

NiFeB anode catalyst for anion exchange membrane water electrolysis

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ABSTRACT

In this work, the Ni₂Fe₁B oxygen evolution reaction (OER) catalyst was scaled up to 5 g per batch and tested as an anode electrode in anion exchange membrane electrolysis. The Ni₂Fe₁B membrane electrode assemblies (MEAs) display outstanding performance of 3.3 A/cm² at 2 V and durability for 60 h at 1 A/cm² in 1 M KOH and 60 °C compared to state of art iridium (Ir) black catalyst.

1. Introduction

Hydrogen can be produced from any energy source (fossil, nuclear or renewable), and electricity represents 70–90% of the electrolytic hydrogen cost [1]. Hydrogen is beneficial for storing surplus energy from renewables in the form of hydrogen from water electrolysis [2]. Low-temperature water electrolysis is a sustainable and efficient hydrogen production technology [3]. Anion exchange membrane (AEM) water electrolysis utilizes non-platinum group metal (PGM) electrocatalysts aiming to achieve high efficiency and economically feasible green hydrogen [3,4]. Alkaline AEM electrolysis aims to achieve performance comparable to PEM electrolysis, i.e. 1 A/cm² at 2 V with stable performance to offer significant cost savings [3]. Recently Paul A. Kohl's group showed AEM performance similar to PEM electrolysis by optimizing ionomer chemistry and content [5–7].

Active, durable, and commercially viable non-PGM oxygen evolution reaction (OER) catalysts are needed for scaling up electrolyzer technology to giga-scale; [8] the OER kinetics are sluggish and consequently, it controls the performance of water electrolysis [8,9]. Metal borides/borates exhibit promising OER performance in a high-pH regime; incorporating highly electronegative boron diminishes oxidation reaction energy barrier under positive bias and assists charge transfer [8]. The durability of metal borides has been limited to < 60 h at a modest current density of ~ 20 mA/cm² [8,9]. The synthesis methods for borides/borates are less energy-intensive and less toxic compared to those needed for other electrocatalysts (metal phosphides and sulfides) [10]. The stability of the boride-based electrocatalysts, earth abundance, and simplicity of preparation make them promising OER catalysts [11]. Thus scientific attention should be paid to their electrocatalytic performance

and durability at high currents to meet the industrial demand.

2. Experimental

2.1. Catalyst synthesis

To synthesize 5 g of Ni₂Fe₁B catalyst: 15 mM of total precursors (Ni₂Fe₁) were added to 150 ml water where the Ni and Fe precursors were NiCl₂·6H₂O and FeCl₃·6H₂O, respectively. The precursors were stirred for 15 min at 750 rpm. The precursors were added once to 750 ml of 0.1 M of sodium borohydride under continuous stirring at room temperature. The resulting precipitate was stirred for another 15 min to ensure complete reduction and then centrifuged four times at 8000 rpm for 6 min. The produced precipitate was then dried in the air in a fume hood till used.

3. Structural and electrochemical characterization

Catalyst morphology and composition were evaluated by scanning electron microscopy (SEM) [Zeiss Supra 55 VP] and an energy-dispersive X-ray spectroscopy (EDX) detector in the device. In-depth transmission electron microscopy (TEM) and EDX mapping investigation was done using the JEOL JEM-2100F microscope. To examine catalyst crystalline characteristics, X-ray diffraction (XRD) [Bruker D8 with CuK α radiation, $\lambda = 1.5425 \text{ \AA}$] was used. The catalysts' electrochemical properties were investigated with an Ivium-n-Stat potentiostat in a three-electrode cell, where glassy carbon (GC) electrode (diameter 5 mm), Pine Research), Hg/HgO electrode (Pine Research), and platinum foil served as working, reference, and counter electrodes,

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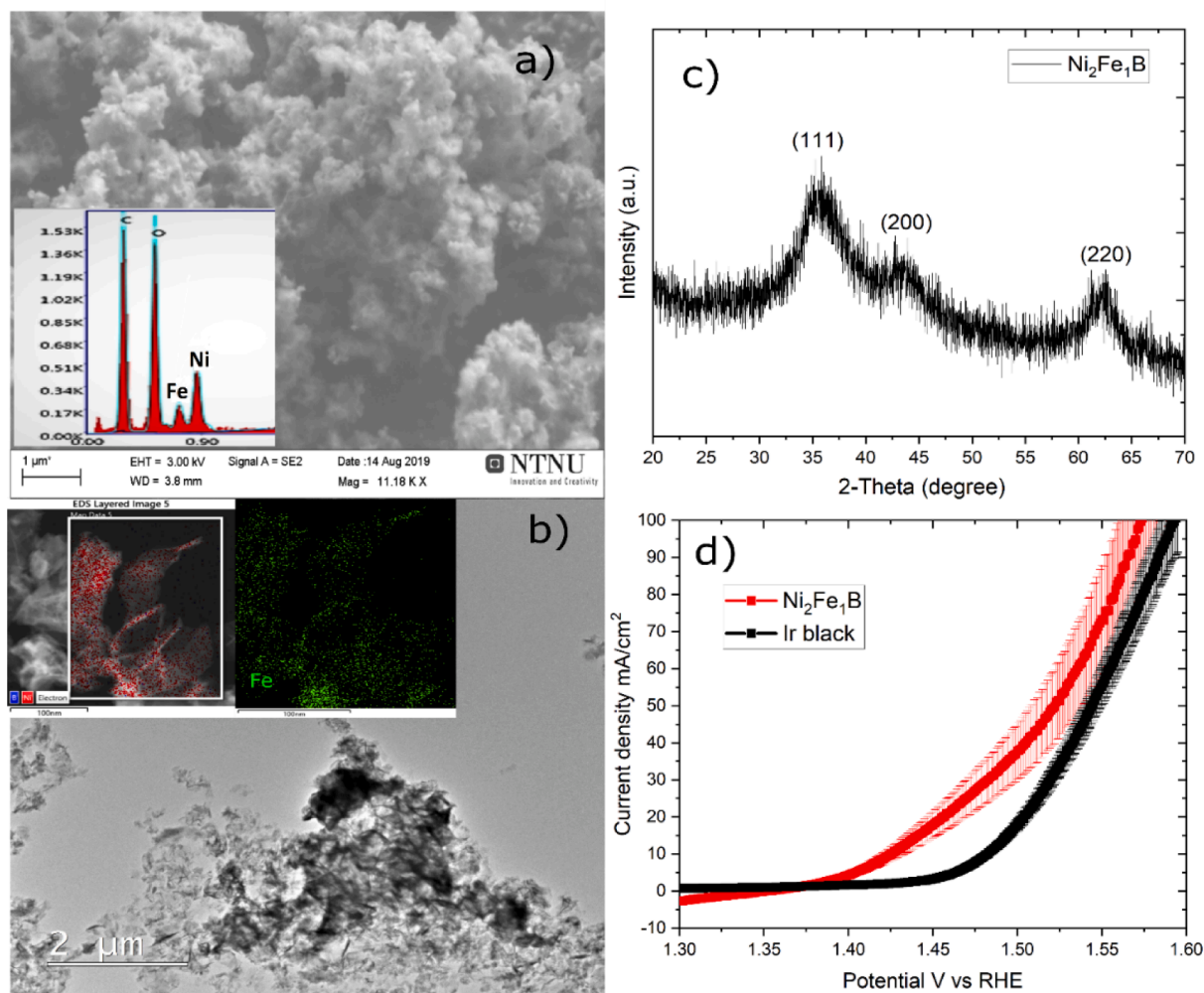


Fig. 1. a) SEM, inset EDX spectra b) TEM image, inset EDX mapping, and c) XRD pattern of $\text{Ni}_2\text{Fe}_1\text{B}$ d) linear sweep voltammetry of $\text{Ni}_2\text{Fe}_1\text{B}$ and iridium (Ir) black catalysts for 5 inks.

respectively. The GC electrodes were polished and thoroughly cleaned before use.

4. Membrane electrode assembly (MEA) fabrication and testing

Inks for catalyst electrode layers were prepared as follows: The required amount of water, ethanol, and ionomer was added to the anode and cathode catalyst powder, and the mixture was ultrasonicated in an ice bath for 15 min. The electrodes and MEA have been fabricated similarly as described earlier by Faid et al. [12,13]. The cathode or anode electrode area was 6.25 cm^2 . To assemble the cell: The membrane was secured with a gasket and sandwiched between cathode and anode electrodes. The cell has an anode and cathode Ni current collectors. 1 M KOH was fed to both the anode and cathode sides at $T = 60^\circ \text{C}$ with flow rates of 250 ml/min. The electrochemical analysis (recording of polarization curves and impedance measurements) was done using a high-current potentiostat (HCP-803 Biologic, France). The cells were controlled at a constant current. The polarization curve was measured at constant current mode from 0 to 3 A/cm^2 with 50 steps with a dwell time of 30 s. Durability testing was carried out for cells at galvanostatic mode at 1 A/cm^2 with a cut-off cell voltage of 2 V.

5. Results and discussions

SEM, TEM, EDX, and XRD were used to evaluate catalyst structure,

composition, and morphological features. Fig. 1 shows an SEM image of scaled-up $\text{Ni}_2\text{Fe}_1\text{B}$. The scaled-up $\text{Ni}_2\text{Fe}_1\text{B}$ showed an agglomerated nanosheet structure as confirmed in the TEM image. EDX analysis and TEM EDX mapping displays are shown in Fig. 1 with the evident presence of Ni, Fe, and B elements. XRD diffraction pattern of $\text{Ni}_2\text{Fe}_1\text{B}$ is shown in Fig. 1c. The $\text{Ni}_2\text{Fe}_1\text{B}$ XRD pattern reveals three broad peaks at 2θ values of 35.57, 43.46, and 62.38 corresponding to (111), (200), and (220) of face-centered cubic phase NiO (JCPDS card no. #47-1049) [14].

Testing the catalyst in three electrode cells using RDE configuration for 5 inks of scaled-up $\text{Ni}_2\text{Fe}_1\text{B}$ powder is shown in Fig. 1d. The OER performance of $\text{Ni}_2\text{Fe}_1\text{B}$ in 1 M KOH is revealed in LSV curves in Fig. 1d which proves that $\text{Ni}_2\text{Fe}_1\text{B}$ has exceptional OER performance compared to state of art Iridium (Ir) black catalyst (Alfa Aesar) with achieving the standard current density of 10 mA/cm^2 at an overpotential of only 190 mV.

To test the scaled-up $\text{Ni}_2\text{Fe}_1\text{B}$ catalyst as an anode electrode for an AEM water electrolysis, the MEA has been fabricated with Pt/c cathode, $\text{Ni}_2\text{Fe}_1\text{B}$ anode, and Fumion FAA membrane. The MEA is then inserted between cathode and anode current collectors in the cell as shown in Fig. 2a. The cells with $\text{Ni}_2\text{Fe}_1\text{B}$ anode catalysts were compared to state of art Ir black catalysts of the same loading and ink composition.

Two ionomer compositions of 9 and 20 wt% have been used for $\text{Ni}_2\text{Fe}_1\text{B}$ and Ir black catalyst layers. The spraying was carried out with a (Coltech) airbrush to be 3 mg/cm^2 for anode ($\text{Ni}_2\text{Fe}_1\text{B}$ or iridium (Ir)

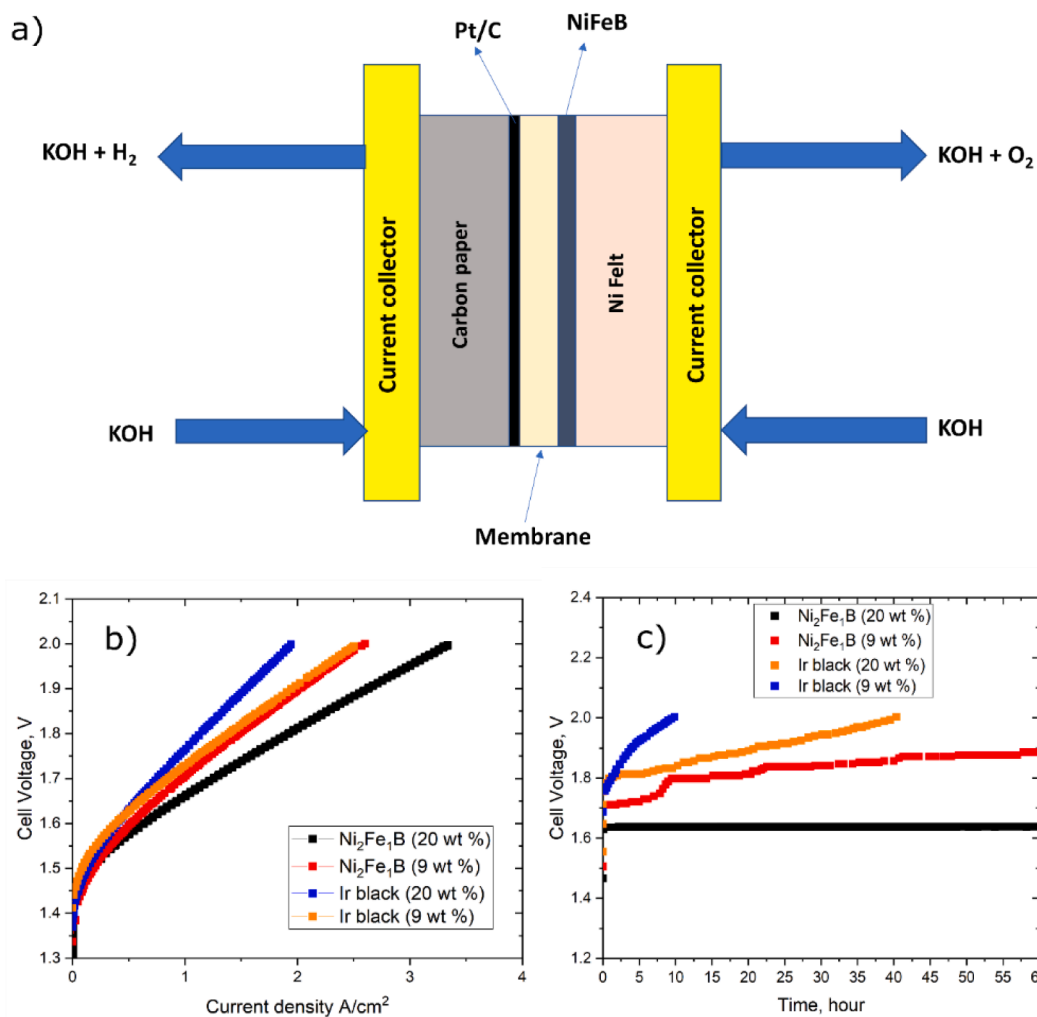


Fig. 2. a) schematic of electrolysis cell used in this work, b) Polarization curves c) stability curves for 60 h at 1 A/cm².

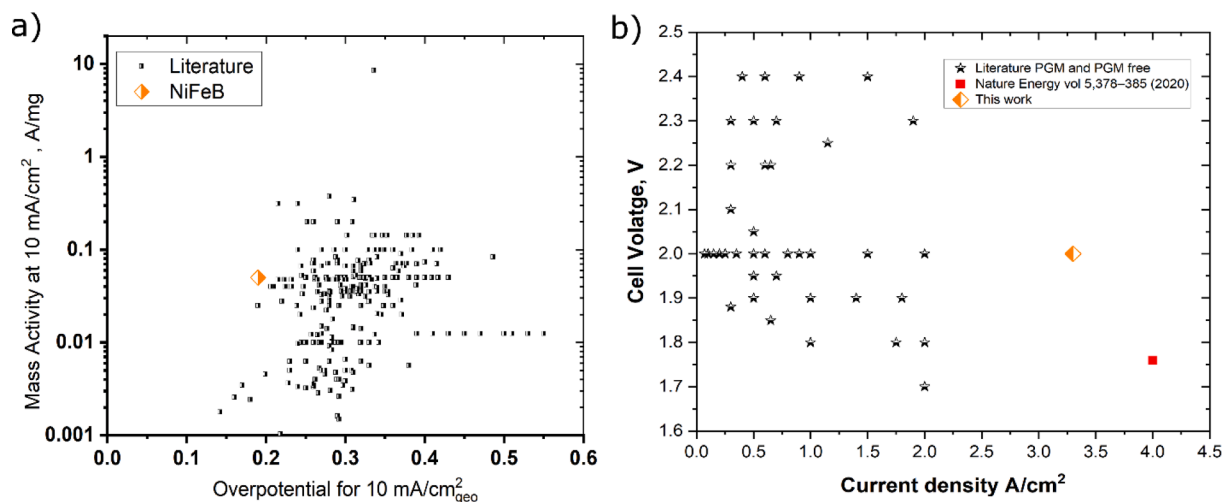


Fig. 3. Performance comparison of Ni₂Fe₁B at a) three electrode systems [15] and b) electrolysis cell system [16,17].

black) and (1 mg/cm² for Pt/C) as the cathode. Ni₂Fe₁B layers at every ionomer content reveal better electrolysis performance and stability than Ir catalyst. Ni₂Fe₁B with 20 wt% ionomer achieves 3.3 A/cm² at 2 V compared to 2.6 A/cm² at the same cell voltage for Ni₂Fe₁B layers with 9 wt% ionomer while the Ir black anode electrode achieves cell

performance of 2.5 and 1.95 A/cm² at 2 V for ionomer content of 9 and 20 wt%. The Ni₂Fe₁B and Ir black cells were then tested for stability at 1 A/cm² with a cut-off cell voltage of 2 V where a cell with a decreasing performance will result in an increased cell voltage with time. Ni₂Fe₁B layers display superior stability for 60 h compared to the expensive Ir

black-based electrode layers. The ionomer content performance-durability influence is different for Ni₂Fe₁B and Ir black where the higher ionomer content for Ir black layers results in lower performance and higher durability while for Ni₂Fe₁B leads to higher performance and durability. The Ni₂Fe₁B catalyst and electrode layers achieve state of art OER performance for AEM water electrolysis of 1 A /cm² at 1.67 V in 1 M KOH, 60 °C as in Fig. 3.

6. Conclusions

Ni₂Fe₁B OER catalyst scaled up to 5 g was tested as anode electrode in anion exchange membrane electrolysis 1 A /cm² at 1.67 V and exceptional durability for 60 h in 1 M KOH and 60 °C compared to state of art Ir black catalyst.

CRedit authorship contribution statement

Alaa Y. Faid: Conceptualization, Methodology, Investigation, Writing – original draft. **Svein Sunde:** Funding acquisition, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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