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REDHY

Redox-Mediated economic, critical raw material free, low capex and highly efficient green hydrogen production technology

REDHY - Deliverable report

D5.2 - Heterogeneous catalysts scaling up

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Public Summary

The purpose of this deliverable is to present a comprehensive description of the scaling up procedure for the synthesis of heterogeneous catalysts based on non-critical row material, to operate outside the electrolytic cell in various catalytic-bed reactors. These catalysts enable the regeneration of redox mediators, thereby promoting the production of oxygen and hydrogen from water. Heterogeneous catalysts were synthetized by co-precipitation and hydrothermal processes and analysed by physico-chemical characterizations. The scaling up procedure were demonstrated for all catalysts, in particular for the oxygen evolution reaction, in alkaline environment, of NiFeOxHy; for the hydrogen evolution reaction, in acidic environment, MoS2/C and in alkaline environment, NiMo unsupported. To ensure a robust and reliable scale-up process, CNR-ITAE carefully addressed reactor design and operating conditions, batch size optimization, and the implementation of rigorous quality-control procedures.

Content

List of abbreviations and definitions

Abbr.	Meaning
SOA	state-of-the-art
CRM	critical raw material
CROC	cathodic redox couples
AROC	anodic redox couples
RHE	Reversible hydrogen electrode
XRD	x-ray diffraction
XRF	x-ray fluorescence
EIS	Electrochemical impedance spectroscopy
FRA	Frequency-Response Analyzer
TGA	Thermogravimetric analysis
PEM	Proton exchange membrane
AEM	Anion exchange membrane
MEA	Membrane-electrode assembly
TPR	Temperature-programmed reduction

1 Introduction

REDHy project offers a highly adaptable, durable, sustainable, intrinsically safe and cost-effective alternative to produce H_2 by using water technology. This innovative approach overcomes the drawbacks of SoA electrolysers, supporting the development of an efficient and scalable hydrogen economy. It enables the production of cost-effective green hydrogen at significantly higher current densities. Unlike conventional systems, REDHy eliminates the use of critical raw materials and avoids fluorinated membranes or ionomers.

REDHy project will use a redox mediator (cathodic redox couples, CROC) in contact with the heterogenous catalyst outside of the electrochemical cell in the catalytic bed to initiate the hydrogen evolution at a redox potential range of 0.15 – 0.05 vs. RHE. Similarly, another redox mediator (anodic redox couples, AROC) coupled with a specific heterogeneous catalyst will enable oxygen evolution, with a redox potential range of 1.65 – 1.8 V vs. RHE.

In this report is reported a comprehensive description of the scaling up procedure for the synthesis of heterogeneous catalysts based on non-critical row material, to operate outside the electrolytic cell in various catalytic-bed reactors. These catalysts enable the regeneration of redox mediators, thereby promoting the production of oxygen and hydrogen from water. Heterogeneous catalysts were synthetized by co-precipitation and hydrothermal processes and analysed by physico-chemical characterizations. The scaling up procedure were demonstrated for all catalysts, in particular for the oxygen evolution reaction, in alkaline environment, of NiFeOxHy; for the hydrogen evolution reaction, in acidic environment, MoS_2/C and in alkaline environment, NiMo unsupported. To ensure a robust and reliable scale-up process, CNR-ITAE carefully addressed reactor design and operating conditions, batch size optimization, and the implementation of rigorous quality-control procedures.

2 Heterogeneous Hydrogen Evolution Catalyst scaling up and optimization

2.1 Acidic Environment

For the hydrogen evolution reaction (HER) under acidic conditions, a MoS_2-based material supported on Ketjenblack EC carbon was selected and developed as the cathodic catalyst, in order to maximize the catalytic activity with a low metal catalyst loading.

The catalyst was prepared via a cost-effective hydrothermal route, which was then scaled up from a 1 g small batch (reported in D5.1) to a 20 g large batch, while preserving their physico-chemical properties.

2.1.1 Synthesis and physico-chemical characterization

2.1.1.1 Synthesis of MoS_2/C

The synthesis method originally established for small batches (1 g of MoS_2/C-based cathode catalyst) was subsequently adapted for scale-up, enabling the production of about 20 g of material in a large batch. To obtain reproducible, large-batch catalyst, the hydrothermal synthesis process in a 2 L high-capacity autoclave (Fig. 1) was optimized by appropriately adjusting the reagent volumes, concentrations, and operating conditions.

Fig. 1. Autoclave (2 L capacity) for the scale up of the syntheses of MoS_2/C heterogeneous catalyst

MoS_2/C synthesis is carried out by dissolving ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, Sigma-Aldrich) and thiourea ($SC(NH_2)_2$, Sigma-Aldrich) in ultrapure distilled water, together with

Ketjenblack as the carbon support. The mixture is stirred in a beaker for about 15 minutes to ensure complete dissolution of the precursors.

The clear solution is then poured into a 2 L high-capacity autoclave with a heating jacket to set a controlled temperature of 200 °C, where the hydrothermal reaction is carried out overnight.

The scheme of synthesis is reported in Fig.2.

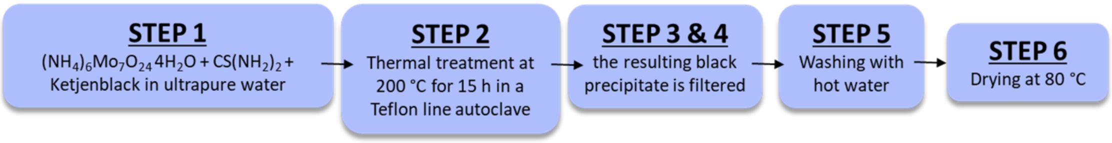


Fig. 2 Synthesis scheme of MoS_2/C heterogeneous catalyst

2.1.1.2 Physico-chemical properties

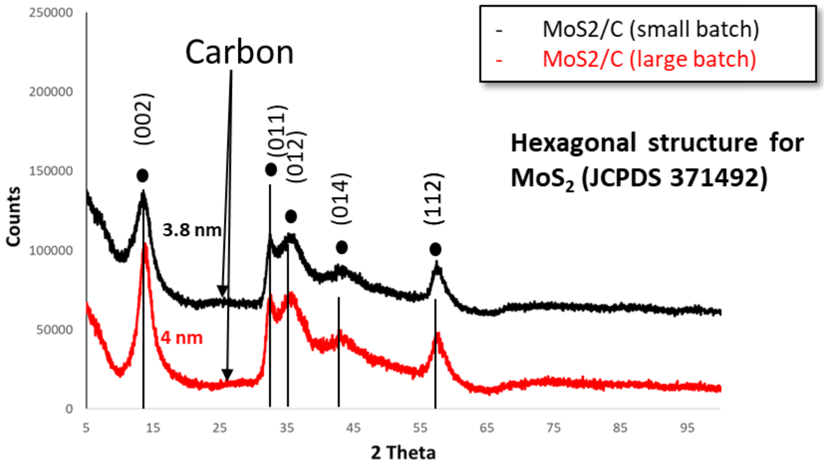
To investigate the physico-chemical properties of the synthesized catalyst, various characterization techniques were employed, including x-ray diffraction (XRD), x-ray fluorescence (XRF) and transmission electron microscopy (TEM).

XRD pattern was recorded using a D8 Advance diffractometer (Bruker AXS, Germany) equipped with Ni β-filtered Cu Kα radiation ($\lambda = 1.5406$ Å), over a 2θ range of 5–100°, at 40 kV and 20 mA, with a scan step of 0.03° s^{-1}. XRD measurement was used to identify and characterize the crystalline phases of the synthesized catalyst.

In Fig. 3, the XRD patterns of both the large-batch and small-batch MoS_2/C samples indicate a predominantly amorphous hexagonal structure (JCPDS 371492), as evidenced by the broad and low-intensity diffraction peaks. The calculated particle size is approximately 4 nm for the large-batch sample (red pattern) and 3.8 nm for the small-batch sample (black pattern).

The atomic composition of the catalysts was determined by X-ray fluorescence (XRF) using an S8 TIGER spectrometer (Bruker AXS, Germany) equipped with a rhodium anode tube (4 kW power, 75 µm Be window) and a LiF 220 crystal analyser.

XRF analysis showed that the synthesized electrocatalysts exhibit comparable atomic compositions, with 59.90% molybdenum and 40.10% sulphur for the small batch, and 61.70% molybdenum and 38.30% sulphur for the large batch, as reported in Fig. 3, on the right.



%at	Mo	S
small	59.90	40.10
large	61.70	38.30

Fig. 3 XRD and XRF comparison between small-batch (black) and large-batch (red) MoS_2 catalysts.

The morphology of the electrocatalyst was examined by transmission electron microscopy (TEM) using a JEOL JEM-F200 instrument equipped with an EDX spectrometer. The catalyst was dispersed in isopropyl alcohol and a suspension was prepared by ultrasonication; a drop of this suspension was then deposited onto a holey carbon-coated Cu grid.

Fig. 4 shows TEM images at different magnifications of the small-batch MoS_2/C (1500 kx, left) and large-batch MoS_2/C (1000 kx, right) heterogeneous catalysts. In both cases, TEM reveals aggregates of 2D MoS_2 nanosheets. HR-TEM images of these supported samples show an intimate intermixing of the phases, which makes them difficult to distinguish except at the edges. The ultra-high-surface-area carbon support (Ketjenblack EC-600JD®, ~1400 m^2 g^{-1}) promotes electronic percolation and reduces ohmic losses in the semiconducting MoS_2.

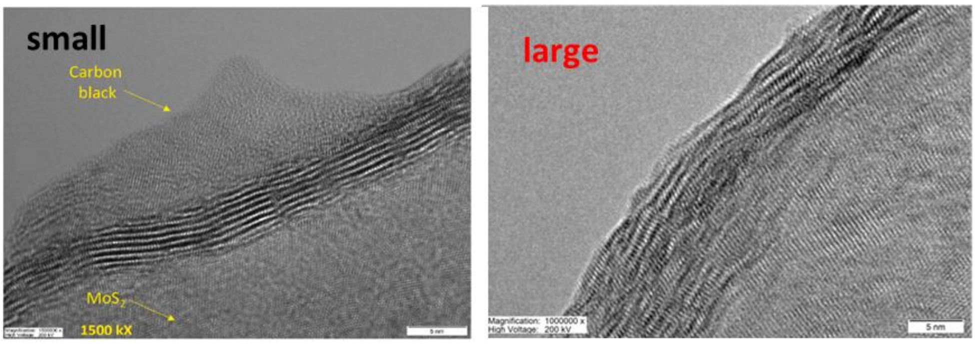


Fig. 4 Transmission electron microscopy images of the small-batch (left) and large-batch (right) MoS_2/C heterogenous catalysts

2.2 Alkaline Environment

Nanosized NiMo heterogeneous catalysts, both unsupported and supported on carbon black, were developed previously (see D5.1) for operation in alkaline environments with an AEM membrane as a backup solution. Among these, only the unsupported NiMo catalyst was selected for scale-up, from a 1 g small batch to a 12 g large batch in a reactor by optimizing the procedure to maintain its physico-chemical properties.

2.2.1 Synthesis and physico-chemical characterization

2.2.1.1 Synthesis of NiMo

The scale-up of the NiMo catalyst synthesis was carried out using a dedicated 25 L continuous stirred-tank reactor (CSTR) setup, as shown in Fig. 5. The synthesis of unsupported NiMo catalyst follows a co-precipitation method. The process protocol is schematically reported in Fig. 6. The precursors, nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, Sigma-Aldrich) and ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, Sigma-Aldrich), were dissolved in ultrapure distilled water.

The resulting solution was placed in a hot-water bath and stirred at 60 °C. A 2 M NaOH solution was added dropwise until pH 9 was achieved. The suspension was then stirred at pH 9 and 60 °C for 3 h. Finally, the precipitate was filtered, washed with hot (~40 °C) ultrapure distilled water, and dried at 80 °C for 24 h. The final product was reduced at 550°C under a 5% hydrogen flow for 6 hours.

Fig. 5 25 L Reactor for scale up of the syntheses of NiMo heterogenous catalyst

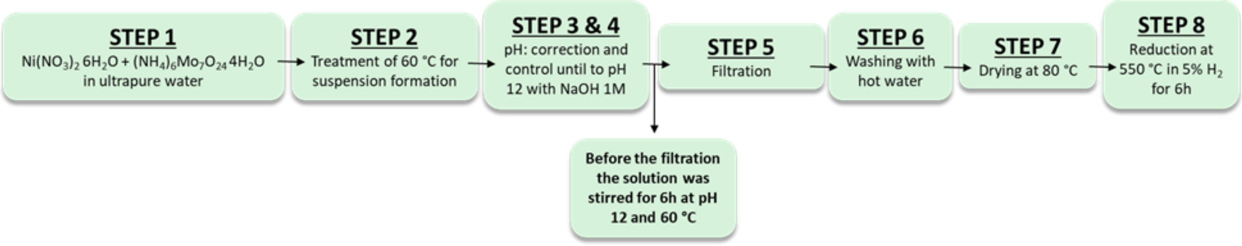


Fig. 6 Synthesis scheme of NiMo heterogenous catalyst

2.2.1.2 *Physico-chemical properties*

Several techniques, including TPR (Temperature-programmed reduction), XRD and XRF, were employed to investigate the physico-chemical properties of the large-batch NiMo catalyst and to compare it with the previously synthesized small-batch NiMo catalyst.

In order to confirm the reduction's temperature, a TPR analysis was carried out to study changes in a material's physical properties as a function of temperature. Firstly, the sample underwent a purification step under an argon flow of 38 cc/min at 300 °C. Subsequently, the reduction was performed up to a maximum temperature of 900 °C under a gas mixture consisting of argon (38 cc/min) and hydrogen (2 cc/min). After the reduction phase, the experiment concluded with a final treatment under an argon flow of 5 cc/min, during which the sample was cooled from 850 °C to 40 °C at a rate of 10 °C/min. The curve reported in Fig. 7 shows the peaks associated with the reduction of the oxide phases formed during the co-precipitation synthesis. On the basis of these results, a reduction temperature of 550 °C was selected to obtain the NiMo alloy.

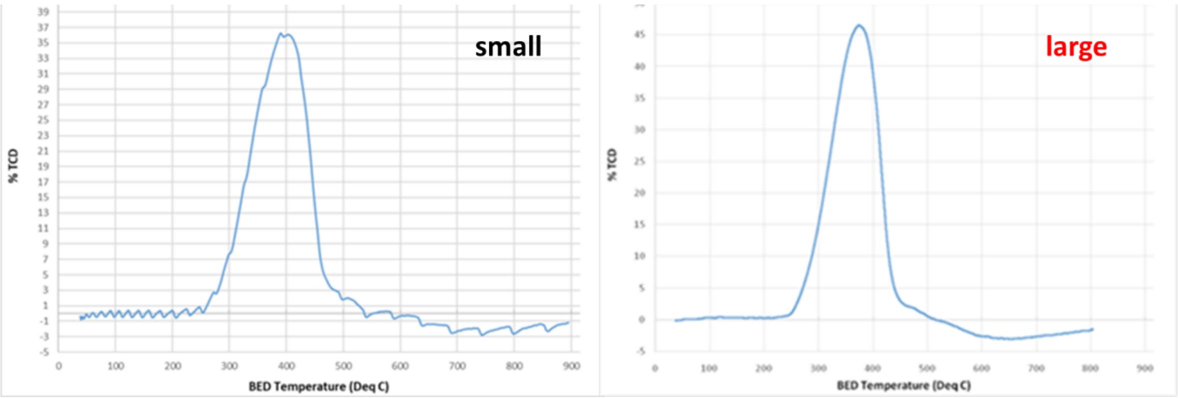
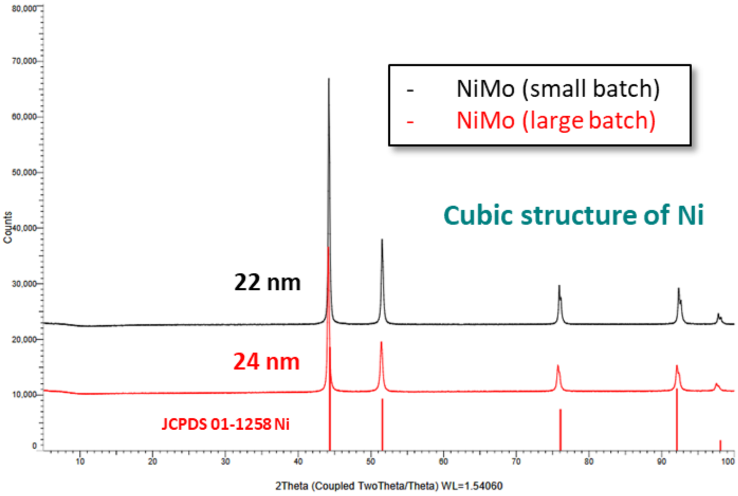


Fig. 7 TPR patterns of the supported NiMo catalyst small batch (on the left) and large batch (on the right)

Fig. 8 compares the XRD patterns of the unsupported NiMo catalysts prepared as small (black line) and large (red line) batches. In both cases, the diffraction peaks are consistent with a cubic Ni phase (JCPDS 01-1258). A slight shift of the reflections toward lower angles confirms the successful formation of the NiMo alloy. Using the Scherrer equation, the average crystallite size was estimated to be 22 nm for the small batch and slightly larger, 24 nm, for the large batch.

Complementary X-ray fluorescence (XRF) analysis further highlights the close similarity between the two materials; the small-batch NiMo exhibits an atomic composition of 92.22% Ni and 7.78% Mo, while the large-batch NiMo shows 93.96% Ni and 6.04% Mo, as reported in the XRF data on the right side of Fig. 8.



%at	Ni	Mo
small	92.22	7.78
large	93.96	6.04

Fig.8 XRD patterns of small-batch (black) and large-batch (red) NiMo heterogeneous catalysts on the left, and XRF analysis on the right

3 Heterogeneous Oxygen Evolution Catalyst scaling up and optimization

3.1 Alkaline Environment

Heterogeneous oxygen evolution catalyst operating in basic media is essential for enhancing the efficiency of oxygen production during water electrolysis. NiFe oxide-hydroxide (LDH)-based anode catalyst was developed via cost-effective and reliable co-precipitation routes.

In particular, the synthesis was scaled up from a 2 g small batch to a 20 g large batch, while preserving the favourable physico-chemical properties previously reported for the oxygen evolution reaction (OER) in alkaline environment (see D5.1).

NiFe layered double hydroxides (LDH) heterogeneous oxygen evolution catalysts is based on non-critical raw material (non-CRM). In this structure, iron (Fe) partially substitutes nickel (Ni) atoms, which is expected to introduce additional electronic levels into the band gap and thereby promote oxygen evolution. Catalyst architectures such as highly active layered double hydroxides, e.g. ($Ni_{1-x}Fe_xOOH$), were investigated for their performance in the OER.

XRD, XRF and BET (Brunauer–Emmett–Teller), were employed to investigate the physico-chemical properties and specific surface area of the large-batch NiFe catalyst and to compare it with the small-batch NiFe catalyst previously synthesized.

3.1.1 Synthesis and physico-chemical characterization

3.1.1.1 NiFeOxHy

The anode catalyst was prepared via a co-precipitation route. Nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, Sigma-Aldrich) and iron nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, Sigma-Aldrich) were first dissolved in ultrapure distilled water to obtain a clear precursor solution. This solution was transferred to a dedicated 25 L continuous stirred-tank reactor (CSTR) setup, as shown in Fig. 5, and stirred at 60 °C. Once the desired temperature was reached, a 1 M NaOH solution was slowly added dropwise until the pH was adjusted to 9. The suspension was then maintained under stirring at pH 9 and 60 °C for 4 h. The resulting precipitate was subsequently filtered, rinsed with hot ultrapure distilled water, and dried at 80 °C for 24 h. A schematic representation of the anode electrocatalyst preparation procedure is shown in Fig. 9.

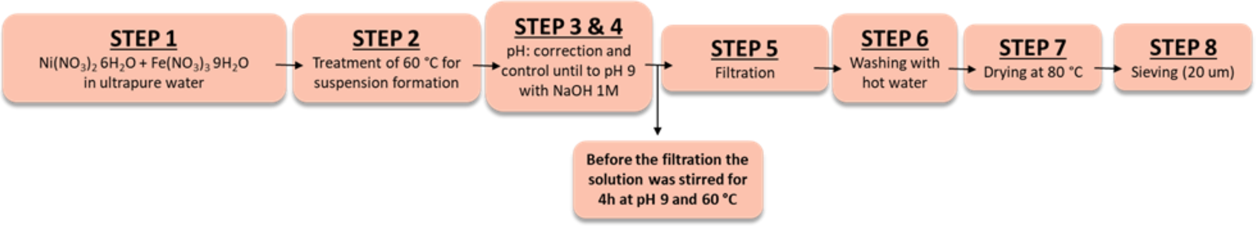


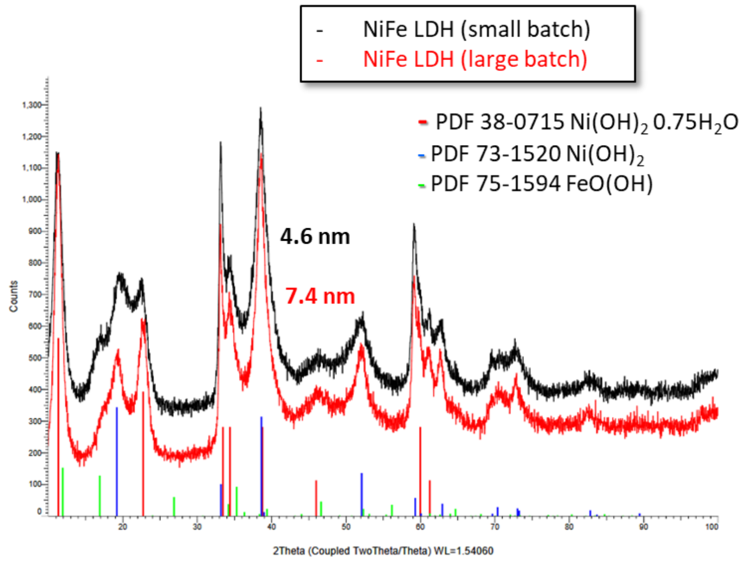
Fig. 9 Synthesis scheme of NiFeOxHy heterogeneous catalyst

3.1.1.2 Physico-chemical properties

The XRD patterns in Fig. 10 compare the diffraction spectra of the NiFe oxide–hydroxide catalyst prepared as a small batch (black line) and as a large batch (red line). Both samples exhibit very similar patterns, corresponding to three phases: $Ni(OH)_2 \cdot 0.75H_2O$, $Ni(OH)_2$, and $FeO(OH)$.

XRD was also used to estimate the average crystallite size by the Scherrer equation, yielding values of approximately 7.4 nm for the large batch and 4.6 nm for the small batch.

The catalyst atomic composition was determined by X-ray fluorescence (XRF), providing semi-quantitative information on the Ni/Fe ratio. The results indicate similar compositions for both batches, with about 85% nickel and 15% iron, as shown on the right in Fig. 10.



%at	Ni	Fe
small	85.24	14.74
large	85.18	14.82

Fig. 10 XRD patterns of small-batch (black) and large-batch (red) NiFe LDH heterogenous catalysts on the left, and XRF analysis on the right

The BET surface areas of the oxide materials was determined by N_2 adsorption–desorption isotherms on powder samples using a Micromeritics ASAP 2020 gas adsorption analyser. The isotherms were evaluated to obtain the active surface area for both the small and large batches. The measured values are very similar for the two samples of about 100 $m^2 g^{-1}$ in both cases, as shown in Fig. 11.

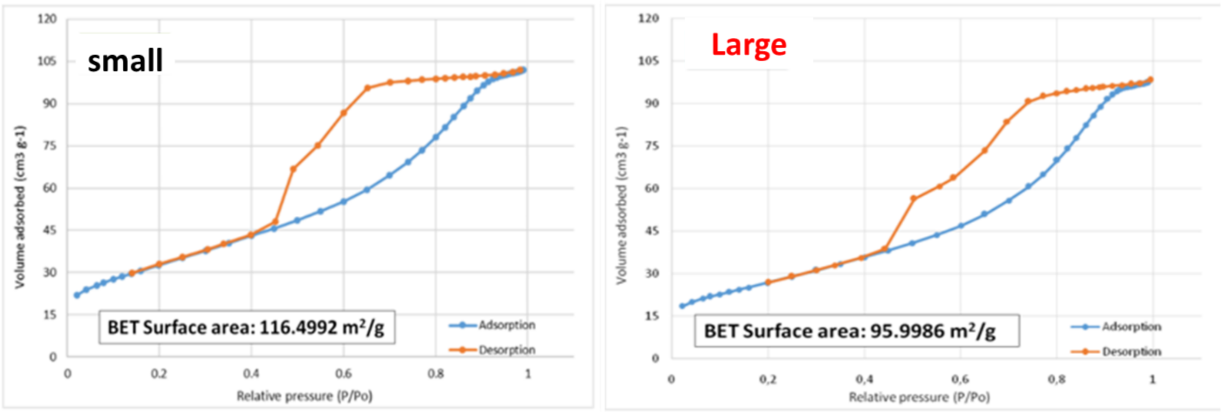


Fig. 11 BET analysis of NiFe small-batch (black) and large-batch (red) heterogenous catalysts.

4 Conclusion

The deliverable D5.2 demonstrates that the heterogeneous electrocatalysts developed at small scale can be successfully scaled up from 1–2 g to 20 g without significantly altering their physico-chemical properties. For the acidic HER environment, the MoS_2/C cathode catalyst synthesized via hydrothermal treatment in a 2 L autoclave maintained its predominantly amorphous hexagonal structure upon scale-up, with only minor differences in crystallite size (≈3.8 nm for the small batch and ≈4.0 nm for the large batch). XRF analysis further confirmed that the Mo/S atomic ratios remain essentially unchanged between batches, while TEM evidenced similar nanosheet-like morphologies and intimate interaction with the high-surface-area Ketjenblack carbon support in both cases.

In alkaline HER conditions, the unsupported NiMo catalyst synthesized by co-precipitation and subsequently reduced at 550 °C in H_2 was likewise reproduced at large scale using a 25 L CSTR setup. TPR profiles for small and large batches showed the same reduction features associated with Ni- and Mo-containing oxides, confirming equivalent reducibility and supporting the selected reduction temperature. XRD measurements revealed consistent cubic Ni-based alloy phases with only a slight increase in crystallite size from 22 nm (small batch) to 24 nm (large batch), while XRF analysis showed very similar Ni/Mo atomic ratios.

For the alkaline OER, the NiFe LDH-based anode catalysts prepared from non-critical raw materials were also successfully scaled up from 2 g to 20 g via co-precipitation in a 25 L CSTR. XRD patterns of small and large-batches NiFeOxHy samples displayed the same phase composition ($Ni(OH)_2 \cdot 0.75H_2O$, $Ni(OH)_2$ and FeO(OH)), with comparable crystallite sizes. XRF analysis confirmed consistent Ni/Fe ratios of about 85/15 for both batches, while BET measurements showed comparable specific surface areas of ~100 $m^2\,g^{-1}$.

Overall, the scale-up routes developed for MoS_2/C, NiMo, and NiFe LDH heterogeneous catalysts enable the production up to 20 g batches that faithfully reproduce the physico-chemical characteristics of the original 1–2 g laboratory-scale materials. This validates the robustness of the synthetic protocols and confirms that the transition from small-batch to larger pre-industrial scales can be achieved without altering catalyst structure, composition, or surface area.

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*IND-Industry; SME-Small and medium enterprise; RTO-Research organization; HES-Higher Educational Establishment

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