

"Development of new and novel electrocatalysts based on metal-carbonyl cluster compounds for renewable energy generation by hydrogen PEM-Fuel Cells"

Jorge Uribe-Godínez¹, Alejandro Altamirano-Gutiérrez²

¹ Centro Nacional de Metrología, km 4.5 Carretera a Los Cues, Municipio El Marqués, 76246 Querétaro, México

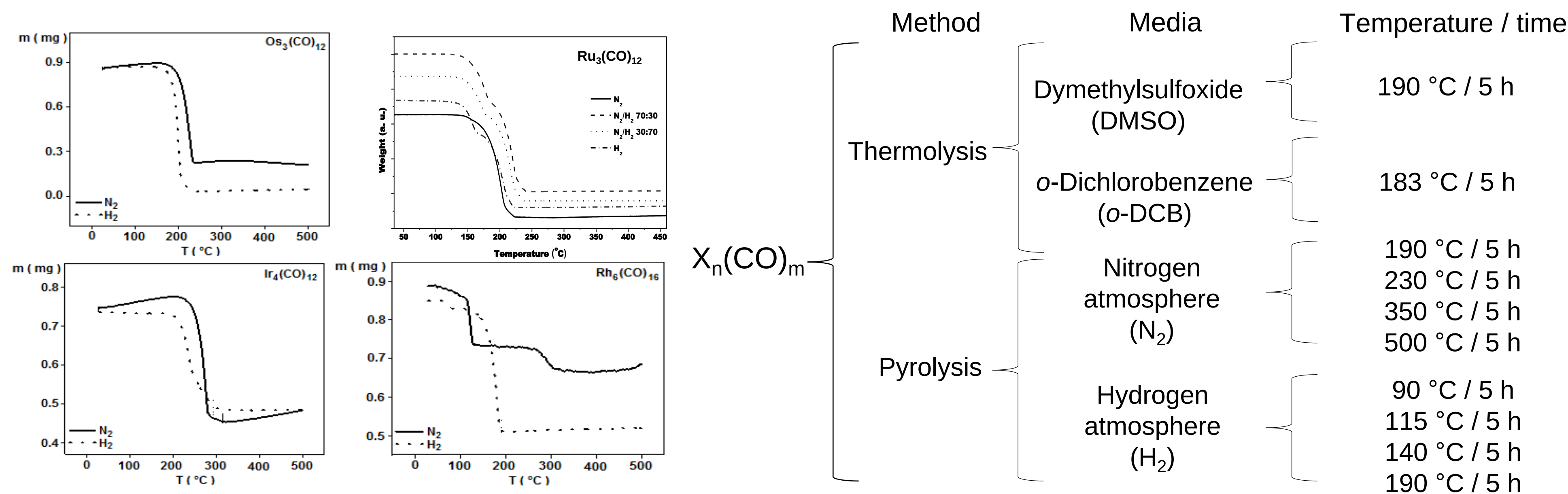
² Centro Universitario de Tonalá, Universidad de Guadalajara, Av. Nuevo Periférico No. 555 Ejido San José Tateposco, C.P. 45425, Tonalá, Jalisco, México

juribe@cenam.mx

ABSTRACT

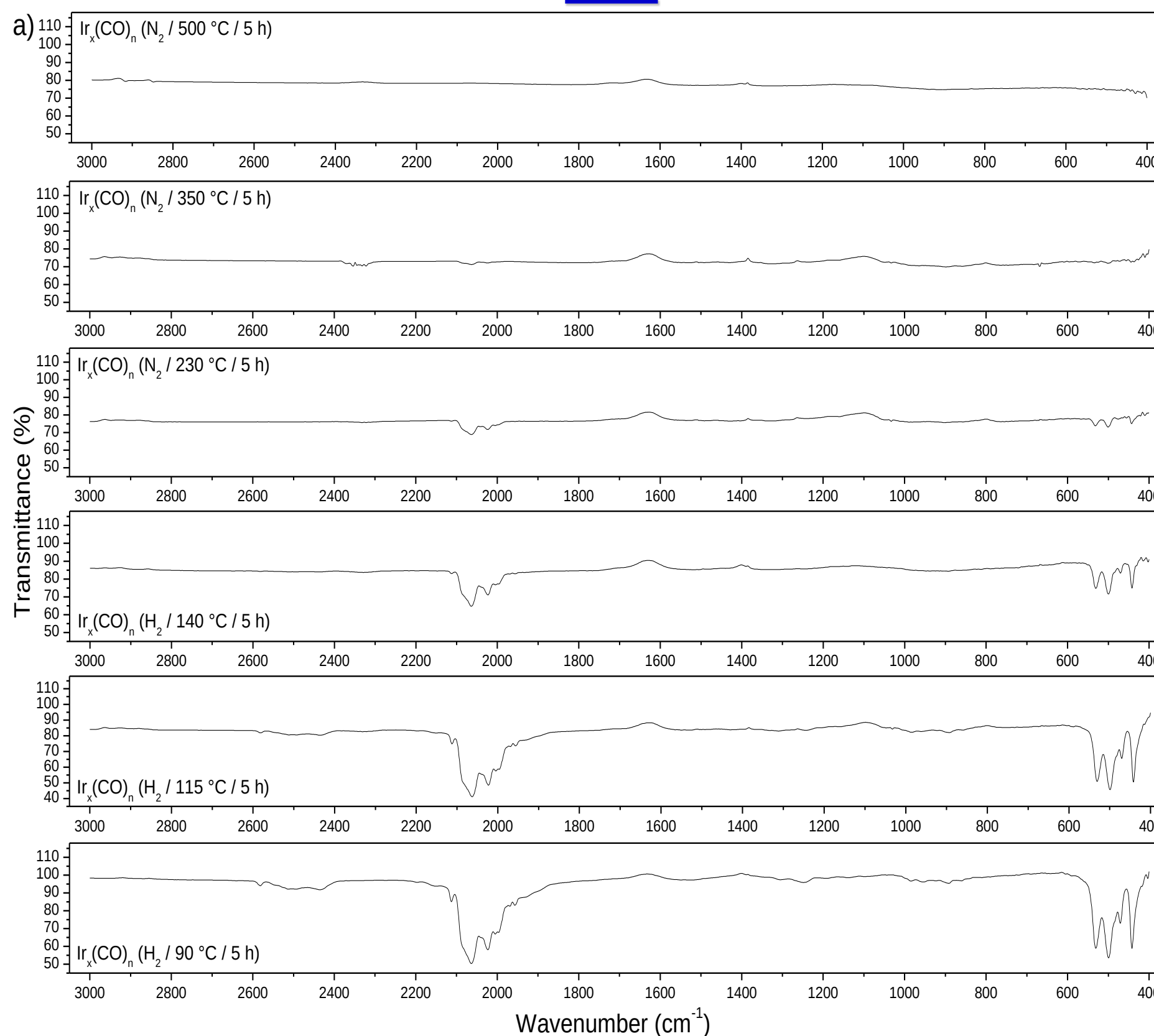
In this work, we have used $\text{Rh}_6(\text{CO})_{16}$, $\text{Ru}_3(\text{CO})_{12}$, $\text{Ir}_4(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$ as precursor compounds to obtain by pyrolysis and thermolysis new nanomaterials, which were evaluated as electrocatalysts of the Oxygen Reduction Reaction (ORR) and the Hydrogen Oxidation Reaction (HOR), in the absence and presence of fuel cell contaminant, as methanol and carbon monoxide (in different concentrations), respectively. The electrochemical study was performed in acid media ($0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$) by cyclic voltammetry (CV) and linear sweep voltammetry (LSV) using the rotating disk electrode technique in a typical electrochemical cell, at room temperature. On the other hand, different analytical techniques, such as FTIR, EDS, XRD and SEM were used to characterize structural and morphologically the electrocatalysts.

Representative thermograms of carbonyl clusters and synthesis conditions of the materials by thermolysis and pyrolysis methods



STRUCTURAL AND MORPHOLOGICAL CHARACTERIZATION OF REPRESENTATIVE CATALYTIC MATERIALS

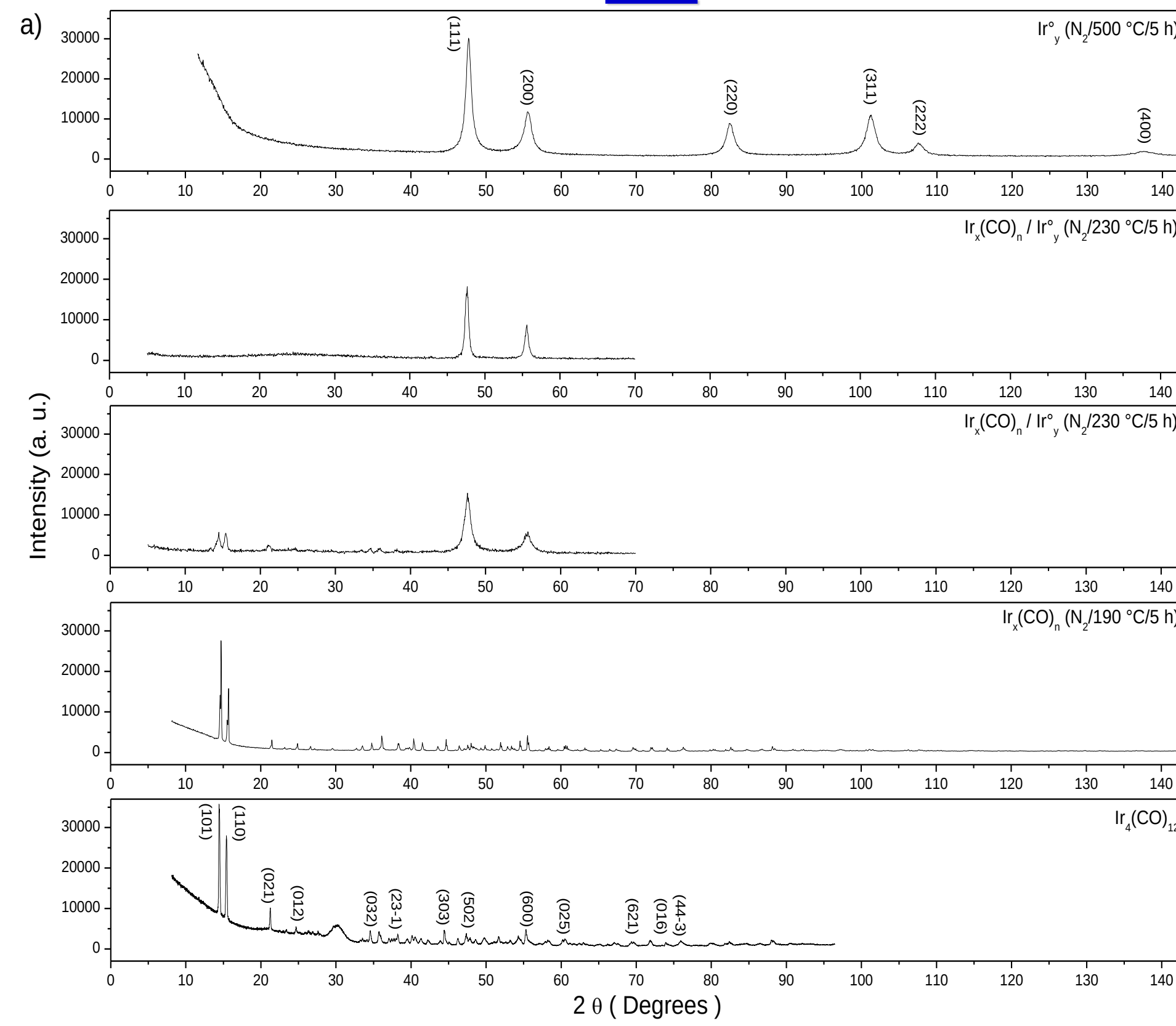
- FTIR



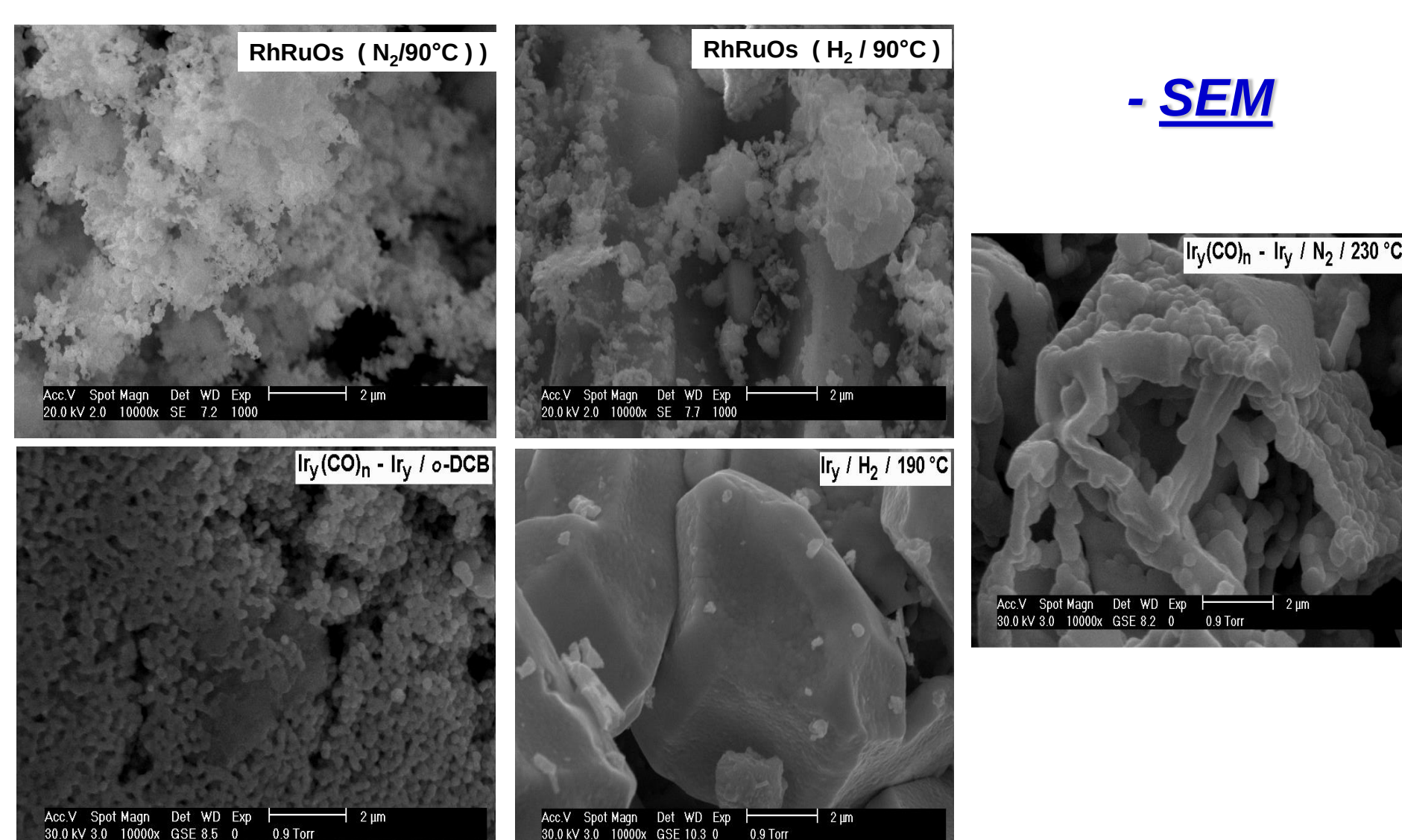
- EDS

Catalyst (Synthesis conditions)	% weight			
	Ir	C	O	Cl
$\text{Ir}_x(\text{CO})_n$ (N_2 / 190 °C)	72.3	17.1	10.6	-
$\text{Ir}_x(\text{CO})_n - \text{Ir}_y$ (N_2 / 230 °C)	90.9	7.6	1.4	-
$\text{Ir}_x(\text{CO})_n - \text{Ir}_y$ (N_2 / 350 °C)	93.5	5.8	0.7	-
Ir_y (N_2 / 500 °C)	93.1	6.9	-	-
$\text{Ir}_x(\text{CO})_n$ (H_2 / 90 °C)	61.2	22.8	16.0	-
$\text{Ir}_x(\text{CO})_n - \text{Ir}_y$ (H_2 / 115 °C)	75.4	15.2	9.3	-
$\text{Ir}_x(\text{CO})_n - \text{Ir}_y$ (H_2 / 140 °C)	78.3	13.5	8.2	-
Ir_y (H_2 / 500 °C)	100	-	-	-
$\text{Ir}_x(\text{CO})_n - \text{Ir}_y$ (o-DCB/ 183 °C)	74.0	14.4	5.7	5.9
$\text{Ir}_4(\text{CO})_{12}$	54.8	27.6	17.6	-

- XRD



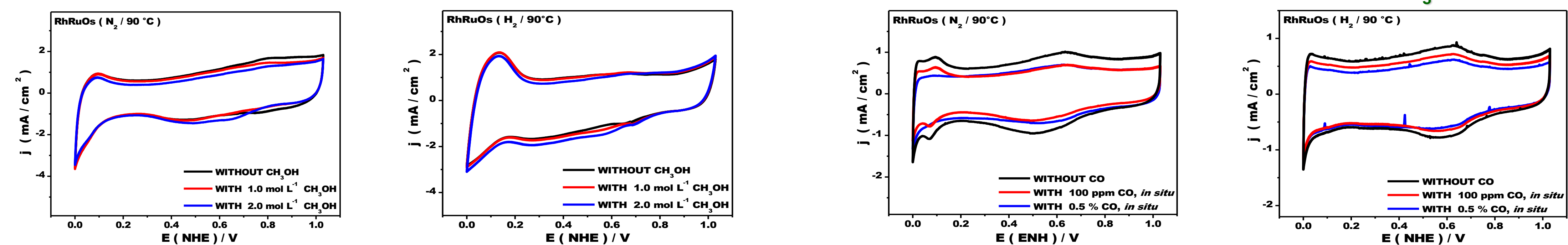
- SEM



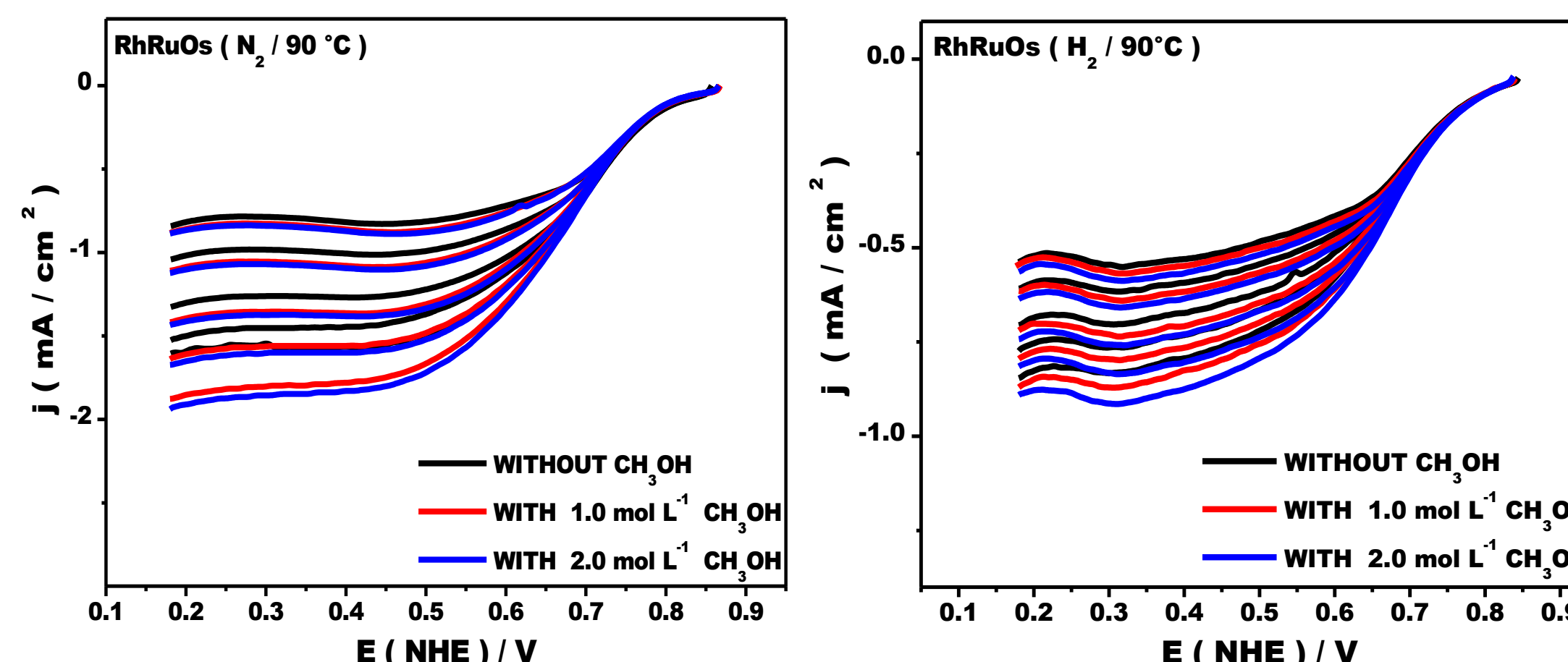
RESULTS

ELECTROCHEMICAL CHARACTERIZATION AND CATALYTIC EVALUATION

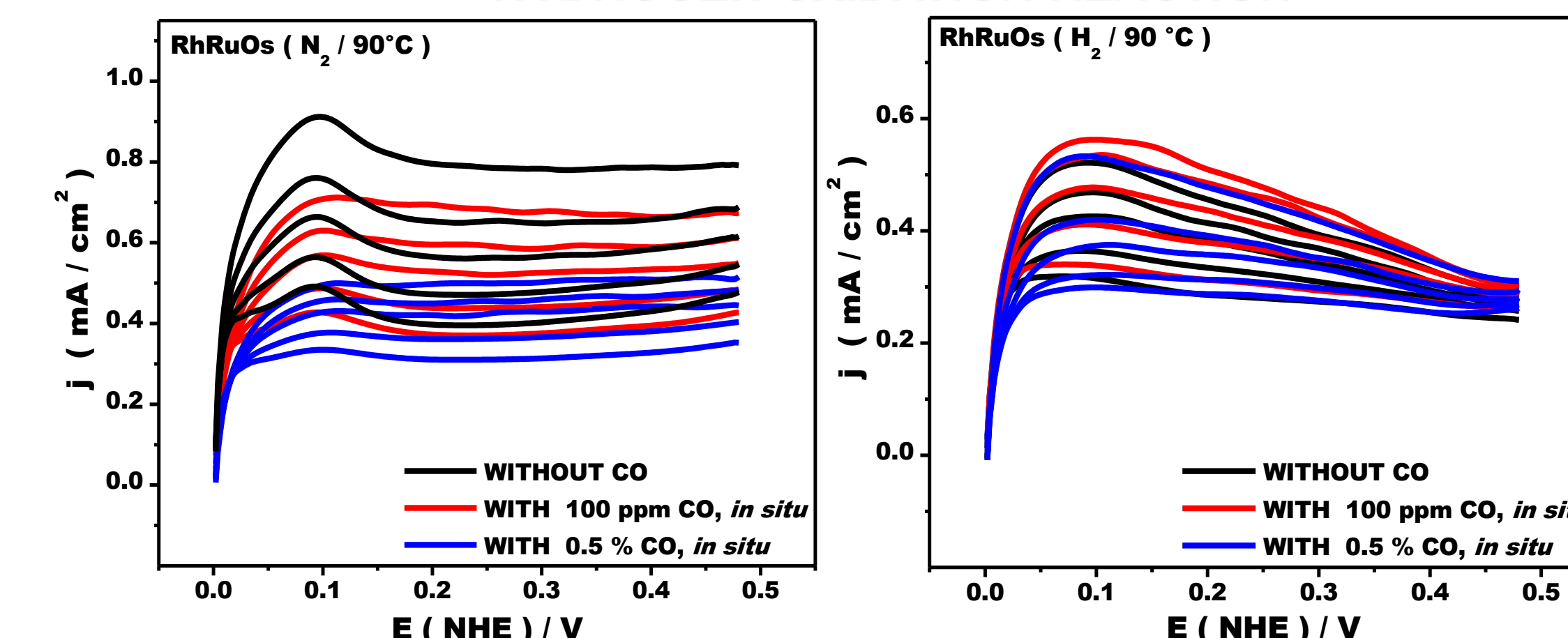
- REPRESENTATIVE TRIMETALLIC-BASED CATALYSTS CVs AND LSV CURVES IN THE ABSENCE AND PRESENCE OF CH_3OH AND CO



- OXYGEN REDUCTION REACTION



- HYDROGEN OXIDATION REACTION



ORR KINETIC PARAMETERS

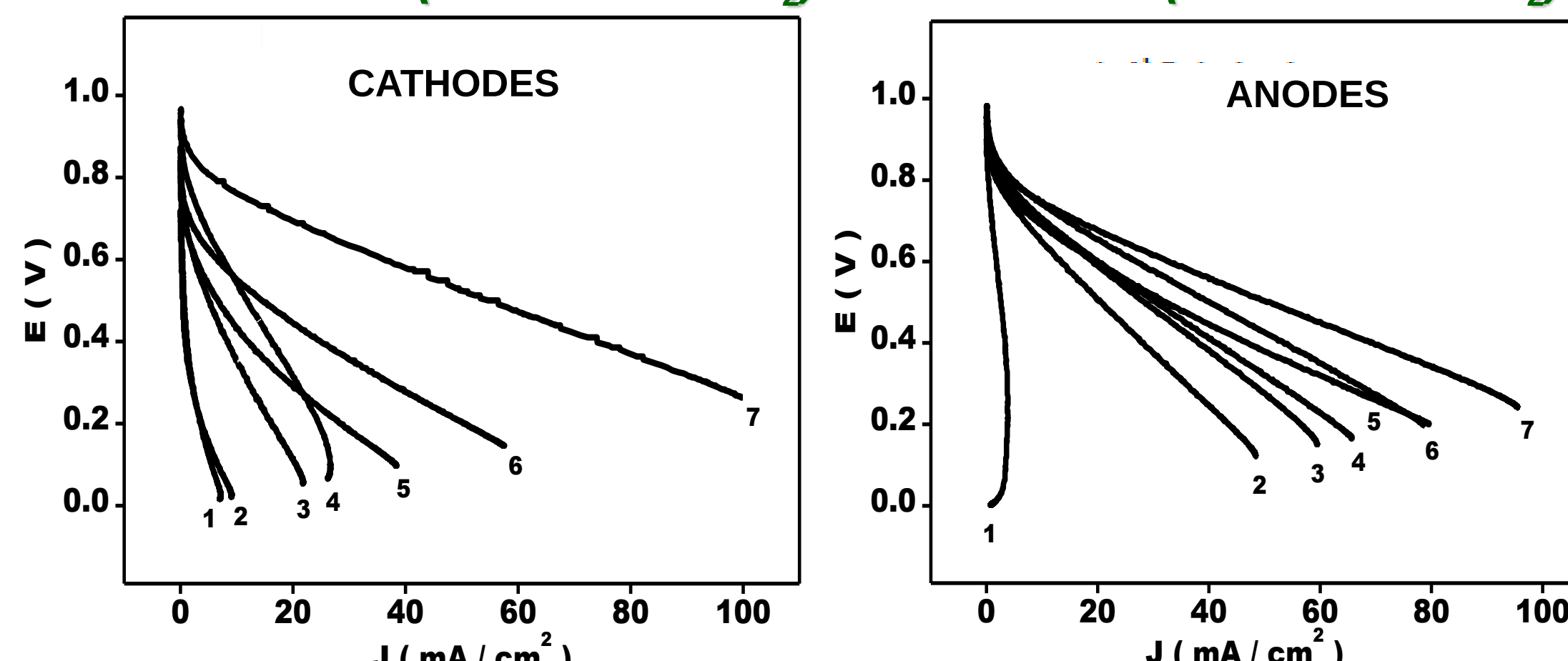
Catalyst	Methanol C (mol L ⁻¹)	E _{oc} (V / NHE)	m	b (mV dec ⁻¹)	α	j ₀ (mA cm ⁻²)
RhRuOs (N_2 / 90 °C)	0.0	0.856	0.98	150.29	0.42	2.26×10^{-5}
	1.0	0.855	0.99	137.54	0.46	8.79×10^{-6}
	2.0	0.844	1.00	139.19	0.46	8.24×10^{-6}
RhRuOs (H_2 / 90 °C)	0.0	0.842	0.99	193.21	0.31	5.62×10^{-5}
	1.0	0.839	0.99	184.63	0.32	4.50×10^{-5}
	2.0	0.835	0.98	179.72	0.33	4.31×10^{-5}
Pt / Vulcan® (30%)	0.0	1.01	1.00	74.56	0.81	1.41×10^{-6}

HOR KINETIC PARAMETERS

Catalyst	[CO]	b (mV dec ⁻¹)	α	j ₀ (mA cm ⁻²)
RhRuOs (N_2 / 90 °C)	0.0	60.67	0.99	0.45
	100 ppm	62.49	0.96	0.30
	0.5%	59.06	1.00	0.21
RhRuOs (H_2 / 90 °C)	0.0	66.95	0.99	0.25
	100 ppm	63.61	0.94	0.24
	0.5%	60.15	0.90	0.19
Pt / Vulcan® (30%)	0.0	31.58	0.90	0.80

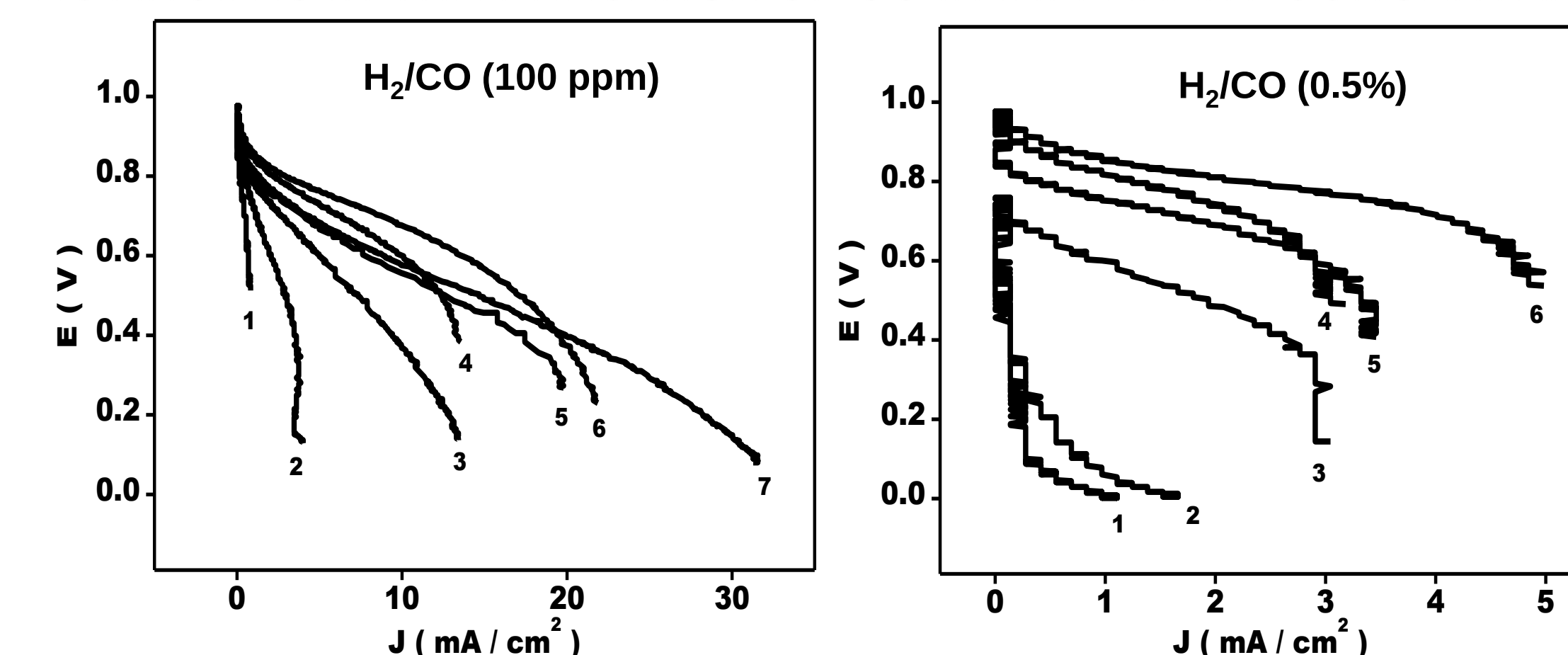
FUEL CELL PERFORMANCE EVALUATION

- REPRESENTATIVE POLARIZATION CURVES OF CATALYSTS EVALUATED AS CATHODES (USING PURE O_2) AND ANODES (USING PURE H_2)



1) $\text{Ir}_y(\text{CO})_n - \text{Ir}_x(\text{N}_2/230^\circ\text{C})$, 2) $\text{Ir}_4(\text{CO})_{12}$, 3) $\text{Ir}_y(\text{H}_2/190^\circ\text{C})$, 4) $\text{Rh}_2(\text{N}_2/190^\circ\text{C})$, 5) $\text{Rh}_6(\text{CO})_{16}$, 6) $\text{Rh}_2(\text{o-DCB})$, 7) Pt/Vulcan® (30 %). For all cases, the anode was Pt/Vulcan® (30 %).

- REPRESENTATIVE POLARIZATION CURVES OF CATALYSTS EVALUATED AS ANODES IN THE PRESENCE OF CO IN DIFFERENT CONCENTRATIONS



1) $\text{Ir}_4(\text{CO})_{12}$, 2) $\text{Rh}_2(\text{o-DCB})$, 3) $\text{Ir}_y(\text{CO})_n - \text{Ir}_x(\text{N}_2/230^\circ\text{C})$, 4) $\text{Rh}_2(\text{N}_2/190^\circ\text{C})$, 5) $\text{Ir}_y(\text{H}_2/190^\circ\text{C})$, 6) $\text{Rh}_6(\text{CO})_{16}$, 7) Pt/Vulcan® (30 %). For all cases, the cathode was Pt/Vulcan® (30 %).

CONCLUSIONS

The new and novel catalysts were obtained under different synthesis conditions by pyrolysis and thermolysis; some of these materials show terminal carbonyl stretching vibration bands around 2000 cm^{-1} , however these bands are very weak for the materials obtained by pyrolysis in a reductive atmosphere, which is an indicative that thermal process decarbonylated completely the precursor materials, as we can corroborated by XRD and EDS, since the corresponding peaks of metal particles are observed and the % weight for carbon and oxygen are very poor or even they are not present in the material, respectively. The most of catalytic materials can perform the ORR and HOR even in the presence of methanol (1.0 and 2.0 mol L^{-1}) and carbon monoxide in different concentrations (100 ppm and 0.5% in mixtures with H_2), respectively. The kinetic parameters of the novel catalysts do not change importantly even in the presence of fuel cell contaminants. These results contrast those of platinum commercial fuel cell catalysts, which become easily deactivated by CO levels of a few ppm. The results show that the new materials are good potential candidates to be used as both cathodes and anodes in PEMFCs, not only using pure or green hydrogen but also using reformed or grey hydrogen. However, it is important that measurements made with this type of technology are reliable and traceable, using appropriate calibrators and, above all, evaluating the performance of the catalysts and fuel cells, using reference systems that allow the different input magnitudes to be controlled, such as pressure, flow and relative humidity of the reactive gases, as well as the output magnitudes, for example, open circuit potential, current density and power density.

REFERENCES

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