Electro-reforming of glucose/xylose mixtures on $Pd_{1-x}Au_x$ nanostructured catalysts

T. Rafaïdeen *and C. Coutanceau*

Université de Poitiers
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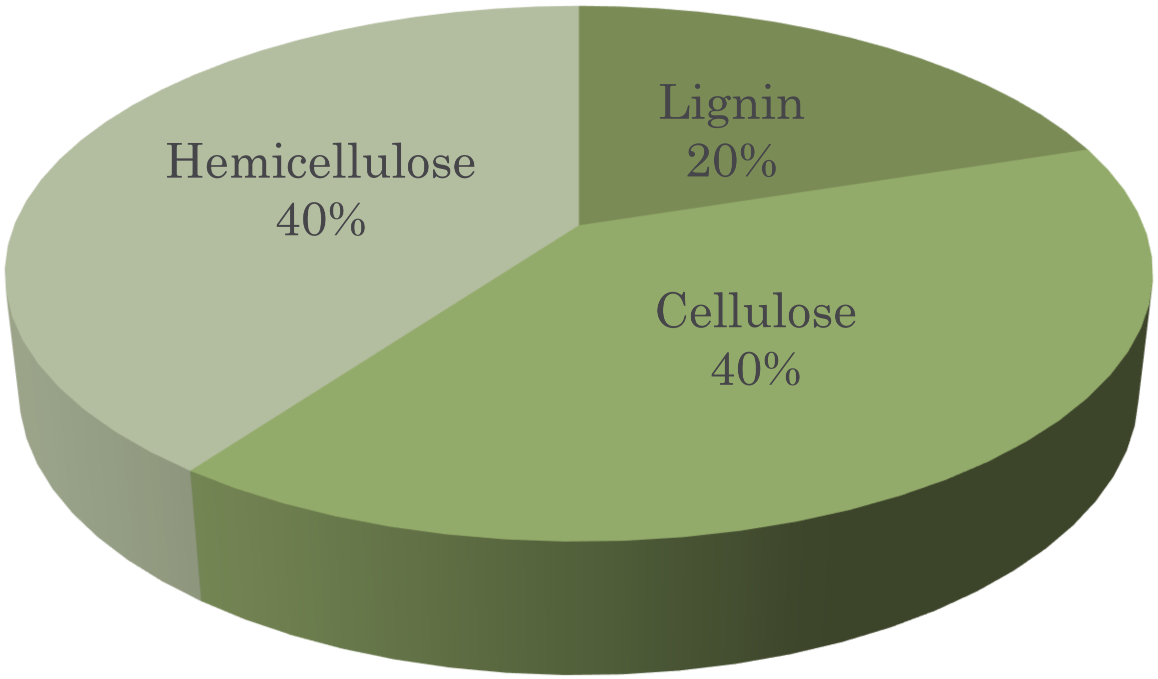
Institut de Chimie des Milieux et Matériaux de Poitiers
cnrs

Ligoncellulosic biomass composition



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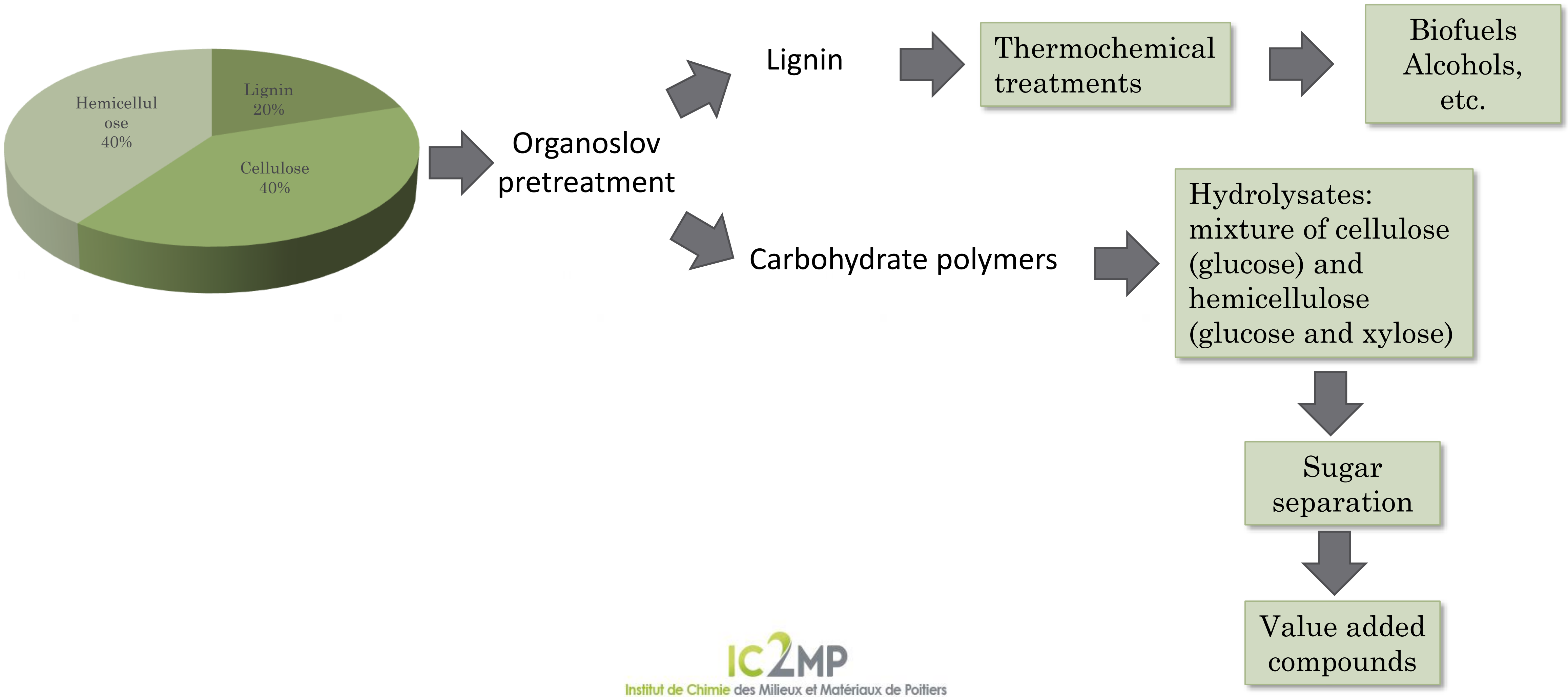
Introduction



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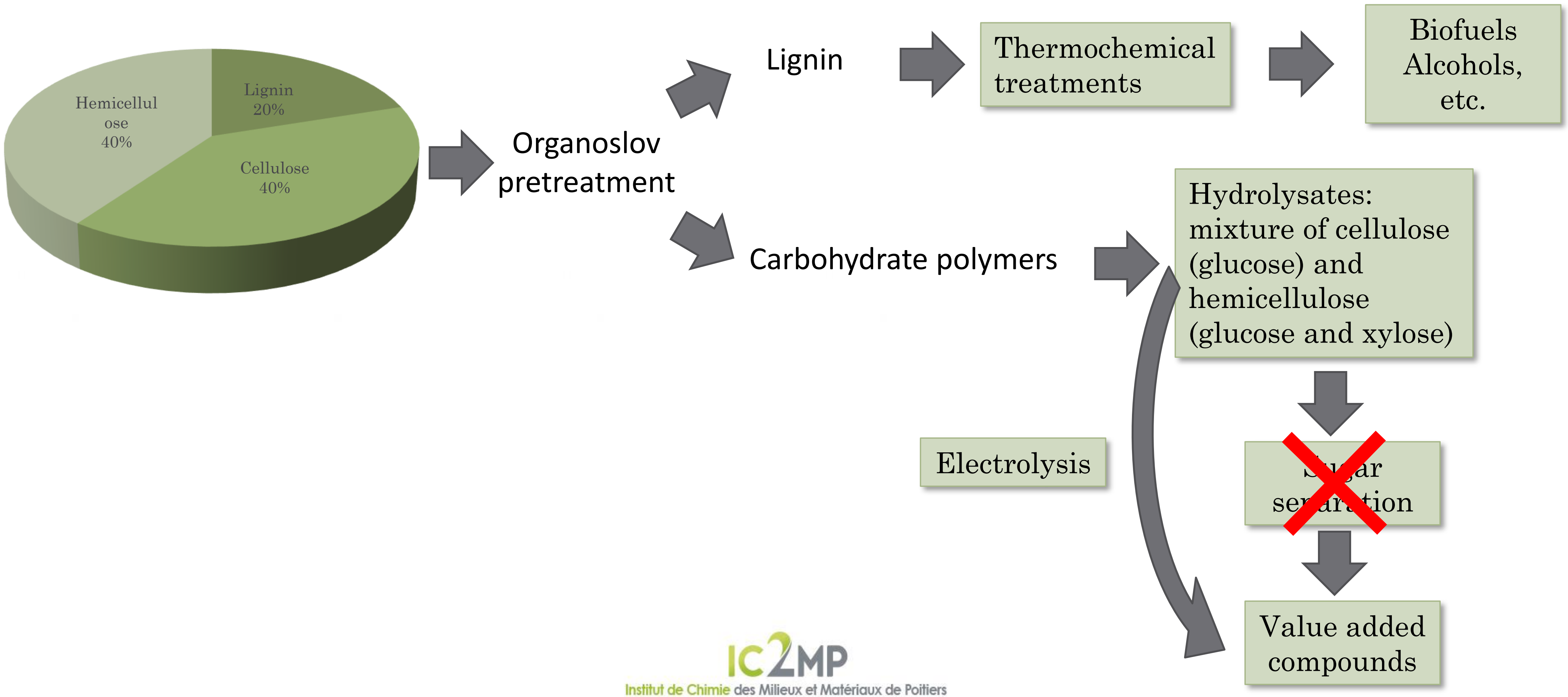

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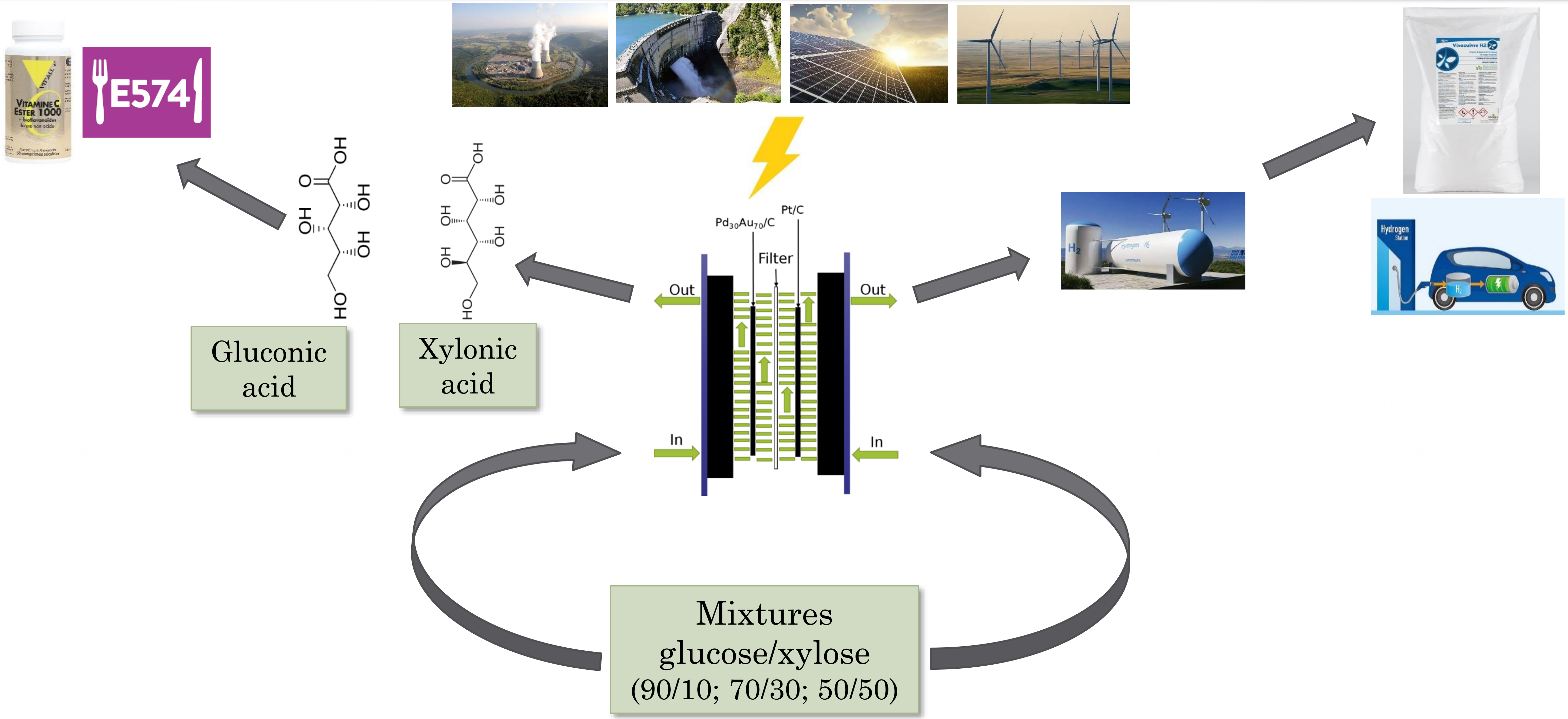
Introduction



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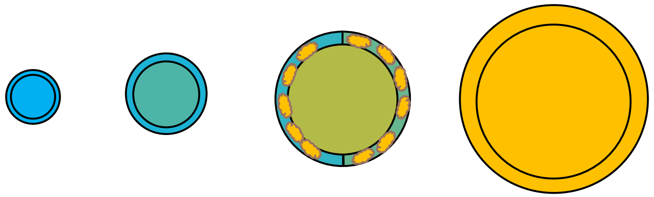
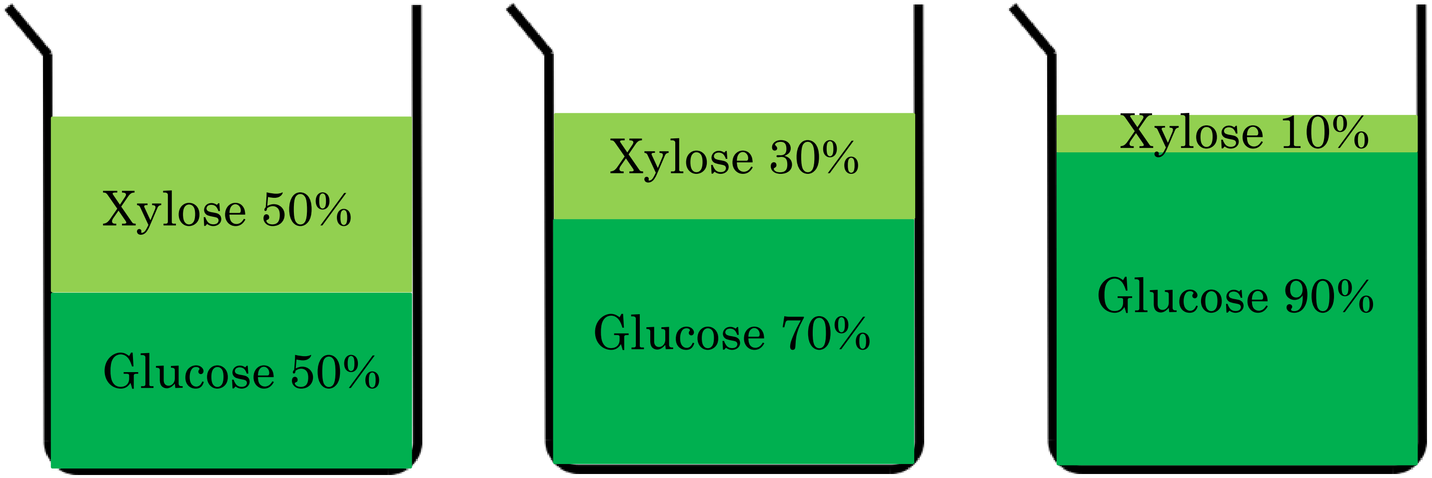
Objective

$Pd_{10-x}Au_x/C$ materials:

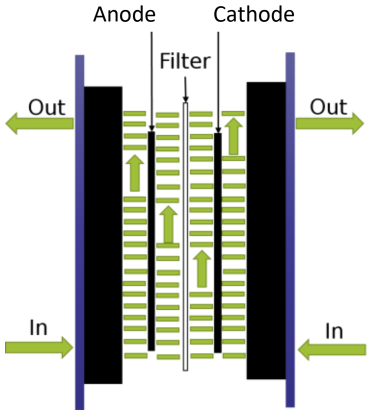
Pd/C; Pd_7Au_3/C; Pd_3Au_7/C; Au/C

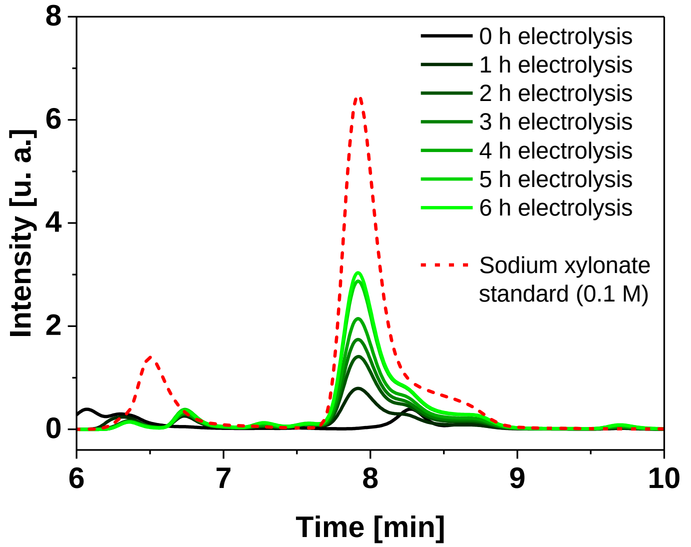


Evaluation of electrocatalytic behavior of all materials for



For the most promising anodic catalyst





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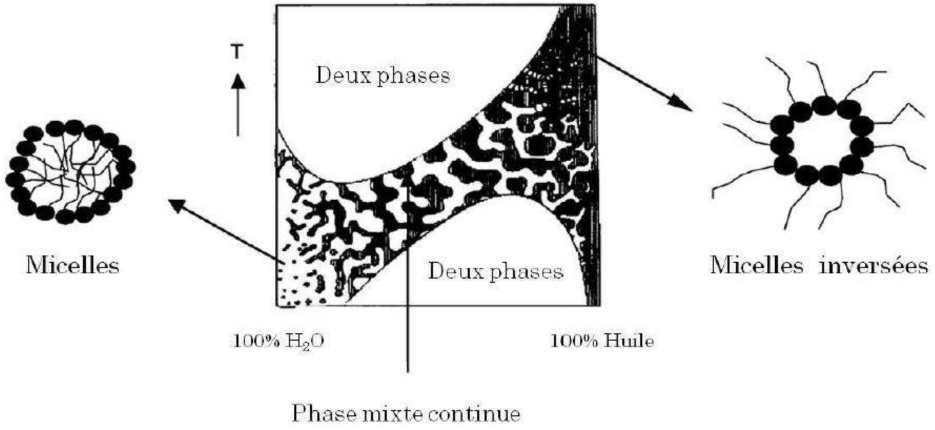
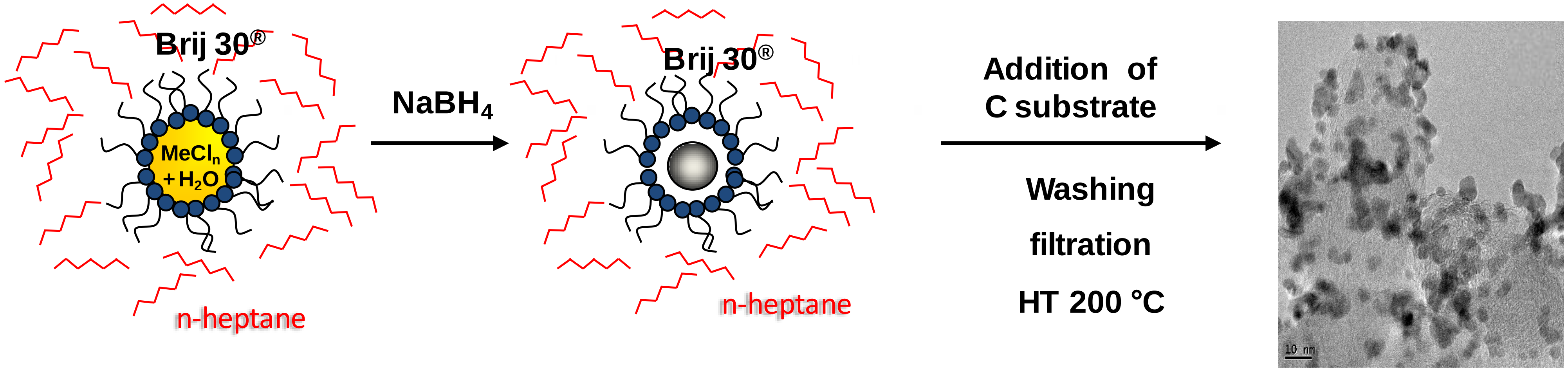
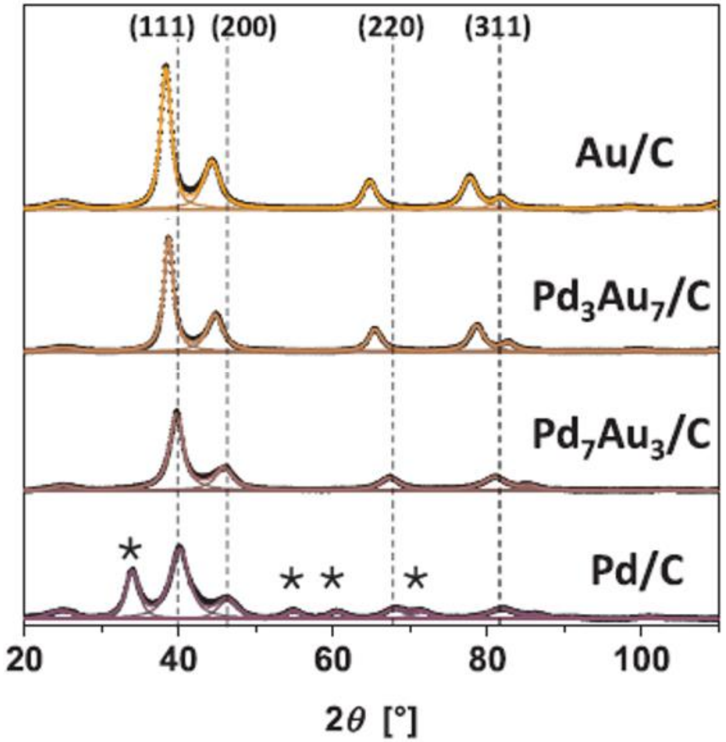
Nanoparticles synthesis

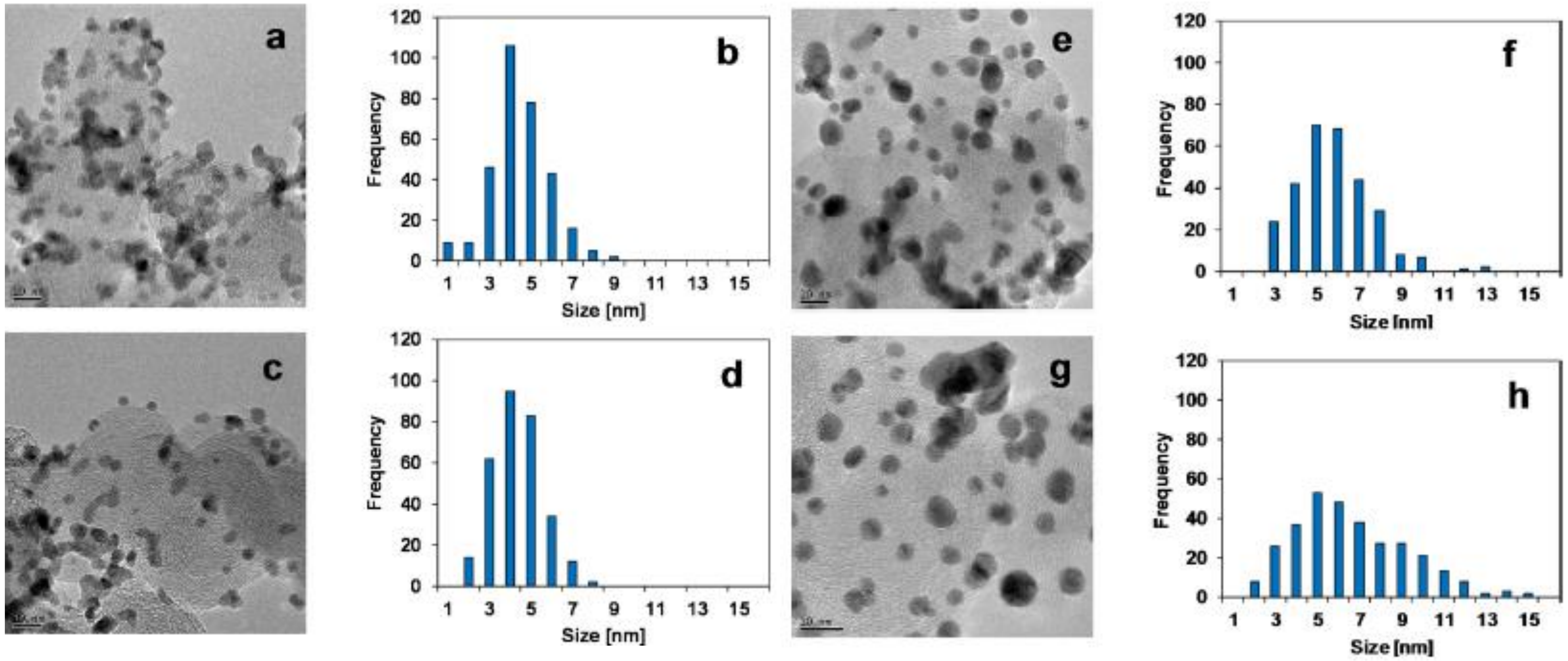




XRD and TEM

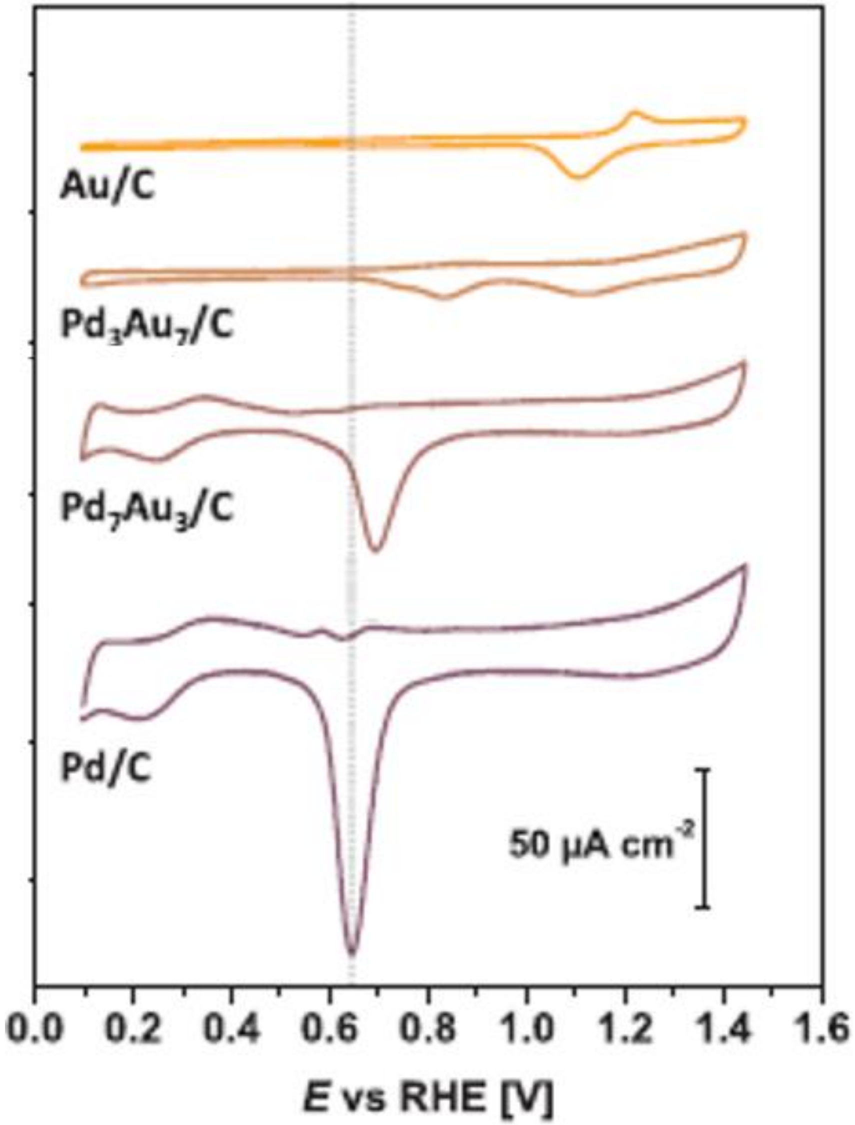


XRD patterns of the Pd_xAu_{10-x}/C (x=0, 3, 7, 10) catalysts
(☆ indicates the diffraction peak relates to the tetragonal PdO structure)



TEM images and histograms of particle size distribution from TEM observations on (a,b) Pd/C, (c,d) Pd_7Au_3/C, (e,f) Pd_3Au_7/C and (g,h) Au/C

Electrochemical characterization



Experimental conditions:

T = 293 K

Electrolyte : N_2 purged, 0.1 M NaOH

Scan rate : 5 mV s^{-1}

Electrode diameter : 3 mm

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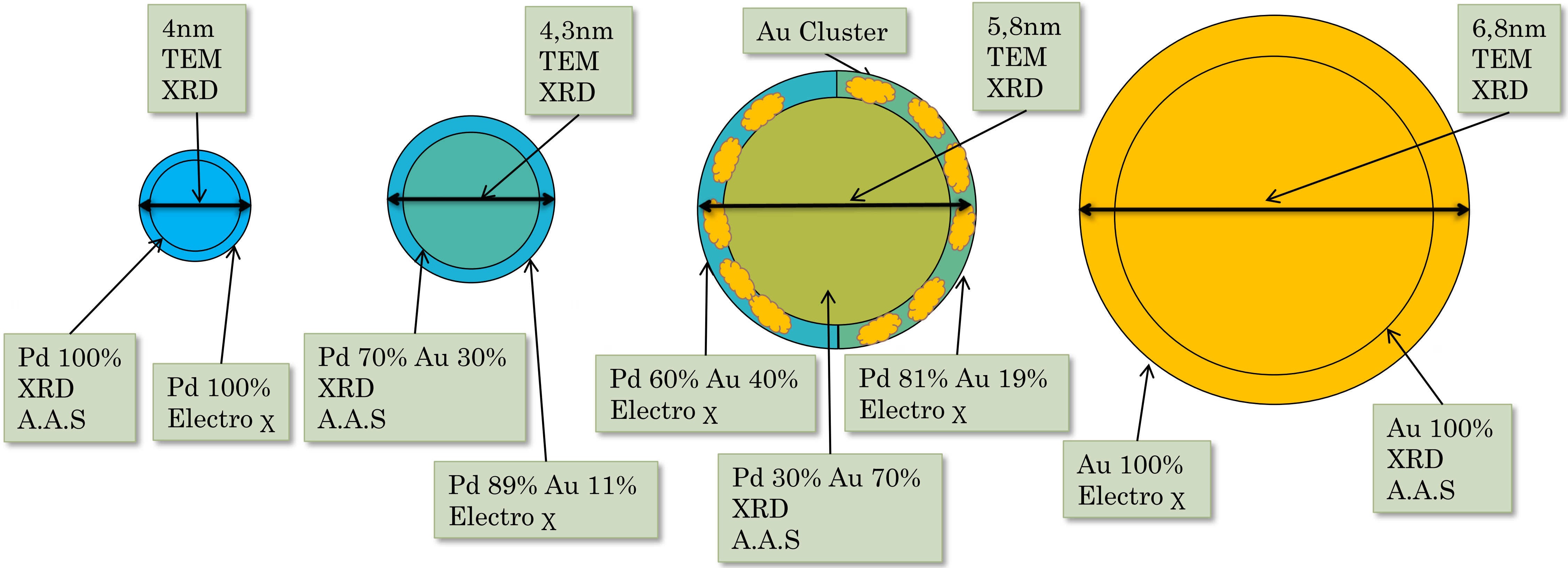
Characterizations results



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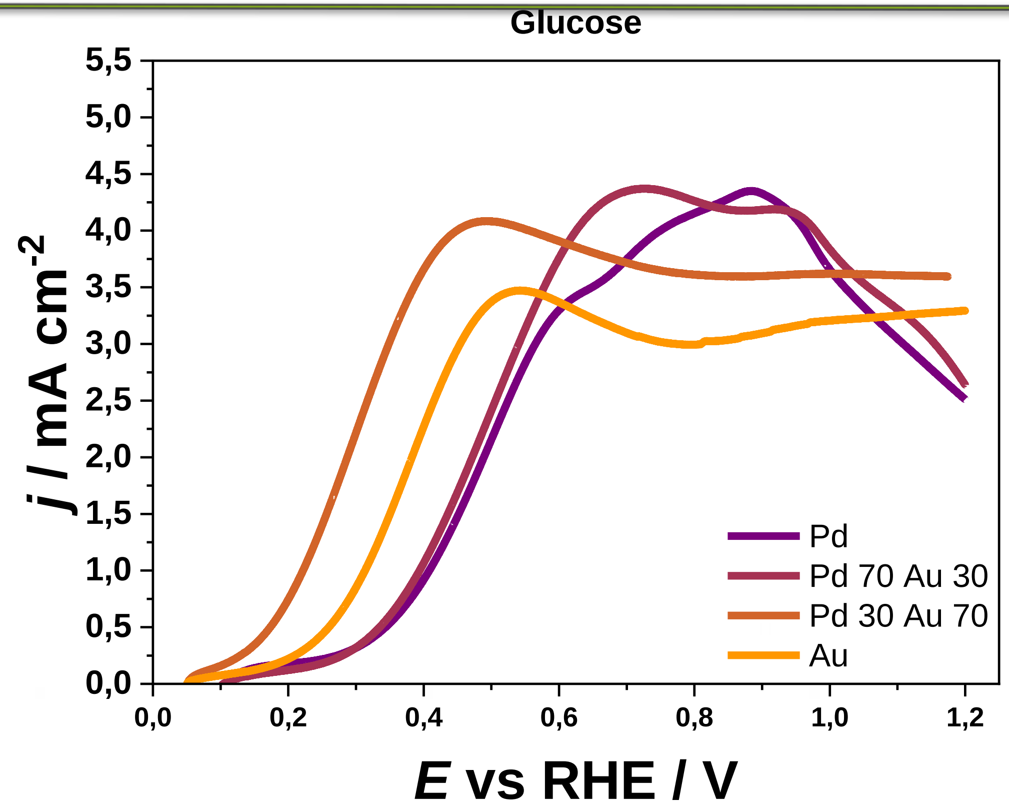
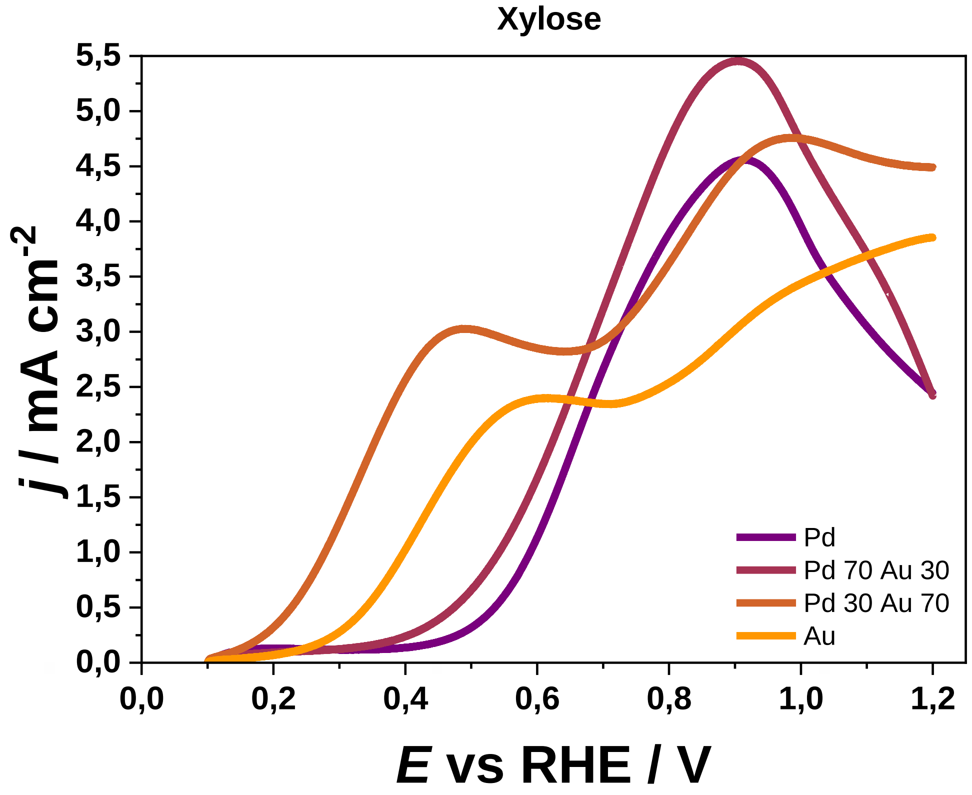
Linear scan voltametry of glucose and xylose





Experimental conditions:

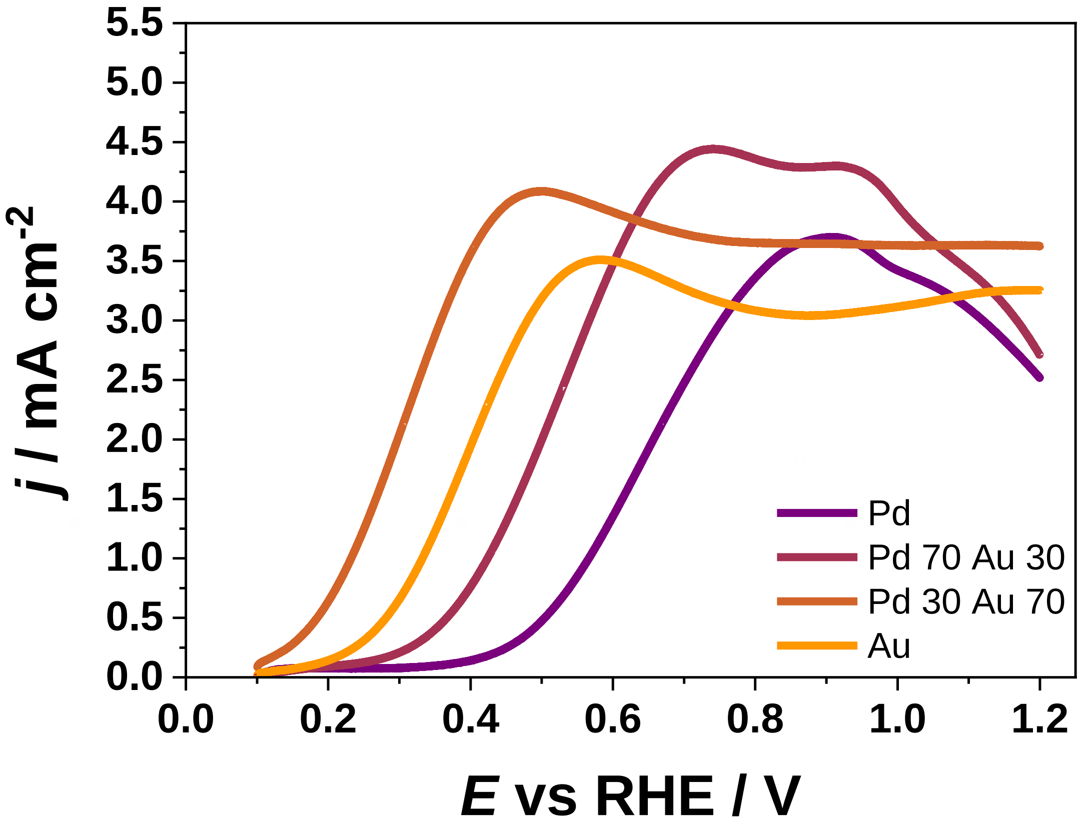
T = 293 K

Electrolyte : N_2 purged, 0.1 M aldose + 0.1 M NaOH

Scan rate : 5 mV s^{-1}

Electrode diameter : 3 mm

Linear scan voltametry of 90 mol% glucose + 10 mol% xylose mixture



Experimental conditions:

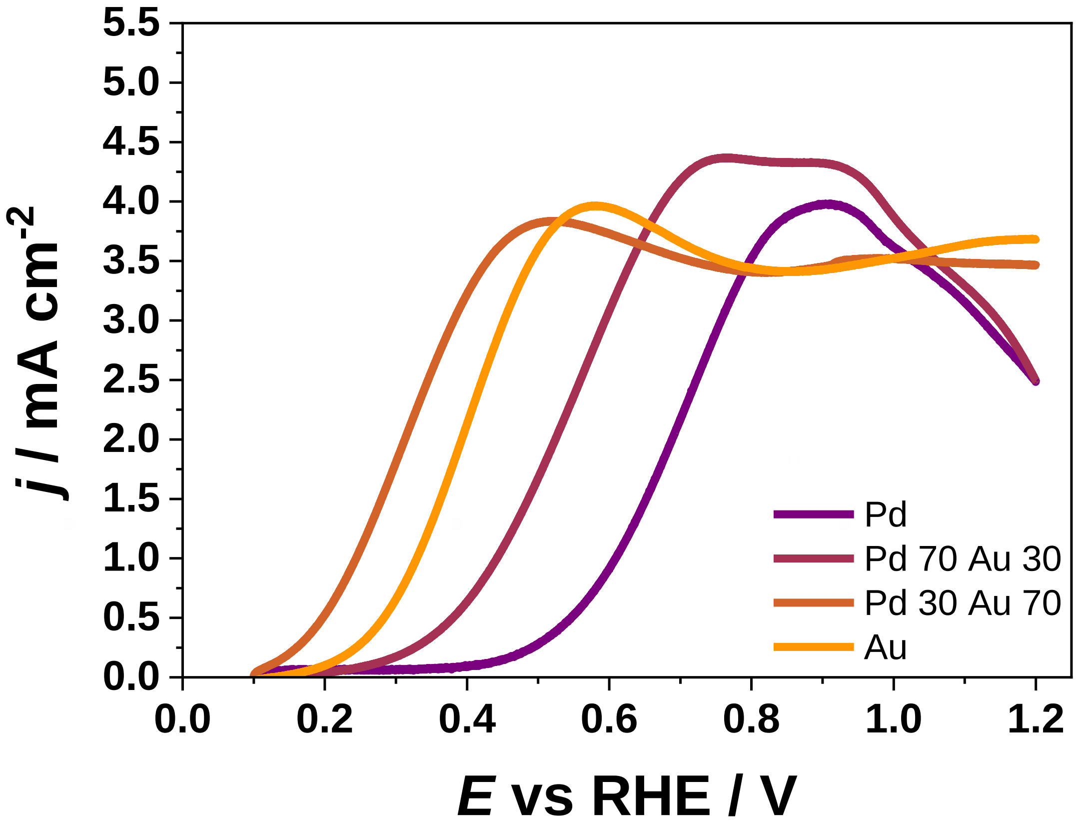
T = 293 K

Electrolyte : N_2 purged, 0.1 M Aldose + 0.1 M NaOH

Scan rate : 5 mV s^{-1}

Electrode diameter : 3 mm

Linear scan voltametry of 70 mol% glucose + 30 mol% xylose mixture



Experimental conditions:

T = 293 K

Electrolyte : N_2 purged, 0.1 M Aldose + 0.1 M NaOH

Scan rate : 5 mV s^{-1}

Electrode diameter : 3 mm

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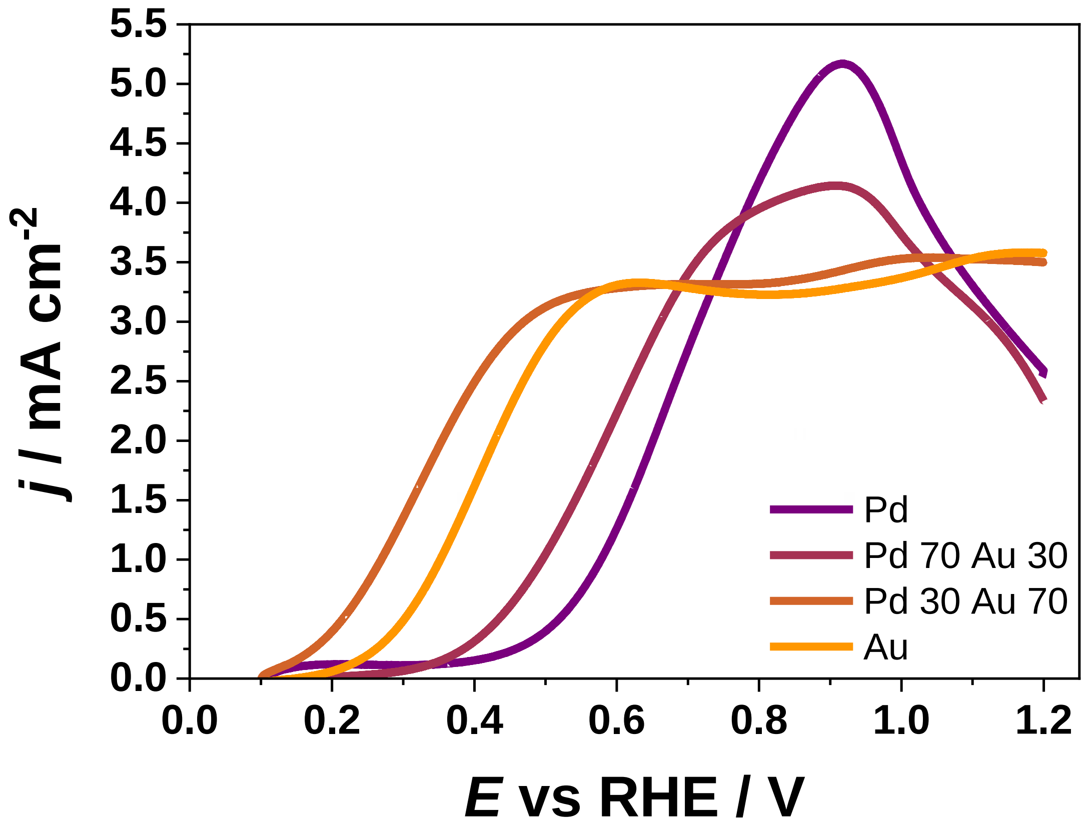
Linear scan voltametry on xylose of a 50 mol% glucose + 50 mol% xylose mixture



Experimental conditions:

T = 293 K

Electrolyte : N_2 purged, 0.1 M Aldose + 0.1 M NaOH

Scan rate : 5 mV s^{-1}

Electrode diameter : 3 mm

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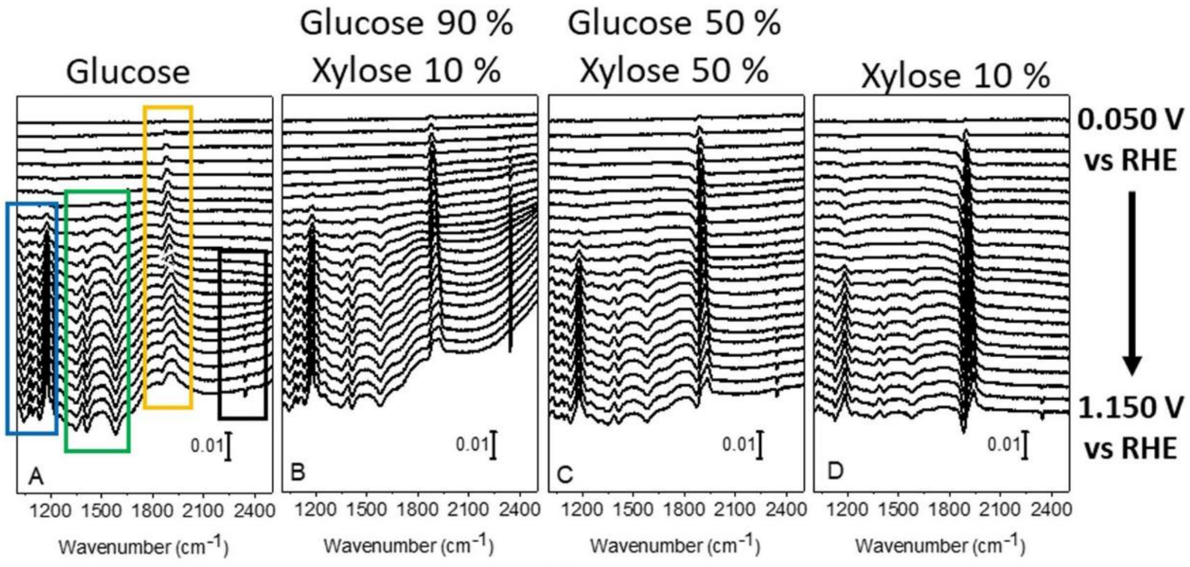
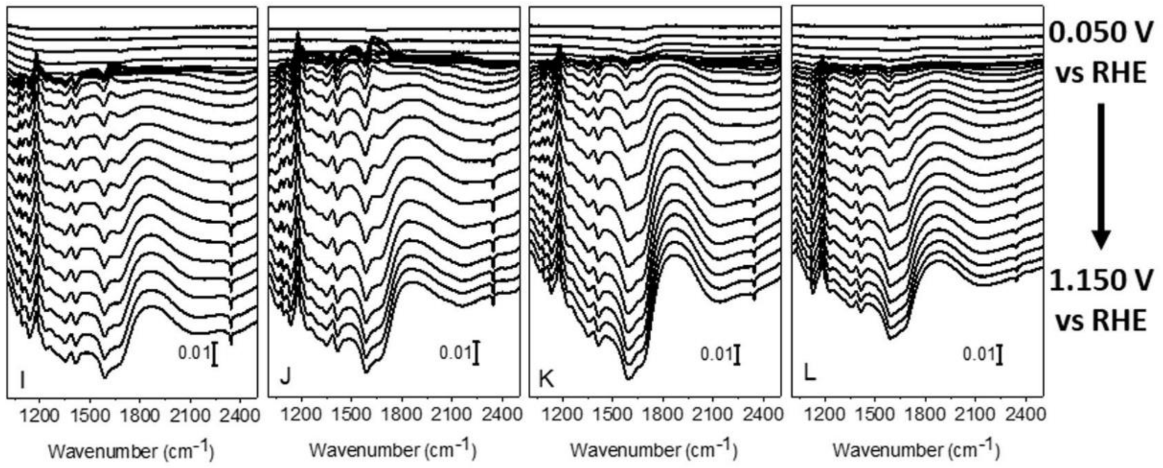
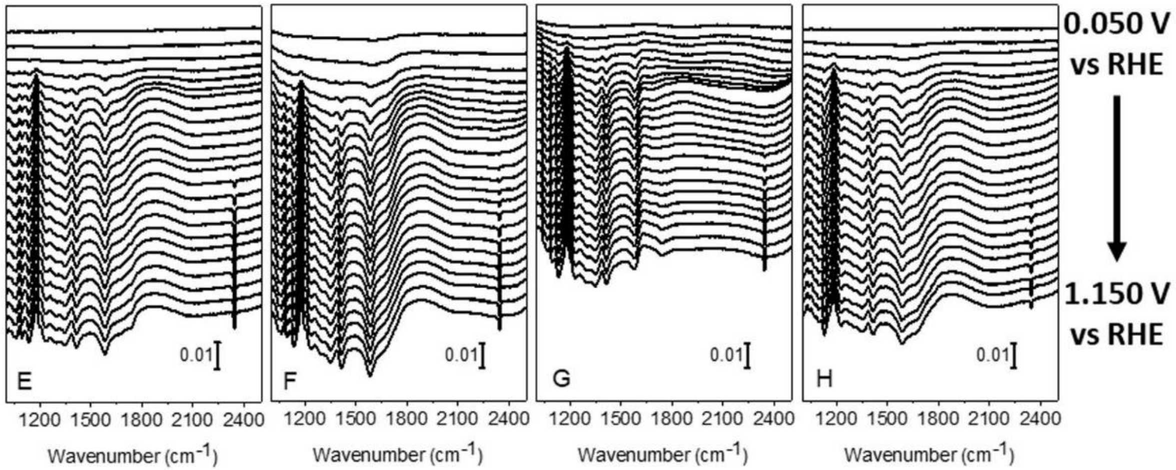


Pd/C



Au/C



$Pd_{0.3}Au_{0.7}/C$

Experimental conditions:

Scan rate: 0.001 V s^{-1},

Resolution 4 cm $^{-1}$,

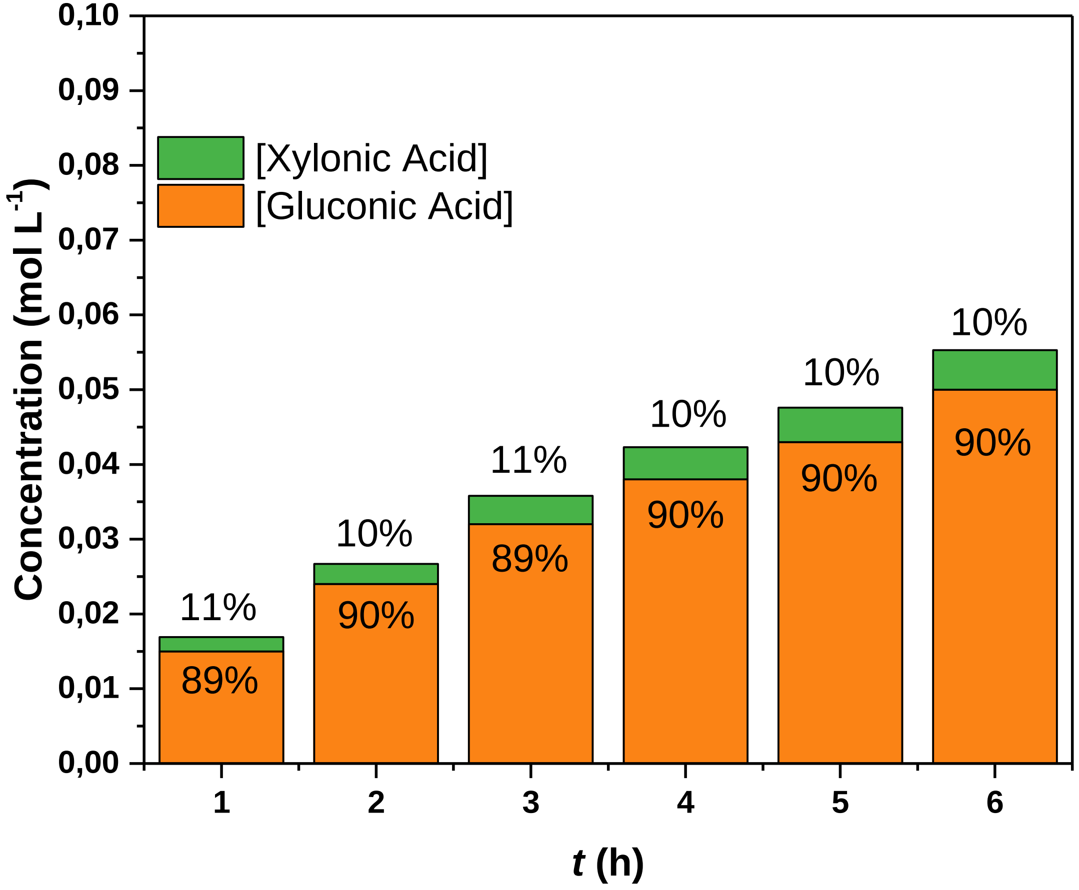
N_2-purged 0.10 mol L^{-1} NaOH electrolyte,

T=293 K.

Vertical scale: $\Delta R/R$.

In Figure 3A. The blue box highlights the C-O stretching region, the green one the bands from O-C-O vibration modes, the orange one the CO_{ads} band and the black one the interfacial CO_2 band.

HPLC analysis for the electrolysis of 90 mol% glucose + 10 mol% xylose mixture



Experimental conditions of the electrolysis:

T = 293 K

Electrolyte : 0.1 M Aldose + 0.1 M NaOH

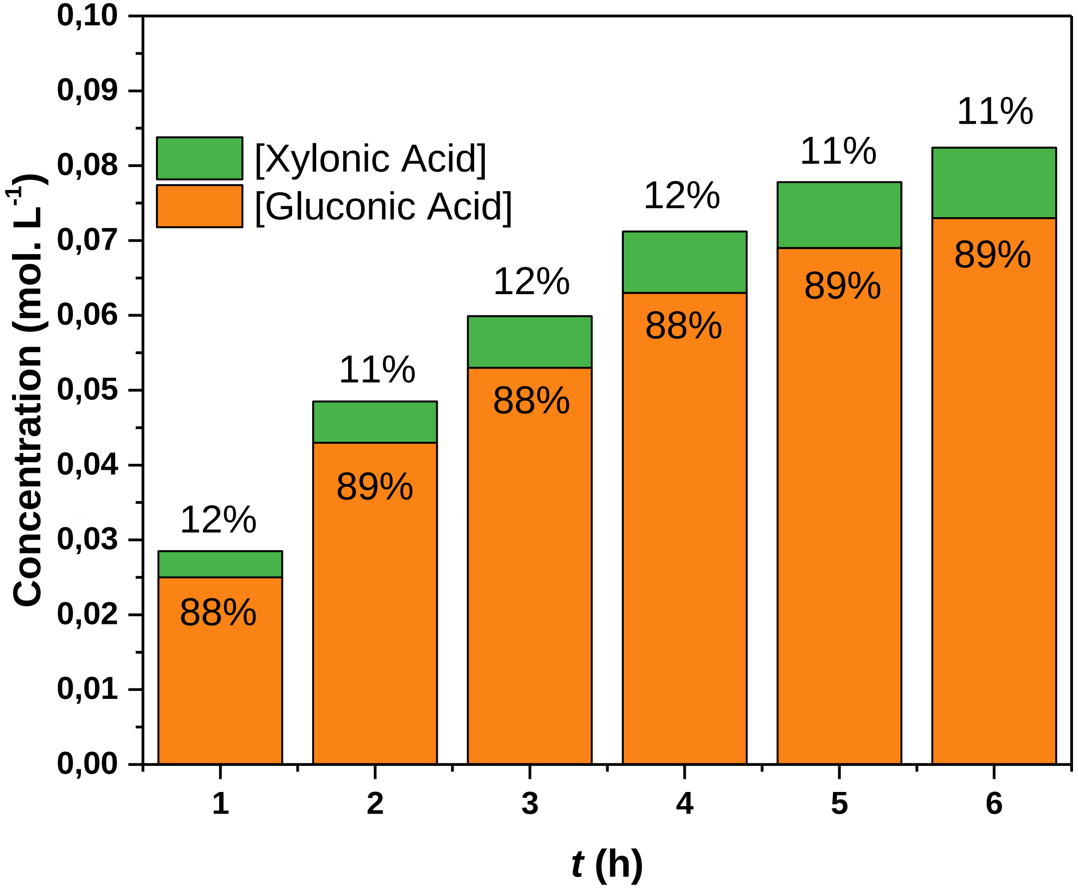
Debit: 30 mL min^{-1}

Electrode surface : 25 cm^2

Cell voltage : 0.4 V

Duration : 6 hours

HPLC analysis for the electrolysis of 90 mol% glucose + 10 mol% xylose mixture



Experimental conditions of the electrolysis:

T = 293 K

Electrolyte : 0.1 M Aldose + 0.1 M NaOH

Debit: 30 mL min^{-1}

Electrode surface : 25 cm^2

Cell voltage : 0.6 V

Duration : 6 hours

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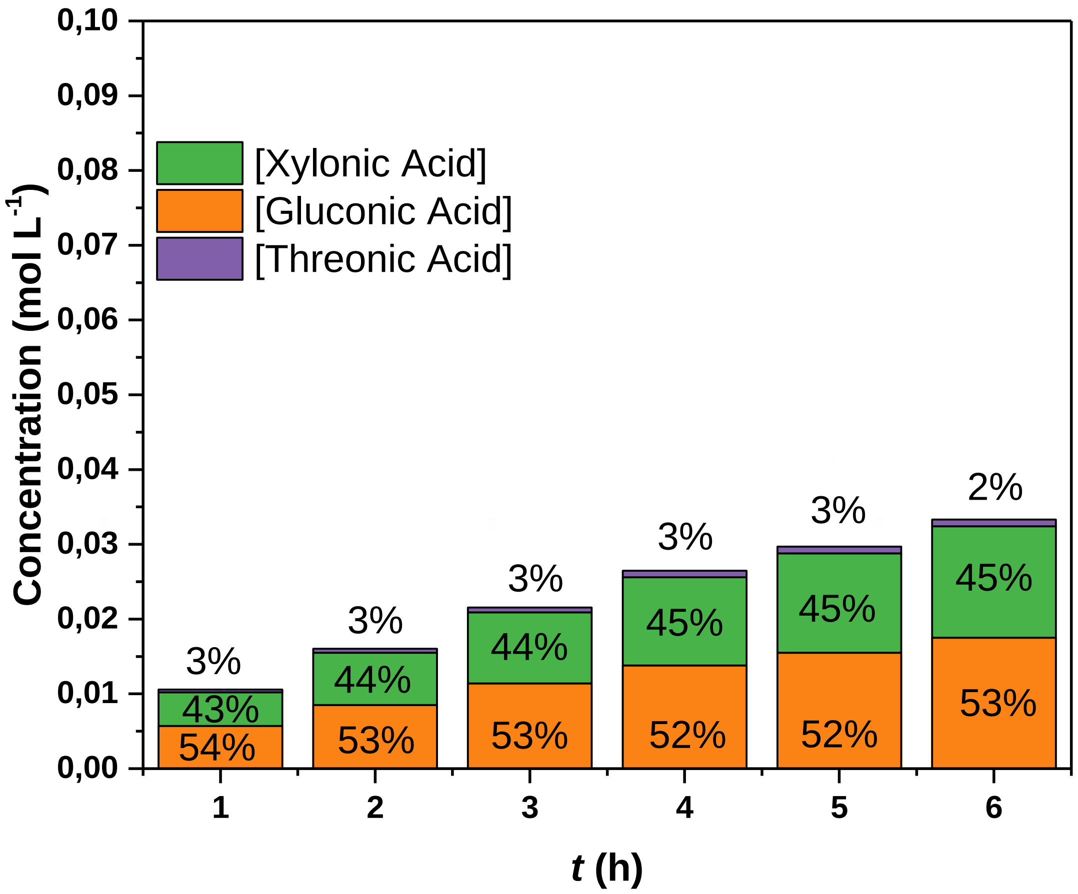
HPLC analysis for the electrolysis of of a 50 mol% glucose + 50 mol% xylose mixture



Experimental conditions of the electrolysis:

$T = 293$ K

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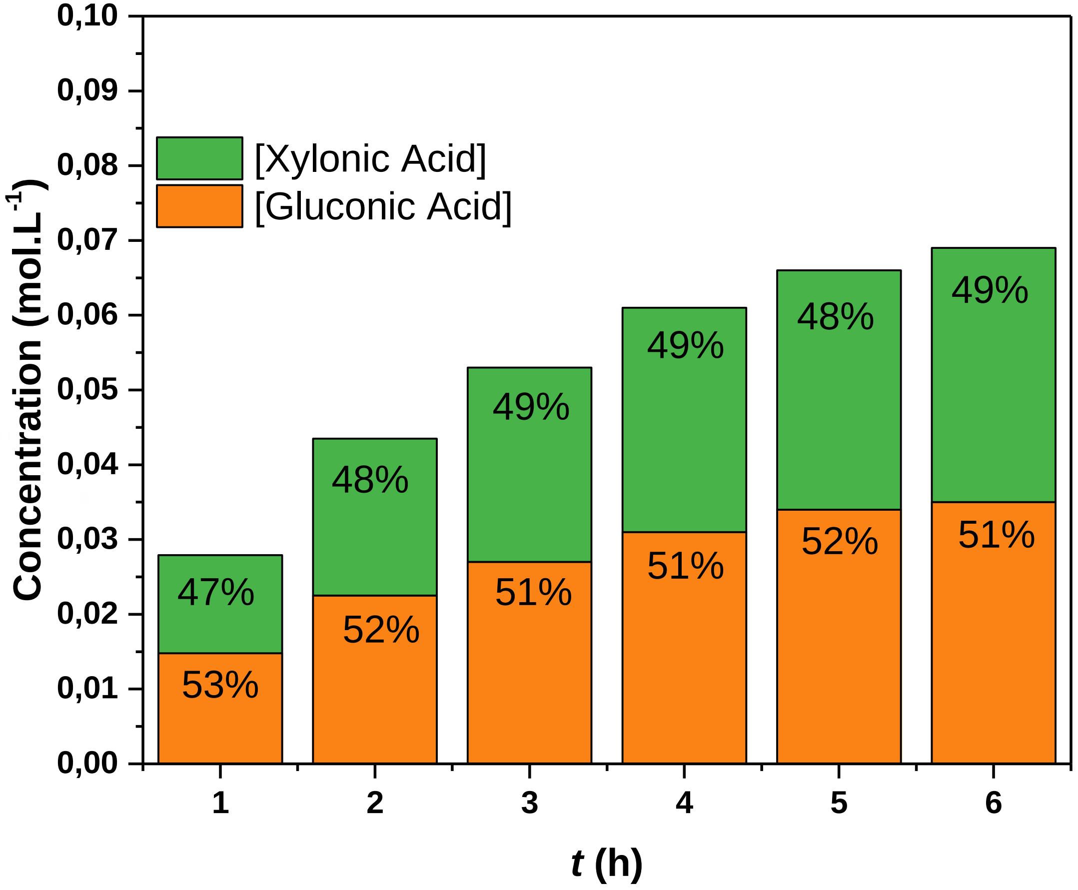

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Data from the electrolysis of glucose + xylose mixtures

Table 2. Data from the electroreforming of glucose 90 %/xylose 10 % and glucose 50 %/xylose 50 % determined from HPLC analysis of the reaction products.

	glucose 90 %/xylose 10 %		glucose 50 %/xylose 50 %	
Cell voltage [V]	+0.4	+0.6	+0.4	+0.6
$C_{gluconate}$ [mol L^{-1}[a]]	0.0500	0.0730	0.0175	0.035
$C_{xylonate}$ [mol L^{-1}[a]]	0.0053	0.0094	0.0149	0.034
$C_{threonate}$ [mol L^{-1}[a]]	0	0	0.0009	0
$C_{products}$ [mol L^{-1}[a]]	0.0553	0.0824	0.0333	0.069
% gluconate	90.4	88.6	52.5	50.1
% xylonate	9.6	11.4	44.7	49.7
% threonate	0	0	2.8	0
x	0.35	0.44	0.21 ($y=0$) 0.27 ($y=1$)	0.69
Glucose contribution [%]	96.7	95.	90.6 ($y=0$) 87.9 ($y=1$)	66.0
Xylose contribution [%]	3.3	5.0	9.4 (y=0) 12.1 (y=1)	34.0

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Possible reactions

Glucose oxidation into gluconate:

$$C_6H_{12}O_6 + 3\,OH^- \rightarrow C_6H_{11}O_7^- + 2\,H_2O + 2\,e^- \qquad (1)$$

Glucose oxidation into xylonate:

$$C_6H_{12}O_6 + 9\,OH^- \rightarrow C_5H_9O_6^- + CO_3^{2-} + 6\,H_2O + 6\,e^- \qquad (2)$$

Glucose oxidation into threonate (considering only co-formation of carbonates):

$$C_6H_{12}O_6 + 15\,OH^- \rightarrow C_4H_7O_5^- + 2\,CO_3^{2-} + 10\,H_2O + 10\,e^- \qquad (3)$$

Xylose electrooxidation into xylonate:

$$C_5H_{10}O_5 + 3\,OH^- \rightarrow C_5H_9O_6^- + 2\,H_2O + 2\,e^- \qquad (4)$$

Xylose oxidation into threonate (considering only co-formation of carbonate):

$$C_5H_{10}O_5 + 9\,OH^- \rightarrow C_4H_7O_5^- + CO_3^{2-} + 6\,H_2O + 6\,e^- \qquad (5)$$

Equation between the electrical charge (Q) and the concentration of the different products

$$Q = FV(2C_{gluconate} + 2xC_{xylonate} + 6(1-x)C_{xylonate} + 6yC_{threonate} + 10(1-y)C_{threonate})$$

$$Q = 2FV(C_{gluconate} + 3C_{xylonate} - 2xC_{xylonate} - 2yC_{threonate} + 5C_{threonate})$$

F is the Faraday constant (F=96,485 C mol^{-1})

V is the volume of anolyte electro-reformed (V = 30mL)

x is the proportion of xylose used to produce xylonate considering equation (4) ($0 \leq x \leq 1$)

y is the proportion of xylose used to produce threonate according to equation (5) ($0 \leq y \leq 1$)

2 is the number of electrons involved in Equation (1) and (4) to produce gluconate from glucose and xylonate from xylose.

6 the number of electrons involved in Equation (2) and (5) to produce xylonate from glucose and threonate from xylose.

10 the number of electrons involved in Equation (3) to produce threonate from glucose.

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Conclusion & perspectives

- Pd-rich surface favoring the dissociative adsorption of sugar with poisoning of the surface by strongly adsorbed CO species.

- Au-rich surface avoided the formation of adsorbed CO species.

- Pd-rich surface displayed higher affinity towards xylose adsorption, whereas Au-rich surface adsorbed preferentially glucose.

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Thank for your attention

Any questions ?

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