The impact of ultrasonic parameters on the exfoliation of NiFe LDH nanosheets as electrocatalysts for the oxygen evolution reaction in alkaline media

Tshimangadzo S. Munonde\textsuperscript{a,b}, Haitao Zheng\textsuperscript{a,*}

\textsuperscript{a} Energy Centre, Council for Scientific and Industrial Research (CSIR), P.O Box 395, Pretoria 0001, South Africa
\textsuperscript{b} Department of Chemical Sciences, University of Johannesburg, Doornfontein Campus, P.O Box 17011, Johannesburg 2028, South Africa

\textbf{A R T I C L E   I N F O}

Keywords:
NiFe LDH
Exfoliation
OER
Ultrasonication
Water

\textbf{A B S T R A C T}

The ultrasonic process has been examined to exfoliate layered materials and upgrade their properties for a variety of applications in different media. Our previous studies have shown that the ultra-sonication treatment in water without chemicals has a positive influence on the physical and electrochemical performance of layered materials and nanoparticles. In this work, we have probed the impact of ultrasonication on the physical properties and the oxygen evolution reaction (OER) of the NiFe LDH materials under various conditions, including suspension concentration (2.5–12.5 mg mL\textsuperscript{-1}), sonication times (3–20 min) and amplitudes (50–90%) in water, in particular, sonication times and amplitudes. We found that the concentration, amplitude and time play significant roles on the exfoliation of the NiFe LDH material. Firstly, the NiFe LDH nanosheets displayed the best OER performance under ultrasonic conditions with the concentration of 10 mg mL\textsuperscript{-1} (50% amplitude and 15 min). Secondly, it was revealed that the exfoliation of the NiFe LDH nanosheets in a short time (<10 min) or a higher amplitudes (>80%) has left a cutdown on the OER activity. Comprehensive, the optimum OER activity was displayed on the exfoliated NiFe LDH materials under ultrasonic condition of 60% (amplitude), 10 mg mL\textsuperscript{-1} and 15 min. It demanded only 250 mV overpotentials to reach 10 mA cm\textsuperscript{2} in 1 M KOH, which was 100 mV less than the starting NiFe LDH material. It was revealed from the mechanism of sonochemistry and the OER reaction that, after exfoliation, the promoted OER performance is ascribed to the enriched Fe\textsuperscript{3+} and Fe\textsuperscript{3+} during the OER process. This work provides a green strategy to improve the intrinsic activity of layered materials.

1. Introduction

Electrochemical water splitting remains an efficient and promising approach to generate clean energy in the form of oxygen and hydrogen fuels [1–3]. Nonetheless, the oxygen evolution reaction (OER) involving a four electron transfer process is kinetically slow, which consequently requires extra potential to drive the reaction [4,5]. Subsequently, a highly effective electrocatalyst is required to advance the reaction kinetics and therefore decrease the overpotential [6,7]. Although the precious metal oxides such as IrO\textsubscript{2} and RuO\textsubscript{2} electrocatalyst have shown substantial electrolycatalytic properties, their high cost limit their large scale applications [8–10]. Alternatively, the fabrication of highly efficient, low cost and prosperous transition metal based OER electrocatalysts have been investigated [11–17]. Amongst the identified alternatives, Layered double hydroxides (LDHs) have shown greater potential owing to their unique tunable metal species, exchangeable interlayer spacing and excellent catalytic performances [18,19], especially in the oxygen evolution reaction (OER) in alkaline media [20–22]. The intensive researches were found on NiFe LDH as electrocatalysts for water electrolysis [5,10,21,23–25]. The initial synthesized NiFe LDH materials possess stacked nanosheets that limited exposure of catalytically active sites. However, the most researches are focused on incorporating carbon materials with NiFe LDH to elevate charge transfer kinetics and further improve the catalytic activity [26–28]. Obviously, the lack of attention is paid to the expansion of active sites or intrinsic activity of the NiFe LDH electrocatalyst. Accordingly, it is critical to initialize the packed basal planes for escalating the catalytic activity of the NiFe LDH. Eventually, some interesting findings...
show that the electrochemical performance of the LDH material was enhanced after being exfoliated into single or thinner nanosheets. It is believed that exfoliation exposes more active sites, which leading to increased mass transfer, accelerating electron transfer, and stronger structural stability [29–31]. In general, the most exfoliation processes for layered materials mainly involved chemical methods (liquid-phase with various organic or inorganic solvents) and mechanical methods (sonication, ball milling and fluid dynamics) [32]. Recently, the use of sonochemistry for the synthesis of catalysts, especially as energy materials, has offered many merits in the light of rapidity, simplicity, efficiency, and environmentally friendliness. [33–35]. In the other hand, the morphology of nanomaterials can be affected greatly by ultrasonication, power, frequency and as well as the solution volume [36–38]. Furthermore, regarding the effect of ultrasonic condition, Yadav et al. [39] indicated that during the MnFe₂O₄ synthesis, the sonication time and percentage of amplitude have significantly affected the structural, cationic distribution and physical property of the MnFe₂O₄. In addition, Cai et al. [40] have investigated the effects of sonication power and time on generating graphene nanoplatelets from graphite using liquid-phase exfoliation. A remarkable finding was that the bulk graphene, h-BN, MoS₂, WS₂ and MoSe₂ layered materials can be ultrasonic exfoliated into atomically thin plates in pure water [41]. The authors observed that apart from low cost, the method not only favor exfoliation, but also leads to high dispersion stability. However, the method involves a very long sonication period of 60 h in a bath ultrasound. Our recent work show that ultrasonic treatment on nano-materials in water in a short time (10 min) have a great impact on the properties and the electrochemical performance of NiFe₂O₄/C and CoFe₂O₄/C nanoparticles [42,43]. However, to the best of our knowledge, there are no detailed reports on the roles of the ultrasonic parameters play in the exfoliation of layer materials using water as media.

From our previous study, we have observed that carbon has a negative influence on the exfoliation of the NiFe LDH/C layer materials [44]. To limit the carbon interference, in this work, we explore the effect of ultrasonic condition on the properties of the NiFe LDH materials without carbon additives as well as electrocatalyst for OER. The NiFe LDH concentration in water, percentage of amplitude and sonication time were investigated in detail.

2. Experimental section

2.1. Synthesis of NiFe LDH materials and the procedures of the ultrasonic exfoliation

The preparation of NiFe LDH followed the same method as our previous study without carbon additives [44] (seen details in Supplementary). The Ni:Fe molar ratio was ~ 2.6:1.

The ultrasonic exfoliation was conducted using tip sonication (UP500hd-230, Hielscher). The synthesized materials were exfoliated in deionised water under various conditions. After exfoliation, the 0.5 mL NiFe LDH suspension was dispensed into 1.5 mL of the prepared Naftion aqueous solution to make the ink which was then deposited onto the GC electrode.

The ultrasonic exfoliation was performed in various concentrations of NiFe LDH suspension with the value of 2.5, 5.0, 7.5, 10 and 12.5 mg mL⁻¹ at 50% amplitude (named as 50A) for 15 min.

To optimize the sonication time, five aqueous NiFe LDH suspensions with concentration of 10 mg mL⁻¹ were sonicated for 3, 5, 10, 15 and 20 min, respectively, under 50% amplitude.

Following the optimizations of concentration and sonication time, five suspensions with each concentration of 10 mg mL⁻¹ were sonicated under the different ultrasound amplitude (50–90%) for 15 min.

2.2. Characterization

The physical properties of the synthesized materials were characterised using the following instruments: the transmission electron microscopy (TEM, JEM-2100, JEOL, Tokyo, Japan). Scanning electron microscopy (SEM-EDX, Auriga Cobra FIB FE-SEM, Germany). Fourier transform infrared spectrometer (Waltham, MA, USA), The X-ray diffractometer (XRD, λ = 0.15406 nm, Rigaku). X-ray photoelectron spectroscopy (XPS) and Thermogravimetric analysis (TGA, NETZSCH, STA 429CD analyser, Germany. 20–900 °C in a nitrogen atmosphere.

2.3. Electrochemical measurements

The electrochemical measurements were conducted on an AUTOLAB (PGSTAT 302) with a three-electrode system, the counter and reference electrode used were platinum rod and Ag/AgCl, respectively. The glassy carbon (GC) electrode (3 mm in diameter) was used as the working electrode. The loadings of the catalyst were ca. 0.16 mg cm⁻². The linear sweep voltammetric (LSV) data were measured after activation of the catalyst with cyclic voltammetric (CV) experiments. Electrochemical impedance spectroscopy (EIS) was tested between 0.1 to 10⁵ Hz at 1.5 V vs RHE. Cyclic voltammetry was conducted at scan rates of 5 to 50 mV s⁻¹ for the estimation of the electrochemical surface area (BES) through the double layer capacitance (Cdl). The chronopotentiometric measurements were conducted on Ni foam (working electrode) with electrocatalysts loaded at the current of 10 mA cm⁻². The IR corrected potentials were converted to RHE (reversible hydrogen electrode) by the equation: \( E_{RHE} = E_{Ag/AgCl} + 0.059 \, pH + E_{Ag/AgCl} \), where: \( E_{Ag/AgCl} = 0.1976 \, V \).

3. Results and discussion

This work mainly focuses on the effects of ultrasonic amplitude and sonication time (due to space limitations) on the OER activity of the NiFe LDH electrocatalysts in 1 M KOH. Previously, the concentration of the NiFe LDH was optimised in water at 50% amplitude for 15 min, as presented in Fig.S1(Supplementary) and the OER activities were summarized in Table S1(Supplementary). The sample with concentration of 10 mg mL⁻¹ demonstrates the best OER performance. Therefore, the concentration of 10 mg mL⁻¹ was used as a constant while investigating effect of the amplitude and exfoliation time.

The SEM images, and XRD patterns of the original NiFe LDH and the Exf NiFe LDH materials at different conditions were shown in Fig. 1. From Fig. 1a, the pristine NiFe LDH show stacked nanosheets with larger sizes with the range of ~70–800 nm and a thickness ranging from ~25 to ~40 nm. After exfoliation, the sizes and thickness of the Exf NiFe LDH materials were significantly decreased, in particular, under low power input (50A-60A) and short time (10–15 min), with narrowed sizes ranging from ~30–300 nm and a thickness of ~12–20 nm (Fig. 1b, 1c), indicating that the stacked NiFe LDHs had been successfully exfoliated by ultrasonication in water. However, the stacked nanosheets resurfaced after a long sonication time (20 min) (Fig. 1e) or high power input (80A) (Fig. 1d), because high sonication amplitude and longer sonication times promote aggregation that leading to the inconsistent exfoliation [40,41].

The XRD patterns in Fig. 1f indicate the typical characteristic peaks of the NiFe LDH on all the samples at 11.3°, 22.6°, 33.1°, 34.2°, 35.2°, 38.3°, 46.3°, 60.1° and 61.1°, indexed as (003), (006), (101), (012), (009), (015), (018), (110) and (113), respectively, that were matched to the NiFe LDH material (JCPDS card No. 40–0215) [46–47]. The peaks at 39.2°, 52.2° and 62.8° correspond to the (101), (012) and (111) planes of β-Ni(OH)₂ (JCPDS card no. 14–0117) [4]. Additionally, the diffraction peaks at 16.4°, 26.7°, 43.1°, 55.9° and 67.9° indexed as (200), (310), (321) and (401) can be attributed to β-FeOOH (JCPDS 75–1549), resulting from the possible hydrolysis of Fe(III) in solution [48]. After exfoliation, the (003), (310), (321) and (018) diffraction peaks became sharper with increased intensities in all exfoliated materials, which indicates increased periodicity in these crystallographic directions, which is the typical characteristic of LDHs [3].
Meanwhile, the basal peaks are shifted. This indicates the increase in the intercalation anions (CO$_3^{2-}$) that were detached from the surface into the interlayer space leading to an extension on the interlayer distance, which signifies a successful exfoliation process [49–51]. Additionally, the interlayer spacing was calculated by the Bragg’s law based on the (003) planes, the value of interlayer spacing is 0.747 for the pristine NiFe LDH, and 0.751, 0.781, 0.753 nm for Exf-NiFe LDH under different conditions (10mins, 50A), (15mins, 60A), (20 min, 60A), (15mins, 80A), respectively. It can be seen that interlayer spacing is increased after exfoliation, the largest interlayer spacing is display in the Exf-NiFe LDH under the mild condition (15mins, 60A). Fig.S3g show the elements mappings of Ni, Fe and O as the main components in all the samples. All the three elements have shown similar patterns with a homogeneous distribution on each sample. Table 1 shows the EDX analysis extracted from Fig.S3. It is worth noting that the atomic ratio of Ni/Fe is 3.2 on the pristine NiFe LDH that is higher than the original experimental ratio of 2.6, which implies the possible loss of Fe ions during the synthesis. After exfoliation, the ratio of Ni/Fe dramatically decreased to 1.1–1.4, which was probably due to the ultrasound power that detached Ni$^{2+}$ from the surface and varied according to the ultrasonic condition and the compounds stabilities [52,53]. As an evidence from the water changed to greenish solution after the ultrasonication. However, specific effect of the ultrasonic condition on the ratio of Ni/Fe still need to be further investigated.

Further insights on the morphology of the NiFe LDH and the Exf NiFe LDH were explored using TEM /SAED as shown in Fig. 2. The Exf NiFe LDH (15 min, 60%) as an example to compare with the pristine NiFe LDH materials are confirmed by the characteristic peaks between 3000 and 3500 cm$^{-1}$ can be allocated to the O–H stretching vibrations in the brucite-like layers [27]. The 2185 cm$^{-1}$ band can be attributed to vibrations of CO$_3^{2-}$ anions [28]. The 1621 cm$^{-1}$ band can be attributed to vibrations of the cohering H$_2$O molecules [58]. The 1345 cm$^{-1}$ band belong to the intercalated CO$_3^{2-}$ anions vibrations [28,58]. The presence of the intrinsic stretching vibrations of Fe-O, Ni-O and Ni-O-Fe bonds in all NiFe LDH materials are confirmed by the characteristic peaks between 400 and 700 cm$^{-1}$ (Fig. 3B) [27,58]. The reduced intensity of CO$_3^{2-}$ band observed in all exfoliated materials due to the increased inter-layer spacing as a result of forming mono-/few layer sheets after exfoliation [49,59]. After exfoliation, the metal–oxygen (M–O) bands around 640 cm$^{-1}$ and 450 cm$^{-1}$ became weaker, suggesting a decrease in the metal–oxygen bonding (Fig. 2B). Meanwhile, the band of 450 cm$^{-1}$ shifts to low energy. In addition, the M–O bands around 450 cm$^{-1}$ show the decrease of the intensities with narrower peaks. Comprehensively, the CO$_3^{2-}$ bands and the M–O bands are reduced after ultrasonication, indicating the exfoliation of the NiFe LDH occurred during ultrasonication in water.

The thermal behaviour of the NiFe LDH and the Exf NiFe LDH were evaluated by TGA/DTA in Fig. 4. The TGA (Fig. 4a) and DTA (Fig. 4b) curves show two-steps weight loss on the pristine and two of the Exf-NiFe LDH with longer time (20 min) and high amplitude (80A). However, the rest of the Exf NiFe LDH materials show two main steps with small multi-steps. On the first main step, the weight loss arose at about

---

**Table 1** Summary of EDX analysis.

| Sample          | Pristine NiFeLDH | Exfoliation condition |
|-----------------|------------------|-----------------------|
|                 | (Pristine)       | (Exfoliation)         |
|                 | NiFeLDH          | 10mins (50A) | 20mins (50A) | 60A (15mins) | 80A (15mins) |
| Ratio of Ni/Fe  | 3.2:1            | 1.1:1                | 1.0:1        | 1.3:1        | 1.4:1        |

---

Fig. 1. SEM images (a-e) and XRD patterns (f) of NiFe LDH and Exf-NiFe LDH under different sonication conditions; (The pristine NiFe LDH (a); Exf-NiFe LDH (b, c, 15mins, 60A; d, 20 min, 60A; e, 15mins, 80A)).
220°C, which is ascribed to the removals of the surface and intercalated water molecules. Further weight loss belongs to the decomposition and elimination of interlayer CO$_3^{2-}$ anions, as well as the dehydroxylation of metal hydroxide layers to metal oxides [34,40,44]. Furthermore, the Exf NiFe LDH with a short time (10 min) and low amplitude (60A) has shown extra steps around 240-290°C and around 400°C that emancipates from the β-Ni(OH)$_2$ and β-FeOOH indicated in the XRD. The total weight loss of the NiFe LDH is 23.5% at 800°C. However, the weight loss of the Exf NiFe LDH under different conditions with varying degrees of weight loss can be ascribed to the high amount of intercalated water and anions freed from the LDH surface during exfoliation [60,61]. The order of weight loss of all the Exf NiFe LDH at 800°C is 45.1% (10 min, 50A) > 29.8% (20 min, 50A) > 24.4% (15 min, 80A), which is higher than the initial NiFe LDH with 23.5% loss. The TGA results suggested that the ultrasonic exfoliation had no significant effect on the thermal stability of the NiFe LDH material, and all synthesized materials have shown to be stable below ~ 220°C.

XPS analysis was also evaluated on the NiFe LDH and the Exf NiFe LDH (15 min, 60A), as seen in Fig. 5 and the peaks percentages of the deconvoluted Ni2p, Fe2p, O1s were listed in Table S2-S4. The survey spectra in Fig. 5a confirm the existence of O, Ni and Fe in all the prepared samples, which is in line with the EDX results. Furthermore, the intensities are reduced after exfoliation in the survey spectra, which is consistent with the weaker energy of the M–O bands after exfoliation from the FTIR results. In Fig. 5b, the Ni 2p doublet was deconvoluted into Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ located at 853.87 and 871.55 eV, alongside
two corresponding satellite peaks found at 859.54 and 877.50 eV, highlighting the presence of Ni$^{2+}$ [62]. The Fe 2p deconvoluted doublet (Fig. 5c) shows the presence of Fe$^{2+}$ and Fe$^{3+}$ in each of the Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ located around 708.99 and 720.70 eV, respectively, alongside two satellite peaks at ~ 715 and ~ 731 eV, indicating the attributes of Fe ions [63]. It is noteworthy that the Fe$^{3+}$ content increased after exfoliation (Table S3). During the ultrasonic exfoliation, firstly, water molecules was dissociated by sonolysis to yield hydrogen radicals (H•) and hydroxyl radicals (OH•) during the bubble collapse triggered by the ultrasonic cavitation in water [36,37,64] (Eq.1). Since the exfoliation was performed under the atmosphere, in the presence of O$_2$, the H$^*$ reacted with O$_2$ to form HO$_2$ (Eq.2) that suppressed the reaction of the radicals (H• and OH•) to recombine to H$_2$O, remaining with OH• in the solution [65,66]. Furthermore, the OH• radicals combine to form H$_2$O$_2$ (Eq.3). Meanwhile, HO$_2^*$ radicals are re-associated lead to a further increase of H$_2$O$_2$ (Eq.4) [67]. Then Fe$^{3+}$ reacted with H$_2$O$_2$ to produce Fe$^{2+}$ due to high temperature (ca. 5000 K)/pressure (ca. 2000 atms) generated from the collapsing of cavitation bubbles (Eq.5) [37,68,69].

\[
\begin{align*}
H_2O &\rightarrow H^*+OH^* (1) \\
H^*+O_2 &\rightarrow OH^*_2 (2) \\
OH^*+OH^* &\rightarrow H_2O_2 (3) \\
2HO^*_2 &\rightarrow H_2O_2 + O_2 (4) \\
Fe^{2+} + H_2O_2 &\rightarrow Fe^{3+} + OH^* + OH^- (5)
\end{align*}
\]

The O 1s deconvolution (Fig. 5d) resulted in five peaks representing the surface labile oxygen (O, 528.31 eV, metal–oxygen bonds (M–O, 528.93 eV), metal-surface hydroxyl bond (M–OH, 529.58 eV), and surface adsorbed water (H$_2$O, 530.45 eV) and intercalated anions (M–CO$_3^{2−}$, 531.46 eV). The Exf NiFe LDH showed similar results with...
3.1. Electrochemical performance

The effects of sonication time and ultrasonic amplitude on the OER performance of the NiFe LDH electrocatalysts were studied in 1 M KOH solution with a constant concentration of 10 mg mL$^{-1}$. The comparisons were displayed in Figs. 6-8.

3.1.1. Effect of ultrasound-sonication time

The ultrasound-sonication time is one key parameter that plays a very crucial role in the sonication-assisted liquid exfoliation process [39]. We explored the influence of the sonication time (3–20 min) on the OER activity of NiFe LDH nanosheets with the constant amplitude (50%) and concentration (10 mg mL$^{-1}$). The LSV plot was shown in Fig. 6 and the summary of analysis was listed in Table S5. As a reference, the original NiFe LDH was also tested for the OER performance. Noticeably, NiFe LDH catalysts exfoliated for a short period (3–5 min) have shown deterioration on the OER performance when compared with the original NiFe LDH (Table S5). It is difficult to explain this phenomenon because its OER activity should be the same as the starting material if exfoliation has not occurred. However, NiFe LDH catalysts exfoliated at prolonged periods (10 min, 15 min and 20 min) have shown improvements on the OER performance when compared to the original NiFe LDH. The prolonged exfoliation period might have increased the inertial cavitation which is responsible for the exfoliation [45]. When the exfoliation time was increased to 15 min, the optimum OER performance was achieved, affording a current density of 10 mA cm$^{-2}$ at the expense of 270 mV overpotential. This result is higher than the Exf NiFe LDH (20 min), Exf NiFe LDH (10 min) and the original NiFe LDH by 20 mV, 40 mV and 80 mV, respectively (see Table S5). Additionally, it is obvious that the prolonged exfoliation periods (10–20 min) have caused electron redistribution that made the oxidation of Ni$^{2+}$ to Ni$^{3+}$ easily occur during the OER process as revealed in Fig. 6 [26], which is an active site for OER electrocatalysis [30]. However, over the 15 min exfoliation, the Exf NiFe LDH nanosheets started to agglomerate/fusion occurred as shown in SEM images (Fig. 1), leading to the loss of some exposed active sites [40].

3.1.2. Effect of ultrasound-sonication amplitude

Ultrasound amplitude, as a measure of the acoustic output, is one of the most influential parameters in the ultrasound exfoliation process [70]. The effect of the ultrasonic amplitude (50–90%) was investigated with the concentration of 10 mg mL$^{-1}$ for 15 min, as displayed in Fig. 7 and a summary listed in Table S6. Under the 60% exfoliation amplitude, the Exf NiFe LDH shows the lowest overpotential of 250 mA at the current density of 10 mA cm$^{-2}$, which was 20 mA less than that under the 70% exfoliation amplitude. We can see that the higher ultrasonic amplitudes (80–90%) are not beneficial to the exfoliation of NiFe LDH, requiring 390 and 490 mV overpotentials to drive a current density of 10 mA cm$^{-2}$, respectively, which was 40 and 149 mA more than the pristine NiFe LDH (Table S6). When the high amplitudes were applied on the ultrasonic process that caused the fusion/aggregation of nanosheets instead of exfoliations [45,70,71], as reflected by the SEM images. On the other hand, the Exf NiFe LDH with greater OER performances (50–70% exfoliation amplitude) show a higher Ni$^{2+}$/Ni$^{3+}$ oxidation peak (inset of Fig. 7), which was believed to influence greatly the OER performance [30].

Through the optimizations under various conditions, the Exf NiFe LDH (60%, 15 min) was identified as the optimum candidate for the OER performance, which was subjected to further assessment for electrocatalytic performances compared with the pristine NiFe LDH, as exhibited in Fig. 8. From Fig. 8a, the Exf NiFe LDH needs 250 mV of overpotential to reach the current density of 10 mA cm$^{-2}$, which was 100 mV lower than that of the pristine NiFe LDH. This indicates the significant improvement of the OER activity on the NiFe LDH after the exfoliation process. Additionally, the Exf NiFe LDH delivered 3.6 times current density than that of the pristine NiFe LDH at 1.5 V. In addition, this result is superior/comparable to recent studies through alternative approaches to obtain single/thin LDH layers for OER (Table S7). The inset graph of Fig. 8a depicts the Tafel slopes of the NiFe LDH and the Exf NiFe LDH calculated as 68 and 43 mA dec$^{-1}$, respectively. The slopes are similar to type A and type B observed in other studies in alkaline solution [72,73], respectively, suggesting the OER kinetic mechanism changed after exfoliation. Obviously, the Exf NiFe LDH with a smaller Tafel slope has a faster electrochemical OER kinetics than that of the original NiFe LDH, which is comparable with the 40 mA dec$^{-1}$ of the benchmark IrO$_2$ electrocatalyst.

In general, the Tafel slopes of 60 and 40 mA dec$^{-1}$ approximately represent the first and second electron transfer as the rate determining step in the OER with 4 electron transfer process, respectively [74]. Thus, the pristine NiFe LDH (68 mA dec$^{-1}$) and the Exf NiFe LDH (43 mA dec$^{-1}$) follow the first and second electron transfer as the rate determining step, respectively. These results strongly suggest the improvement of the charge-transfer process, as indicated by the Nyquist plots in Fig. 8b.
These results indicate the fast electron transfer ability of the Exf NiFe LDH, which is consistent with the Tafel slope analysis. Furthermore, the fast electron transfer ability of the Exf NiFe LDH could be related to the abundantly exposed intrinsic active sites, leading to more adsorption of OH⁻ on the surface of the Exf NiFe LDH, as there might be a virtuous contact between the electrode surface and the electrolyte, benefitting the OER process [1,75,76]. To rationalize this, the electrochemical surface areas (ECSA) were estimated by the CVs at various scan rates (Fig. 8(a and d)). The linear slope of the capacitive current against scan rate is illustrated in Fig. 8(b). The ECSA of Exf NiFe LDH catalyst exhibits the ECSA (6.48 mF/cm²) that was around 5 times larger than that of the pristine NiFe LDH (1.32 mF/cm²), which could have benefitted from the single/thinner nanosheets and was responsible for the higher OER activity [23,49]. This is in concordance with the XRD, FTIR, SEM and TEM results showing the effectiveness of the ultrasonic exfoliation process. Additionally, the unit activity of each site (intrinsic activity) was evaluated by measuring the turnover frequency (TOF) as it influences the OER performance [23]. Assuming that all metal sites are active sites, the TOFs of Exf NiFe LDH (60%) and NiFe LDHwere obtained as 0.035 and 0.01 s⁻¹, respectively, indicating better intrinsic activity of the Exf NiFe LDH.

The chronopotentiometry was carried out to evaluate the stability of the OER catalysts for 12 h, as shown in Fig. 8f. Nickel form (NF) was used as the working electrode. Thus, a bare NF was tested under the same experimental conditions as a reference. During the first 6 h of the OER process, the Exf NiFe LDH/NF shows a constant overpotential without degradation. However, after 6 h, Exf NiFe LDH/NF shows a slight rise in overpotentials that may be ascribed to a slow release of gas bubbles from the working electrode [75]. However, the NiFe LDH/NF displays unstable overpotentials with a wave trend during the first 6 h of the OER electrolysis. After 6 h, it kept constant trend for 2 h, then rising slowly, suggesting the surface passivation of the catalyst under the OER process [77]. Compared to our previous study [44], the exfoliated NiFe LDH/C has shown improved electrochemical stability, although most of the NiFe LDH nanosheets bonding with carbon were not exfoliated. In this work, the exfoliation of the NiFe LDH nanosheets without carbon became easier, however, the exfoliated NiFe LDH without carbon does not benefit the stability.

For the reaction path of the OER in NiFe LDH, it was suggested that OH⁻ was adsorbed onto the Fe site at a low potential, while at a higher potential, H₂O prefered to bind to the Ni site. Hereafter, the reaction intermediates that were generated by adsorbed OH⁻ reacted with other OH group in alkaline electrolyte, then further oxidized to O₂ and H₂O [78]. Generally, the Fe³⁺ interacted strongly with OH than the Ni²⁺ at a higher potential, as Fe³⁺ is a stronger Lewis acid. Meanwhile, the electronic effect of Fe³⁺ could boost a higher Ni valence, leading to a bond with OH⁻ that easily promote H₂O dissociation in alkaline solution [26,78]. From the XRD and XPS analysis, the intensity of the (3 1 0) peak of FeOOH (Fe³⁺) and the percentage of Fe³⁺ after exfoliation was increased, which implies that the water dissociation could be accelerated through the depressing reaction of Ni(OH)₂ to NiOOH complex. It was also evident that the OER activity was increased by increasing Fe³⁺ doped in the β-Ni(OH)₂ [79]. According to the EDX analysis, the ratio of Ni/Fe was changed remarkably after exfoliation. The changes of Ni²⁺/Fe³⁺ in the NiFe LDH could be due to the undergoing charge transfer during ultrasonic cavitation. For this reason, the electron density and cationic ions coordination rearranged as the oxidation of Ni²⁺ was boosted accordingly and its OER catalytic activity was increased accordingly [80]. In addition, the exfoliation process could be beneficial to the adsorption of the Fe species at the defect or edge sites of the Ni complex, which could effectively improve Ni²⁺ catalytic behaviour [81]. Furthermore, the increased Fe³⁺ could create cation defects in the NiFe LDH after ultrasonication, which can promote the OER performance [82,83]. Most studies show that both Ni and Fe are indispensable in Ni (Co)FeOOH for the OER activity [26,84]. To further understand the Fe role in the OER activity, some advanced characterizations and computational methods were applied on the Ni(Co) Fe (oxy) hydroxides [74,85,86]. The authors claim that Fe³⁺ has a higher intrinsic activity than Ni²⁺ or Co²⁺, Ni or Co sites in Ni (Co) Fe OOH are the host of Fe rather than active centres for the OER. Additionally, it was suggested that Ni (Co) OOH has a higher electrical conductivity and chemical stability than FeOOH, as strong electrical coupling between Fe and Ni (Co) are essential to the OER activity. In this work, the best OER
performance was obtained on the ExF NiFe LDH with a Ni/Fe ratio of 1.0 that is the lowest ratio. From EDX analysis (Table 1 in Fig. 1), which means that the higher Ni/Fe is not beneficial to the OER activity, because Fe occupies the active sites.

4. Conclusion

In summary, to explore the impact of the ultrasonic exfoliation, various suspension concentrations, ultrasound amplitudes, and sonication times were conducted for the exfoliation of NiFe LDH, with the OER activity on the respective exfoliated sample tested. It was found that, firstly, the concentration of 5 mg mL−1 in water is beneficial to the exfoliation of NiFe LDH nanosheets. Secondly, the short time (< 10 min) or high ultrasonic amplitudes (80–90%) show a negative effect on the exfoliation of the NiFe LDH nanosheets, as well as the OER activity. The optimum OER activity was achieved on the sample under exfoliation in a suspension concentration of 10 mg mL−1 at an amplitude of 60% for 15 min. The best exfoliated NiFe LDH catalyst shows advanced performance with 250 mV overpotential at a current density of 10 mA cm−2, which is 100 mV less than the initial NiFe LDH catalyst. Furthermore, it was found that Ni2+ can be oxidized to Ni3+ easily on the exfoliated NiFe LDH, which enhances the OER activity by acting as an active site for OER catalysis. Moreover, the improved OER activity is also as a result of the faster charge transfer on the exfoliated NiFe LDH caused by the Fe and Ni strong electrical coupling. The durability of the exfoliated NiFe LDH nanosheets was maintained similar as the pristine NiFe LDH during the 12 h OER electrolysis. This work provides a green strategy to improve the intrinsic activity of layered materials. To achieve a best catalyst with a balance of activity and stability, we suggest that it is necessary to incorporate suitable amount of carbon or conductive materials into the nanosheets to expand the activity and stability.

CRediT authorship contribution statement

Tshimangadzo S. Munonde: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - original draft, Visualization. Haitao Zheng: Conceptualization, Methodology, Investigation, Formal analysis, Writing - review & editing, Visualization, Supervision, Funding acquisition.

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.

Acknowledgement

The authors are thankful for the financial support from the CSIR and the National Research Foundation of South Africa.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ulsonch.2021.105664.
[83] J. Suntivich, K.J. May, H.A. Gasteiger, J.B. Goodenough, Y. Shao-Horn, A perovskite oxide optimized for oxygen evolution catalysis from molecular orbital principles, Science 334 (6061) (2011) 1383–1385, https://doi.org/10.1126/science.1212856.

[84] M. Gong, H. Dai, A mini review of NiFe-based materials as highly active oxygen evolution reaction electrocatalysts, Nano Res. 8 (1) (2015) 23–39, https://doi.org/10.1007/s12274-014-0591-z.

[85] L. Trotzchaud, S.L. Young, J.K. Ranney, S.W. Boettcher, Nickel-Iron oxyhydroxide oxygen-evolution electrocatalysts: The role of intentional and incidental iron incorporation, J. Am. Chem. Soc. 136 (18) (2014) 6744–6753, https://doi.org/10.1021/ja502379c.

[86] D. Friebel, M.W. Louie, M. Bajdich, K.E. Sanwald, Y. Cai, A.M. Wise, M.-J. Cheng, D. Sokaras, T.-C. Weng, R. Alonso-Mori, R.C. Davis, J.R. Bargar, J.K. Nørskov, A. Nilsson, A.T. Bell, Identification of highly active Fe sites in (Ni, Fe)OOH for electrocatalytic water splitting, J. Am. Chem. Soc. 137 (3) (2015) 1305–1313, https://doi.org/10.1021/jacs.5b05586.