Perovskite $LaMn_xCu_{1-x}O_3$ materials for heterogeneous electro-Fenton process

Sara Díaz-Rullo Edreira, Noelia San Segundo, Ana Cruz del Álamo, María Isabel Pariente, Raúl Molina, Juan José Espada, Fernando Martínez

Universidad Rey Juan Carlos

Introduction

Universidad Rey Juan Carlos

Wastewater treatment problems

Water quality spoilage is been a worrying issue around the world in recent years due to human activities and climate change.

UNO

New technologies are necessary to treat wastewater effluents in a more effective and efficient way

Electro Fenton → Heterogeneous Electro Fenton

REACTIONS IN THE CATHODE

$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$

FENTON-LIKE REACTIONS

$Cu^{2+} + e^- \rightarrow Cu^+$

$Cu^+ + H_2O_2 \rightarrow HO^{\cdot} + HO^- + Cu^{2+}$

ADVANTAGES

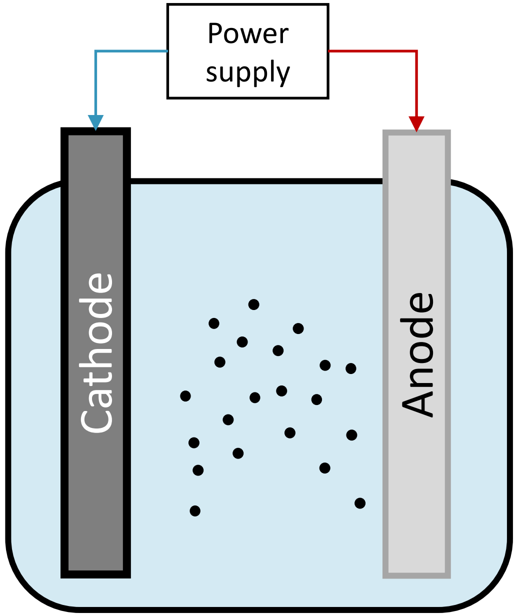
- **Possible neutral pH working.**
- **Easy separation, reusability and recyclability of the catalyst.**
- The on-site production of H_2O_2.
- Continuous regeneration of Fe^{2+} at the cathode.
- Easy automation.

Introduction

Universidad Rey Juan Carlos

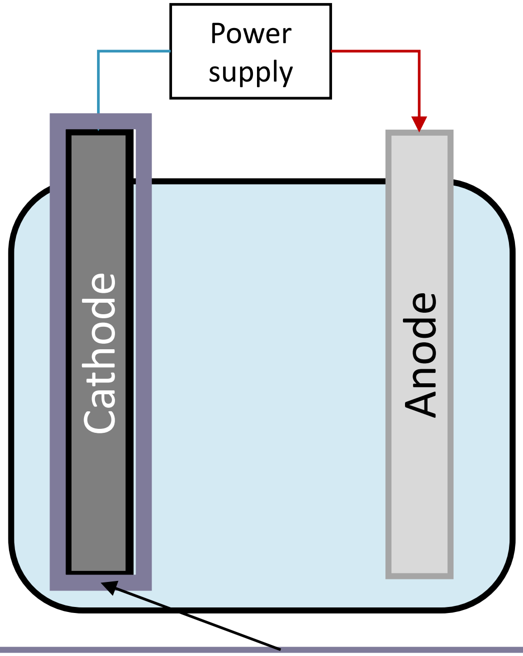
Heterogeneous Electro Fenton Process: System configuration

Powder catalyst (slurry)



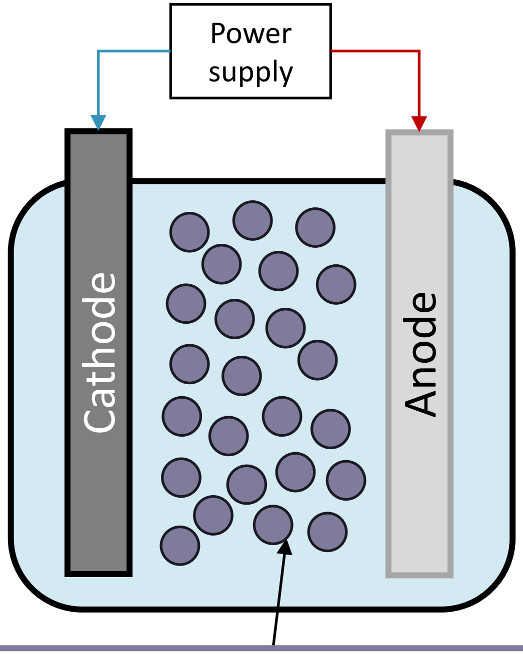
Catalyst added as insoluble powder

Modified cathodic material



Supported catalyst over the electrode

Catalyst supporting material (3D electrodes)



Supported catalyst over conductive material (not an electrode)

S.O. Ganiyu et al. *Applied Catalysis B: Environmental 235 (2018) 103–129*

V. Poza-Nogueiras et al. / Chemosphere 201 (2018) 399e416

Introduction

Universidad Rey Juan Carlos

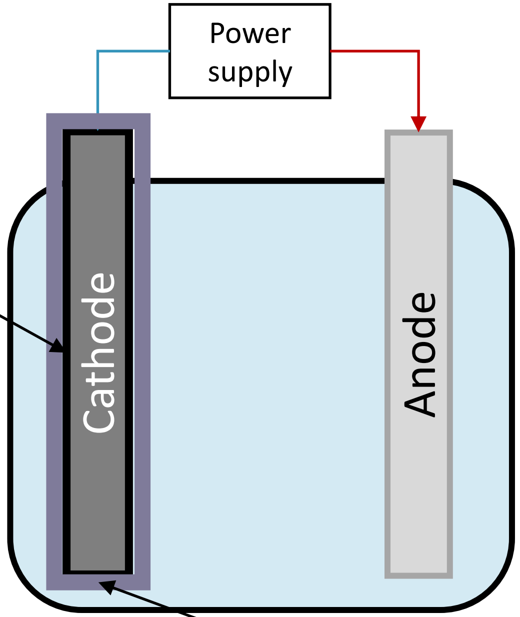
Heterogeneous Electro Fenton Process: System configuration

This type of deposition it could use in different type of cathodes, like **carbonaceous electrode.**

ADVANTAGES

- *In-situ* production of large quantities of H_2O_2
- Good electronic conductivity
- Mechanical and chemical stability
- High surface areas and porosity
- Excellent electrolytic efficiency at relatively low cost

Modified cathodic material



Supported catalyst over the electrode

S.O. Ganiyu et al. *Applied Catalysis B: Environmental 235 (2018) 103–129*

V. Poza-Nogueiras et al. / Chemosphere 201 (2018) 399e416

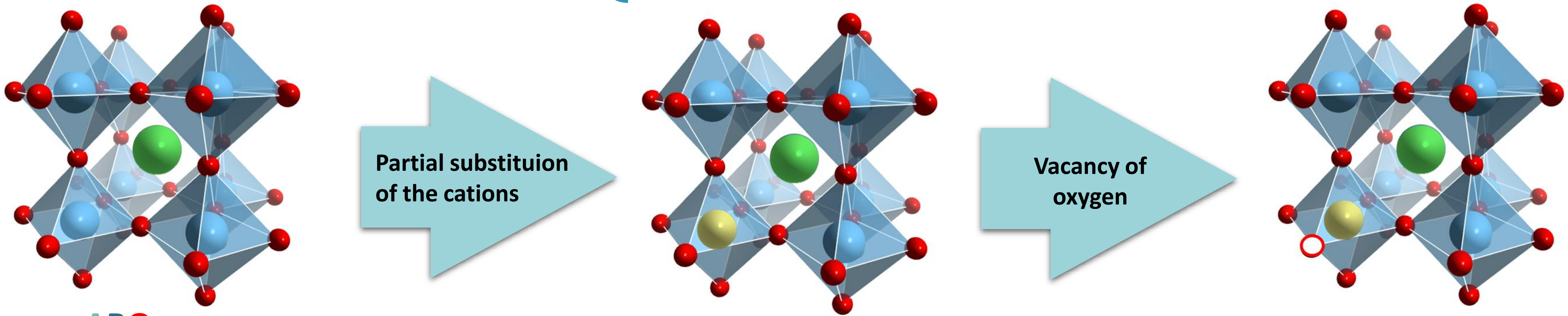
Introduction

Universidad Rey Juan Carlos

Catalyst: Perovskite

Estructure type **ABO_3**

- **A**: Rare earth or alkaline earth metals (La, Sr…)
- **B**: transition metals (Cu, Fe, Mn, …)



ABO_3
$LaMnO_3$

$AB_{1-x}B'_xO_3$
$LaMn_{1-x}Cu_xO_3$

$AB_{1-x}B'_xO_{3-\delta}$
$LaMn_{1-x}Cu_xO_{3-\delta}$

$LaMn_{0.5}Cu_{0.5}O_3$

A, La   B, Mn   B', Cu   O   Vacancy O^{2-}

A.Cruz del Álamo, et al. Catalysis Today 361 (2021) 159–16

Objective

Universidad Rey Juan Carlos

- Study and assessment of different deposition method of $LaMn_{0.5}Cu_{0.5}O_3$ catalyst over the cathode (working electrode) for degradation of **methylene blue (MB)** by heterogeneous electro Fenton process.

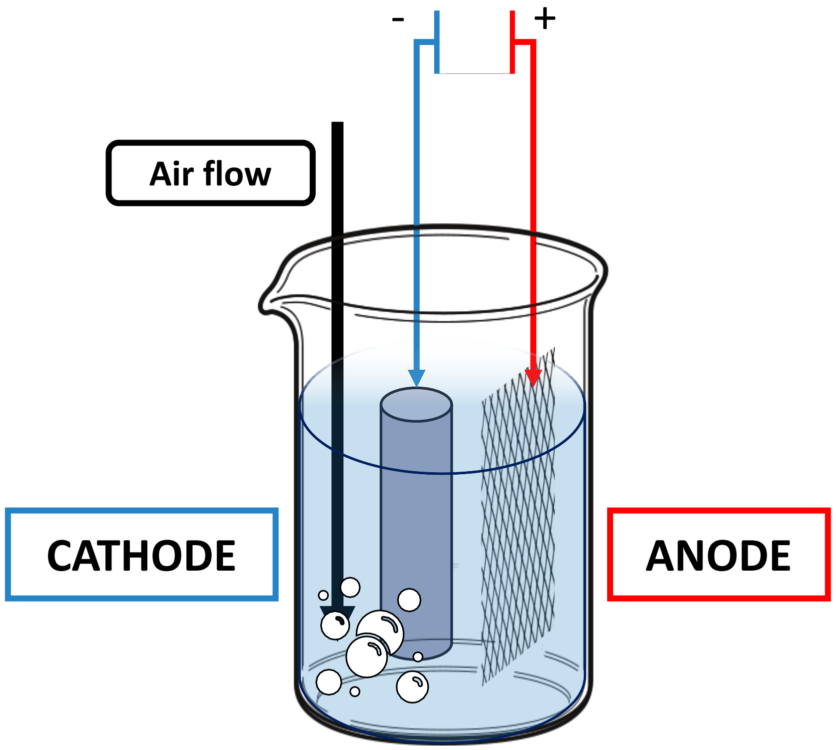
Study of different parameters

- ✓ impregnating conductive agents
  - ➢ Ni as conductive component
  - ➢ Ag as conductive component
  - ➢ Perfluorinated resin (Nafion)
- ✓ Deposition methods
  - ➢ Rolling -press
  - ➢ Sprinkle fixation
- ✓ Curing conditions

Materials and methods

Universidad Rey Juan Carlos

Electro Fenton experimental set-up



V = 100 mL

Galvanostatic conditions

Cathode Surface (graphite bar)	3	cm^2
Anode Surface (Ti/Pt metal rack)	6	cm^2
Distance between electrodes	2.5	cm
Intensity	15	mA
Current density	5	mA/cm^2
Reactor volume	100	mL
Pollutant [Methylene blue]$_o$	50	mg/L
pH	6 ± 0.2	
Na_2SO_4	50	mM
Air flow	300	mL/min
Stirring	600	rpm

Materials and methods

Universidad Rey Juan Carlos

Perovskite $LaMn_{0.5}Cu_{0.5}O_3$ synthesis

Perovskite material was prepared using a modified sol-gel citrated method, using citric acid as quelant agent

Mix of precursors 2h → Drying 70 ºC 24h → Drying 110 ºC 24h → Calcine 700 ºC 5h

A.Cruz del Álamo, et al. Catalysis Today 361 (2021) 159–16

Perovskite precursors:

- $La(NO_3)_3.6H2O$
- $Mn(NO_3)_2.4H2O$
- $Cu(CH_3COO)_2.2H2O$

Characterization

- X-Ray Difraction (XRD)
- Nitrogen adsorption/desorption

Materials and methods

Universidad Rey Juan Carlos

Deposition of perovskite catalyst $LaMn_{0.5}Cu_{0.5}O_3$ over carbon graphite bar cathode

IMPREGNATING ELECTRIC CONDUCTIVE AGENTS

- **Nickel Filled Polymer (Chemtronic CW 2000):**
  - ✓ Nickel ≥50 - ≤75
  - ✓ 2-methoxy-1-methylethyl acetate ≥10 - ≤25
  - ✓ 2-butoxyethyl acetate ≥10 - ≤18
  - ✓ n-butyl acetate ≥10 - <20
  - **Recommended curing conditions**
    - ✓ 15 to 20 minutes at room temperature
    - ✓ 10 - 15 minutes at 80 to 100°C

- **Silver filled polymer (Loctite Edag 5915):**
  - ✓ Ag content is not detailed by the supplier
  - ✓ Epoxy resin
  - **Recommended curing conditions**
    - ✓ 15 minutes @ 130°C
    - ✓ 10 minutes @ 177°C

- **Perfluorinated resin solution containing Nafion (5% w/w)**
  - ✓ 5 wt. % in lower aliphatic alcohols and water
  - ✓ 15-20 % water

Materials and methods

Universidad Rey Juan Carlos

Deposition Method

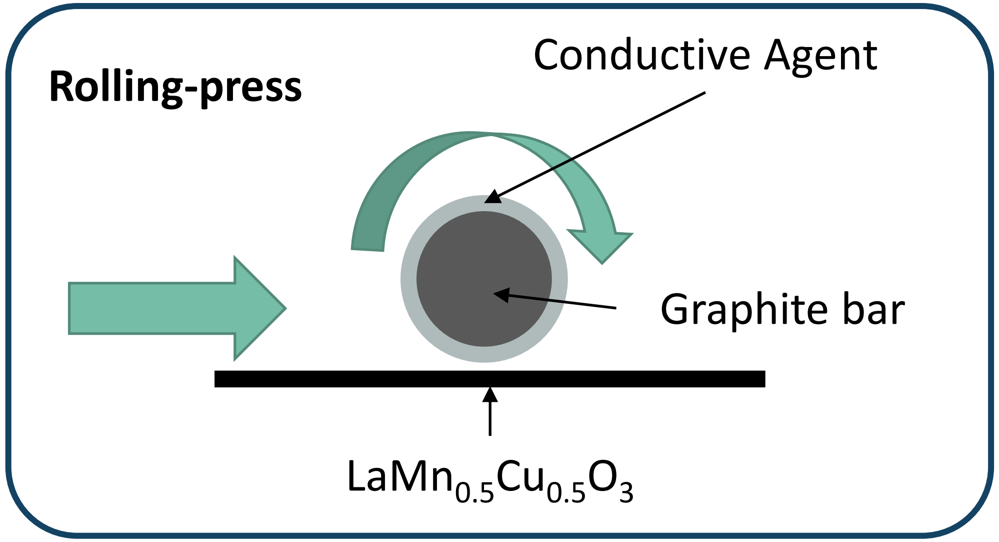
1- Application of electric conductive agents on the electrode surface

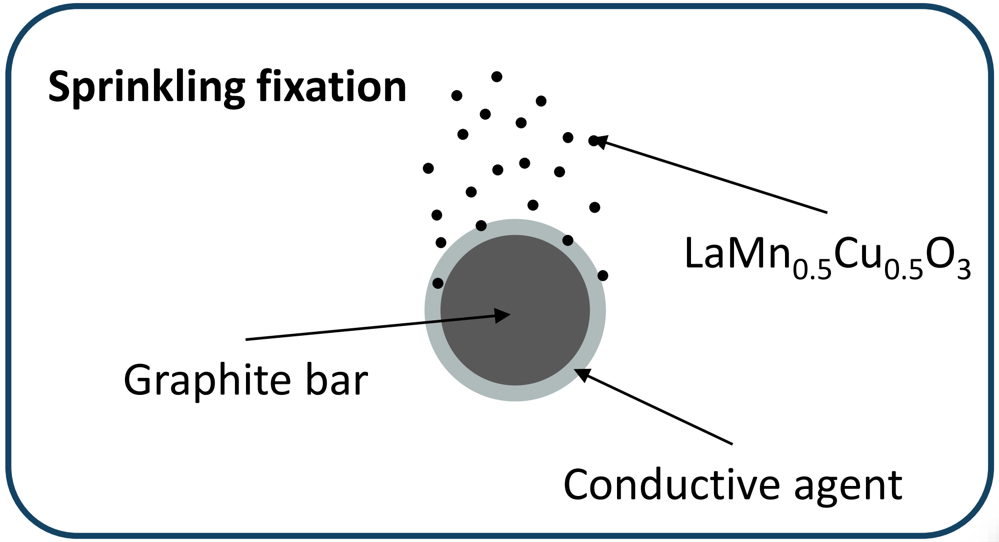
2- Deposition of powder perovskite catalyst

2.1. Impregnation by **rolling** of the graphite bar over a perovskite powder bed

2.2. **Sprinkling** of powder perovskite catalyst over the graphite bar

3- Curing conditions





Materials and methods

Universidad Rey Juan Carlos

Curing conditions

- **Nickel Filled Polymer Chemtronic CW 2000**
  - ✓ Rolling Room temperatura cure (**Ni-R@RT**)
  - ✓ Rolling 100ºC cure (**Ni-R@100**)
- **Silver filled polymer (Loctite Edag 5915)**
  - ✓ Rolling 130ºC cure (**Ag-R@130**)
  - ✓ Sprinkle 130ºC cure (**Ag-S@130)**
  - ✓ Rolling 177ºC cure (**Ag-R@177**)
- **Perfluorinated resin solution containing Nafion (5% w/w)**
  - ✓ Rolling 80 ºC cure (**Nafion-R@80**)

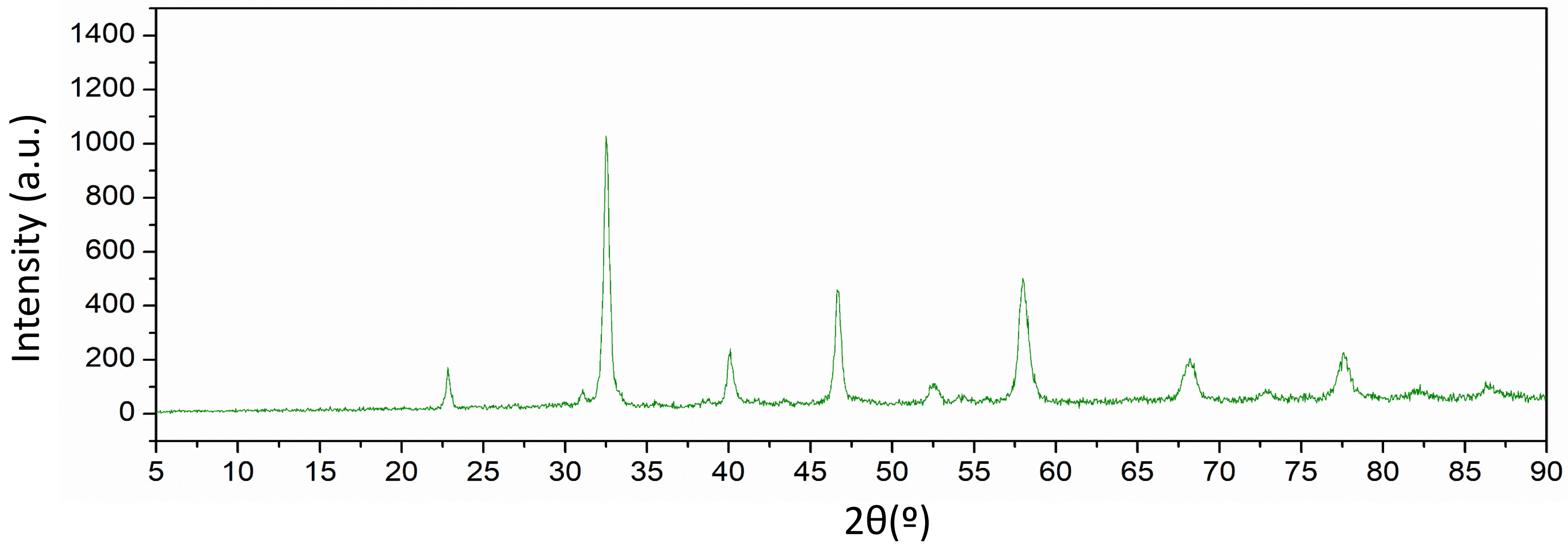
Modified electrodes were inmmersed in water under the same hydrodynamics conditions that used in the EF catalytic runs for 1 h (air bubbling, 300 ml/min but non-voltage potential) as washing and non-attached particles removal

Results

Catalyst Characterization

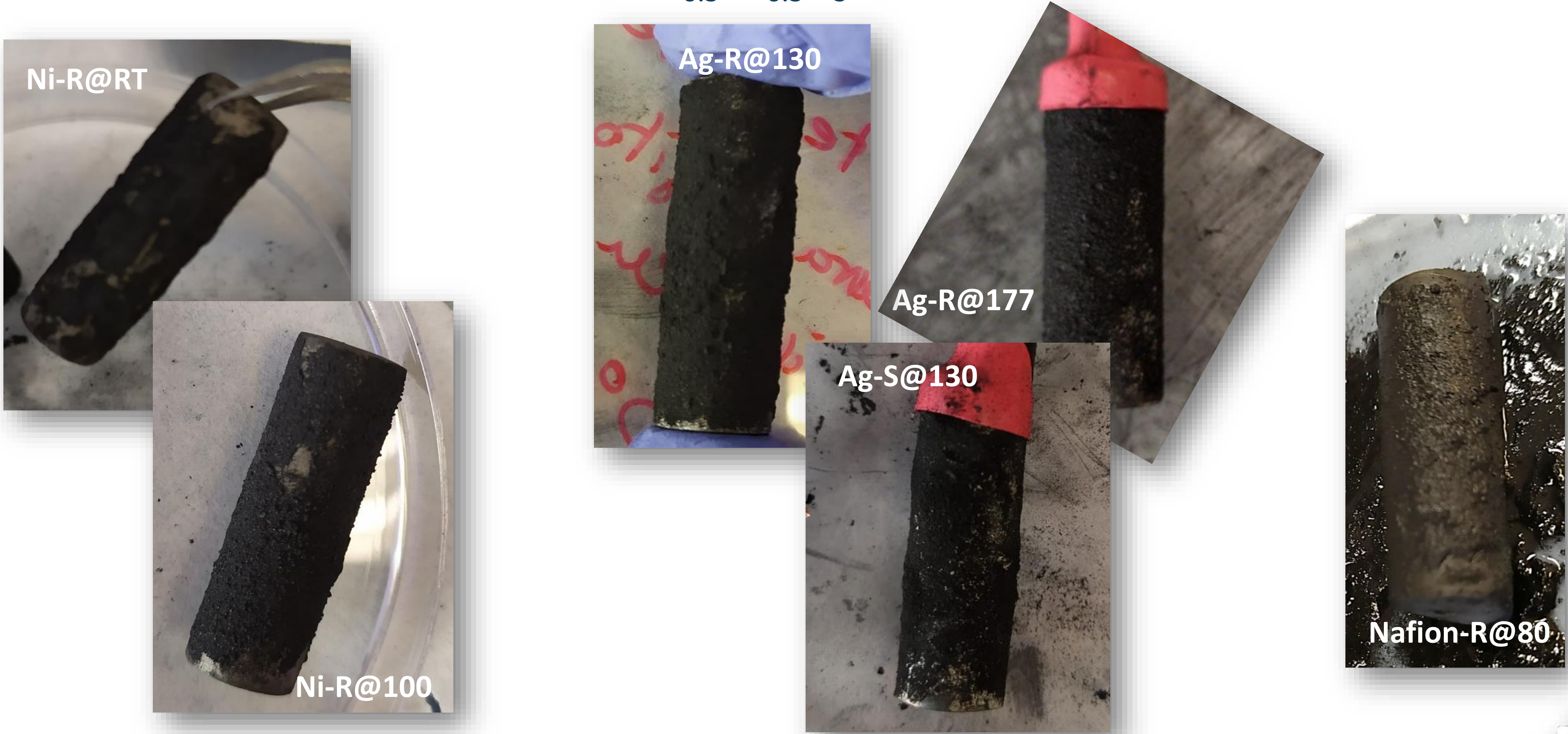
Characterization of perovskite $LaMn_{0.5}Cu_{0.5}O_3$

Perovskite materials	La: xMn: yCu: zCitric acid	BET Surface area (m_2/g)
$LaMn_{0.5}Cu_{0.5}O_3$	1: 0.5: 0.5: 0.3	3.68 ± 0.16



Results

Deposition of perovskite catalyst $LaMn_{0.5}Cu_{0.5}O_3$ over carbon graphite bar cathode



Results

Influence of different conductive agents

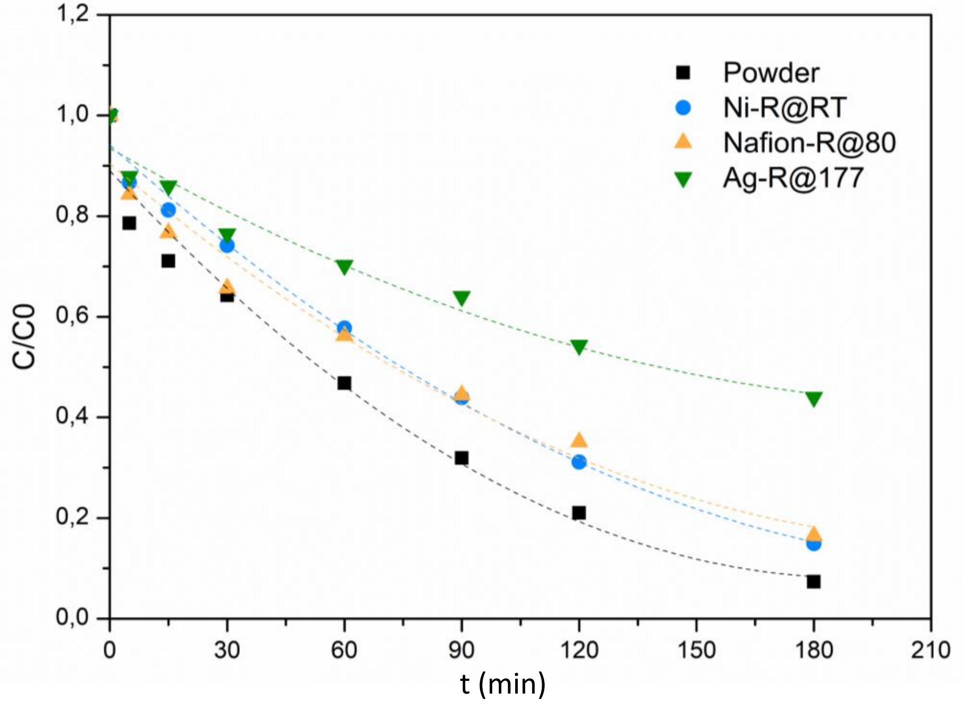
Perovskite content and losses

Perovskite-modified electrode	Perovskite content after curing conditions (mg)*	Perovskite content after inmmersion in water (1h)*	Perovskite loss after inmmersion in water (%)
Ni-R@RT	143.5	115.4	19.6
Ni-R@100	175.0	106.5	39.1
Ag-R@130	183.5	172.0	6.3
Ag-S@130	146.4	139.0	4.9
Ag-R@177	147.9	147.9	< 0.01
Nafion-R@80	203.9	163.3	19.9

*Perovskite mass over 3 cm^2 of cathode surface

Results

Influence of different conductive agents: Comparison



- **Ni-R@100:** High MB removal, less perovskite loading.
- **Ag-R@177: The** lowest MB removal, major perovskite loading.
- **Nafion-R@80:** Similar MB removal than Ni-R@100; similar amount of perovskite than powder catalyst reaction

Presence of perfluorinated resin

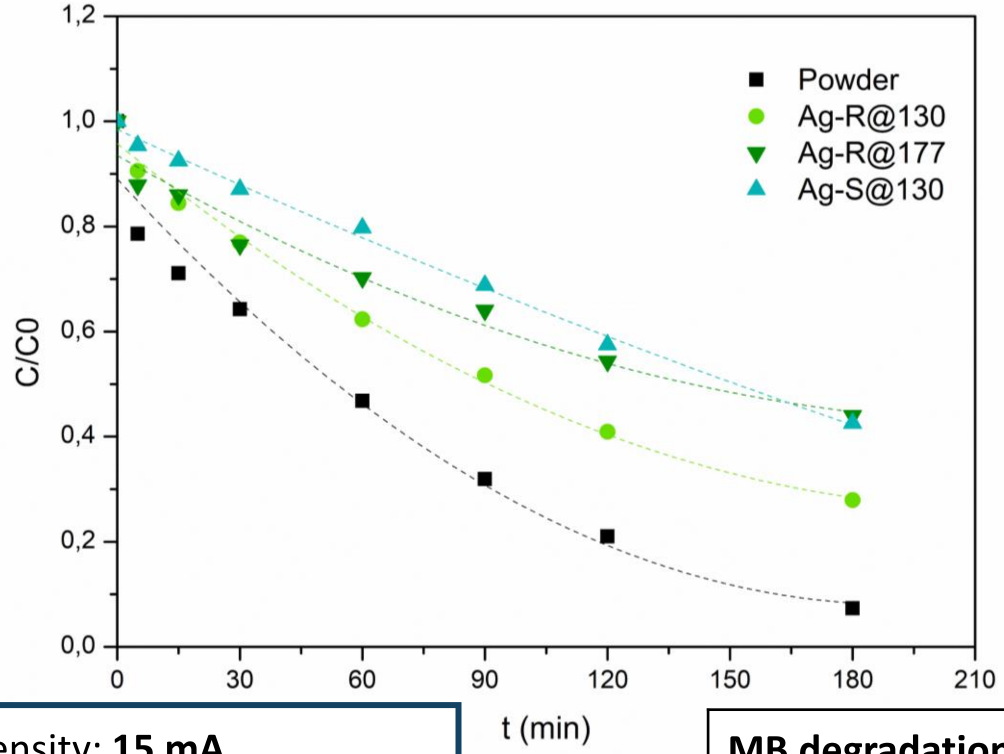
- Intensity: **15 mA**
- Current density: **5 mA/cm²**
- Air Flow: **300 mL/min**
- Initial MB: **50 ppm**
- pH = **6 ± 0.2**
- Reactor volumen: **100 mL**

	Perovskite (mg)	MB degradation (mg/L)					TOC (%)	Perovskite losses (%)
		30'	60'	90'	120'	180'		
Ni-R@RT	1.1	31.2	24.2	18.5	13.1	6.4	31.3	0.3
Ag-R@177	1.5	33.9	31.1	28.3	24.1	19.5	NA	0.3
Nafion-R@80	1.6	30.9	26.5	21.0	16.6	7.8	37.5	0.1
Powder	1.9	31.6	23.0	15.7	10.3	3.6	39.6	--

Results

Universidad Rey Juan Carlos

Influence of different conductive agents: cure conditions - deposition method



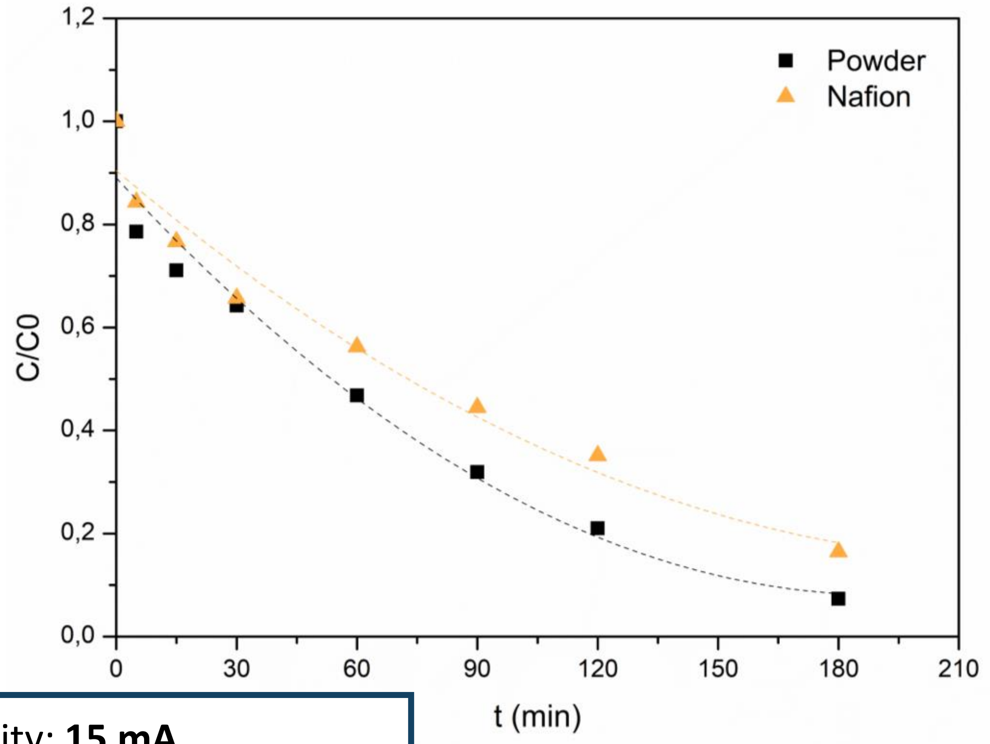
- Ag conductive agent the best adherence. The catalyst losses after washing the lowest registered.
- Catalytic activity of these depositions are lower despite the amount of perovskite over the cathode
- Free surface in contact with oxygenated liquid medium is a key parameter

- Intensity: **15 mA**
- Current density: **5 mA/cm²**
- Air Flow: **300 mL/min**
- Initial MB: **50 ppm**
- pH = **6 ± 0.2**
- Reactor volumen: **100 mL**

	Powder	Ag-R@130	Ag-S@130	Ag-R@177
MB degradation (%)	92.7	72.0	57.4	56.0
Catalyst concentration (g/L)	1.9	1.7	1.4	1.5
Perovskite loss after EF reaction (%)	--	1	0.04	0.3

Results

Influence of different conductive agents: deposition method



- Intensity: **15 mA**
- Current density: **5 mA/cm²**
- Air Flow: **300 mL/min**
- Initial MB: **50 ppm**
- pH = **6 ± 0.2**
- Reactor volumen: **100 mL**

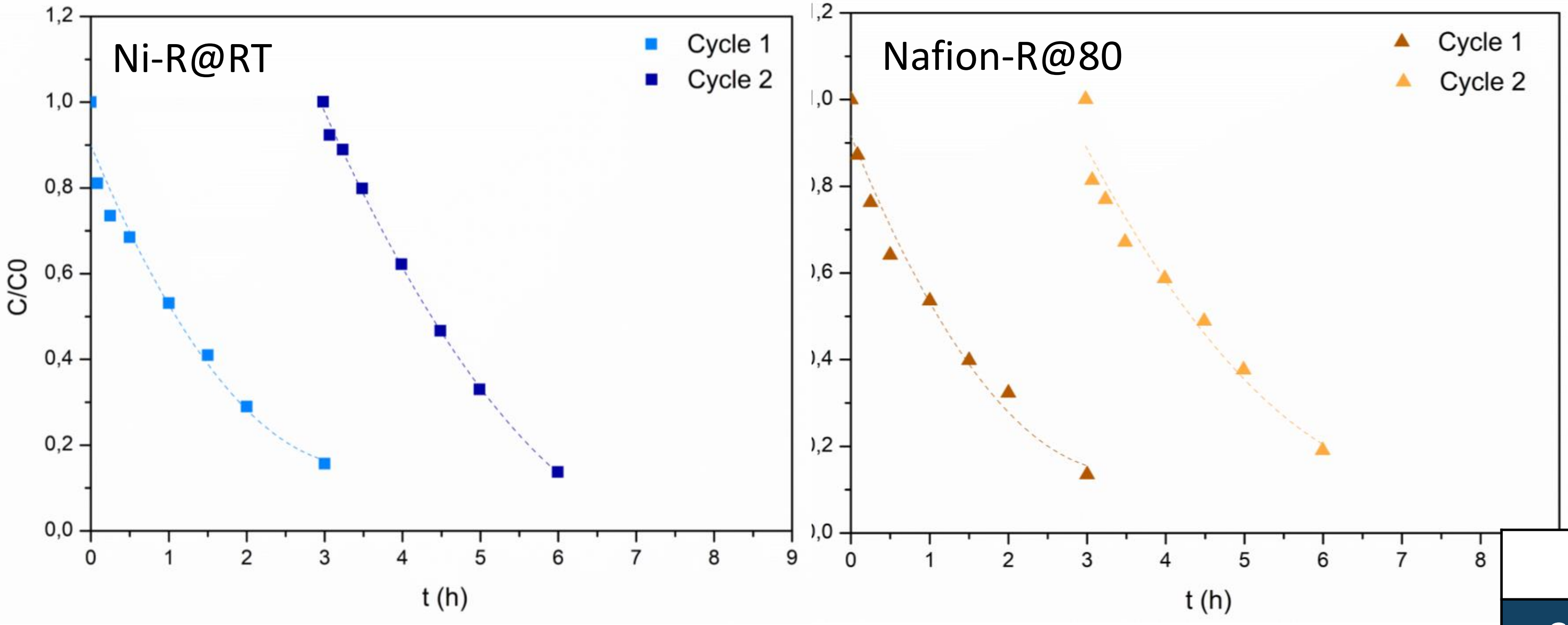
- **Nafion-R@80**: MB degradation similar than powder reactions.
- Perovskite deposited is quite like powder catalyst reaction. The lowest losses of perovskite after reaction of all method tested.
- Conductivity due to perfluorinated resin enhance degradation of MB

	Powder	Nafion-R@80
MB degradation (%)	92.7	83.5
TOC degradation (%)	39.6	37.5
Catalyst conxentration (g/L)	1.9	1.6
Perovskite losses after reaction (%)	--	0.1

Results

Universidad Rey Juan Carlos

Catalyst reuse with Ni and Nafion conductive agent



- Intensity: **15 mA**
- Current density: **5 mA/cm²**
- Air Flow: **300 mL/min**
- Initial MB: **50 ppm**
- pH = **6 ± 0.2**
- Reactor volumen: **100 mL**

Reused catalyst over Ni-R@RT and Nafion-R@80 retains the catalytic activity as efficient as the fresh one during 2 cycles

	Ni-R@RT		Nafion-R@80	
	Cycle 1	Cycle 2	Cycle 1	Cycle 2
MB degradation (%)	84.3	85.9	86.6	80.6
TOC degradation (%)	28.8	33.8	31.9	43.1
Catalyst (g/L)	1.2	1.2	1.6	1.6
Perovskite losses after reaction (%)	0.3	0.3	0.12	< 0.01

Conclusions

Deposition of $LaMn_{0.5}Cu_{0.5}O_3$ over carbon graphite bar cathode

- Results show higher perovskite loading in the cathode reduces the activity of the EF process, suggesting the graphite surface is less effective for the reduction of oxygen to form hydrogen peroxide by a higher covering of the perovskite particles.
- The immobilization of perovskite by the perfluorosulphonic Nafion resin is very active despite the high perovskite loading, probably due to the better conductivity of the perfluorosulphonic polymer
- Both, Sprinkle and Rolling method, and cure temperature present the same effectivity for deposition of catalyst over the electrode.
- The reusability of the catalyst, on Ni-R@RT and Nafion-R@80, shows to retain the catalytic activity as efficient as the fresh one during 2 cycles.

Universidad Rey Juan Carlos