NiFe Oxide Catalysts for Electro-Oxidation of Glucose

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1. Introduction

A new frontier for the chemical industry is the highly selective transformation, by electrochemistry, of raw materials from biomass into intermediates, contributing to the transition from a fossil-based to a bio-based economy. Demonstrating the feasibility of this more sustainable approach is one of the objectives of the EU PERFORM project.

To establish this new infrastructure, the focus was pointed on specific investigations of target paired reactions. One of these reactions concerns glucose electro-oxidation to glucaric acid, a first step in the electrochemical synthesis of adipic acid (AA) [1].

Here we report, progress in development of a new 3D NiFe oxide catalyst (NiFeOx/NF), obtained from Nickel foam (NF) via hydrothermal synthesis for glucose (Glu) electrochemical oxidation [2].

2. Materials and Methods

2.1. Catalysts Preparation

1st step. A 20x20 mm NF is treated with HCl conc. in ultrasonic bath for 5 min, then washed with ultrapure water and ethanol, sequentially.

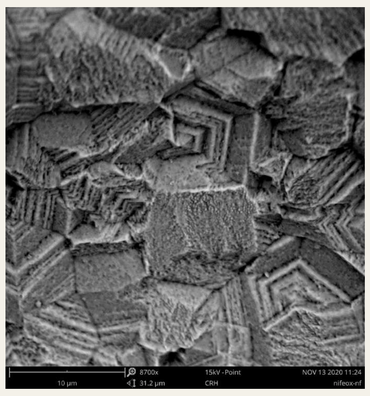
2nd step. The cleaned NF is immersed in a 0.2M Fe^{3+} solution and sonicated for 30 min.

3rd step. 10 mL of a 1.5M $CO(NH_2)_2$ solution and 20 mL of ethanol were added, the mixture containing NF is put in autoclave and heated to 160 °C for 24 h (heating rate 2 °C/min).

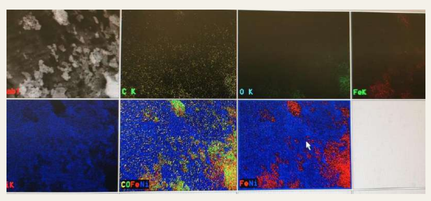
4th step. The sample is removed from the autoclave, washed with ultrapure water and ethanol obtaining the hydroxide nanosheets $NiFe(OH)_x$/NF.

5th step. The sample is thermal treated in muffle at 300 °C for 3 h (heating rate 2 °C/min) obtaining the $NiFeO_x$/NF catalyst.

2.2. Catalyst characterization by SEM

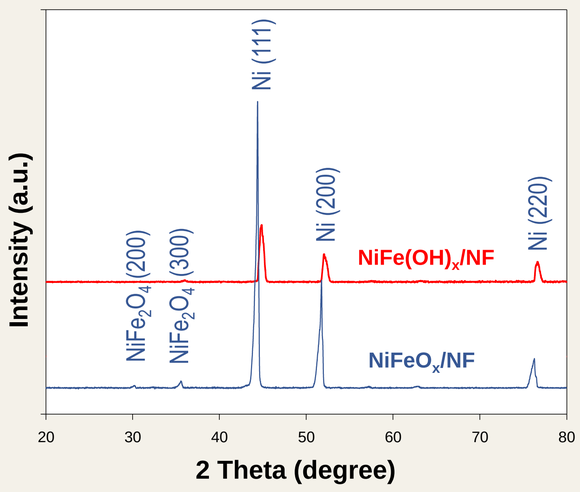


SEM image of the $NiFeO_x$/NF catalyst.



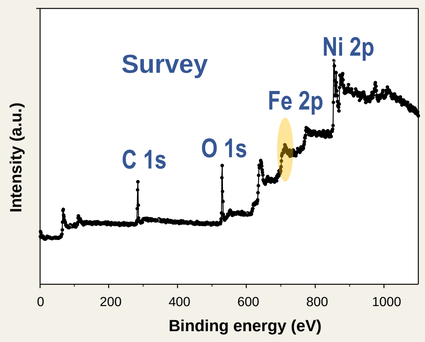
EDX Multi-Element Mapping of the used $NiFeO_x$/NF catalyst.

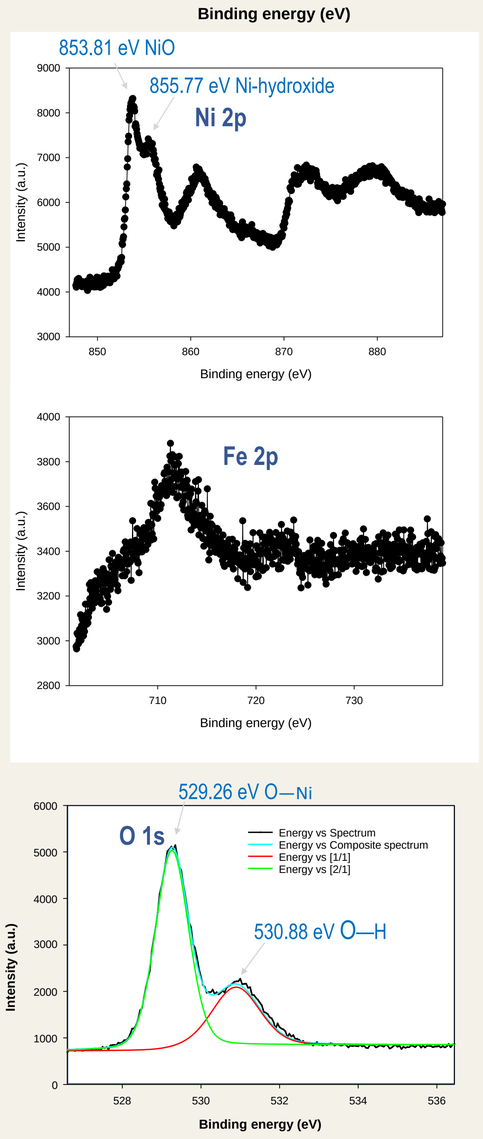
2.3. Catalyst characterization by XRD



XRD patterns of the of the intermediated hydroxide and of the oxide obtained by hydrothermal synthesis.

2.4. Catalyst characterization by XPS





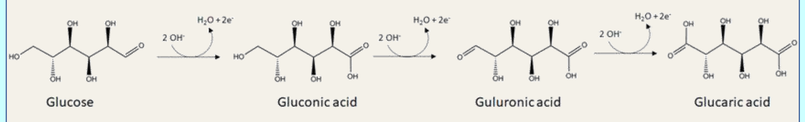
Weight % Table

C1s	O1s	Fe2p3	Ni2p3
15.75	13.30	9.22	61.72

3. Results

3.1. Electrochemical test of glucose oxidation

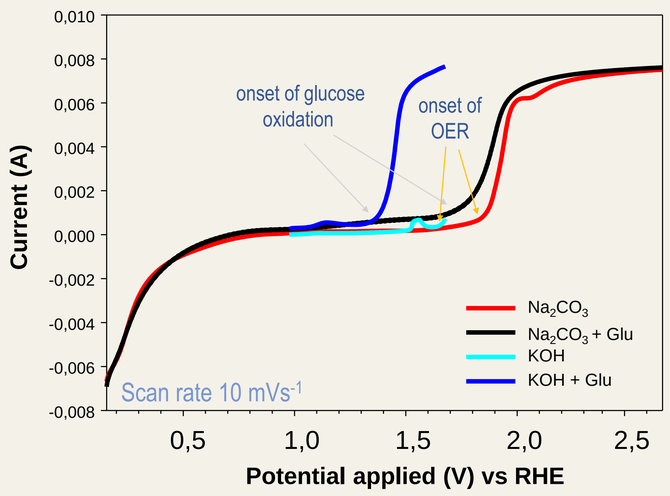
During the reaction, the formation of Gluconic Acid (GA) initially takes place, then its conversion according to **Scheme 1**. For a screening of the capability of the prepared $NiFeO_x$/NF catalysts, the amounts of GA produced in batch by Glucose oxidation was determined by IC.



Scheme 1. Probable Reaction pathway

Electrochemical test conditions	Power supply	PGSTAT30 with a three-electrode set-up
	Reaction mode	CV and LSV in batch cell at rt
	Counter E.	Pt wire
	Reference E.	saturated Ag/AgCl
	Working E.	$NiFeO_x$/NF sample
	Electrolyte	1M KOH Ar purged or 0.1M Na_2CO_3 in air

3.2. Linear Sweep Voltammetry (LSV)



3.3. Determination of Gluconic Acid by IC

IC test conditions:

MagIC Net Metrohm
Column: Metrosep Organic Acids
Eluent: 0.5 mM H_2SO_4
Flow: 0.5 mL/min
Pressure: 5.34 MPa
Injection Volume: 20 µL

Catalyst	Electrolyte	pH	Reaction Time / h	Gluconic Acid / ppm
$NiFeO_x$/NF	KOH 1M	13.52	2	238
$NiFeO_x$/NF	Na_2CO_3 0.1M	10.95	2	143

4. Conclusion

The ongoing research, demonstrating the feasibility of the electro-synthetic approach, open the way toward a more efficient glucaric acid production, helping to promote the emerging electrification of the chemical industry.

The new electrochemical approach, under investigation within the PERFORM project, is inspired to green chemistry, and allows both energy saving and biomass valorisation.

$NiFeO_x$/NF catalysts have been successfully prepared and characterized.

The $NiFeO_x$/NF catalysts have been demonstrated effective in D-glucose oxidation reaction under different reaction conditions, with better results for KOH electrolyte.

Tests will be performed with the best screening catalysts in flow cell by the partners of PERFORM to evaluate the conversion capability under different conditions, and selectivity toward glucaric acid.

Acknowledgements

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References

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