HYDROGEN - a mean to decarbonize the global economy
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Single-stage Synthesis of Nitrogen-doped Graphene and Application as Electrocatalyst for Fuel Cells

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ICSI Energy - has a cluster of exceptional infrastructure for the whole sequence of the new energy revolution (Production → Storage / Transport → Utilization)

BRIEF OVERVIEW

Objectives:

- Promote excellence in fundamental and applied research
- Provide support for development of applied technologies and models
- Support in training activities for students and young researchers

CRYO-HY

Low Temperature Laboratory for energy support – 2012

CNHPC

National Center for Hydrogen and Fuel Cell – 2009

ROMEST

ROManian **E**nergy **ST**orage Laboratory - 2015

- **2009** – ICSI Energy becomes a full **member of the Hydrogen Europe Research**
- **2012** – foundation of the **Romanian Association for Hydrogen Energy**
- **2014 –** ICSI Energy became a **National Interest Facility**
- **2021- founding member of Prahova with Hydrogen Association – Excellence Center (PH2-CE)**

Working with hydrogen since the ‘90s!

Primary research directions

- **Mat4H program** -Development of new materials for hydrogen based technologies.
- **Gas2Power program** (conversion of hydrogen into energy using fuel cells)- Fuel cells development and production.
- **Power2Gas program** (energy storage technologies using hydrogen) – Electrolysers development and production.
- **Lithium-Ion Battery program** –Development of hybrid energy storage technologies.
- **H-mobility & Stationary applications** - Development of "clean" mobility hybrid platforms and stationary integrated systems.

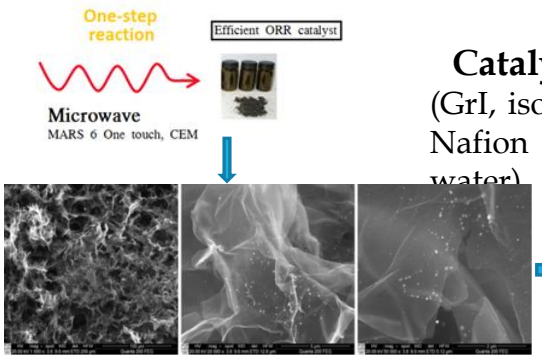
We have 2 directions: (i) **nanoscale area** with materials development and innovative solutions and (ii) **macroscale area** with testing and validation.

It is time to put laboratory innovations into practice - faster than we have been done in the past - and to allow them to expand to the industrial level.

*The main focus is to **support** the “**new energy era**”, with the ambition of **developing technologies, materials** and **systems** that play a **key role** in our **future energy chains.***

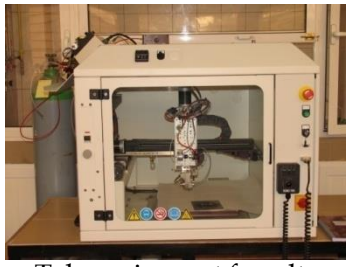
"Mat4H" program

- **Synthesis of metallic/non-metallic catalysts** by physicochemical methods. Morphological and structural characterization of the synthesized materials, evaluation of electrocatalytic performances
- **Gas Diffusion and Microporous Layers** development with improved electrical and mechanical properties
- ORR **Catalysts development** with low Pt content and improved performances due to co-catalysts adding (unfunctionalized graphene materials and functionalized/doped with metal or halogen nanoparticles)
- **Membrane Electrode Assemblies** (MEA) development



Catalytic ink
(GrI, isopropanol, Nafion 5%, water)

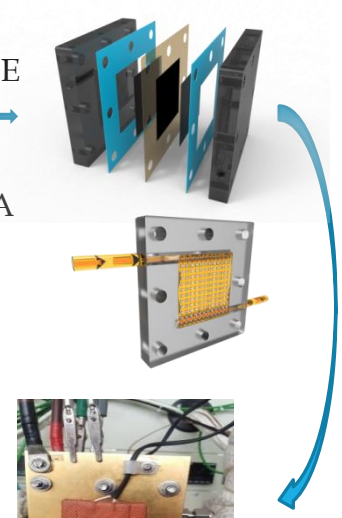
Ultrasonically mixing 2h



SonoTek equipment for ultrasonically spraying

GDE

MEA

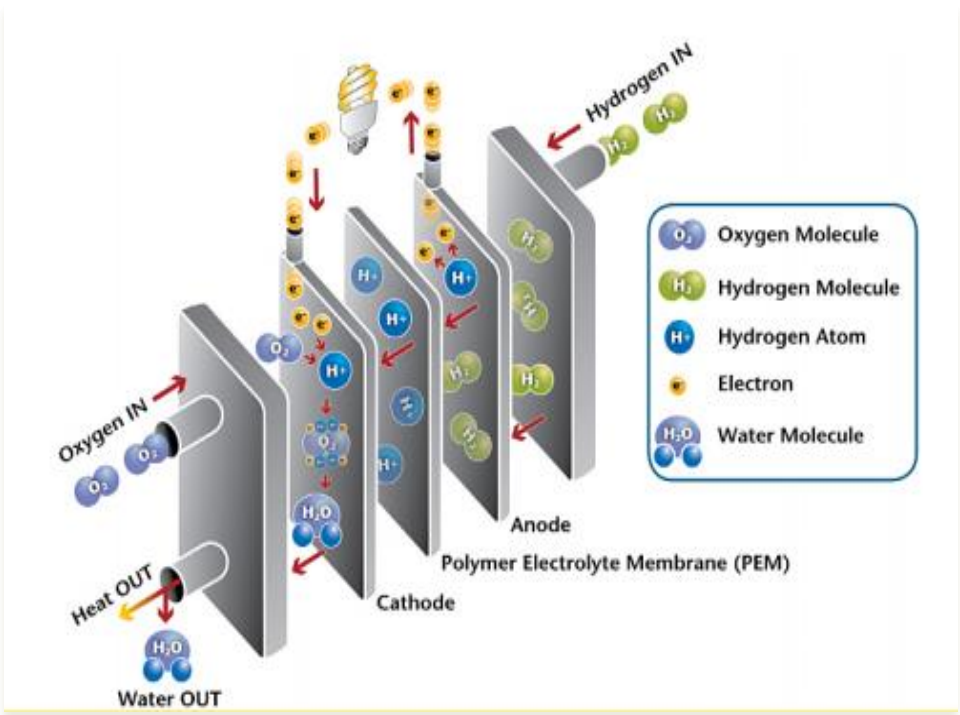


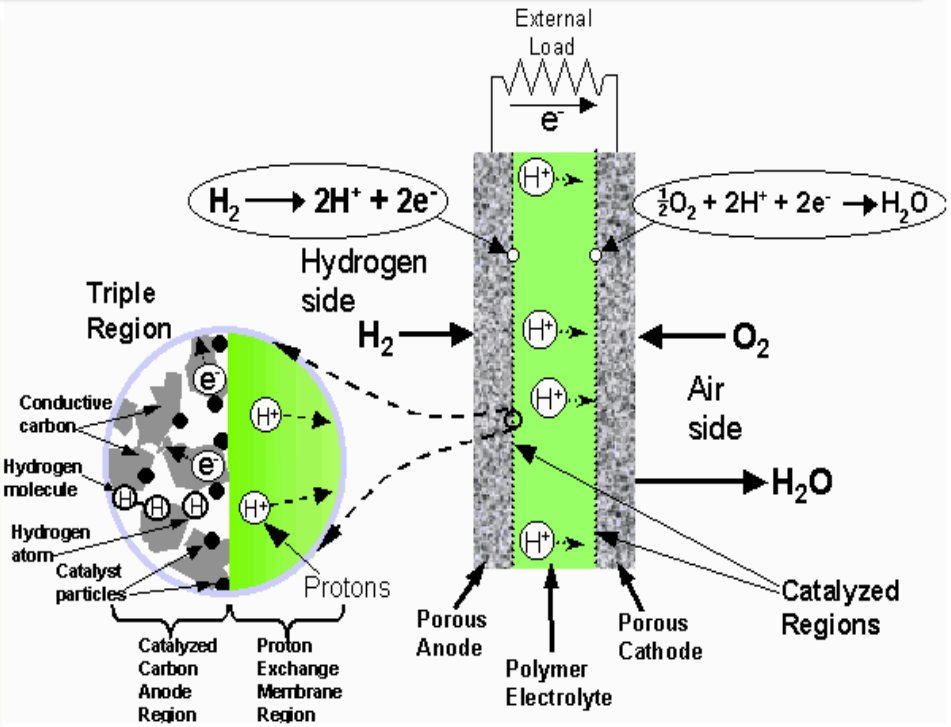
- Polarization plots of a single PEMFC
- Electrochemical tests for active surface area

Summary:

- Introduction to Proton Exchange Membrane Fuel Cells
- Trends in materials for electrodes
- Innovative synthesis method for nitrogen-doped reduced graphene oxide (N/rGO)
- N/rGO samples characterization: physical, chemical, electrochemical
- Conclusions

INTRODUCTION:
Proton Exchange Membrane Fuel Cells





Anode (HOR): $H_2 \rightarrow 2H^+ + 2e^-$

Cathode (ORR): $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$

ORR << HOR

It needs catalysts!

Catalyst electrode layer: Pt/C

Various Alternatives

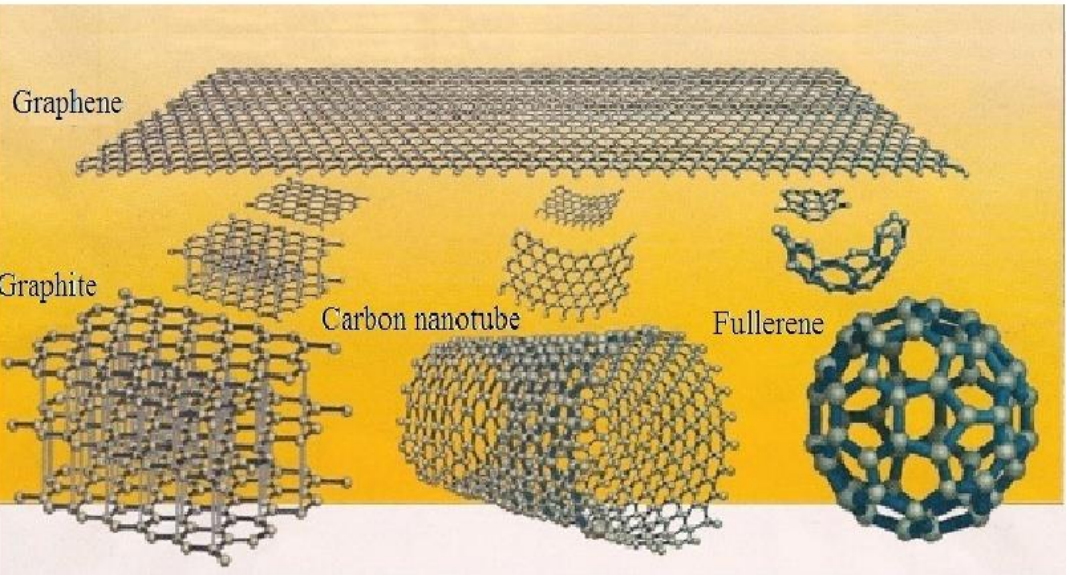
1. Lean-Pt catalysts
   e.g. Pt-M alloys
2. Noble metal catalysts
   e.g. Pd, Ir, or Ru
3. Transition metal catalysts
   e.g. TiN, CoSe, WC
4. Non-metal catalysts
   e.g. Carbon based catalysts

TRENDS IN MATERIALS FOR ELECTRODES

→ Carbon nanomaterials → CNTs , CFs, graphene-based materials

→ Non-carbonic supports → electrically conducting ceramics

→ Less expensive catalysts
→ Using less platinum in the composition
→ Novel platinum-free catalysts



Why the Interest in Graphene for FUEL CELL?

Properties of graphene

Nano-Material :
- High Surface Area
- Nano Thickness
- Low Conc. Required

Multifunctional Material:
- Low Density
- High Stiffness
- High Electrical Conductivity
- High Thermal Conductivity
- Low Thermal Expansion
- High Thermal Stability
- Barrier Properties
- Optically Transparent

Our strategy to decrease the materials costs for MEA

1. **Use of catalytic systems with *high activity* and *low price* by:**

Developing more efficient catalytic supports, which demonstrated improved chemical stability (graphene oxide **GO** and reduced graphene oxide **rGO**)

2. The development of a new class of materials with *low cost* and *efficiency* for oxygen reduction reaction (ORR) by:

-Developing of new catalytic systems with high stability and efficiency for ORR electrodes: Pt/rGO, Au/rGO, Pt-Co/rGO, Ce/rGO, Pt-Ce/rGO, Pt-Co-Ce/rGO

-Developing of non-metal doped catalyst: iodine-doped graphene, bromine-doped graphene, **nitrogen**-doped graphene

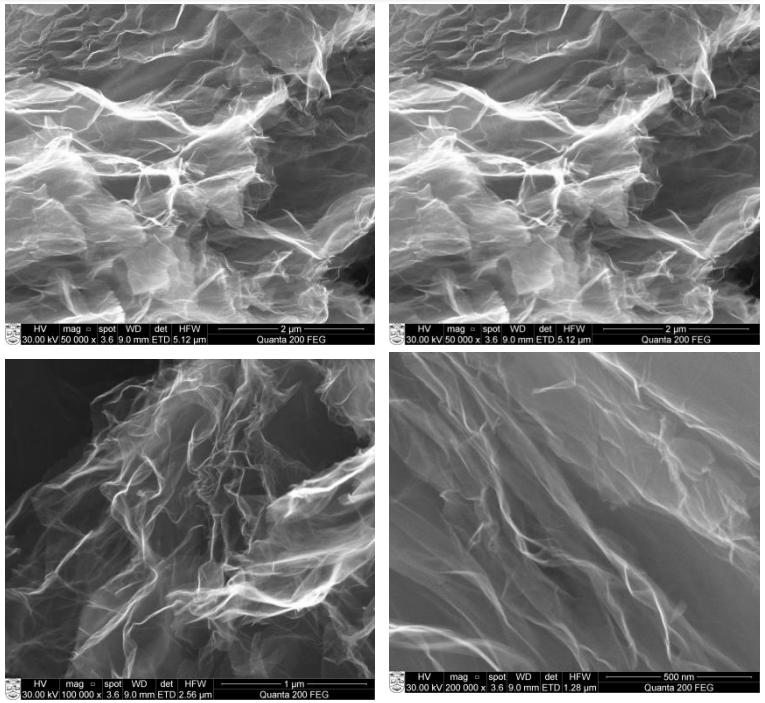
Experimental: Preparation method for N/rGO

rGO
+
DI
+
EG
+
N source
+
$NaBH_4$

One-step reaction

Microwave
MARS 6 One touch, CEM

Efficient ORR catalyst



Proposed working procedure:

-*Graphene oxide (Abalonix)* was dispersed in distilled water (DI) and ultrasonicated (550 W)

-*Nitrogen precursor* (**ammonia**/**nitric acid**/**urea**) was added, then ultrasonicated

-*Reduction agent* ($NaBH_4$ sol., EG, EtOH) was added and the reaction mixture was ultrasonicated

The reaction mixture containing a polar liquid adsorbs the microwave energy rapidly. Thus, the slurry is subjected to rapid heating and elevated pressures, causing the sample to react in a short time.

Reaction conditions: 15 min. reaction time, 50-80°C temperature, 800 W microwave power

The reaction products have been discharged, separated, extensively washed with de-ionized water and alcohol. The final product is dried in the lyophilizer. The product is ***perfectly dispersible*** in de-ionized water (ultrasonic bath, 15 min), it can be dried and redispersed.

Experimental: characterization methods

✓ Micro-structural investigation of N/rGO:

Elemental analisys
-N, H, O determination

Trace metals (K, Mn)
VARIAN AA 240 FS atomic absorption spectrometer

The specific surface areas (BET method)
Quantachrome IQ Autosorbe instrument

FTIR
Nicolet Impact 410, Thermo Fisher spectrometer

FE-SEM
FEI Quanta 200 FEG

X-Ray Photoelectron Spectroscopy
Thermo Scientific ESCALAB 250Xi spectrometer

✓ Electrochemical investigation of N/rGO using *ex-situ* characterization

Electrochemical workstation VersaScan
VersaSTAT F and 3F, Princeton Applied Research

Characterization: Elemental analysis

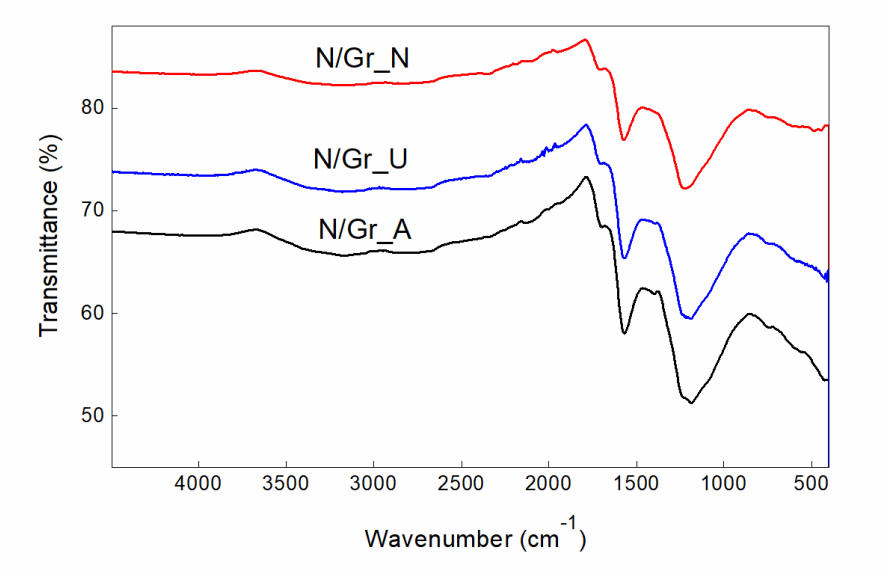
Table 1. Nitrogen-doped graphene materials obtained by using the MW method and comparison on N doping ratio based on experimental condition (inorganic nitrogen precursors: **ammonia** and **nitric acid**)

N/ Gr	Ammonia (A), Nitric acid (N) (mL)	Red. agent	T (°C)	C % (wt.)	N % (wt.)	H % (wt.)	O % (wt.)
1	**40 (A)**	**EG**	**80**	**80.8**	**4.7**	**1.1**	**13.3**
2	36 (A)	EG	80	82.1	4.4	1.1	12.3
3	40 (A)	EG	60	83.5	2.6	1.5	12.4
4	36 (A)	EG	60	84.1	1.9	1.5	12.5
5	**40 (A)**	**BH_4Na**	**80**	**82.4**	**3.2**	**1.3**	**13.1**
6	36 (A)	BH_4Na	80	82.7	2.9	1.4	12.9
7	40 (A)	BH_4Na	60	84.1	2.4	1.4	12.1
8	36 (A)	BH_4Na	60	84.2	2.0	1.6	12.2
9	**40 (A)**	**Et**	**80**	**81.4**	**3.3**	**1.4**	**13.8**
10	36 (A)	Et	80	81.4	3.0	1.5	14.0
11	40 (A)	Et	60	82.0	2.1	1.4	14.5
12	36 (A)	Et	60	82.1	1.9	1.4	14.5
13	**40 (N)**	**BH_4Na**	**80**	**83.0**	**3.5**	**1.2**	**12.3**
14	36 (N)	BH_4Na	80	82.6	3.4	1.3	12.7
15	40 (N)	BH_4Na	60	83.6	2.8	1.3	12.3
16	36 (N)	BH_4Na	60	82.3	2.5	1.4	13.8

Table 2. Nitrogen-doped graphene materials obtained by using the MW method and comparison on N doping ratio based on experimental condition (organic nitrogen precursor: **urea**)

N/Gr	Urea (g)	Red. agent	T (C)	C % (wt)	N % (wt)	H % (wt.)	O % (wt.)
1	**3**	**EG**	**80**	**84.1**	**2.7**	**1.5**	**11.7**
2	2.5	EG	80	83.9	2.4	1.5	12.2
3	2	EG	80	83.7	2.4	1.5	12.4
4	3	EG	60	83.3	2.5	1.5	12.7
5	2.5	EG	60	83.2	2.4	1.5	12.9
6	2	EG	60	83.2	2.2	1.5	13.1
7	3	BH_4Na	80	84.9	1.8	1.6	11.7
8	2.5	BH_4Na	80	83.9	1.4	1.6	13.1
9	2	BH_4Na	80	83.7	1.3	1.6	13.4
10	3	BH_4Na	60	83.4	1.3	1.7	13.6
11	2.5	BH_4Na	60	83.4	1.2	1.7	13.7
12	2	BH_4Na	60	83.4	1.0	1.8	13.8
13	3	Et	80	85.1	1.9	1.5	11.5
14	2.5	Et	80	84.9	1.8	1.5	11.8
15	2	Et	80	85.0	1.5	1.5	12.0
16	3	Et	60	84.9	1.7	1.6	11.8
17	2.5	Et	60	84.8	1.6	1.7	11.9
18	2	Et	60	84.9	1.4	1.7	12.0

Characterization: FT-IR spectra

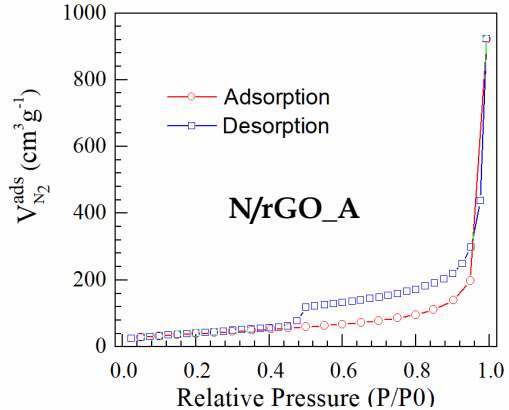


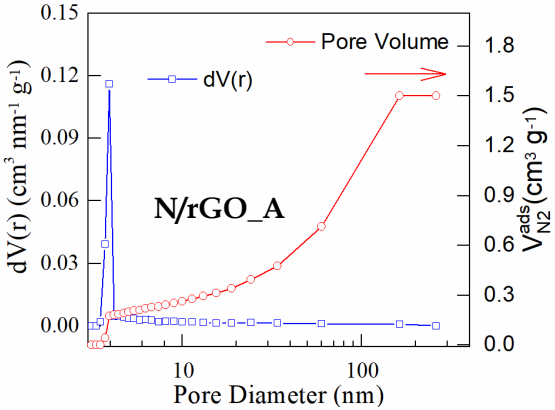
FT-IR spectra of N/rGO

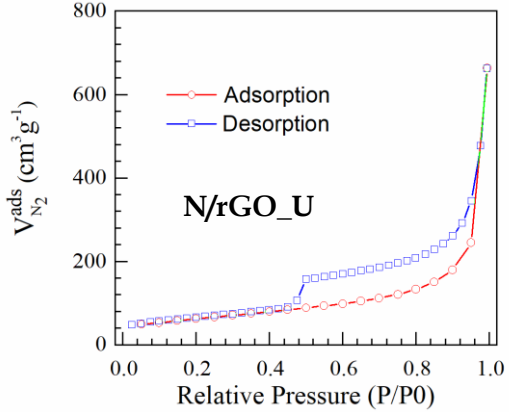
- ✓ 1572 cm^{-1}: skeletal vibrations from un-oxidized graphitic domains from aromatic regions of GO
- ✓ 1725 cm^{-1}: C=O stretching
- ✓ 1150−1600 cm^{-1}: feasible overlapping vibrational modes

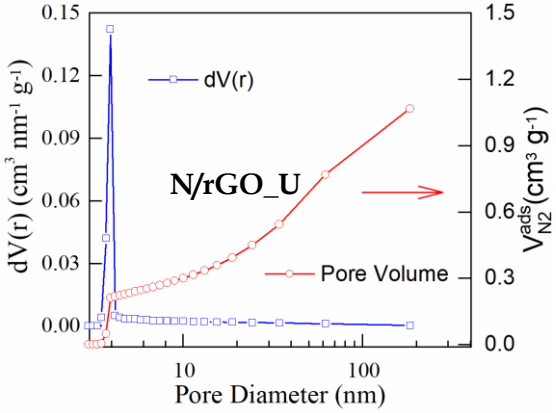
The identification of chemisorbed nitrogen on GO surface is difficult due to its spectral similarity to epoxy oxygen, that usually exist in the graphene lattice, in particular for materials obtained by reduction of GO.

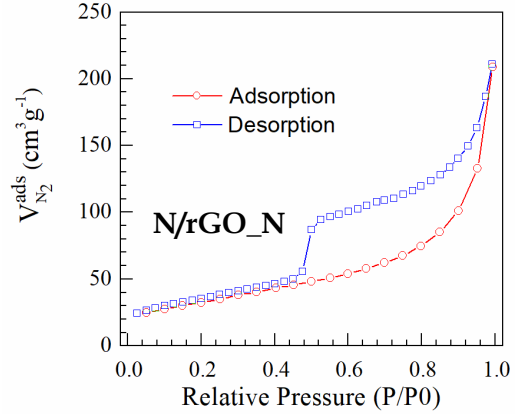
Characterization: BET surface area

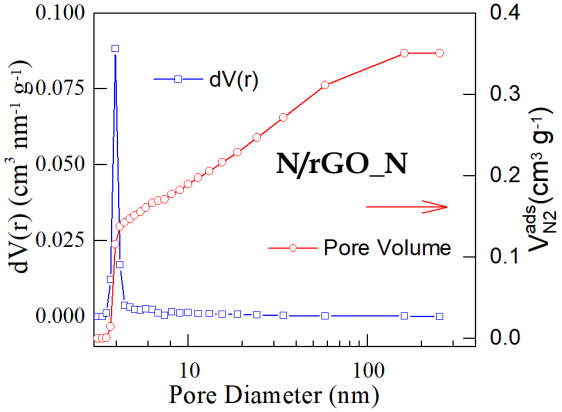












Textural properties of N/rGOs

Samples	S_{BET} ($m^2\ g^{-1}$)	BJH Pore volume ($cm^3\ g^{-1}$)	BJH Pore Radius (A)
N/rGO_A	52	0.193	19.634
N/rGO_U	76	0.168	19.665
N/rGO_N	133	0.253	19.678
rGO	397	0.297	19.722

(a) BET surface area calculated from the linear part of the BET plot ($P/P_0 = 0.1 - 0.3$)

(b) Pore volume, calculated from the volume of N_2 adsorbed at $P/P_0 = 0.99$, using BJH method

Ex-situ electrochemical measurements

An important aim of the present research was ***the fundamental electrochemical characterization of modified nitrogen-doped graphene electrodes*** in KOH electrolyte

The objectives were:

❖Comparative study of electrochemical activity for prepared samples (Cyclic voltammetry)

❖Long term stability (Chronoamperometric response, Cyclic voltammetry) of developed electrodes

A Versa Scan electrochemical workstation (VersaSTAT F and 3F, Princeton Applied Research) was employed for the electrochemical study of N/rGO samples. A three-electrode electrochemical cell was used for CV measurements.

Electrodes: -RE electrode Ag/AgCl

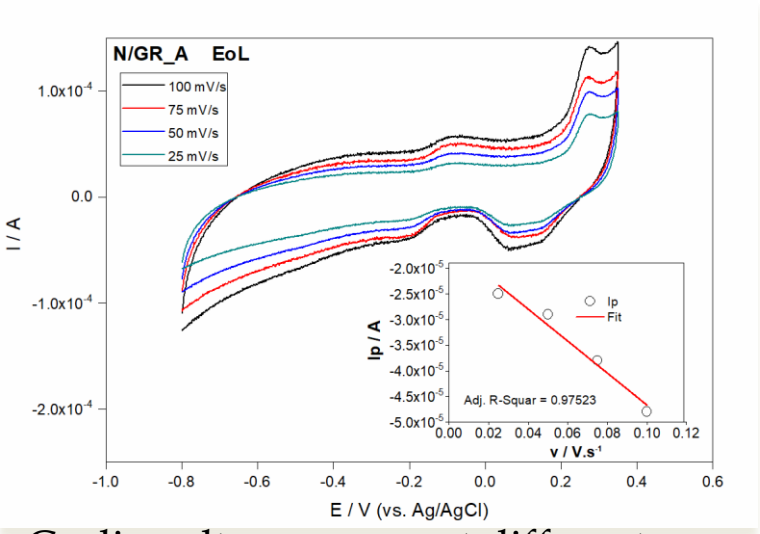
-CE (counter electrod): Pt

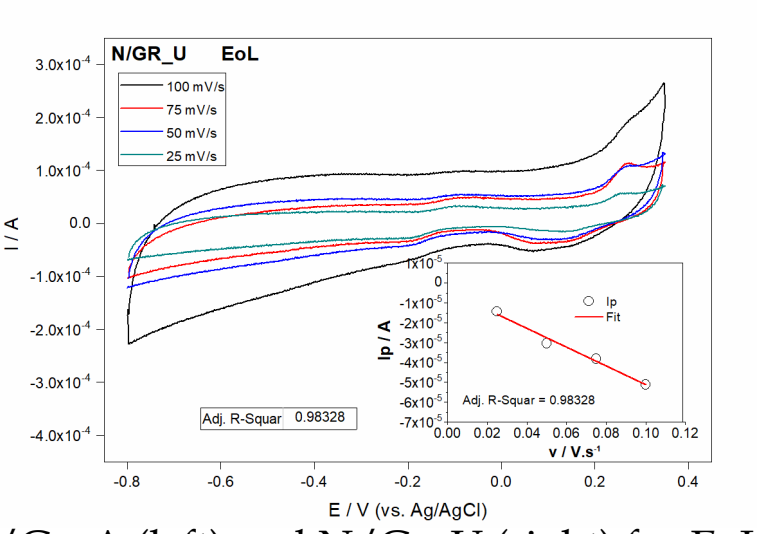
-**WE** (working electrodes): N/Gr_A, N/Gr_U

WE: A homogeneous ink, composed of electrocatalyst, Nafion ionomer, isopropanol

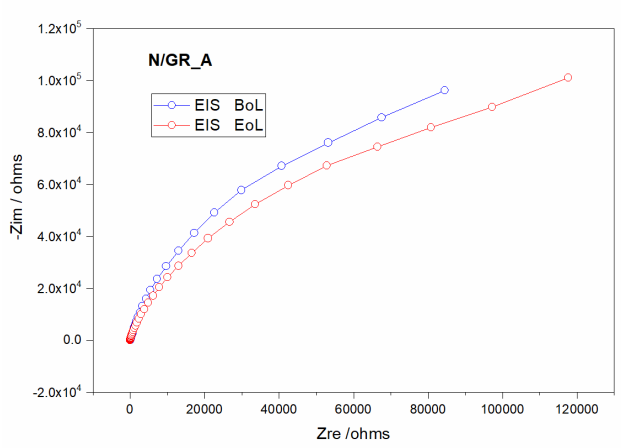
The CV measurements were carried out at room temperature using 0.1 M KOH as the electrolyte solution. CV potential was evaluated between −0.8 V to 0.3 V, using various voltage scan rates (25, 50, 75 and 100 mV s^{-1}). The EIS tests were evaluated by applying the alternating voltage of 10 mV in the frequency domain of 0.01 Hz to 100 kHz

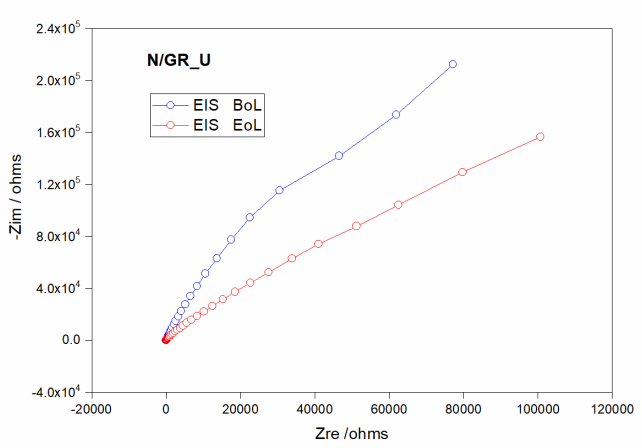
Electrochemical results: stability evaluation





Cyclic voltamograms at different scan rates for N/Gr_A (left) and N/Gr_U (right) for EoL. Right bottom insert plot of the dependency of oxidation peak current on the square root of the rate





Nyquist plots of the catalysts N/Gr_A (left) and N/Gr_U (right)

CONCLUSIONS:

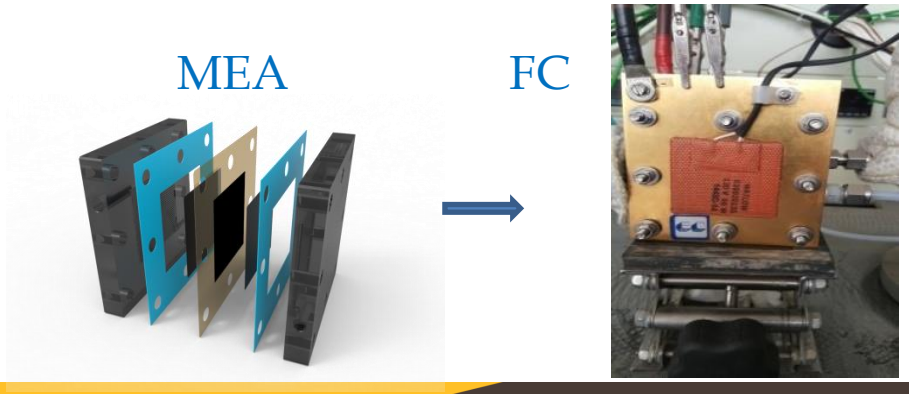
- N/rGOs were successfully prepared using one-step method by microwave synthesis in presence of ammonia, nitric acid or urea

- The presence of N has been confirmed by elementalanalysis and XPS spectroscopy

- The *ex-situ* electrochemical measurements revealed enhanced performances in respect to N/rGO electrodes.

- N/rGO is regarded as potential ORR catalyst for a more comprehensive durability investigation.

- Future work: *In-situ* testing in PEMFC



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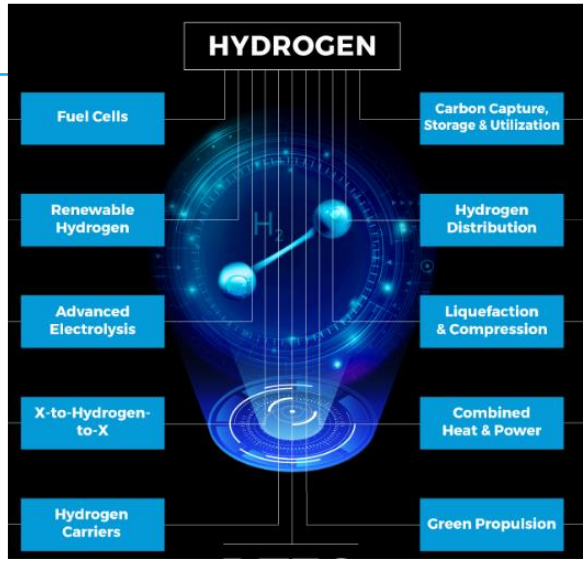
Innovation insights

ICSI involvement in the energy area

- 14 patents and 23 patent applications (2017-2021)
- Over 20 projects at European (Horizon, M-Era-Net, Erasmus) and national level (PED, TE, Structural funds, PFE, PN) (2021-2021)
- Several products, technologies and services ready to be scaled-up from lab-scale to semi-industrial scale or further
- Several agreements for collaboration, especially for pre-feasibility & feasibility studies for the development of projects in the field of energy and hydrogen-based technologies, with private companies, but also with City Halls and Municipalities



What ICSI can offer

- *A strong and reliable partner*
- *Capabilities and experience from material development up to the testing and demonstration of systems based on fuel cells, hydrogen and energy storage technologies.*
- *A network of collaborators both from research and commercial area, partnerships designed in order to create a hydrogen research initiative group.*

ICSI ENERGY

THANK YOU FOR YOUR ATTENTION!

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