ELECTROQUÍMICA CIENCIA Y TECNOLOGÍA

UAM UNIVERSIDAD AUTÓNOMA DE MADRID

Research Plan:

Study of the evolution of FeN_xC_y and Fe_3C species in Fe/N/C catalysts during the oxygen reduction reaction in acid and alkaline electrolyte

ÁLVARO GARCÍA

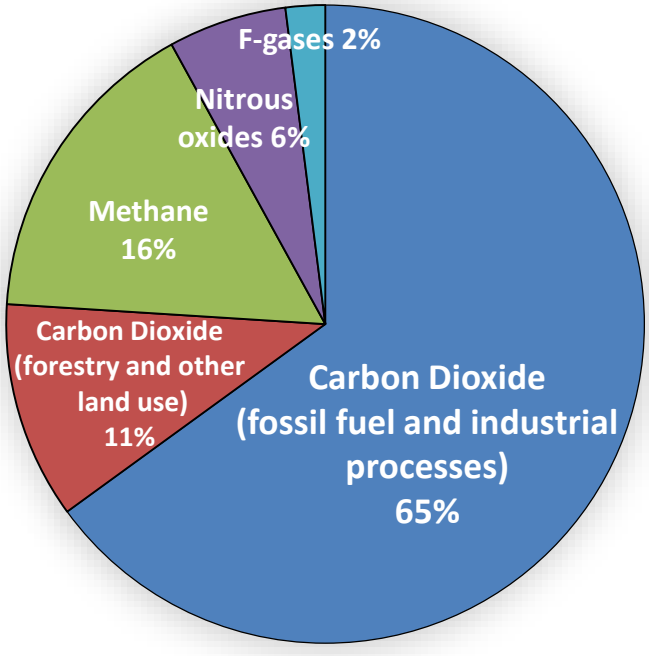
Current Trends in Electrochemistry
41st Meeting of the Electrochemistry Group of the Spanish Royal Society of Chemistry
1st French-Spanish Atelier/Workshop on Electrochemistry

GOBIERNO DE ESPAÑA MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD CSIC Consejo Superior de Investigaciones Científicas

CSIC ICP EQS

GHE-ENVIRONMENTAL CONCERNS

Current state

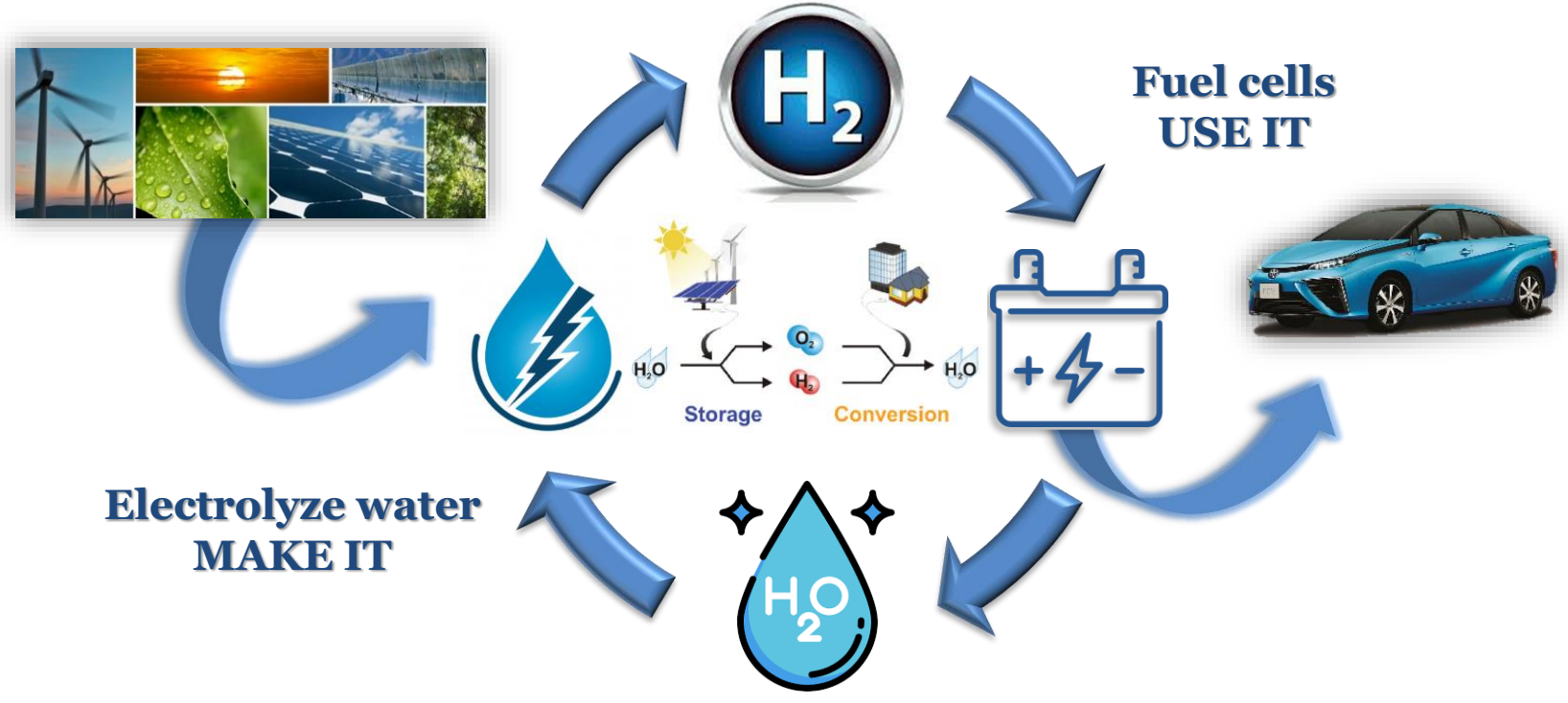


Targets

- Global warming no more than 2 ^{0}C relative to pre-industrial levels

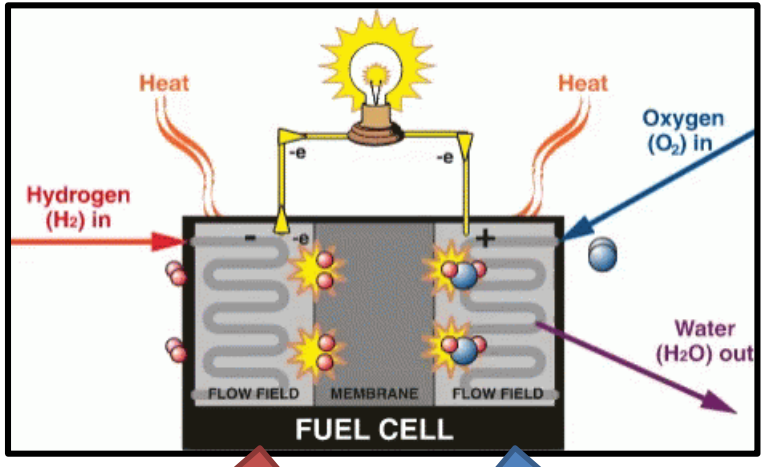
- Reducing CO_2 emissions by 80% in 2050

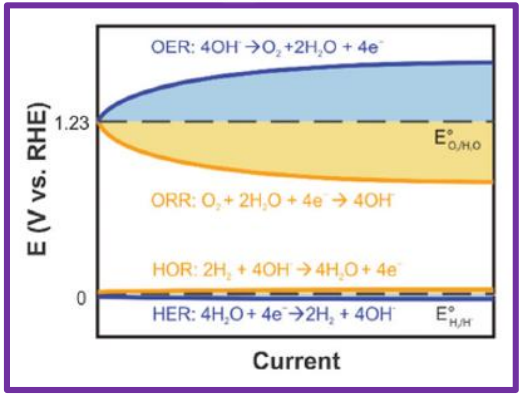
CIRCULAR ECONOMY OF H_2



HOW FUEL CELL WORKS

Low-temperature H_2-feed fuel cells generate direct electrical potential difference (work) by the recombination of O_2 and H_2 with the only bi-product of H_2O





Anode

Cathode

$Hydrogen\ Oxidation\ Reaction (HOR)$:

$2H_2 \rightarrow 4H^+ + 4e^-$

$E^0\ (H^+/H_2) = 0.00\ V\ vs\ RHE$

$Oxygen\ Reduction\ Reaction\ (ORR)$:

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

$E^0\ (O_2/H_2O) = 1.23\ V\ vs\ RHE$

$Global\ Reaction$: $2H_2 + O_2 \rightleftharpoons 2H_2O$ $E_{Global\ reaction} = 1.23\ V\ vs\ RHE$

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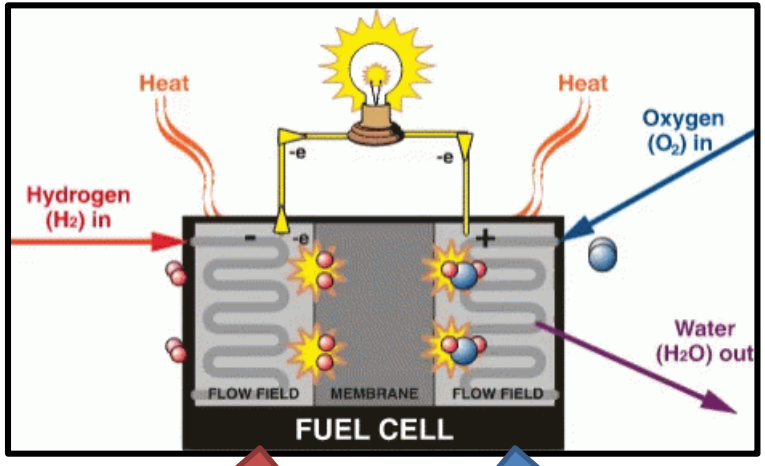
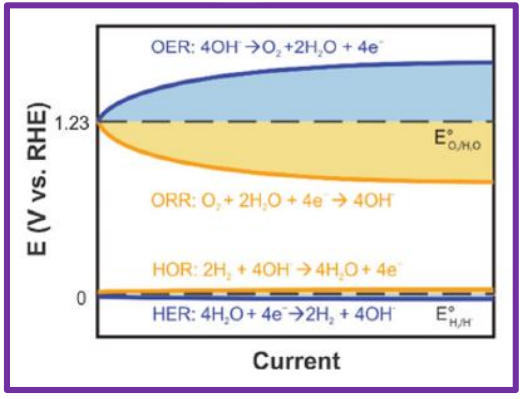




Anode

Cathode

Overall process is limited by the sluggish kinetics of ORR

Hydrogen Oxidation Rea

$2H_2 \rightarrow 4H^+ + 4$

$E^0\ (H^+/H_2) = 0.00$

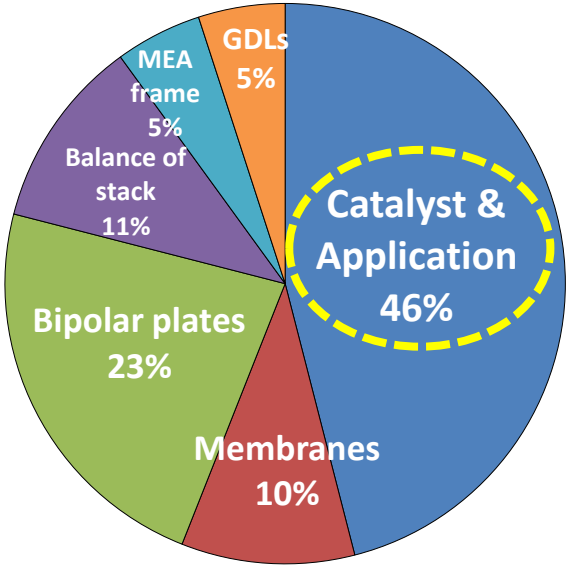
Reduction Reaction (ORR):

$+ 4H^+ + 4e^- \rightarrow 2H_2O$

$O_2/H_2O) = 1.23\ V\ vs\ RHE$

Global Reaction: $2H_2 + O_2 \rightleftharpoons 2H_2O$ $E_{Global\ reaction} = 1.23\ V\ vs\ RHE$

FUEL CELL COST



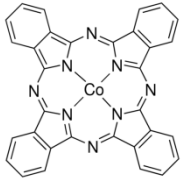
Catalyst is the highest cost component of the PEMFC stack

Significant barrier for PEMFC commercialization

Pt world **production** in 2015: 188 tons
Pt world **demand** in 2015: 235 tons
Pt world **recycling** in 2015: 51,2 tons
Cathode – ORR – 80wt.% Pt

NON-PRECIOUS METAL CATALYST (NPMC)

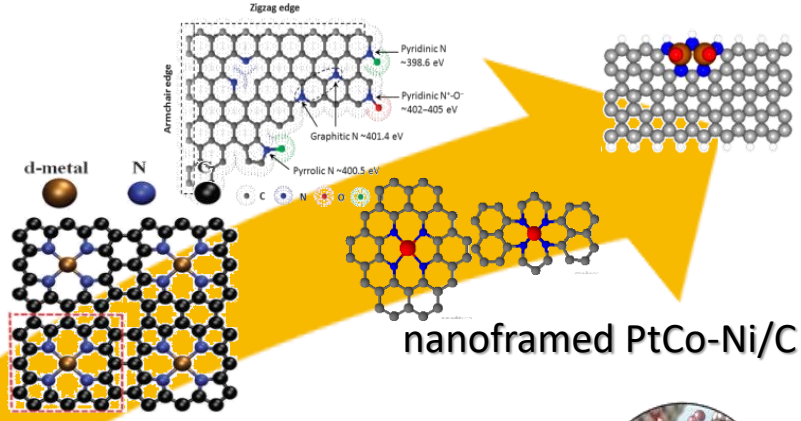
NPMC



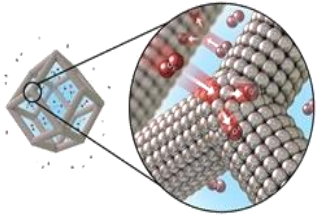
Jasisnki, Nature 201 (1964) 1212

PtM/C

PtNi dealloyed



nanoframed PtCo-Ni/C



$Pt/C \rightarrow 0.18\ A/mg_{Pt} \rightarrow \rightarrow \rightarrow \rightarrow \rightarrow \rightarrow 5.7\ A/mg_{Pt}$ (DOE $0.44\ A/mg_{Pt}$)

- **Impregnation of Fe in graphene, carbon nanotubes or activated carbon**
- **MOF like ZIF-8 replacing Zn with a transition metal**
- **Metallic porphyrins in silica supports**
- **Polymerization of cyanamide and polyaniline with metal salts**
- **Porous organic polymers as precursor**
- **Combinations of two transition metals in the structure**
- **Aerogels by hydrothermal treatment**

PROS VS CONS IN NPMCS

Advantages

- Cheap
- Simple synthesis
- High surface area
- Thermal stability
- High conductivity

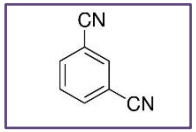
Drawbacks

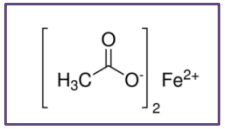
- Nature of active sites unknown:N, Metal…
- Formation of H_2O_2
- Carbon corrosion at high potentials
- Dissolution of the catalyst
- Activity and durability

SYNTHESIS METHOD

Molar Ratio

1 $ZnCl_2$: 1 Dicyanobencene 1 Fe : 4 N





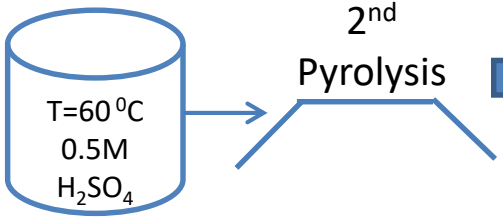
46 h
T= 400 ^{0}C
vacuum

Ball-milling 1 h
(300-350 rpm)

30 min
T= 900 ^{0}C
N_2 / NH_3

20 ^{0}C/min

Acid Leaching

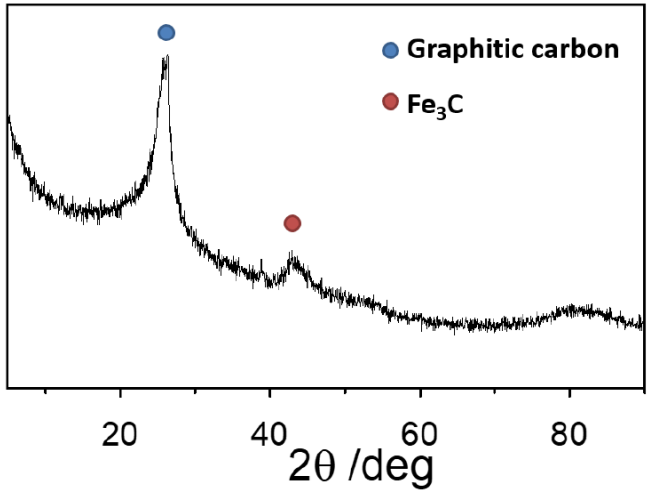


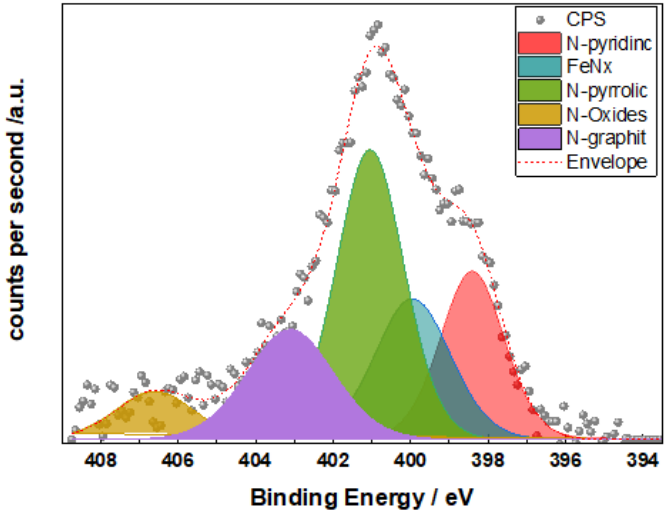
2nd
Pyrolysis

Catalyst
Fe-N-DCB

CHARACTERIZATION RESULTS

Catalyst	Weight Content / %			N/C	Specific surface area
	C	N	H	Atomic ratio	(micropore/external surface) / $m^2 \cdot g^{-1}$
Fe/N/DCB	88.42	1.68	0.92	0.019	537 (253/ 284)





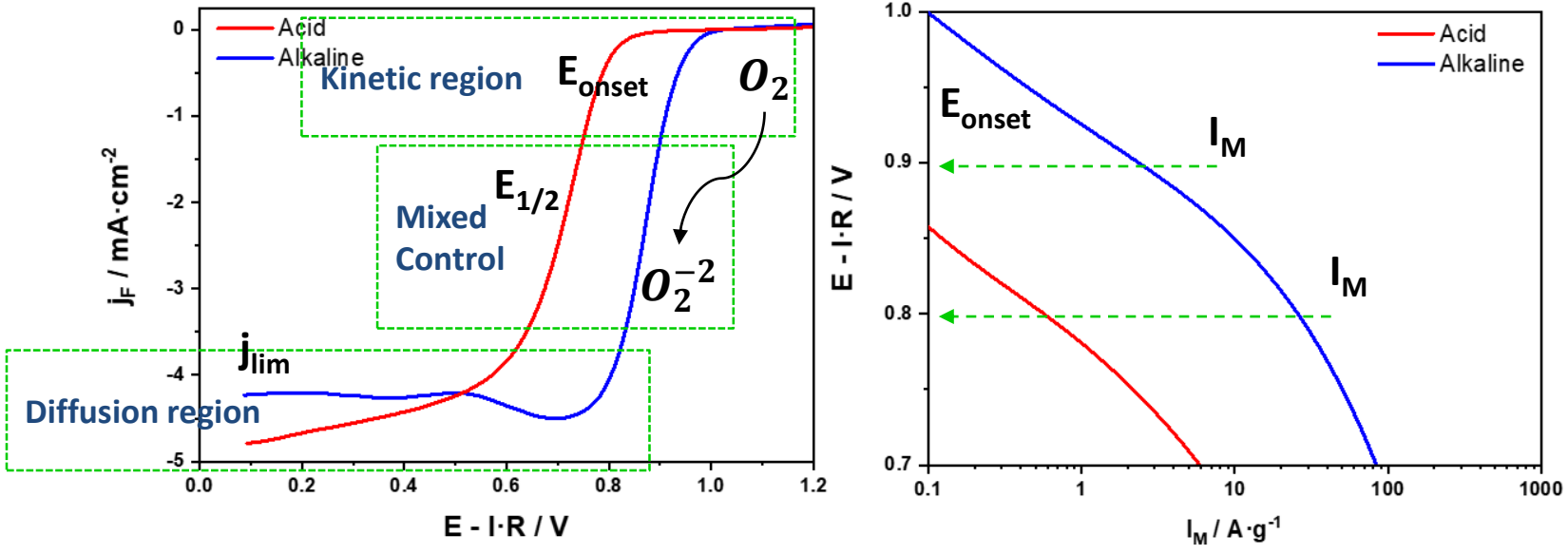
Catalyst	Atomic ratios			Nitrogen species / %				
	C/N	C/O	N/Fe	Pyridinic	FeNx	Pyrrolic	Quaternary	Oxide
Fe/N/DCB	52	13	17	19	21	35	15	10

ELECTROCHEMICAL MEASUREMENTS

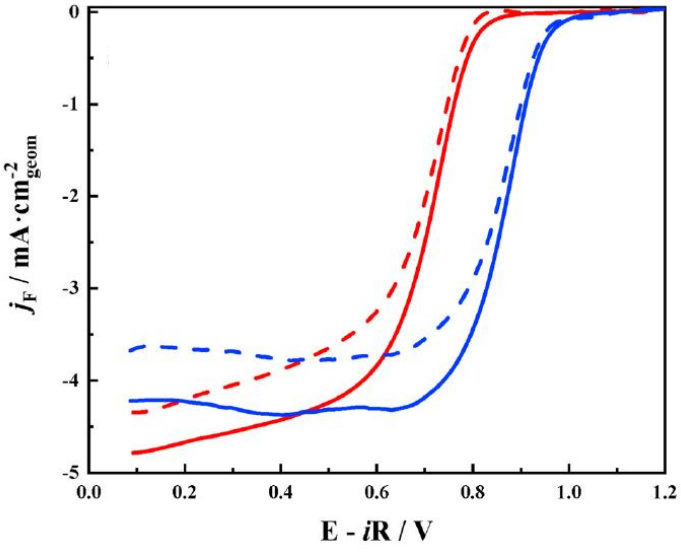
ORR

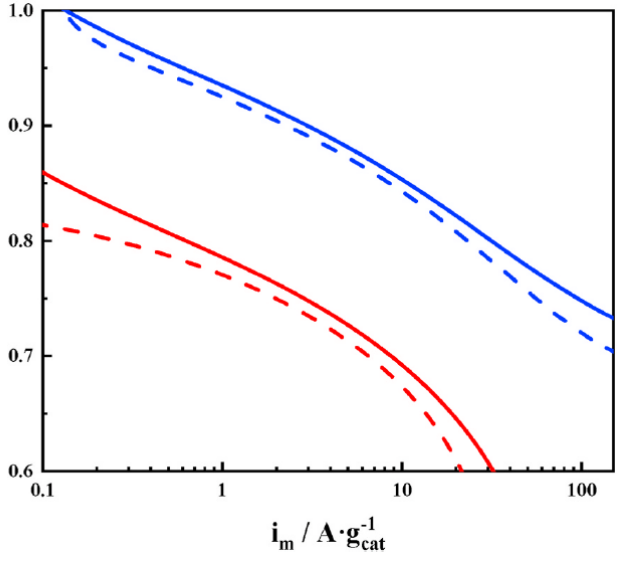
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

Acid = 0.1M $HClO_4$; Alkaline = 0.1 M KOH
Catalyst loading = 0.6 mg/cm^2
RDE area = 0.196 cm^2 with a Rotating speed = 1600 rpm
Cyclic voltamperometry from 0.05 V – 1.2 V vs RHE, Scan rate = 10 mV/s



ELECTROCHEMICAL MEASUREMENTS





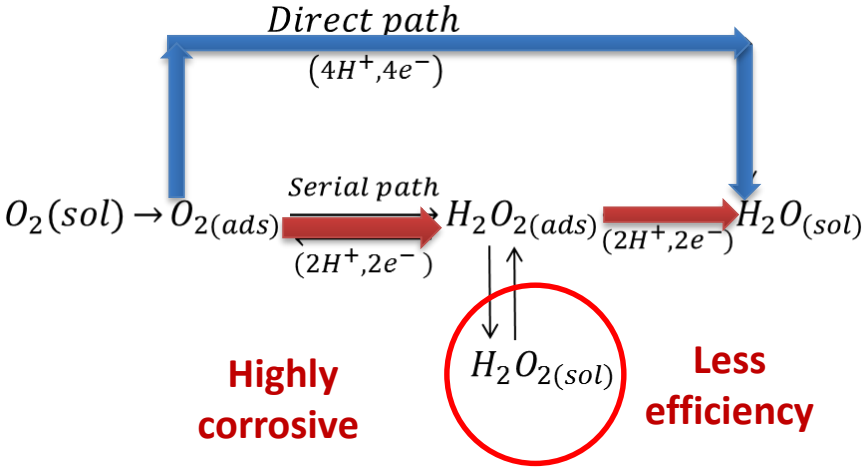
Electrolyte	E_{onset} / V	$E_{1/2}$ / V	i_m / A g^{-1} @ 0.8 V	j_k / mA cm$^{-2}_{geom}$ @ 0.8 V Before AST	j_k / mA cm$^{-2}_{geom}$ @ 0.8 V After AST (250 cycles)
0.1 M $HClO_4$	0.84	0.71	0.57	0.4	0.2
0.1 M KOH	0.98	0.87	27.25	19.2	13.9

Accelerated Stress Test (AST)
250 cycles from 0.05 V to 1.2 V vs RHE at 10mV/s in O_2 saturated electrolyte

+

Active sites study (before and after ORR AST)
by
Identical Location TEM (IL-TEM)
and
XAS study
Fe K-edge and N K-edge

FORMATION OF H_2O vs. H_2O_2



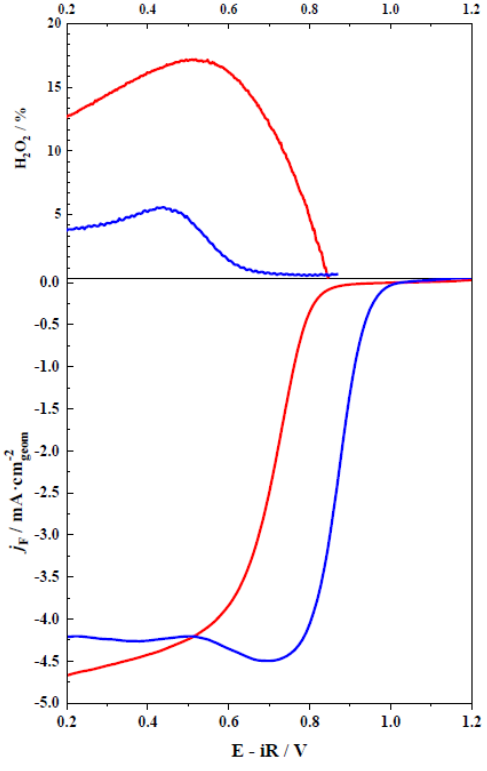
Highly corrosive

Less efficiency

$$\%\,(H_2O_2) = \frac{\frac{2 \cdot i_R}{N}}{i_D + \frac{i_R}{N}}$$

$$n^o\, e^- = 4 - \left(\frac{\%\, H_2O_2}{50\,\%}\right)$$

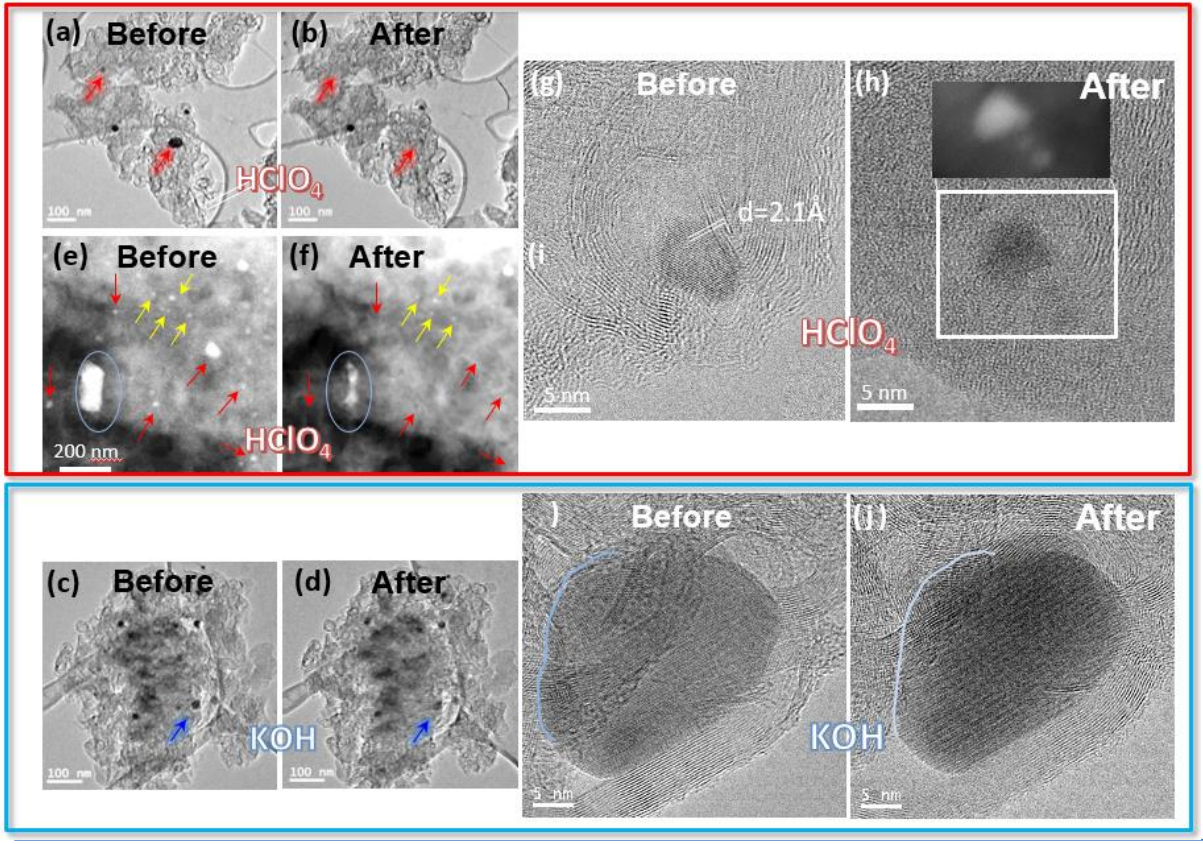
	% H_2O_2	nº e⁻
Acid	17	3.66
Alkaline	6	3.88



Pt ring at 1.2 V (vs RHE) to quantify production of H_2O_2

Oxygen Reduction Reaction in RRDE

IDENTICAL LOCATION TEM STUDY



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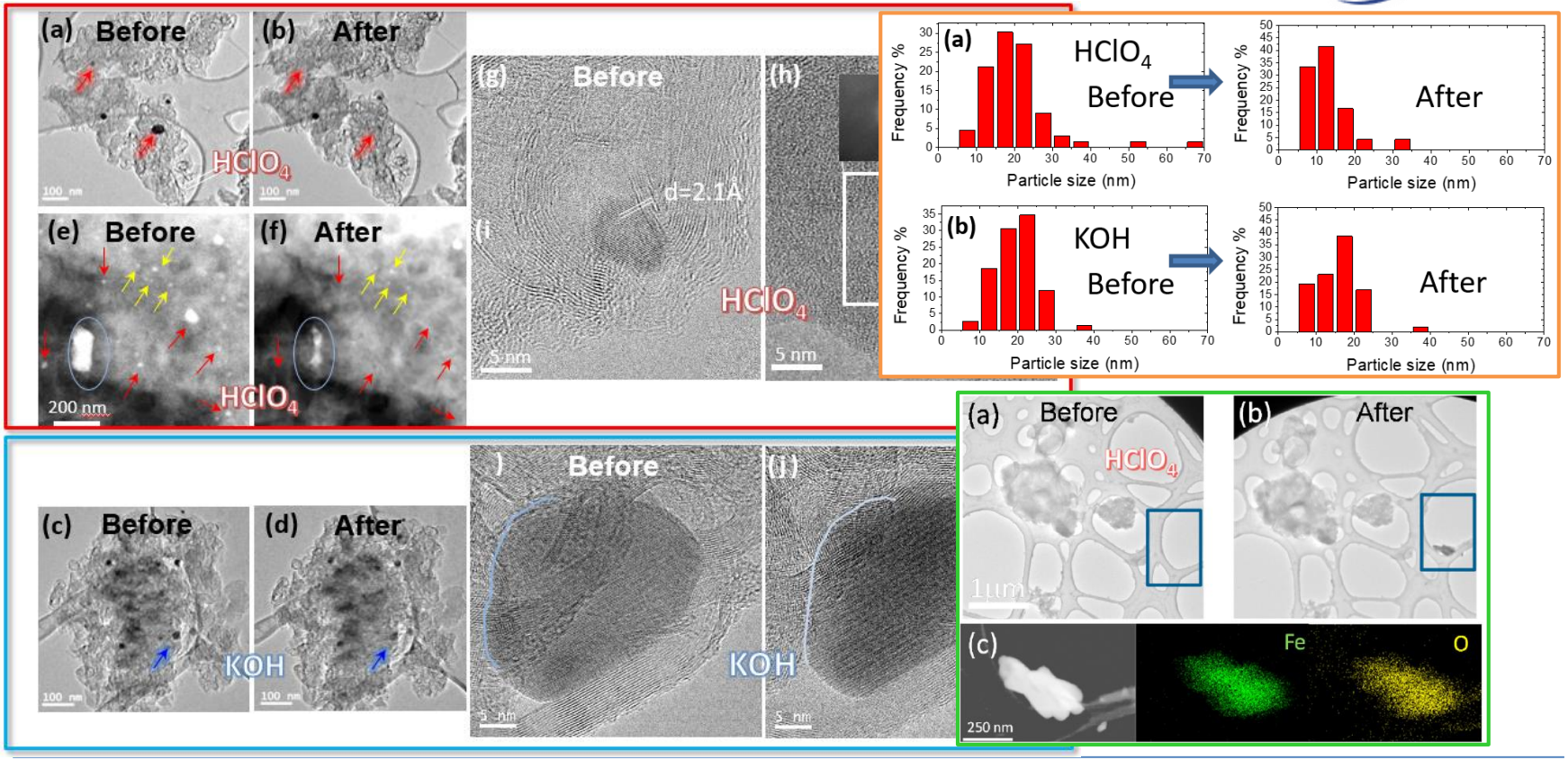
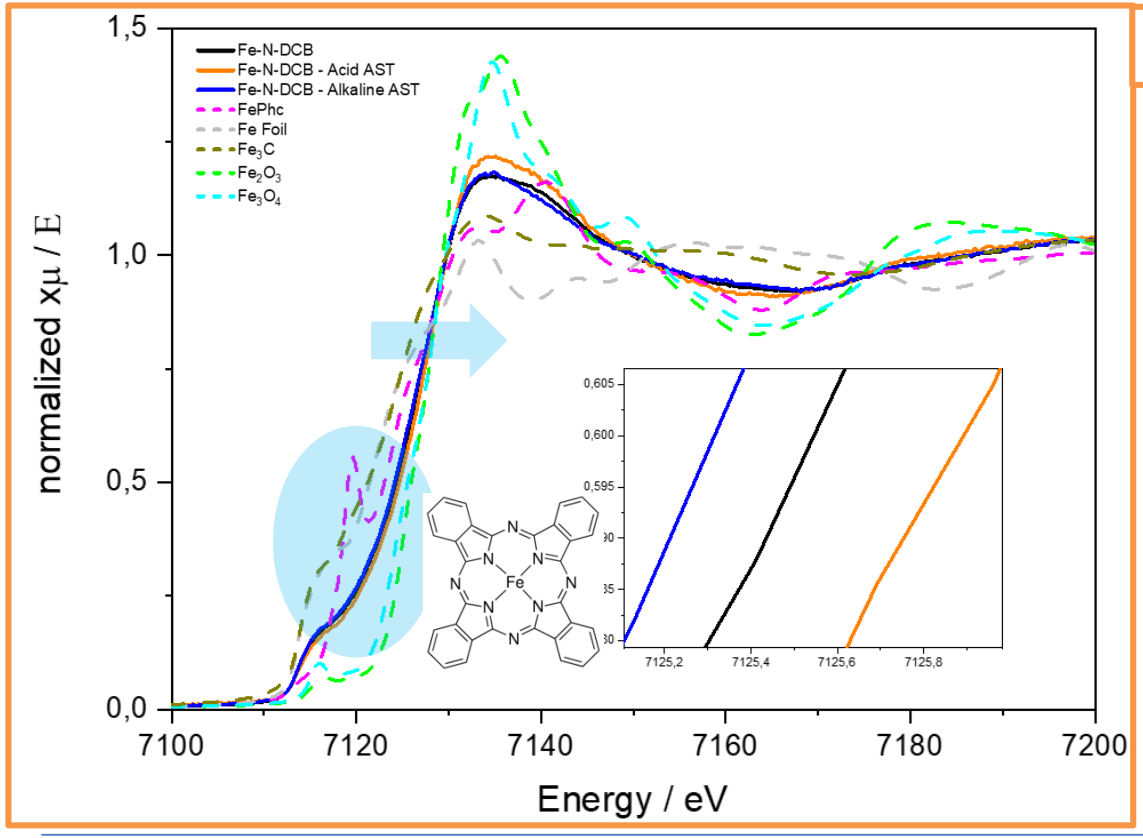


X-RAY ABSORPTION: Fe K-edge



XANES

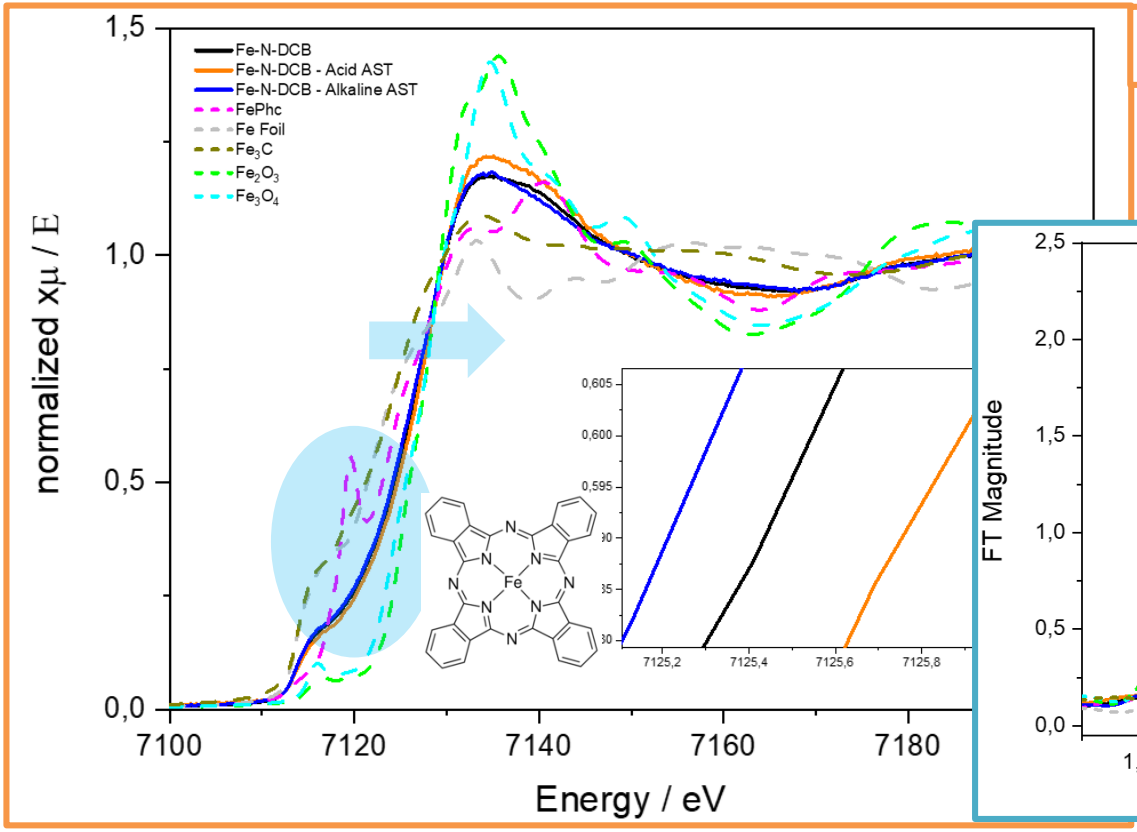
Fe K-edge

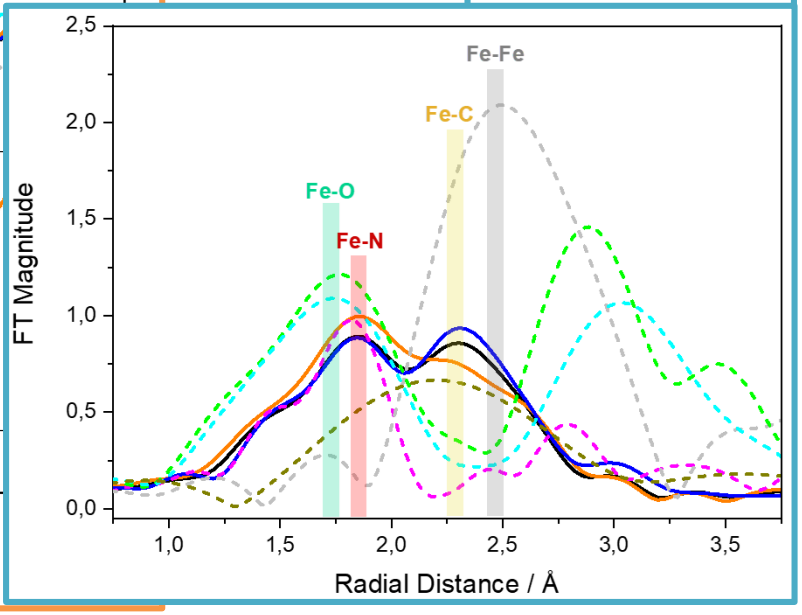
X-RAY ABSORPTION: Fe K-edge

XANES

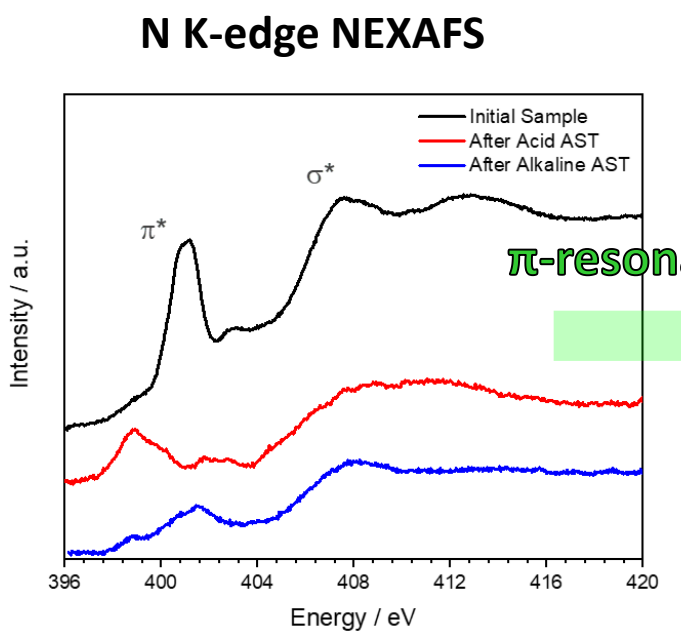
Fe K-edge

EXAFS

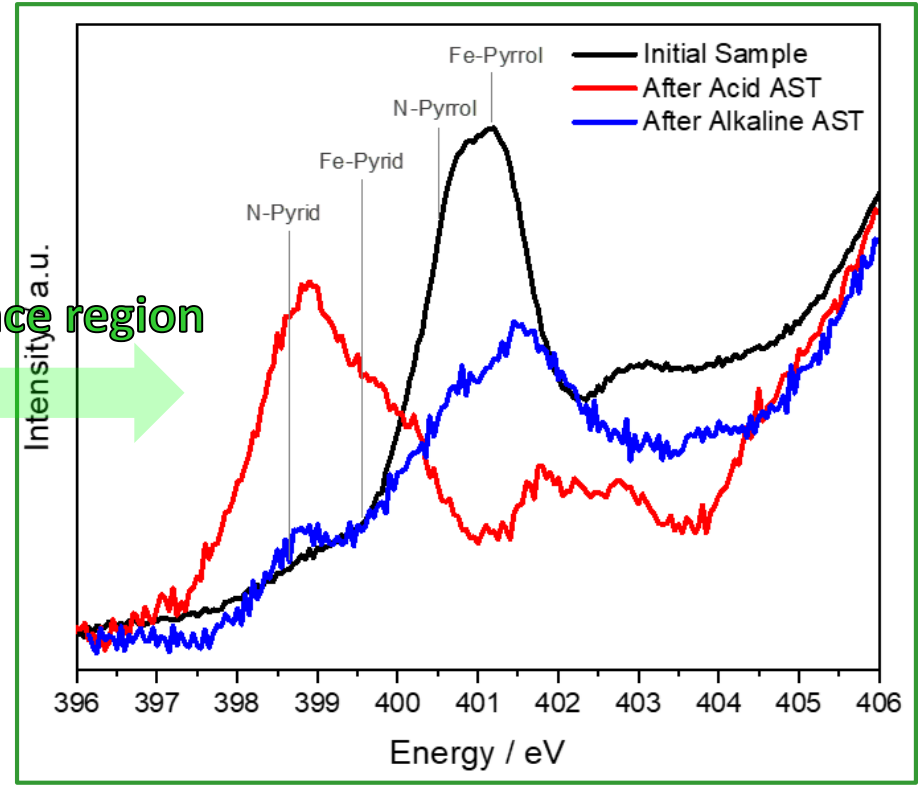




X-RAY ABSORPTION: N K-edge



π-resonance region



CONCLUSIONS

- We have synthetized new NPMC by a new polymerization method with inexpensive starting materials.
- The E_{onset} and mass activity values are excellent for ORR and comparable to the state-of-the-art in alkaline media.
- Characterization techniques reveals the presence of different iron species, Fe_3C and FeN_x ensembles in two configurations FeN_x-pyridinic and FeN_x-pyrrolic.
- Fe_3C particles are solubilized and FeN_x species are lost during the AST in acid and alkaline electrolytes, especially in the former medium, leading to the appearance of iron oxides.
- The FeNx-pyridinic species can be recognized as the actual active sites for ORR in acid electrolyte, because are the Fe sites that have been preserve in the structure after AST.

FUTURE WORK

- **Start with new generations of ORR catalysts: Imine-based framework catalyst and MOF-based catalyst.**
- **Perform more accelerated stress test (durability and corrosion) following DOE protocols.**
- **Deeper studies of the active sites using CO and NO chemisorptions.**
- **Study of the catalyst performance in fuel cell.**
- **Divulgation of the most noticeable results in scientific articles and congress participation.**

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EQS

¡GRACIAS!

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