between  $\square$ - and  $\square$ -NiOx phases has made it difficult to reach a consensus [18,24,25]. We will consider these factors when interpreting and developing our methods and results.

Fig. 3 also indicates the challenge in reproducing results for amorphous NiOx-based catalysts [8]. At the I2CNER seminar [26], Berlinguette explained the difference between amorphous and crystalline NiOx, the importance of Ni(IV) in the OER mechanism, and a new method to make crystalline NiOx films via photochemistry. Berlinguette mentioned that amorphous NiOx is generally more active than its crystalline version. He achieved reproducibility but was not able to produce highly efficient OER catalysts.

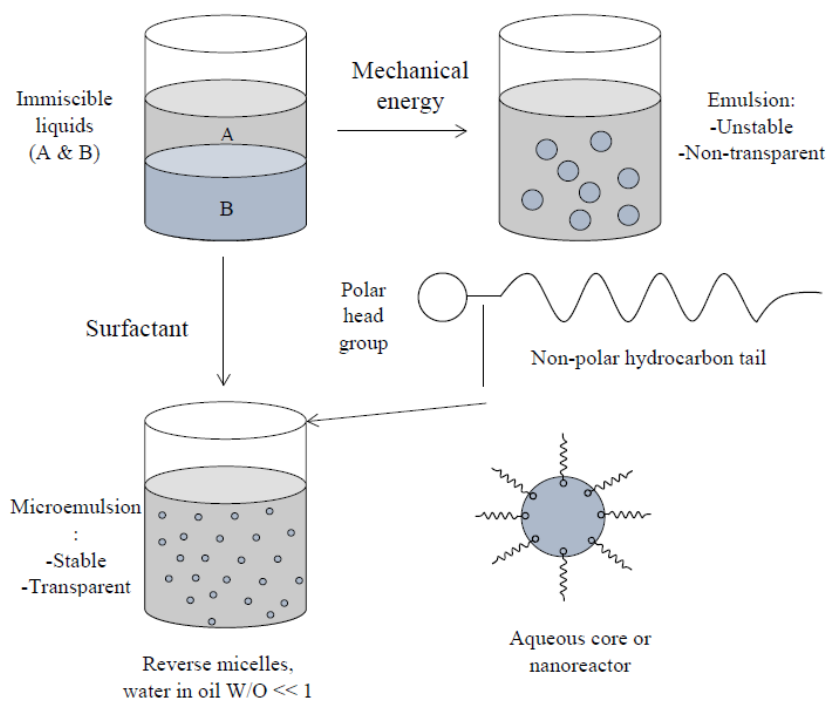


Figure 1. Description of a microemulsion.

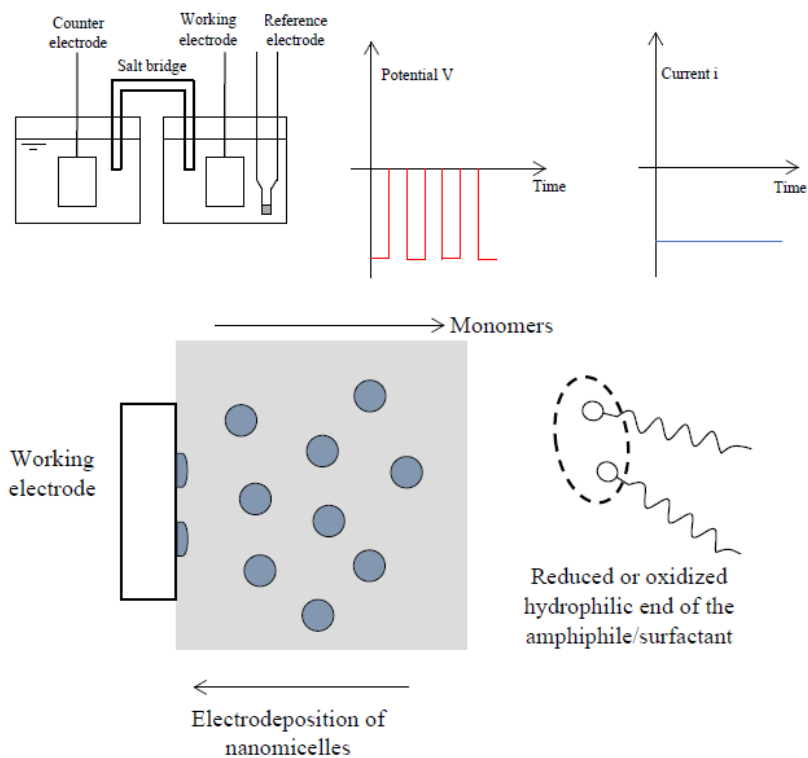
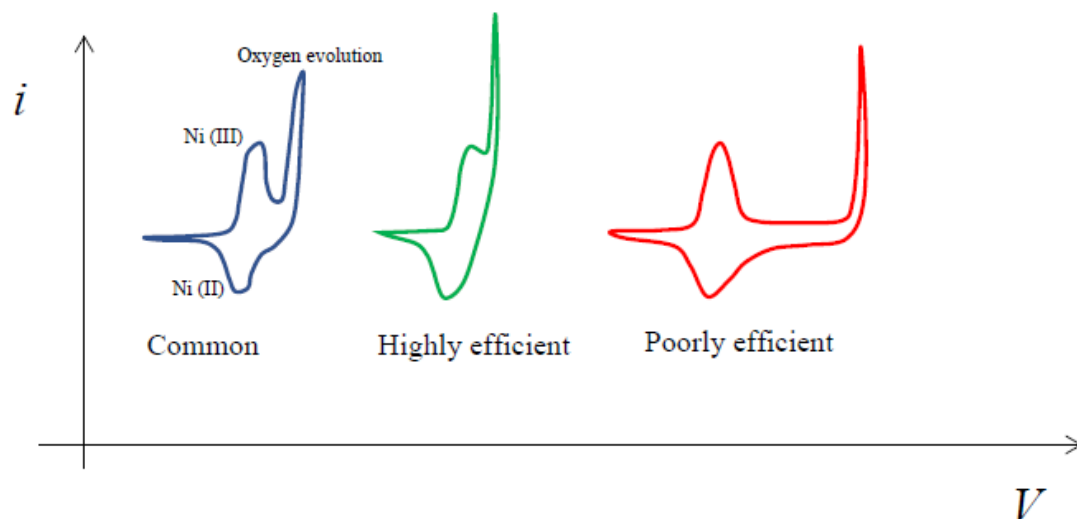


Figure 2. Surfactant-assisted electrodeposition of ( $\gamma$ ,  $\beta$ ) FeNiOx.



**Figure 3.** Common cyclic voltammograms found for electromade NiOx-based catalysts ( $i$  and  $V$  are current and potential, respectively).

### 3. Experimental Setup/Project Description

Fig. 2 (top left) shows a three-electrode setup (plating station) to synthesize nanosized NiOx-based electrocatalysts. Fig. 1 explains how the microemulsion (i.e. plating bath) is made. In the rationale section, we illustrate the potential materials to be used as redox surfactants: a nickel-plating bath and an oil with an inert salt. The deposition mechanism is illustrated in Fig. 2 (bottom) in which the consumed reverse micelle becomes a monomer as it is oxidized/reduced depending on the electric charge of the working electrode. The deposited nano-NiOx is then tested electrochemically by cyclic and linear voltammetry to determine its OER efficiency. Electrochemical impedance, Raman spectroscopy, and scanning electron microscopy equipped with energy-dispersive X-ray spectroscopy are additional techniques considered for further testing of the developed samples. These techniques can help us understand the source of activity of the developed material.

### 4. Expectations/Goals

New synthesis methods for nickel hydroxides can lead to improved materials with higher efficiency and lower cost for batteries and electrocatalysts. Our research aims to develop nanosized NiOx alloys that can improve the overpotential of the OER by several tens of millivolts, which is significant because the cost [27] of hydrogen generation is highly dependent on the overpotential of the reaction. Future work can include using porous catalyst carriers to explore further improvements of the developed NiOx-based electrocatalyst.

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### Conflict of interest

There is no conflict of interest for this study.

## References

- [1] Hall DS, Lockwood DJ, Bock C, MacDougall BR. Nickel hydroxides and related materials: A review of their structures, synthesis and properties. *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences*. 2015; 471: 20140792. doi:10.1098/rspa.2014.0792.
- [2] Bode H, Dehmelt K, Witte J. Zur Kenntnis der nickelhydroxidelektrode—I. Über das nickel (II)-hydroxidhydrat. *Electrochimica Acta*. 1966; 11:1079-IN1071, doi:10.1016/0013-4686(66)80045-2.
- [3] Doyle RL, Lyons MEG. Kinetics and mechanistic aspects of the oxygen evolution reaction at hydrous iron oxide films in base. *Journal of the Electrochemical Society*. 2013; 160(2): H142-H154, doi:10.1149/2.015303jes.
- [4] Louie MW, Bell AT. An investigation of thin-film Ni–Fe oxide catalysts for the electrochemical evolution of oxygen. *Journal of the American Chemical Society*. 2013; 135(33): 12329-12337, doi:10.1021/ja405351s.
- [5] Lyons MEG, Doyle RL, Godwin I, O'Brien M, Russell L. Hydrous nickel oxide: Redox switching and the oxygen evolution reaction in aqueous alkaline solution. *Journal of the Electrochemical Society*. 2012; 159: H932-H944, doi:10.1149/2.078212jes.
- [6] DK, Lassalle-Kaiser B, Surendranath Y, Yano J, Yachandra VK, Nocera DG. Structure–activity correlations in a nickel–borate oxygen evolution catalyst. *Journal of the American Chemical Society*. 2012; 134(15): 6801-6809, doi:10.1021/ja301018q.
- [7] Corrigan DA, Knight SL. Electrochemical and spectroscopic evidence on the participation of quadrivalent nickel in the nickel hydroxide redox reaction. *Journal of the Electrochemical Society*. 1989; 136: 613-619, doi:10.1149/1.2096697.
- [8] Merrill MD, Dougherty RC. Metal oxide catalysts for the evolution of O<sub>2</sub> from H<sub>2</sub>O. *Journal of Physical Chemistry C*. 2008; 112: 3655-3666, doi:10.1021/jp710675m.
- [9] Seh ZW, Kibsgaard J, Dickens CF, Chorkendorff I, Nørskov JK, Jaramillo TF. Combining theory and experiment in electrocatalysis: Insights into materials design. *Science*. 2017; 355(6321), doi:10.1126/science.aad4998.
- [10] H, Xiao H, Goddard WA. In silico discovery of new dopants for Fe-doped Ni oxyhydroxide (Ni<sub>1-x</sub>Fe<sub>x</sub>OOH) catalysts for oxygen evolution reaction. *Journal of the American Chemical Society*. 2018; 140(22): 6745-6748, doi:10.1021/jacs.8b02225.
- [11] Xiao H, Shin H, Goddard WA. Synergy between Fe and Ni in the optimal performance of (Ni,Fe)OOH catalysts for the oxygen evolution reaction. *Proceedings of the National Academy of Sciences U S A*. 2018; 115(23): 5872-5877, doi:10.1073/pnas.1722034115.
- [12] Benck JD, Lee SC, Fong KD, Kibsgaard J, Sinclair R, Jaramillo TF. Designing active and stable silicon photocathodes for solar hydrogen production using molybdenum sulfide nanomaterials. *Advanced Energy Materials*. 2014; 4(18): 1400739, doi:10.1002/aenm.201400739.
- [13] Man IC et al. Universality in oxygen evolution electrocatalysis on oxide surfaces. *ChemCatChem*. 2011; 3: 1159-1165, doi:10.1002/cctc.201000397.
- [14] P, Kibsgaard J, Gallo A, Park J, Mitani M, Sokaras D, Kroll T, Sinclair R, Mogensen MB et al. Effects of gold substrates on the intrinsic and extrinsic activity of high-loading nickel-based oxyhydroxide oxygen evolution catalysts. *ACS Catalysis*. 2017; 7(8): 5399-5409, doi:10.1021/acscatal.7b01070.
- [15] Diaz-Morales O, Ferrus-Suspedra D, Koper MTM. The importance of nickel oxyhydroxide deprotonation on its activity towards electrochemical water oxidation. *Chemical Science*. 2016; 7(4): 2639-2645, doi:10.1039/C5SC04486C.
- [16] Fidelsky V, Toroker MC. Enhanced water oxidation catalysis of nickel oxyhydroxide through the addition of vacancies. *Journal of Physical Chemistry C*. 2016; 120: 25405-25410, doi:10.1021/acs.jpcc.6b07931.
- [17] CCL, Jung S, Peters JC, Jaramillo TF. Benchmarking heterogeneous electrocatalysts for the oxygen evolution reaction. *Journal of the American Chemical Society*. 2013; 135(45): 16977-16987, doi:10.1021/ja407115p.
- [18] Wehrens-Dijksma M, Notten PHL. Electrochemical quartz microbalance characterization of Ni(OH)<sub>2</sub>-based thin film electrodes. *Electrochimica Acta*. 2006; 51(18): 3609-3621, doi:10.1016/j.electacta.2005.10.022.
- [19] Delgado D, Bucher J. 2020. Iron–nickel oxyhydroxide catalyst from watts bath for the oxygen evolution reaction in water electrolysis. ChemRxiv: Cambridge: Cambridge Open Engage.
- [20] Delgado D, Bizzotto F, Zana A, Arenz M. Accelerated durability test for high-surface-area oxyhydroxide nickel supported on Raney nickel as catalyst for the alkaline oxygen evolution reaction. *ChemPhysChem*. 2019; 20(22): 3147-3153.

- [21] Delgado D, Minakshi M, Kim D-J, Kyeong C. Influence of the oxide content in the catalytic power of Raney nickel in hydrogen generation. *Analytical Letters*. 2017; 50(15): 2386-2401.
- [22] Delgado D, Minakshi M, Kim D-J. Electrochemical impedance spectroscopy studies on hydrogen evolution from porous Raney cobalt in alkaline solution. *International Journal of Electrochemical Science*. Volume. 2015; 10: 9379-9394.
- [23] Rosslee CA, Abbott NL. Principles for microscale separations based on redox-active surfactants and electrochemical methods. *Analytical Chemistry*. 2001; 73(20): 4808-4814, doi:10.1021/ac010273s.
- [24] MC, Payne BP, Lau LWM, Gerson A, Smart RSC. X-ray photoelectron spectroscopic chemical state quantification of mixed nickel metal, oxide and hydroxide systems. *Surface and Interface Analysis*. 2009; 41: 324-332, doi:10.1002/sia.3026.
- [25] Mansour AN, Melendres CA. Characterization of KNiIO<sub>6</sub> by XPS. *Surface Science Spectra*. 1994; 3(3): 287-295, doi:10.1116/1.1247758.
- [26] Berlinguette CP. In: *International Institute for Carbon-Neutral Energy Research*.
- [27] Delgado D, Hefter G, Minakshi M. In: G Ferreira (ed.) *Alternative Energies: Updates on Progress*. Berlin Heidelberg: Springer; 2013. p. 141-161.