Clean hydrogen production from electro-reforming of oxygenated organic compounds

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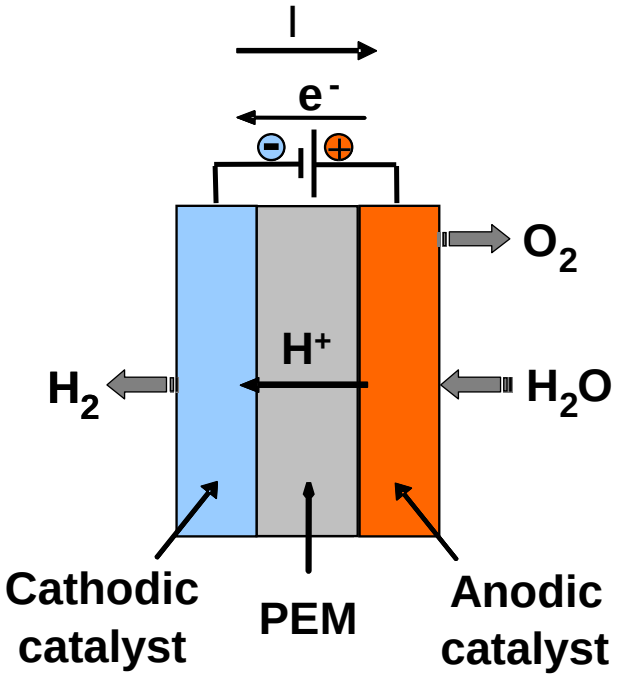
Co-responsible "Catalysis and Non-conventional Media" group of IC2MP
UMR CNRS-University of Poitiers n° 7285

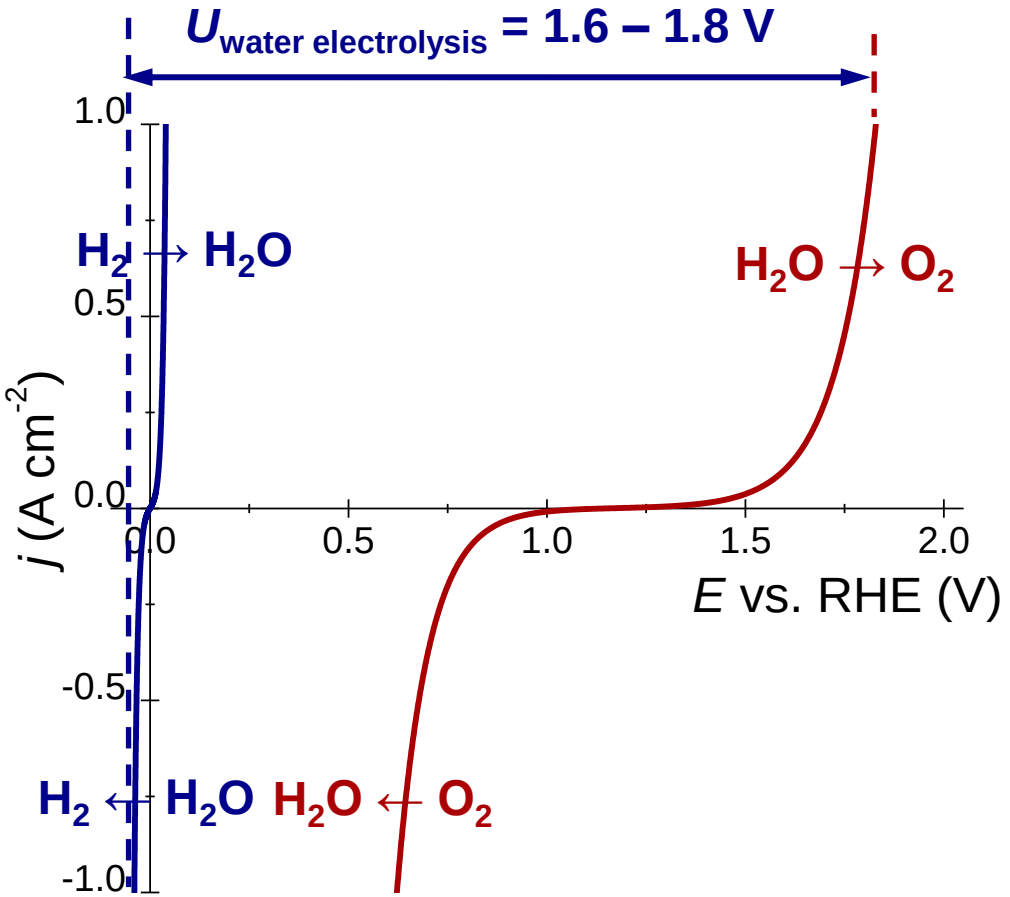
Project manager at the "Energie hub" of CNRS

Water electrolysis



Overall reaction

$H_2O \rightarrow H_2 + ½O_2$



$$W_e \text{ (in kWh/Nm}^3) = \frac{n_e F}{3600 V_m \times 10^3} U_{cell}(j) \approx 2.364\, U_{cell}(j)$$

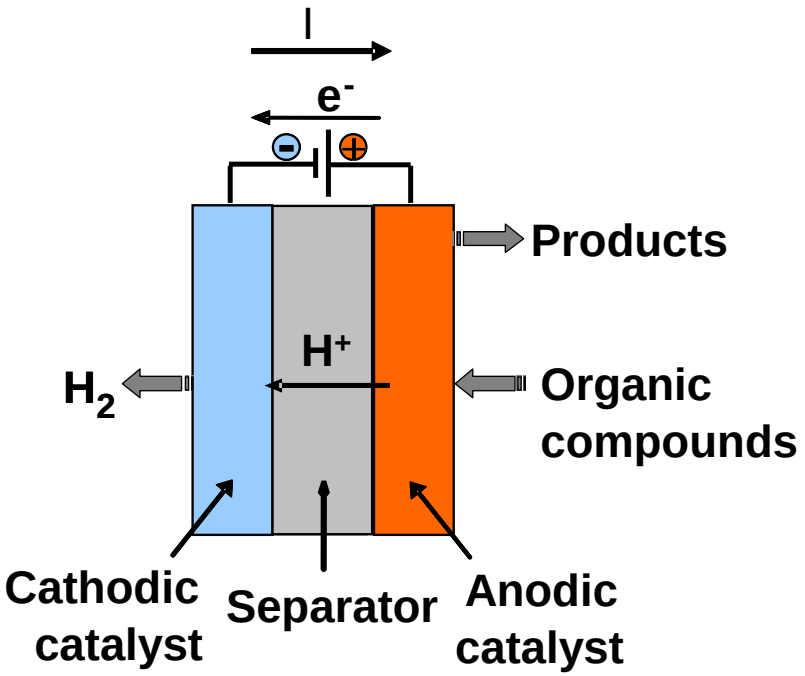
W_e = 3.8 – 4.3 kWh / sm³

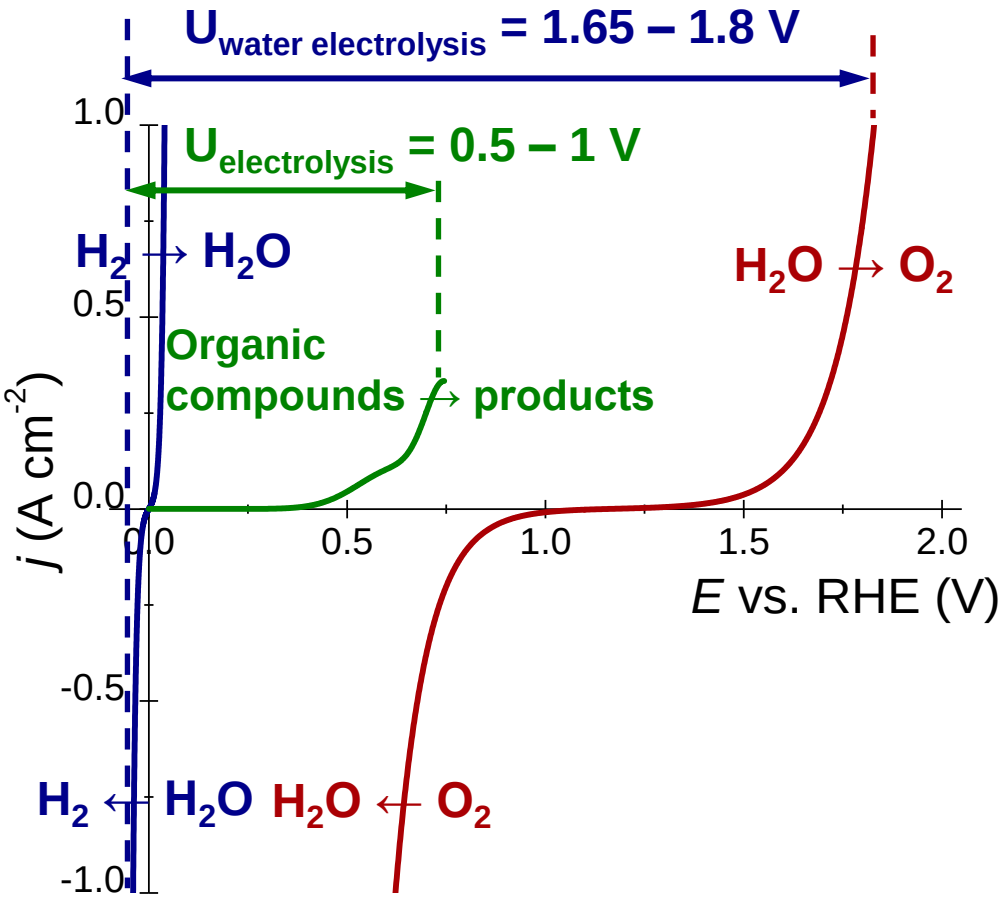
Water electrolysis vs. electroreforming of oxygenated compounds

Compound	n_{H_2} / mole	ΔH^{+0} / kJ mol^{-1}	Δh^{+0} / kJ mol H_2^{-1}	ΔG^{+0} / kJ mol^{-1}	$U_{cell}^{0} \approx + \Delta G^{+0}/nF$ (V vs. SHE)
H_2O	1	+ 286	+ 286	+ 237	1.23
HCOOH	1	+ 32	+ 32	- 33	- 0.17
CH_3OH	3	+ 131.2	+ 44	+ 9.3	0.016
C_2H_5OH	6	+ 348	+ 58	+ 97.3	0.084
CH_2OH-CH_2OH	5	+ 240	+ 48	+ 17.2	0.018
1-C_3H_7OH	9	+ 545	+ 61	+ 170	0.098
DMM $CH_2(OCH_3)_2$	8	+ 340.6	+ 42.6	- 5.6	- 0.004
CH_2OH-CHOH-CH_2OH	7	+ 350	+ 50	- 1	- 0.001
1-C_4H_9OH	12	+ 754	+ 63	+ 205	0.177
Glucose	12	+ 627.1	+ 52.3	- 27.4	- 0.012

C. Lamy, C. Coutanceau, S. Baranton, Production of clean hydrogen by electrochemical reforming of oxygenated organic compounds, in “Hydrogen Energy and Fuel Cells Primers”, B. Pollet (Ed.), Elsevier, Amsterdam, 2020. ISBN: 978-0-12-821500-5.

Co-production of high purity H_2 and value-added products



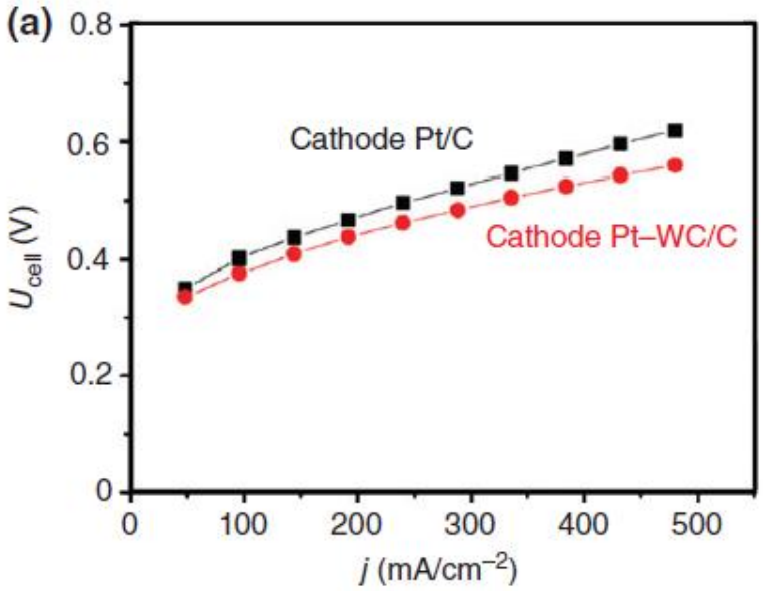


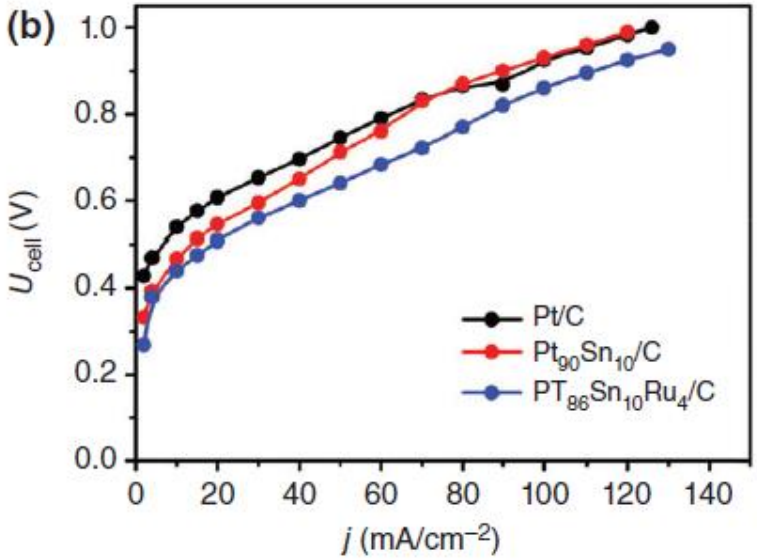
S. Baranton, C. Coutanceau,, Nickel cobalt hydroxide nanoflakes as catalysts for the hydrogen evolution reaction, Appl. Catal. B: environmental 136-137 (2013) 1-8.

Y. X. Chen, A. Lavacchi, H. A. Miller, M. Bevilacqua, J. Filippi, M. Innocenti, A. Marchionni, W. Oberhauser, L. Wang, F. Vizza, Nanotechnology Makes Biomass Electrolysis More Energy Efficient than Water Electrolysis., Nature Comm. 5 (2014)

W_e = 1.2 – 2.4 kWh / sm³

Electroreforming of oxygenated compounds





Electrolysis cell voltage versus current density $U_{cell}(j)$ for the oxidation in proton exchange membrane electrolysis cells (PEMEC)

(a) 2 M MeOH (anode PtRu/C) at 90°C

Hu Z, Wu M, Wei Z, Songa S, Shen PK. Pt-WC/C as a cathode electrocatalyst for hydrogen production by methanol electrolysis. J Power Sources 166 (2007) 458–461.

(b) 2 M EtOH (cathode Pt/C) at 20°C.

Lamy C, Jaubert T, Baranton S, Coutanceau C. Clean hydrogen generation through the electrocatalytic oxidation of ethanol in a proton exchange membrane electrolysis cell (PEMEC). Effect of the nature and structure of the catalytic anode. J Power Sources 245 (2014) 927–936.

Reactions in a Direct Alcohol Proton Exchange Membrane Electrolysis Cell

Méthanol: $CH_3OH + H_2O \rightarrow CO_2 + 3\ H_2$

Ethanol: $CH_3\text{-}CH_2OH + 3\ H_2O \rightarrow 2\ CO_2 + 6\ H_2$

$CH_3\text{-}CH_2OH + H_2O \rightarrow CH_3\text{-}CO_2H + 2\ H_2$

$CH_3\text{-}CH_2OH \rightarrow CH_3\text{-}CHO + H_2$

C. Coutanceau, S. Baranton. Electrochemical conversion of alcohols for hydrogen production: a short overview. WIREs Energy Environ 2016. doi: 10.1002/wene.193

Catalyst		AL	AA	CO_2	Calculated $n_e^{(*)}$
Pt / C	U_{cell} / V		0.92 – 0.97		3.5
	Chemical yield / mol %	**46**	**42**	**12**	
$Pt_{0.9}Sn_{0.1}$ / C	U_{cell} / V		0.92 – 0.97		4.6
	Chemical yield / mol %	**31**	**41**	**28**	
$Pt_{0.86}Sn_{0.1}Ru_{0.04}$ / C	U_{cell} / V		0.80 – 0.96		4.5
	Chemical yield / mol %	**39**	**32**	**29**	

$$C_2H_5OH + H_2O \rightarrow CH_3COOH + 2\ H_2$$

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$CH_3\text{-}CH_2OH \rightarrow CH_3\text{-}CHO + H_2$

Activation of water at U_{cell} <<< 1.23 V

C. Coutanceau, S. Baranton. Electrochemical conversion of alcohols for hydrogen production: a short overview. WIREs Energy Environ 2016. doi: 10.1002/wene.193

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$$C_2H_5OH + H_2O \rightarrow CH_3COOH + 2\ H_2$$

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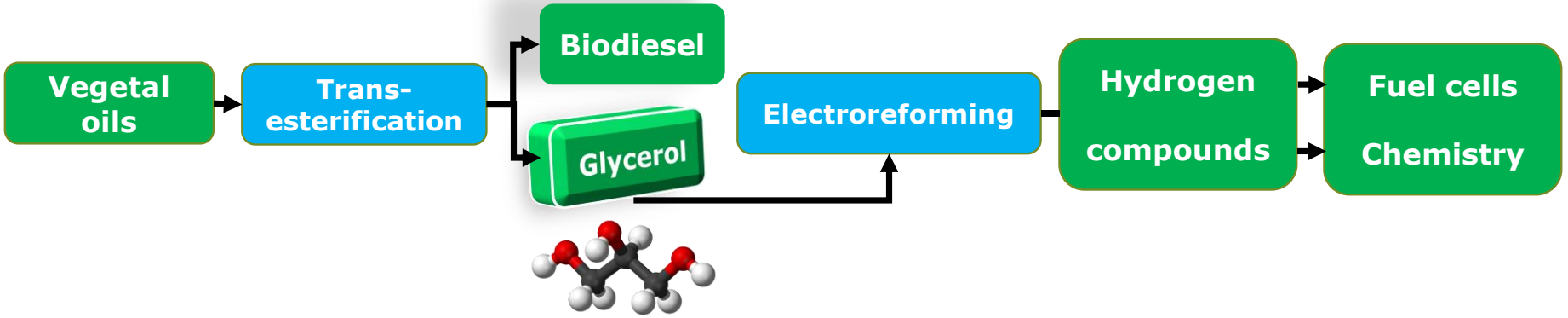
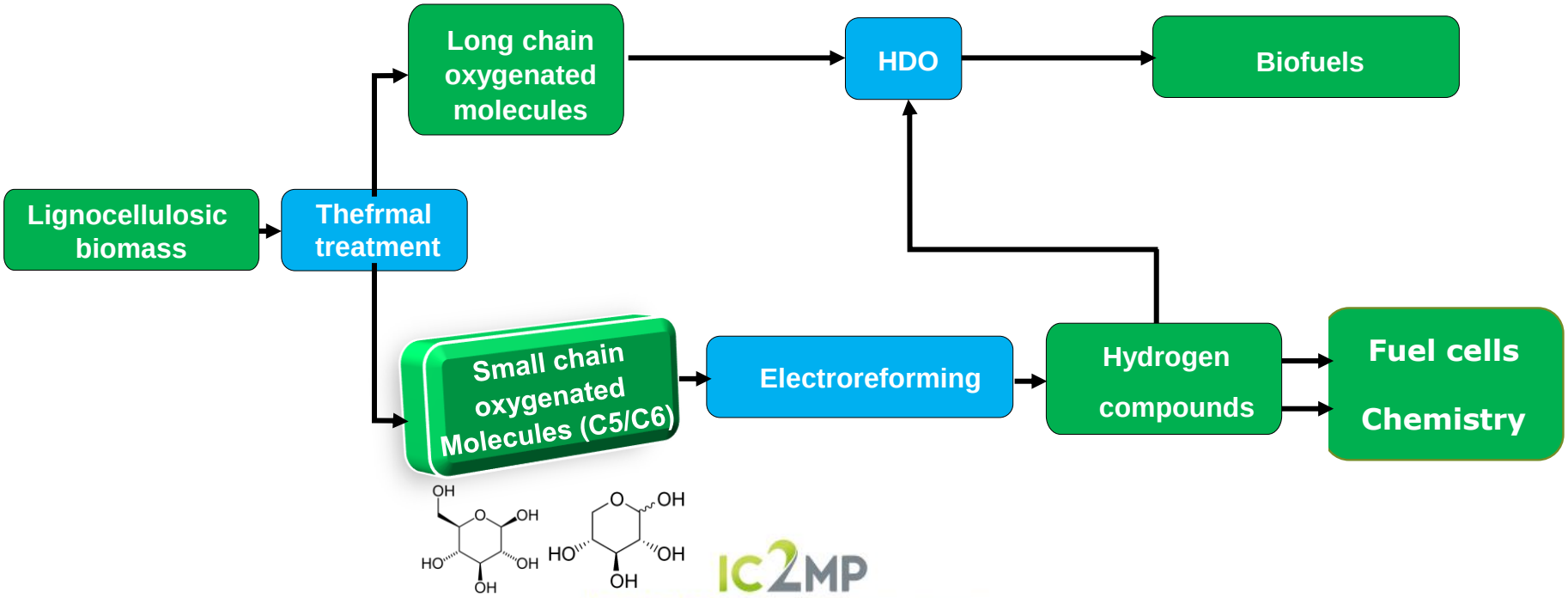
1st generation biofuels



2nd generation biofuels



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Reaction medium

- Molecules such as polyols and sugars more electroreactive in alkaline media
    - Base-catalyzed reaction favoured
    - possibility of using non noble metals

- C-C bond cleavage more difficult in alkaline media at low potentials
    - Enhancement of the selectivity
    - Co-production of hydrogen and high value-added compounds

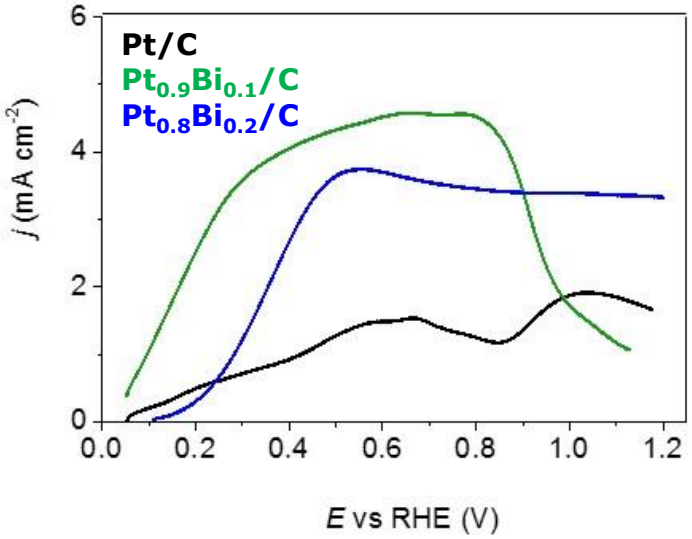
Electrocatalytic materials

PtBi materials known to be catalytically very active towards biomass conversion for a long time

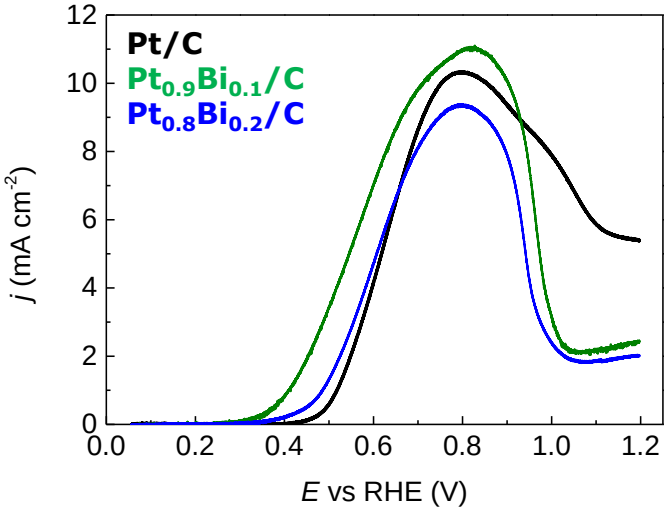
- T. Mallat, A. Baiker, Oxidation of alcohols with molecular oxygen on platinum metal catalysts in aqueous solutions . Catal. Today 19 (1994) 247 – 284
- P. Gallezot, Selective oxidation with air on metal catalysts. Catal. Today 37 (1997) 405 –418

PtBi catalysts are also very electroactive materials for biomass conversion

- M. Simões, S. Baranton, C. Coutanceau. Enhancement of catalytic properties for glycerol electrooxidation on Pt and Pd nanoparticles induced by Bi surface modification . Applied Catalysis B: Environmental 110 (2011) 40 – 49
- J. Cobos-Gonzalez, S. Baranton, C. Coutanceau . Development of Bi-Modified PtPd Nanocatalysts for the Electrochemical Reforming of Polyols into Hydrogen and Value-Added Chemicals ChemElectroChem 3 (2016) 1694–1704
-N. Neha, T. rafaïdeen, R. B. S. Kouamé, S. Baranton, C. Coutanceau , Remarkably Efficient Carbon-Supported Nanostructured Platinum-Bismuth Catalysts for the Selective Electrooxidation of Glucose and Methyl-Glucoside. Electrocatalysis 12 (2021) 1-14.



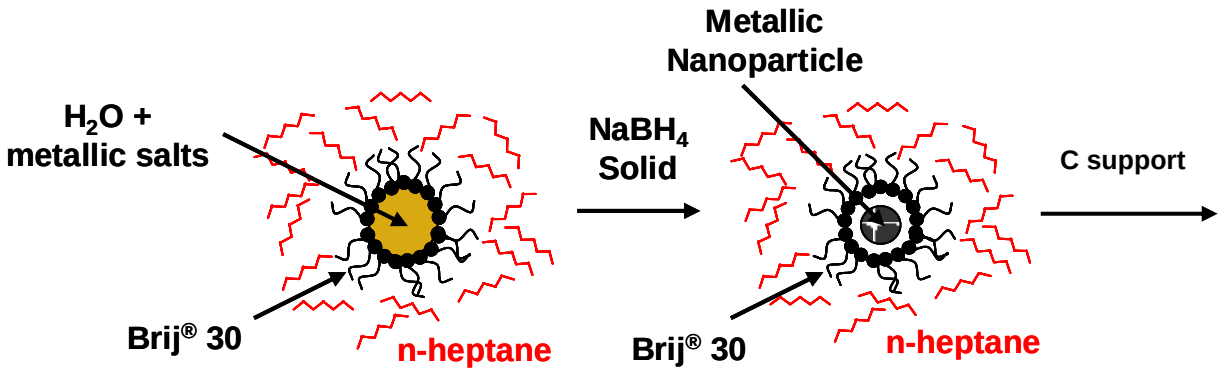
0.1 M glucose electrooxidation in 0.1 M NaOH, 20 °C, scan rate 0,005 V s^{-1}



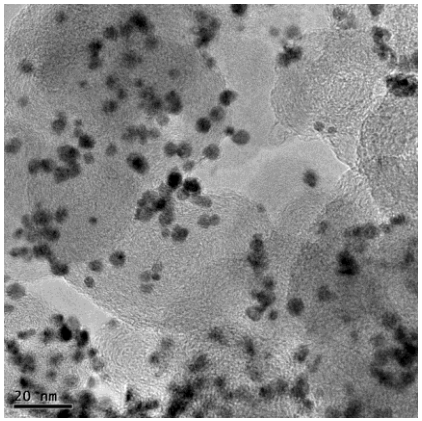
0.1 M glycerol electrooxidation in 0.1 M NaOH, 20 °C, scan rate 0,005 V s^{-1}

Sythesis of electrocatalytic materials

"Water in oil" microemulsion synthesis :



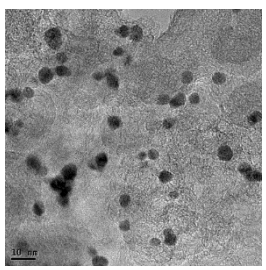
40 wt% M / C

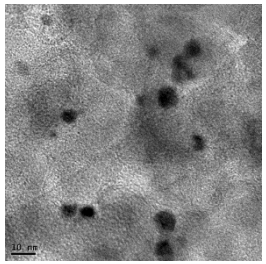


- Easy and rapid to implement
- Formation of nanoparticules from a wide range of metal salts
- Easy cleaning step

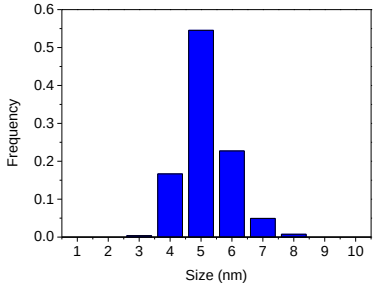
Characterization of electrocatalytic materials

TEM

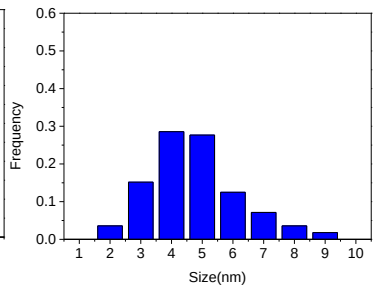




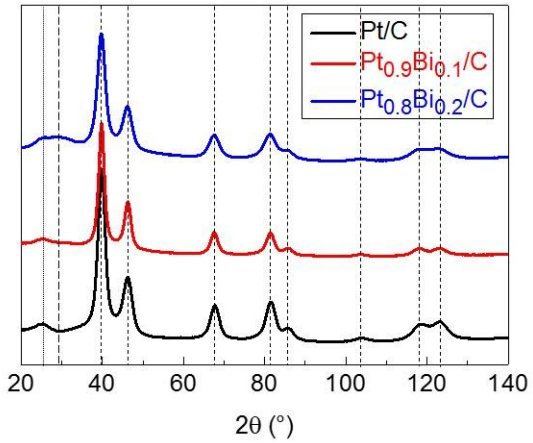
Pt/C



Pt_9Bi_1/C

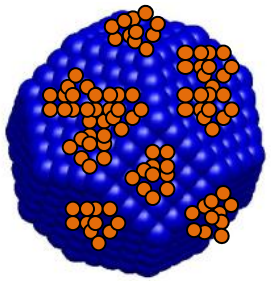


XRD



DRX, AAS, ICP-OES, XPS:

	Pt/C	Pt_9Bi_1/C		Pt_8Bi_2/C	
Comp. ICP-OES (at%)	100	Pt	Bi	Pt	Bi
		92	8	84	16
Comp. AAS (at%)	100	Pt	Bi	Pt	Bi
		88.2	11.8	78.2	21.8
d (nm)	5.2	4.7		4.7	
L_v (nm)	3.5	4.3		3.1	
a (nm)	0.3916	0.3919		0.3926	
Comp. XPS (at%)		Pt^0: 79	Bi_{total}: 21	Pt^0: 72	Bi_{total}: 28
			$Bi(OH)_2$: 72 $Bi(OH)_3$: 22 Bi_2O_4: 6		Bi^0 9 $Bi(OH)_2$: 34 $Bi(OH)_3$: 51 Bi_2O : 6



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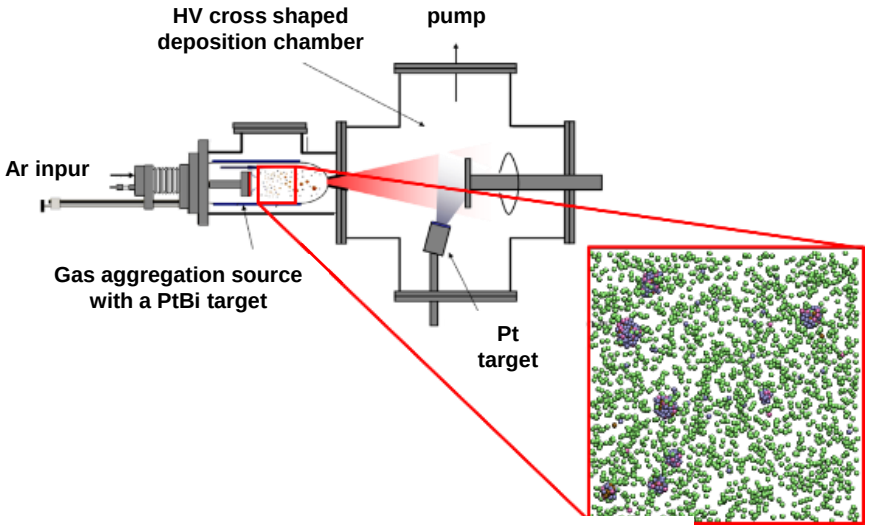
- B. S. R. Kouamé, S. Baranton, C. Canaff, P. Brault, W. Chamorro-Coral, A. Caillard, K. De Oliveira Vigier, C. Coutanceau. Insights on the unique electrocatalytic behavior of PtBi/C materials. Electrochim. Acta 329 (2020) 135161.

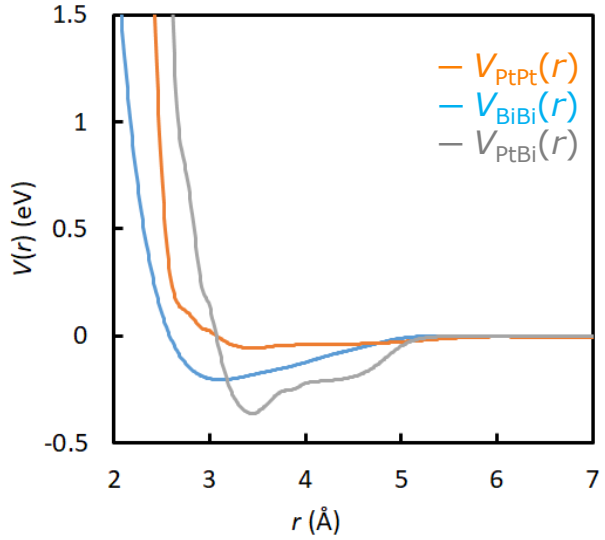
Molecular dynamics

For more information: pascal.brault@univ-orleans.fr
GREMI



Conditions for MDs calculation:

- Growth of Pt_nBi_{500-n} nanoparticles ($n \leq 500$) in GAS configuration
- To mimic the synthesis by wet chemistry
  - T maintained around 300 K (with low fluctuations) using a Berendsen thermostat.
  - The energy of clusters bond formation after collisions is transported and dissipated by the Ar atoms acting as the solvent in the case of the synthesis of nanoparticles by wet chemistry.



Interaction potentials as a function of the interatomic distance (*r*) used in the MD simulations.

- Pt-Bi bond strength > Pt-Pt and Bi-Bi bond strengths
- Pt-Bi equilibrium distance is larger than the Pt-Pt distance

=> Bi should be located on the outermost surface

=> strong electronic interaction between Pt and Bi

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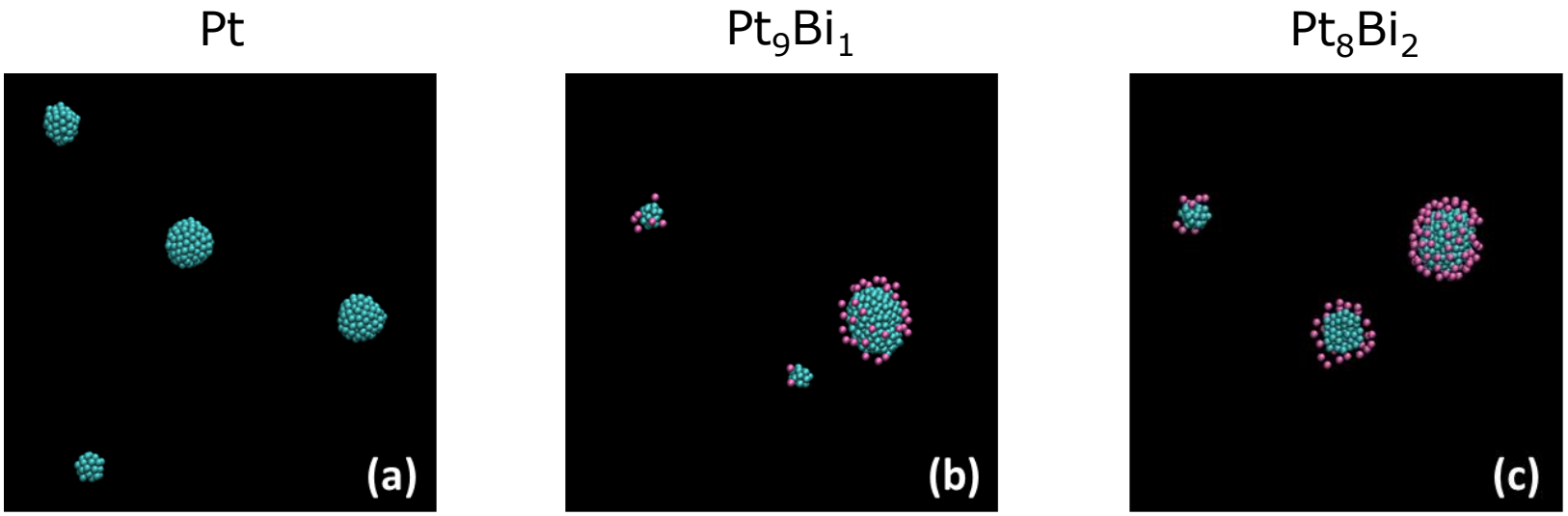
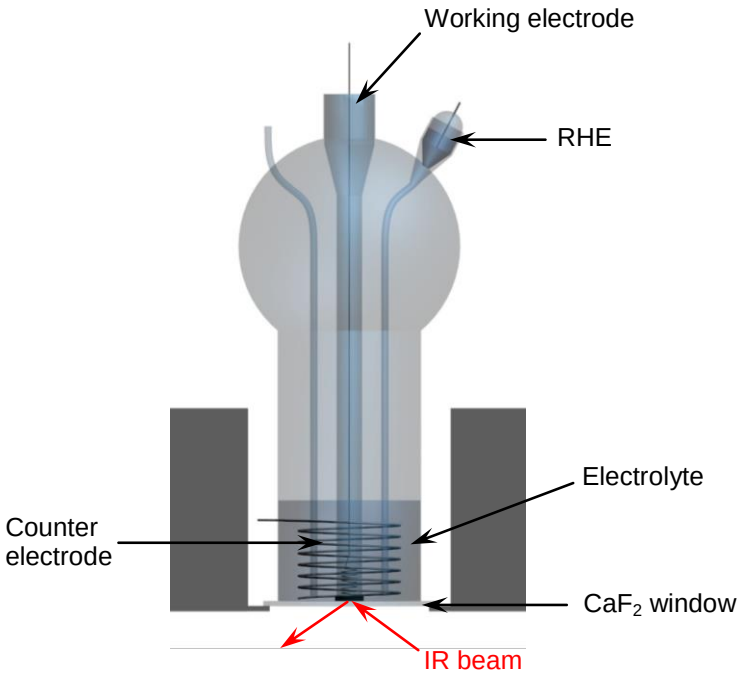


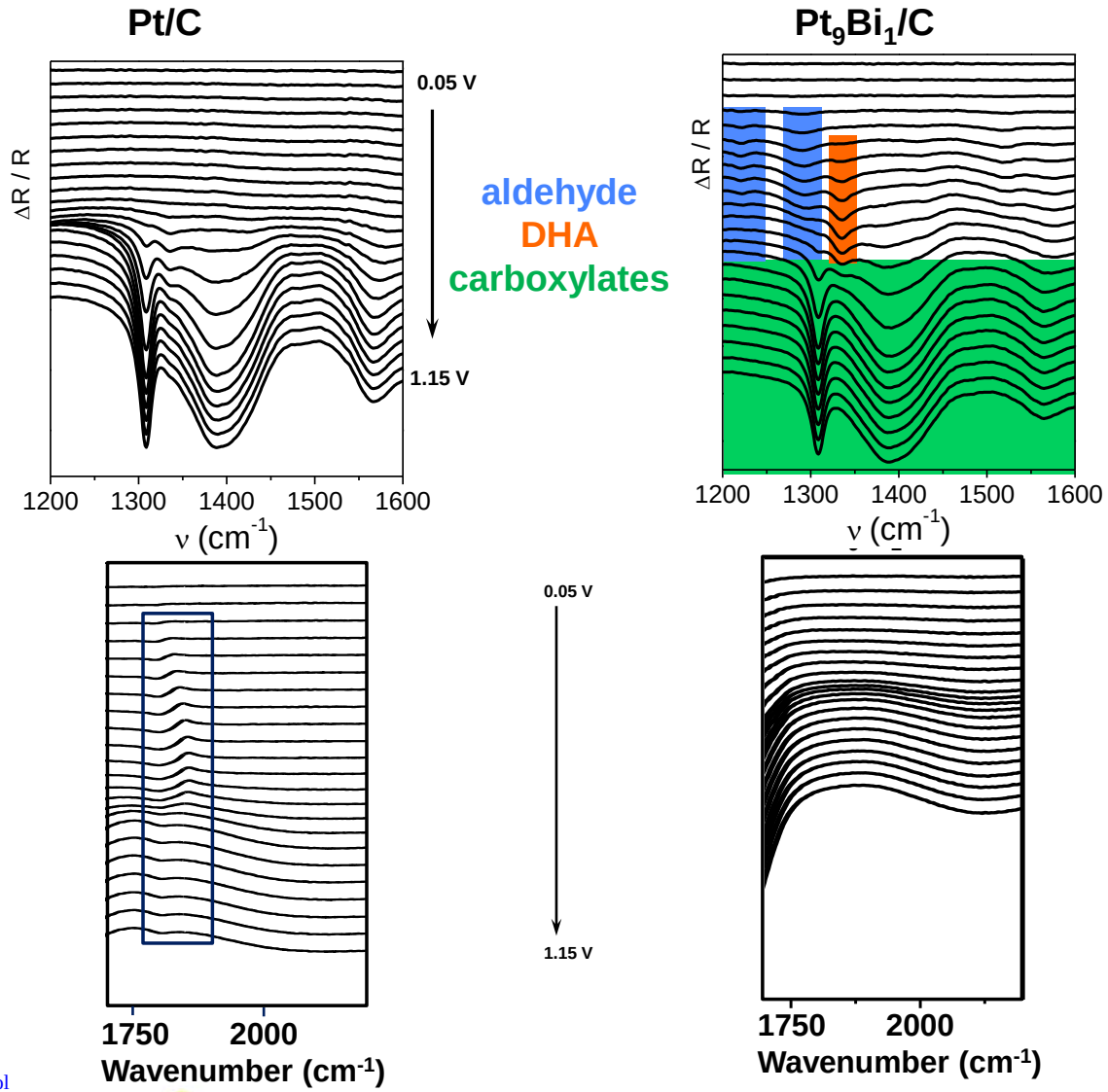
Snapshots at 20 ns for all considered $Pt_{1-x}Bi_x$ atomic compositions

- Bi atoms are always decorating Pt core clusters
- The Pt core is crystalline
- Each cluster is stoichiometric: Pt/Bi atomic composition globally and locally preserved
- For 20 at. % Bi ($Pt_{0.8}Bi_{0.2}$), the Pt core cluster is almost fully hidden by Bi atoms

Selectivity by in situ FTIRS: Glycerol



In situ IR electrochemical cell



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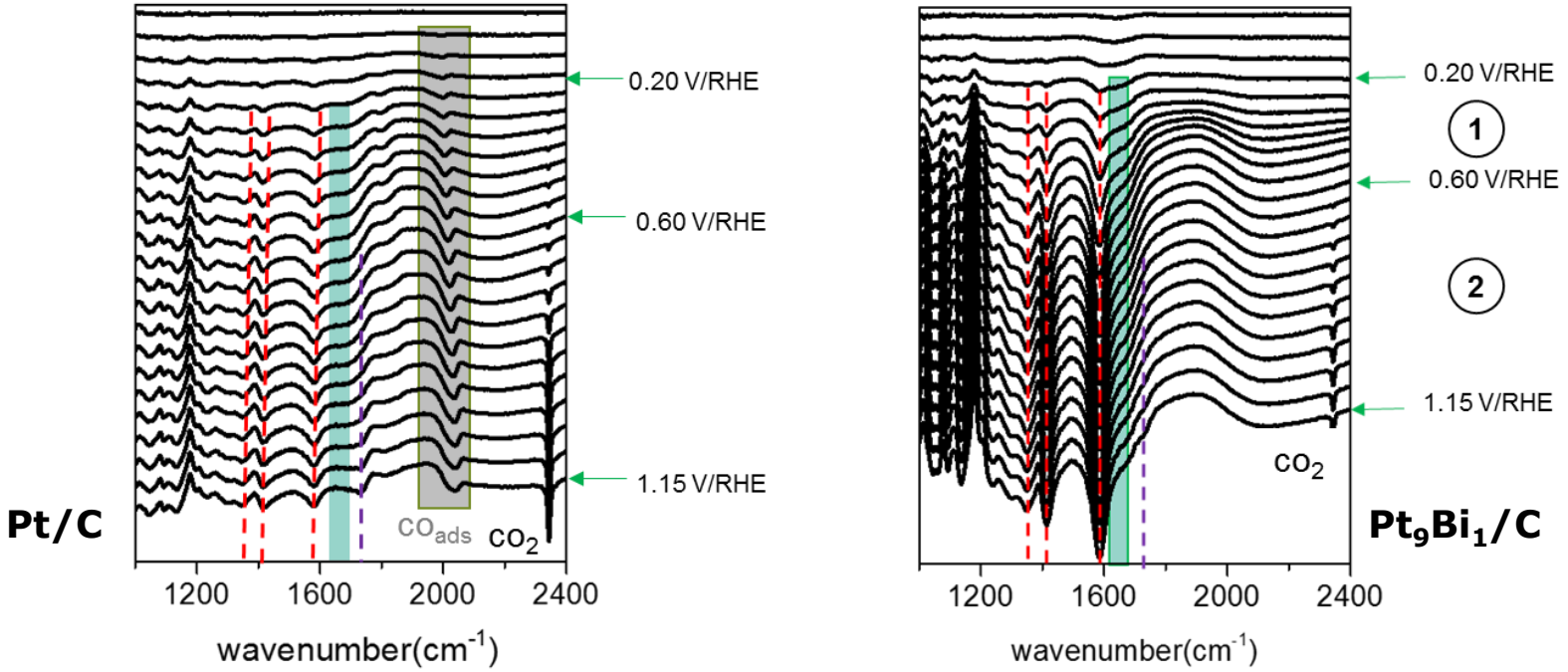
Selectivity by in situ FTIRS: glucose oxidation



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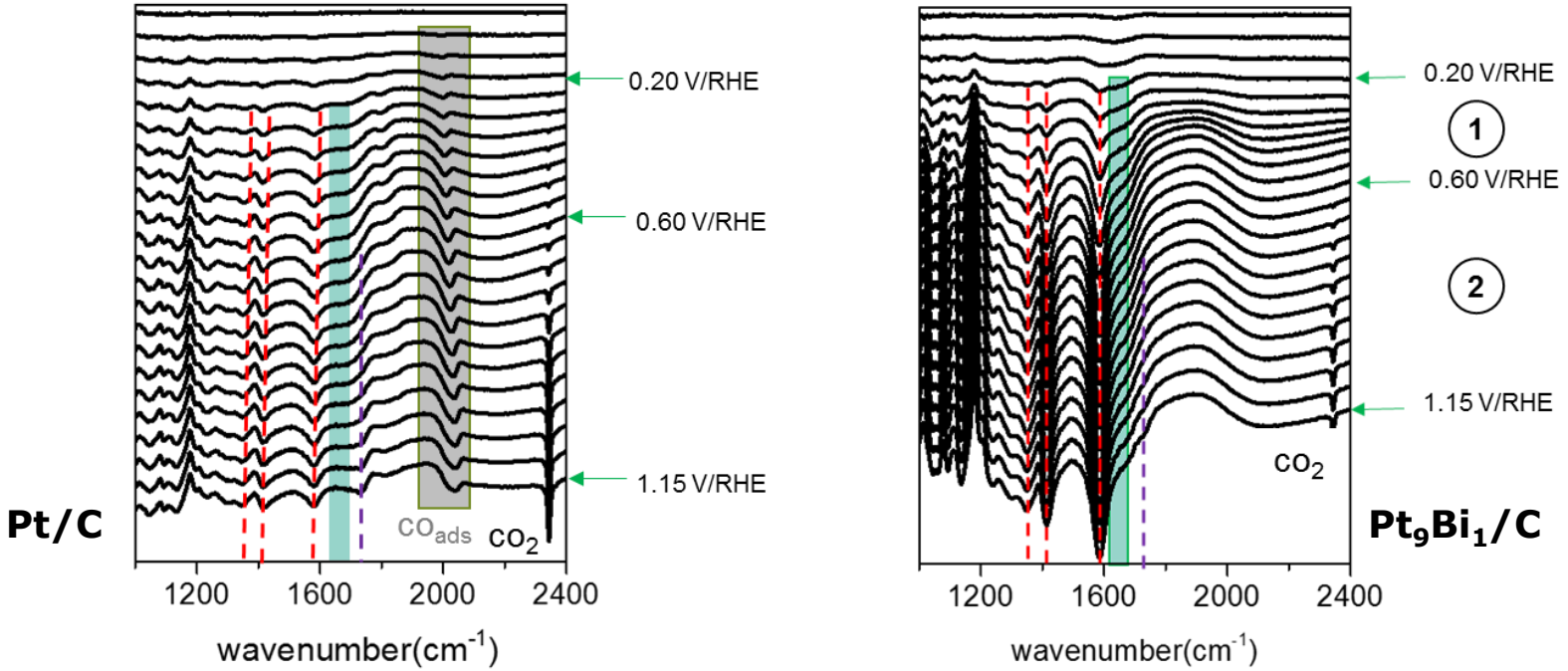

(1) E < 0.60 V/RHE: $Glucose_{sol} \longrightarrow Glucose_{ads} \xrightarrow{(OH^-)_{sol}}$ gluconate (Eley-readeal mechanism)

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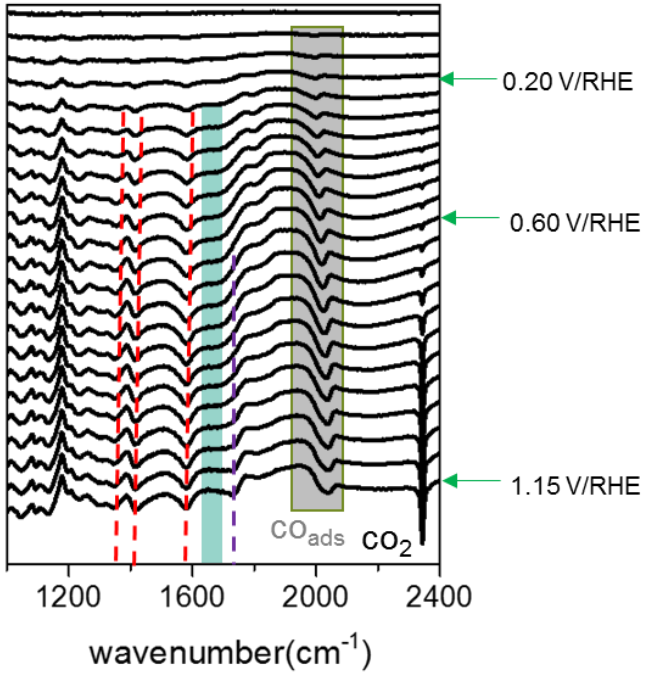
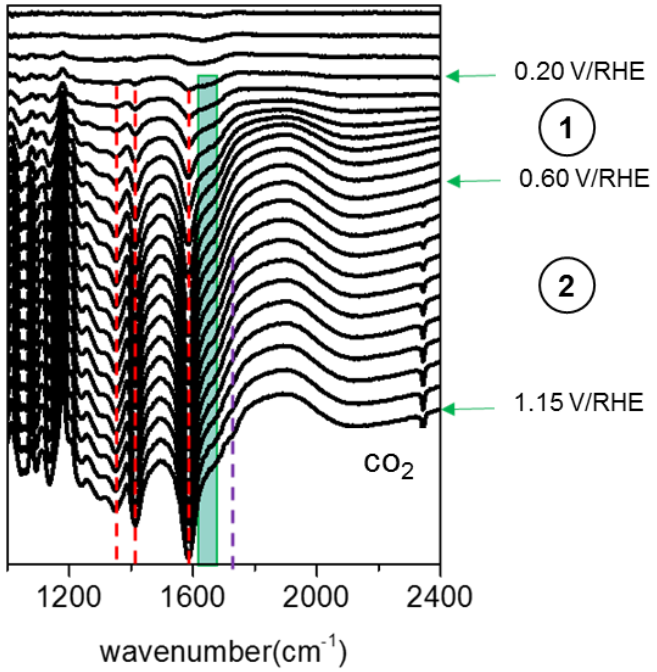




(1) E < 0.60 V/RHE: $Glucose_{sol} \longrightarrow Glucose_{ads} \xrightarrow{(OH^-)_{sol}}$ gluconate (Eley-readeal mechanism)

(2) E > 0.60 V/RHE : $Glucose_{sol} \longrightarrow lactone_{ads}$

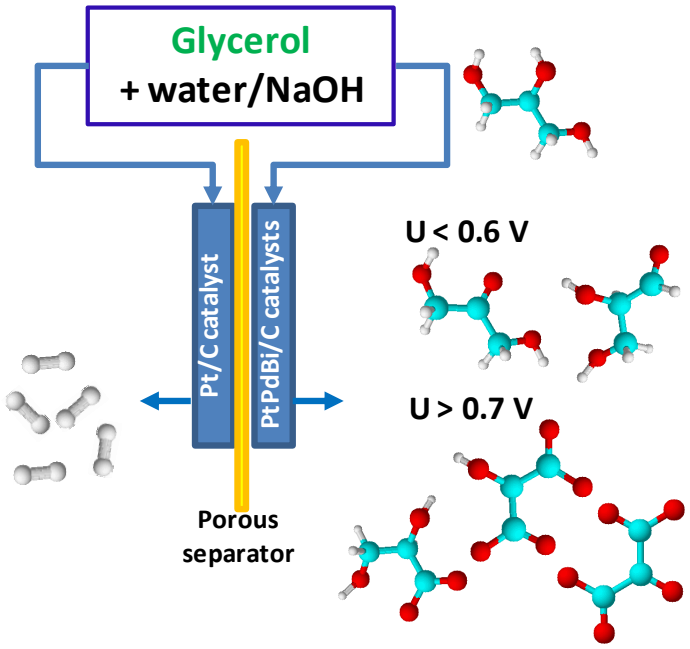
$Lactone_{sol} \xrightarrow{(OH^-)_{sol}}$ gluconate (hydrolysis)

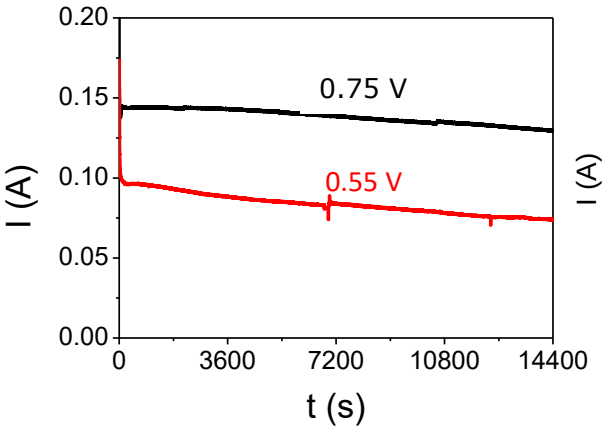
$Lactone_{ads} \xrightarrow{(OH)_{ads}}$ gluconate + CO_2 + dégradation products

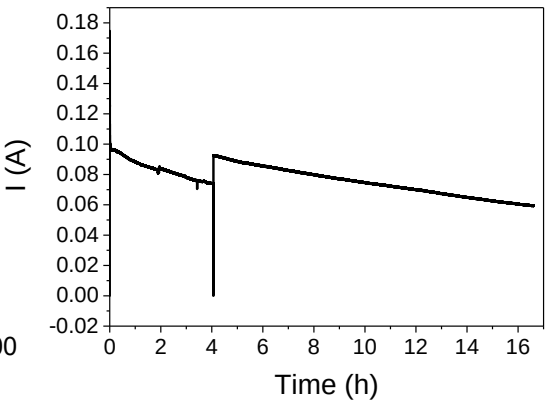
(Bifunctional mechanism)

N. Neha, T. rafaïdeen, R. B. S. Kouamé, S. Baranton, C. Coutanceau , Remarkably Efficient Carbon-Supported Nanostructured Platinum-Bismuth Catalysts for the Selective Electrooxidation of Glucose and Methyl-Glucoside. Electrocatalysis 12 (2021) 1-14.

Glycerol electroconversion







25 cm^{-2} electrolysis cell fitted with a Pt/C cathode and a Pt_9Bi_1/anode (electrodes: 1.6 mg cm_{metal}^{-2}); 2 M glycerol + 0.5 M NaOH, 20 °C flow rate = 2 mL min^{-1}

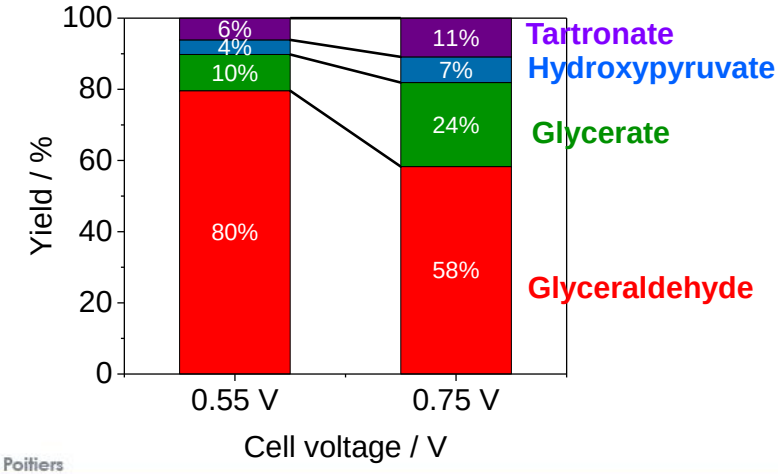
$$W_e \left(\text{in } \frac{\text{kWh}}{\text{Nm}^3}\right) We = \frac{n_e F}{3600 V_m \times 10^3} U_{cell}(j) \approx 2.364\, U_{cell}(j)$$

At 0.55 V: W_e = 1.3 kWh sm_{H2}^{-3}

At 0.75 V: W_e = 1.77 kWh sm_{H2}^{-3}

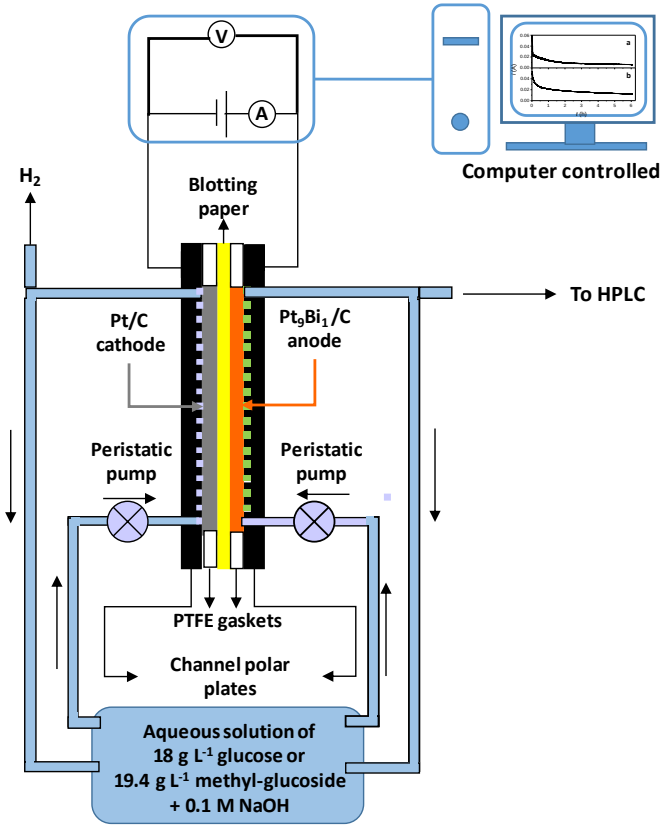
Water electrolysis: 3.8 – 4.3 kWh / Nm^3

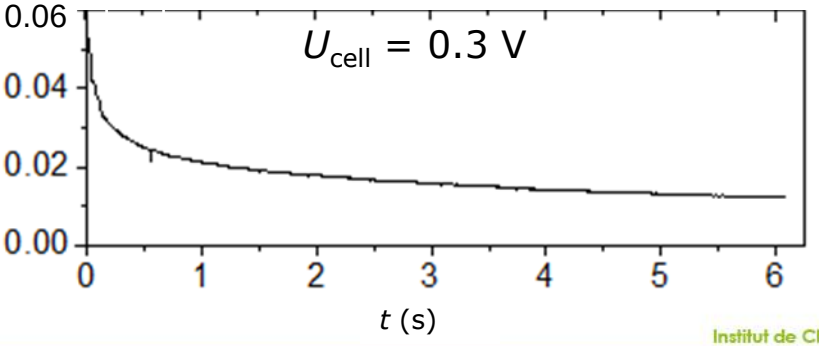
Reaction product distribution
(Except dihydroxyacetone)



J. Cobos-Gonzalez, S. Baranton, C. Coutanceau . Development of Bi-Modified PtPd Nanocatalysts for the Electrochemical Reforming of Polyols into Hydrogen and Value-Added Chemicals ChemElectroChem 3 (2016) 1694–1704

Glucose electroconversion





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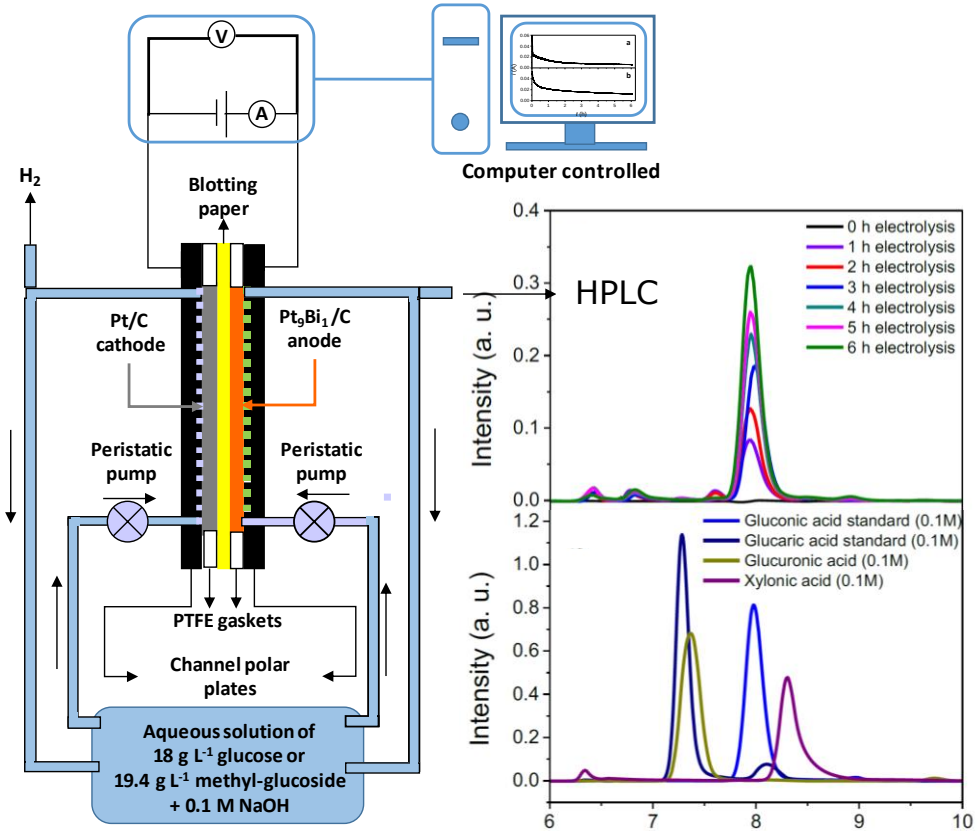
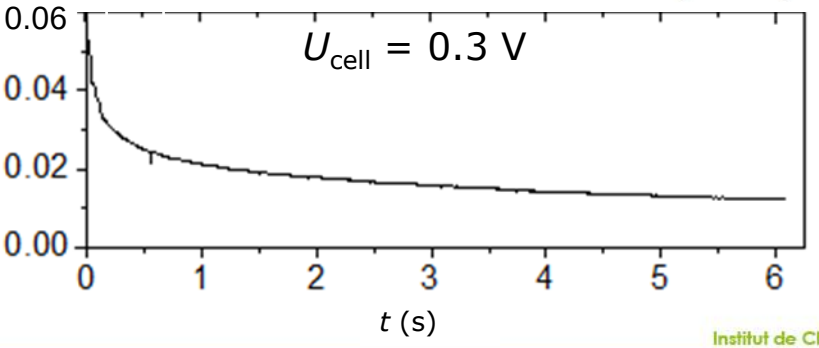
Glucose electroconversion





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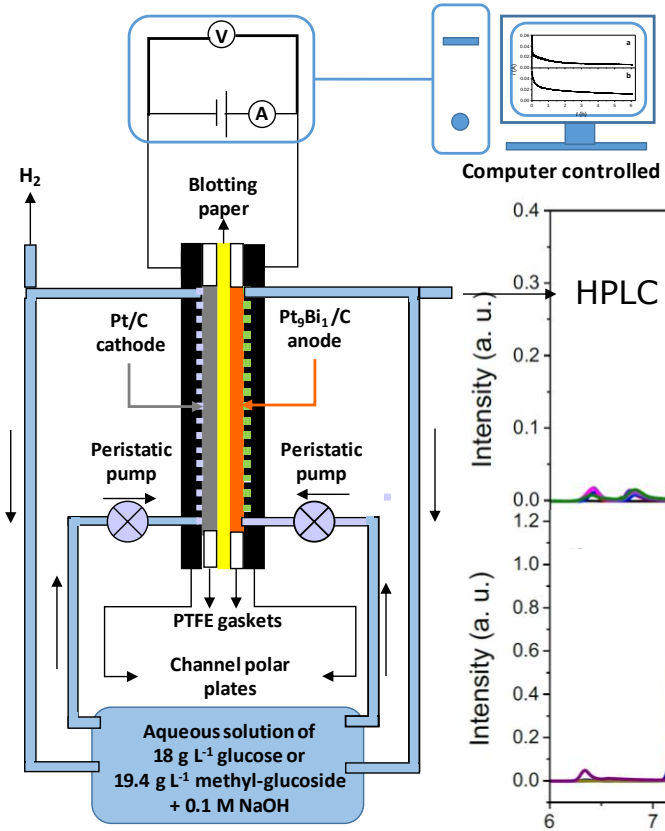
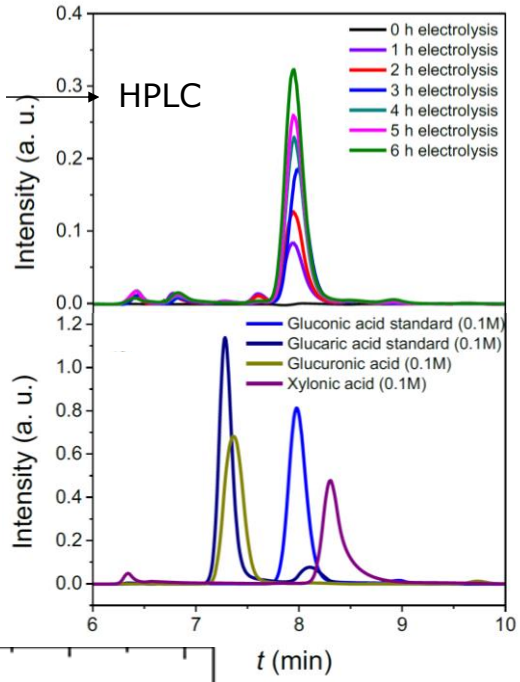
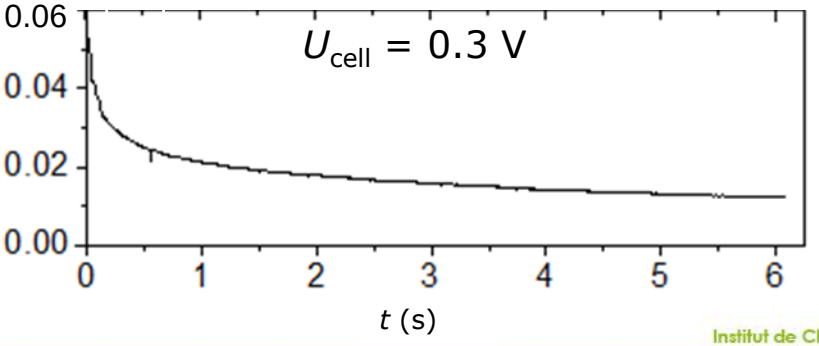
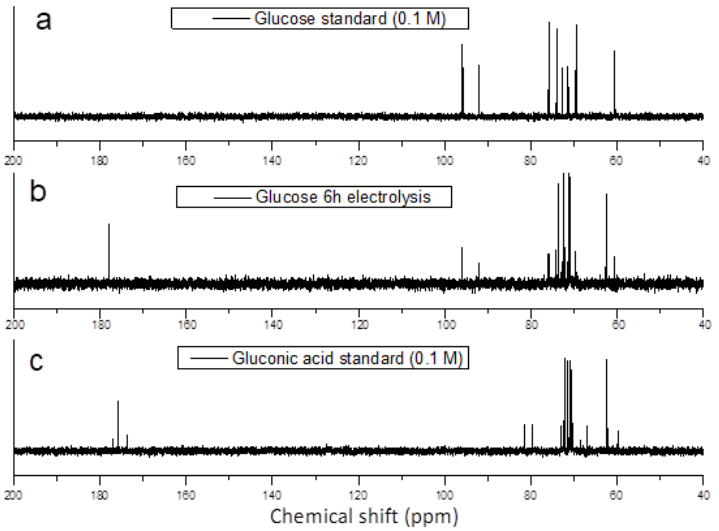
Glucose electroconversion

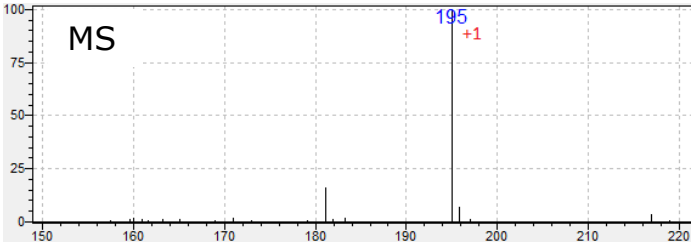


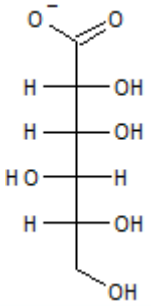




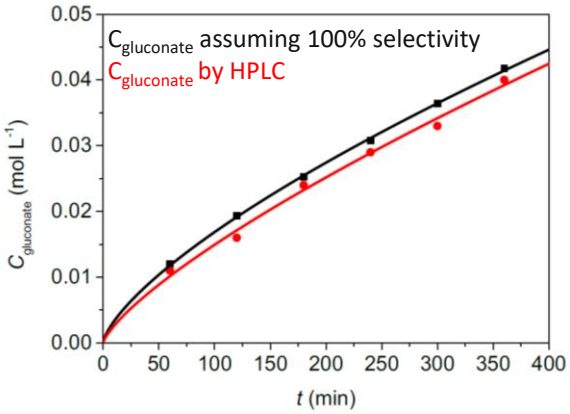
^{13}C NMR







Electroreforming of oxygenated compounds from biomass



Selectivity ~100 %; Faradaic yield ~100 %; ~40 % conversion

At 0.30 V: W_e = 0.71 kWh Nm_{H2}^{-3}
Water electrolysis: 3.8 – 4.3 kWh / Nm^3

Energy cost at 0.3 V: 1 molecule of H_2 is evolved by molecule of gluconate produced

$$C_6H_{12}O_6 + OH^- \rightarrow C_6H_{11}O_7^- + H_2$$

The production of 1 ton sodium gluconate is then accompanied with the evolution of 9 kg H_2

The specific electrical energy consumed at 0.3 V corresponds to ca. 8.05 kWh kg_{H2}^{-1}

Assuming a mean electricity cost of ca. 0.15 €/kWh in Europe, it corresponds to 11 €

Less than 3% of commercial prices for industrially produced sodium gluconate
600 to 750 US $, i.e. 750 to 950 CAD per ton (Dezhou Huiyang Biotechnology Co., Ltd., Wuxi Fengmin Environmental Technology Development Co., Ltd., etc.).

Low current densities

Low hydrogen production rate

Problem of hydroxyl ions migration from cathode to the anode

Reaction of sugars/reaction products at the cathode

=> Use of an AEM + ionomer

Increase of sugars/polyols concentrations

anode reaction $C_6H_{12}O_6 + 3\ OH^- \rightarrow C_6H_{11}O_7^- + 2\ H_2O + 2\ e^-$

cathode reaction $2\ H_2O + 2\ e^- \rightarrow 2\ OH^- + H_2$

Overall reaction $C_6H_{12}O_6 + OH^- \rightarrow C_6H_{11}O_7^- + H_2$

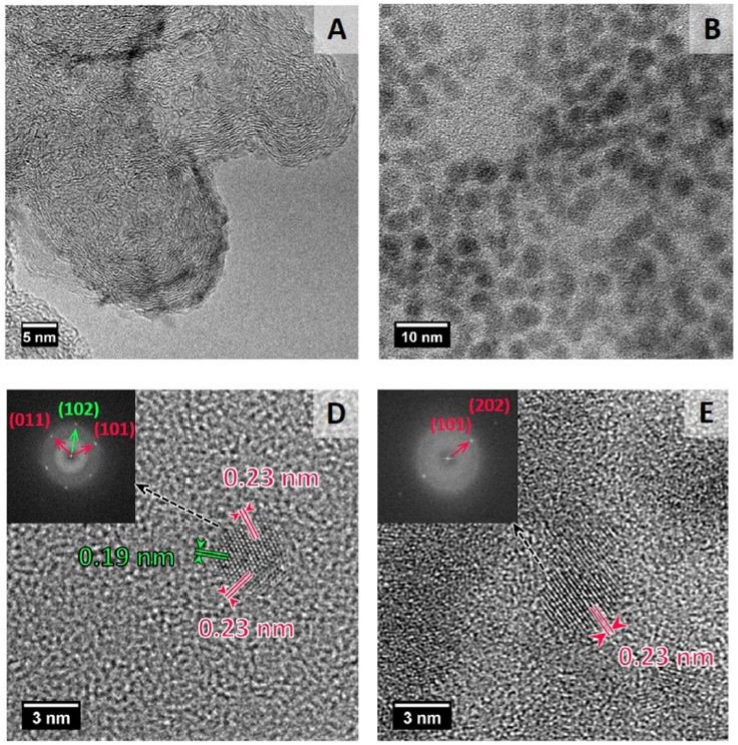
=> increase of the hydroxyl ions concentration => problem of molecules stability

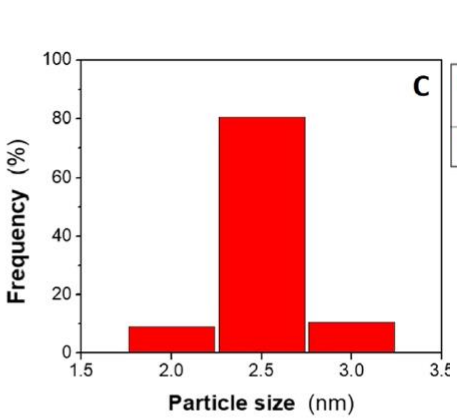
PGM based catalyst: high cost, strategic materials, availability, etc.

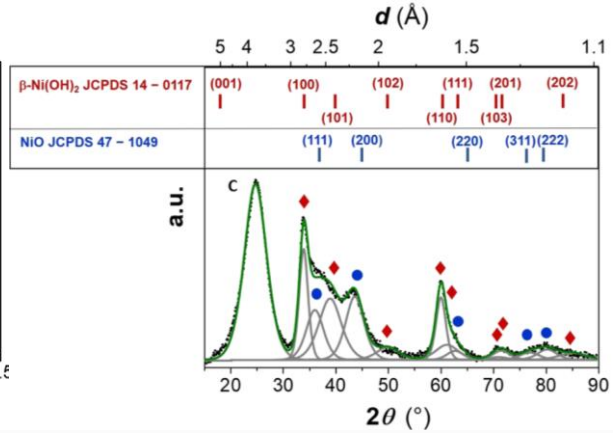
=> development of non-PGM catalysts, electroactive at a potential as low as possible and allowing achieving high current densities

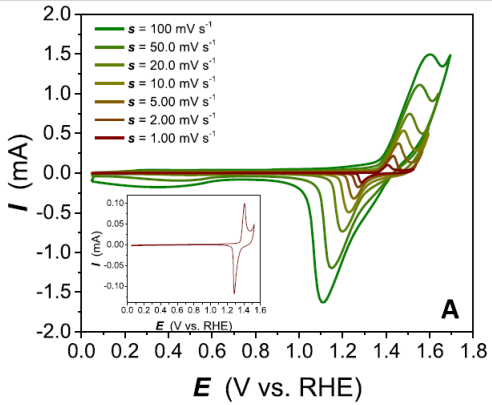
=> Nickel is known to be an active materials for alcohol electrooxidation

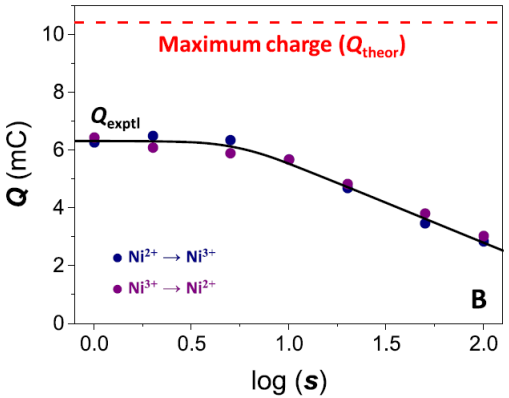
Synthesis on $Ni(OH)_2$ nanoparticles by the water in oil microemulsion method

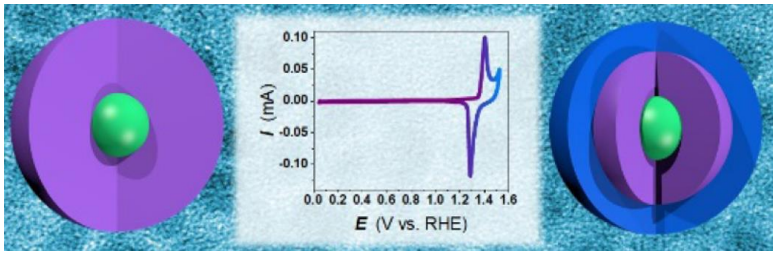








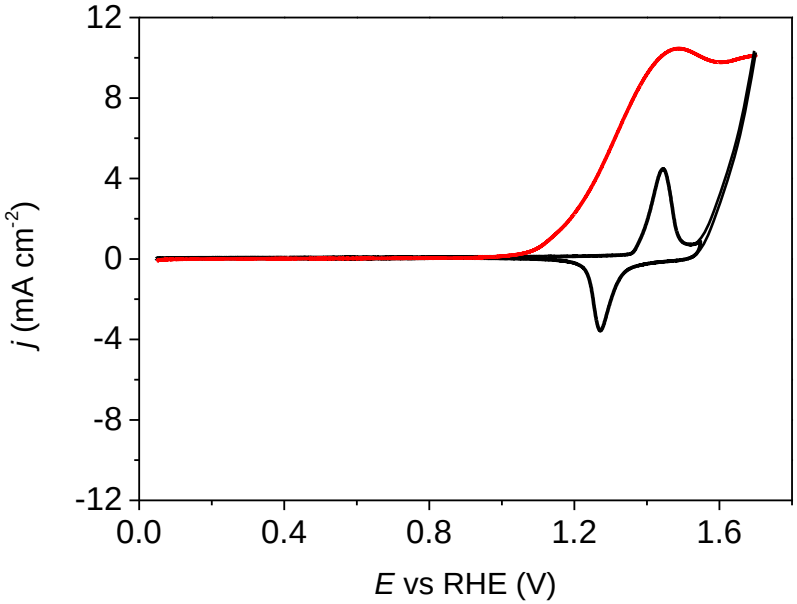




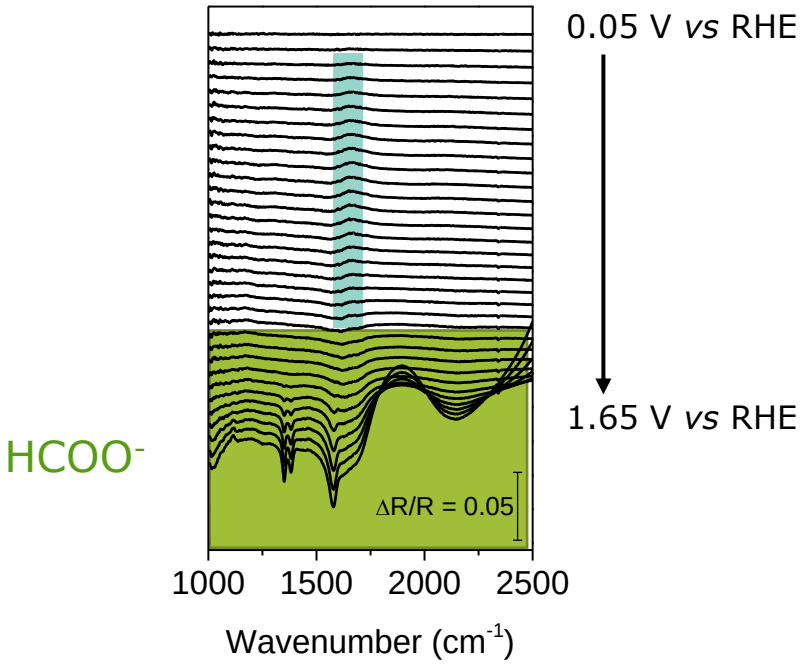
S. Tahmasebi, S. Jahangiri, N. Mosey, G. Jerkiewicz, A. Mark, S. Cheng, G. Botton, S. Baranton, C. Coutanceau. Remarkably Stable Nickel Hydroxide Nanoparticles for Miniaturized Electrochemical Energy Storage. ACS Appl. Energy Mater. 3 (2020) 7294−7305

NiO $Ni(OH)_2$ NiO(OH)

Activity and selectivity of $Ni(OH)_2$ nanoparticles towards glycerol electrooxidation

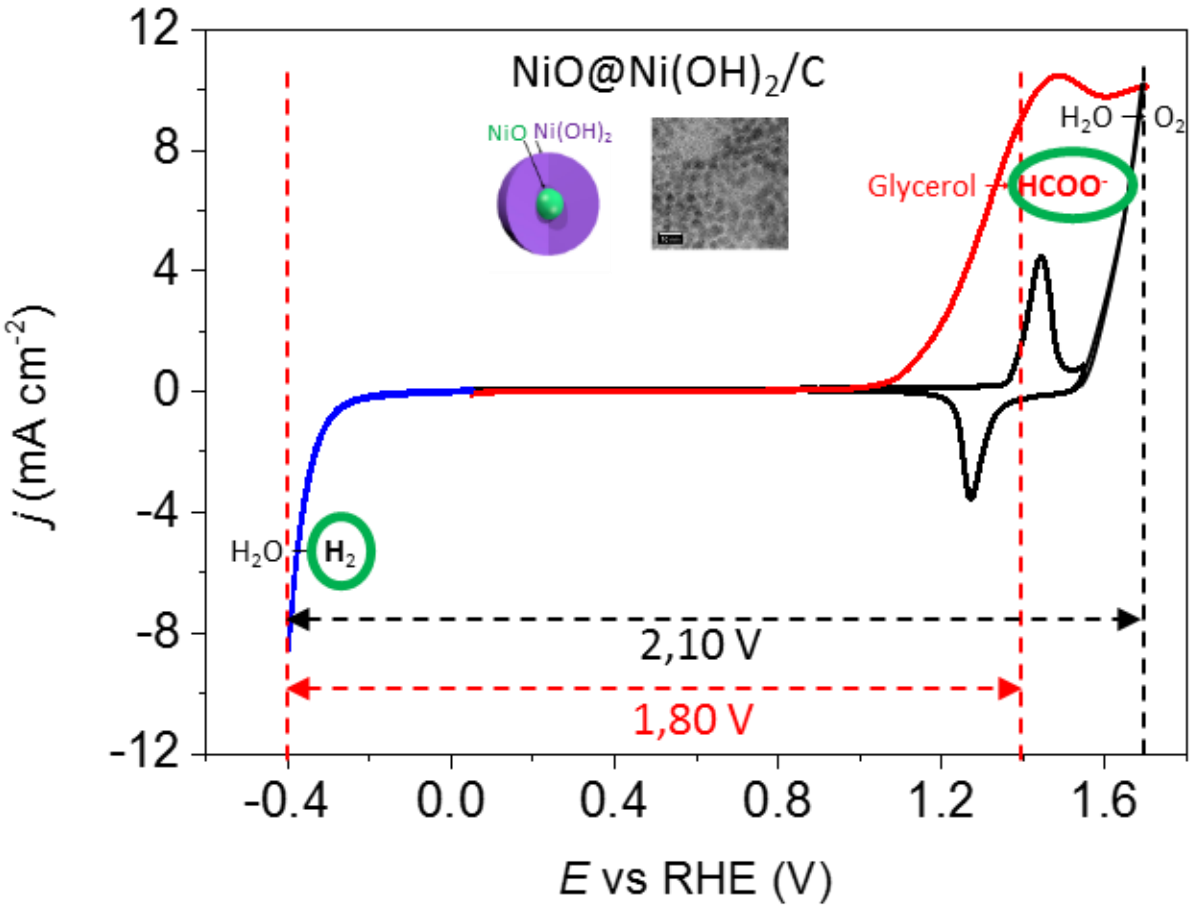


Cyclic voltammetry of a Ni/C catalysts recorded in 0.1 M NaOH (black line) and 0.1 M NaOH + 0.1 M glycerol (red line) media (scan rate = 10 mV s^{-1}, metal loading = 50 µg cm^{-2}, S_{geom} = 0.071 cm^2, T = 20° C)



In situ infrared spectra for the electrooxidation of 0.1 M glycerol in 0.1 M NaOH electrolyte on a carbon-supported Ni/C catalyst (T = 20 ° C. scan rate: 1 mV s^{-1}, resolution 4 cm^{-1}).

Activity and selectivity of $Ni(OH)_2$ nanoparticles towards glycerol electrooxidation



Both H_2 and $HCOO^-$ can serve as fuels in low temperature fuel cells

Conclusion and perspectives

The electroreforming of oxygenated organic molecules allows decreasing the electrolysis cell voltage for hydrogen production

It is better to use wastes from bio-industries such as glycerol, C5 and C6 sugars

=> decrease of the OPEX for biofuels and hydrogen production

But the kinetics of electroreforming reaction are very low on PGM-based catalysts, and more PGM are needed to enhance the reaction rate

=> Increase of the CAPEX

Increase of sugars/polyols and hydroxyl ions diffusion towards catalytic sites

Development of non-PGM based catalysts (Ni-based)

=> decrease of both the CAPEX and the OPEX

Thank you for your attention

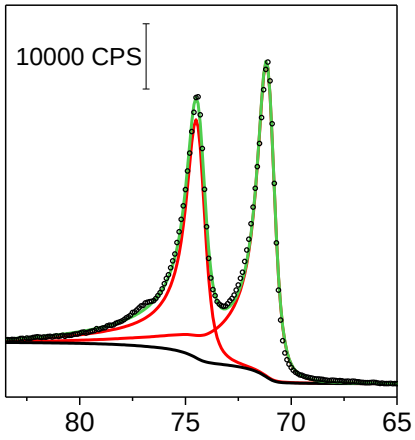
Nouvelle Aquitaine
County Council

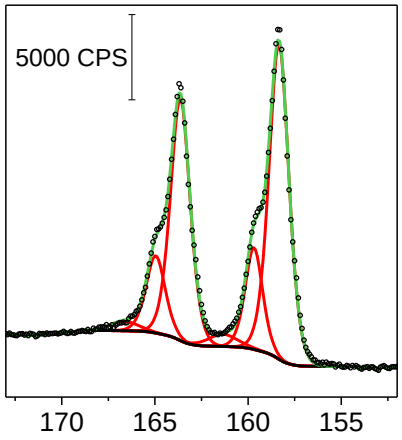
European commission
(ERDF)

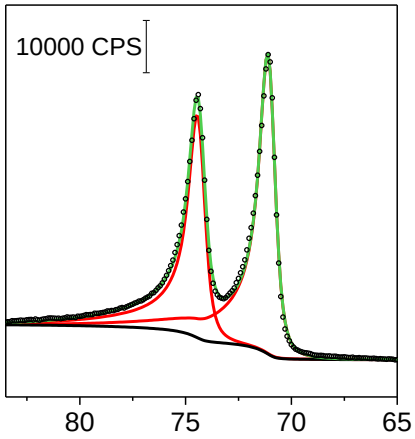
National Agency
for Research

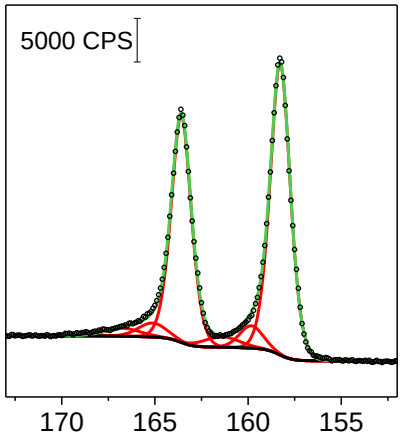
IC2MP
Institut de Chimie des Milieux et Matériaux de Poitiers

Fresh Pt_9Bi_1/C



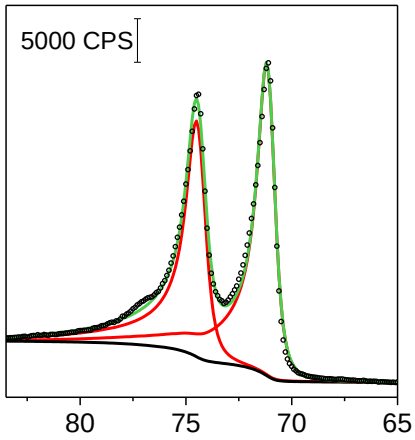


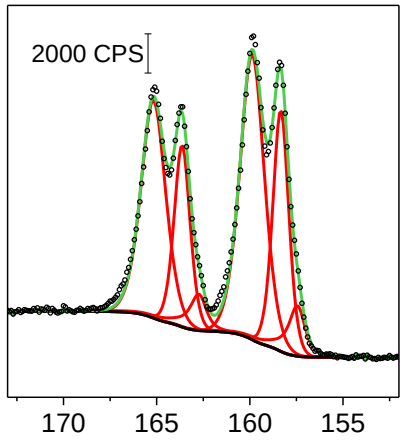


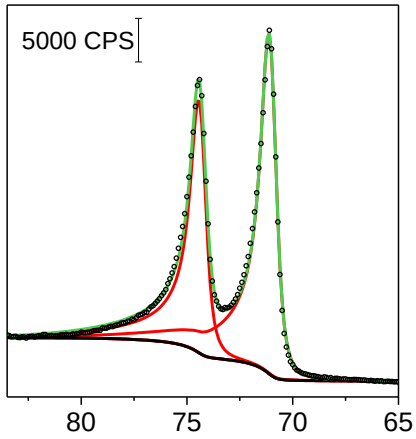


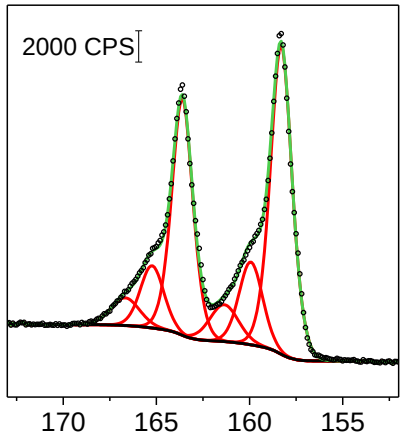
~ Pt^0 (79%), ↑ Bi^{2+} (87%), ↓ Bi^{3+} (8%), ↓ Bi^{4+} (5%)

Fresh Pt_8Bi_2/C

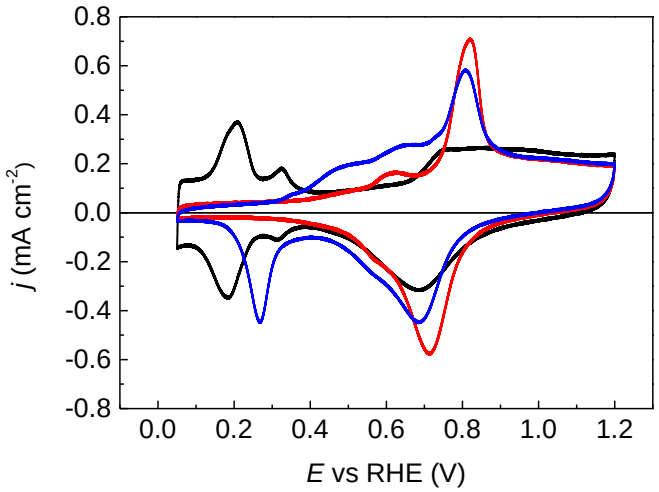




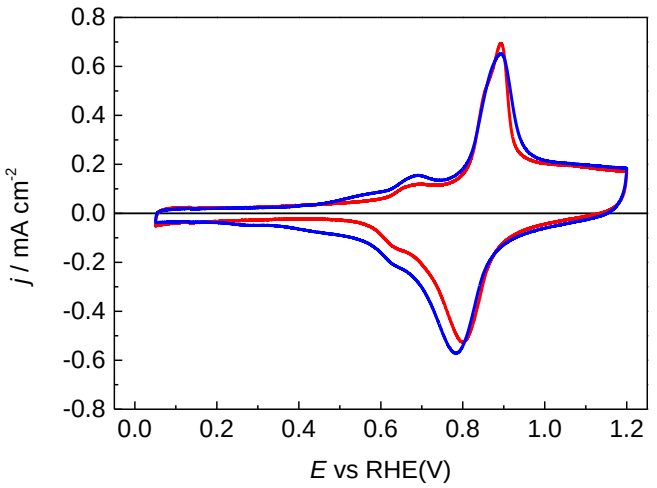




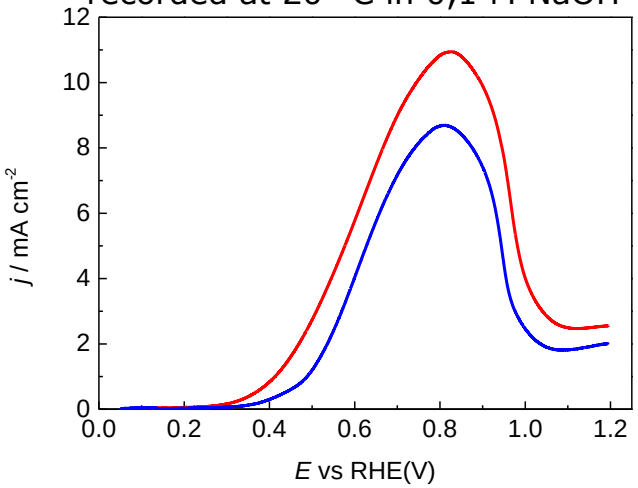
~ Pt^0 (71%), ↓ Bi^0, ↑ Bi^{2+} (69%), ↓ Bi^{3+} (20%), ↑ Bi^{4+} (11%)



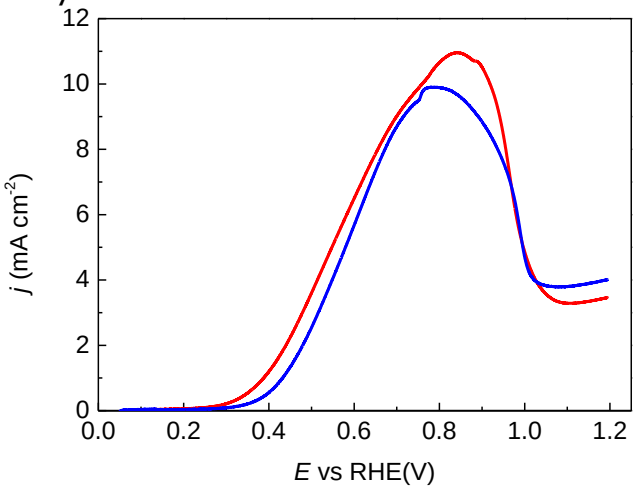
10th stable CVs of Pt/C, Pt_9Bi_1/C and Pt_8Bi_2/C recorded at 20 °C in 0,1 M NaOH



CVs of Pt_9Bi_1/C and Pt_8Bi_2/C recorded at 20 °C after 1000 potential cycles between 0.05 and 1.00 V in 0.1 M NaOH



Initial polarisation curves of 0.1 M glycerol oxidation in 0.1 M NaOH at Pt/C, Pt_9Bi_1/C and Pt_8Bi_2/C



Polarisation curves of 0.1 M glycerol oxidation in 0.1 M NaOH electrolyte at Pt/C, Pt_9Bi_1/C and Pt_8Bi_2/C after 1000 potential cycles