

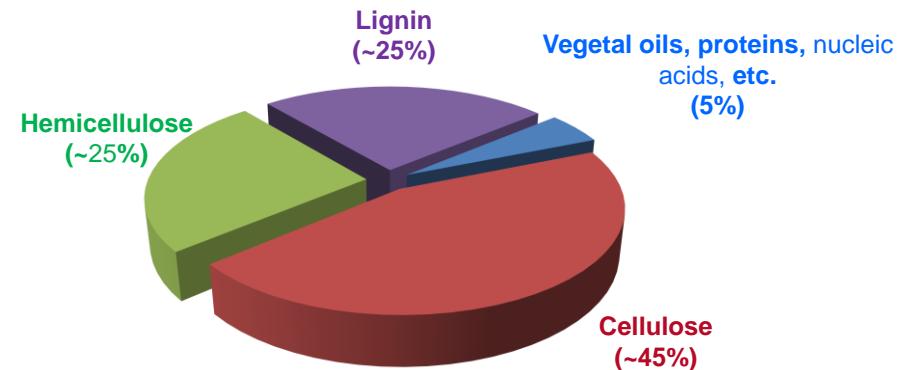
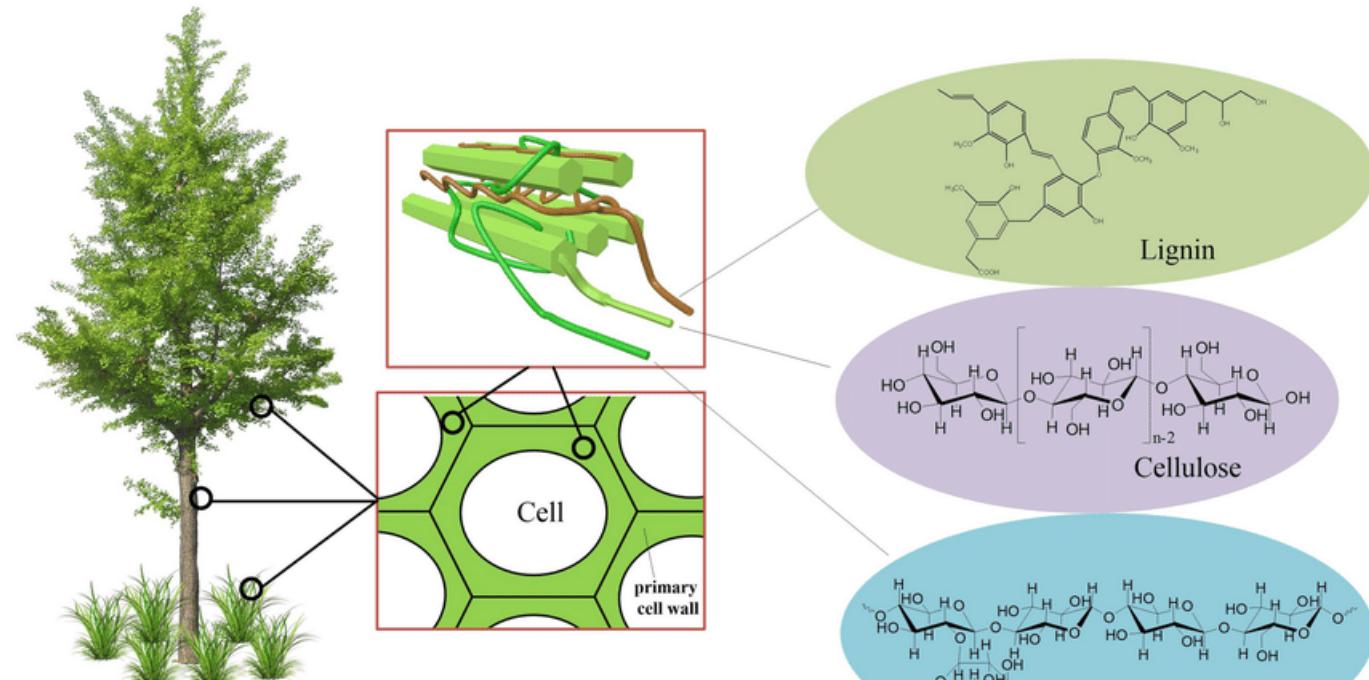
# L'hydrogène comme coproduit de la conversion électrocatalytique du glucose en composés à haute valeur ajoutée

T. Faverge, N. Neha, T. Rafaïdeen, B. Gilles, A. Bonnefont, F. Maillard, M. Chatenet, C. Coutanceau

[christophe.coutanceau@univ-poitiers.fr](mailto:christophe.coutanceau@univ-poitiers.fr)



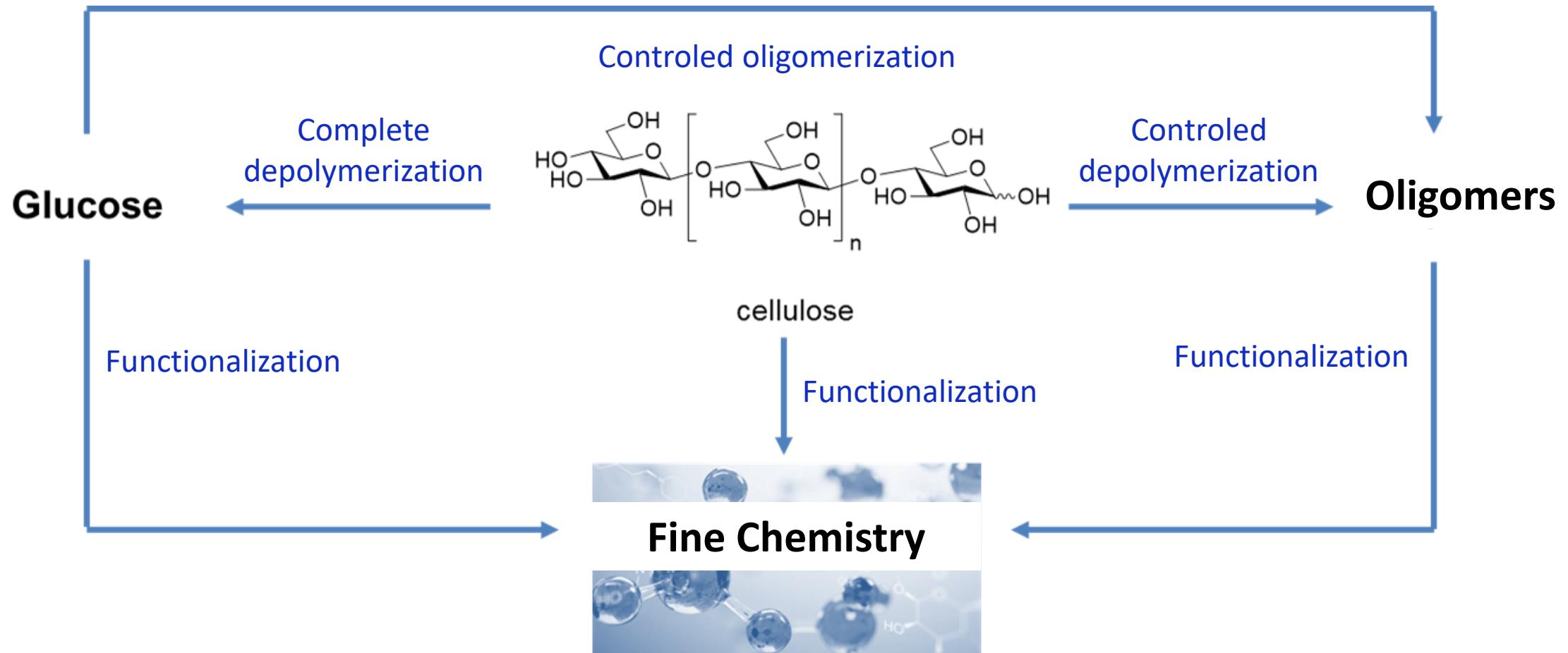
INCREASE



Biomass production > 200 billion tons / y

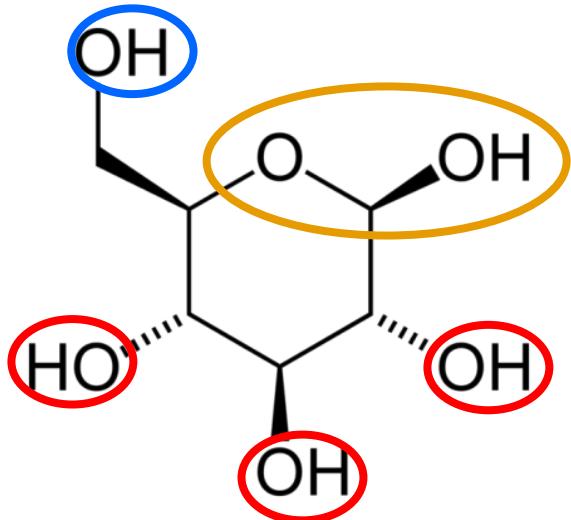
**Fuels**  
ethanol, hydrocarbons, hydrogen, etc.

**Fine chemistry**  
Platfrom molecules :  
glucose, xylose,  
Furanic derivatives,  
bioethanol, glycerol, etc.



**C6 : Primary alcohol**  
**Thermodynamically hard to oxidize**

**Secondary alcohols**  
**Reactivity ?**



**C1 : anomeric function**  
**Can be oxidized or reduced**

Biomass molecules from biorefinery:

=> either reduced or oxidized into valuable compounds,

Paired-electrochemical processes allow decreasing the electrical energy cost

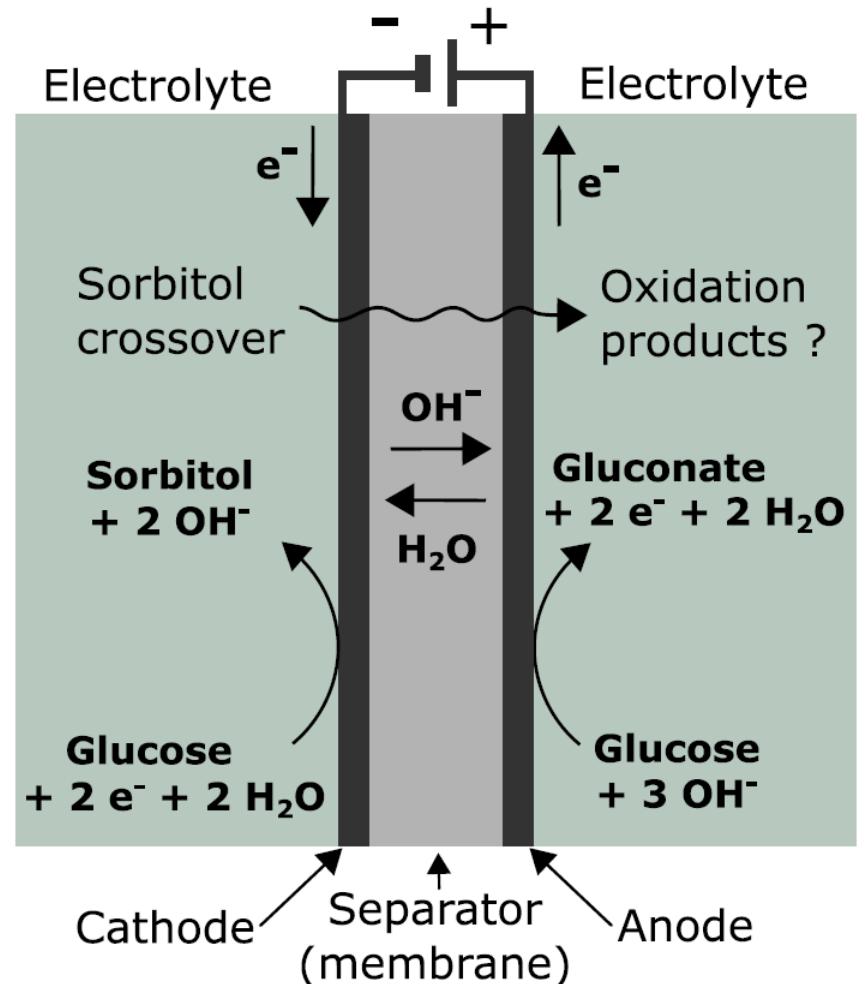
=> value-added compounds formed at both electrodes.

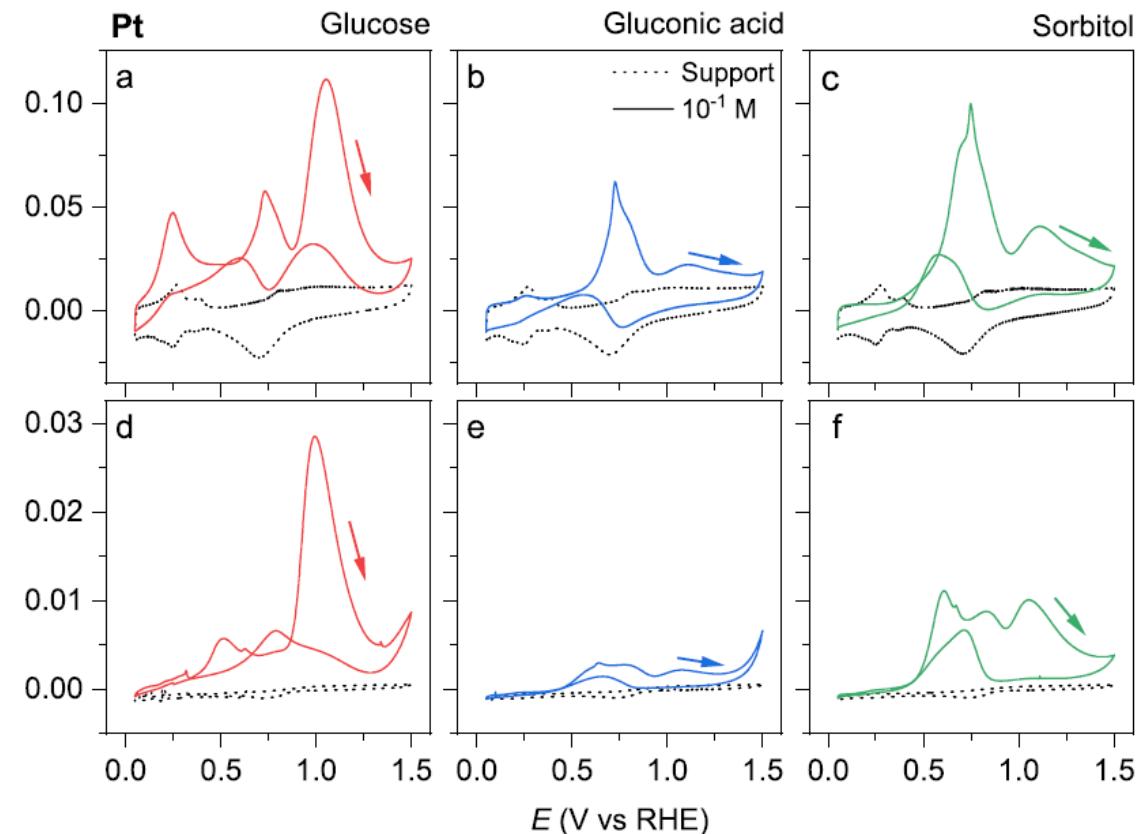
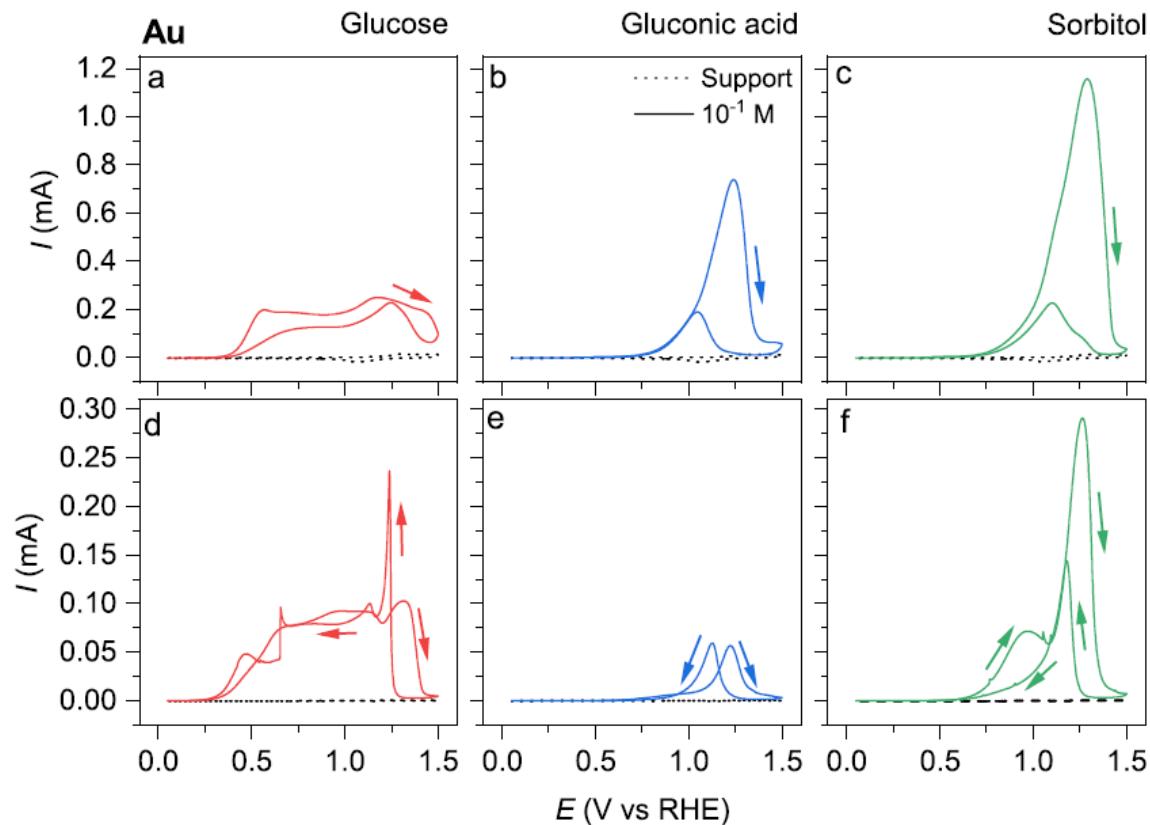
Process intensification can be achieved by the development of microreactors.

High activity of the electrocatalyst

High selectivity towards a given compounds (here gluconate)

Specificity towards a given reactant

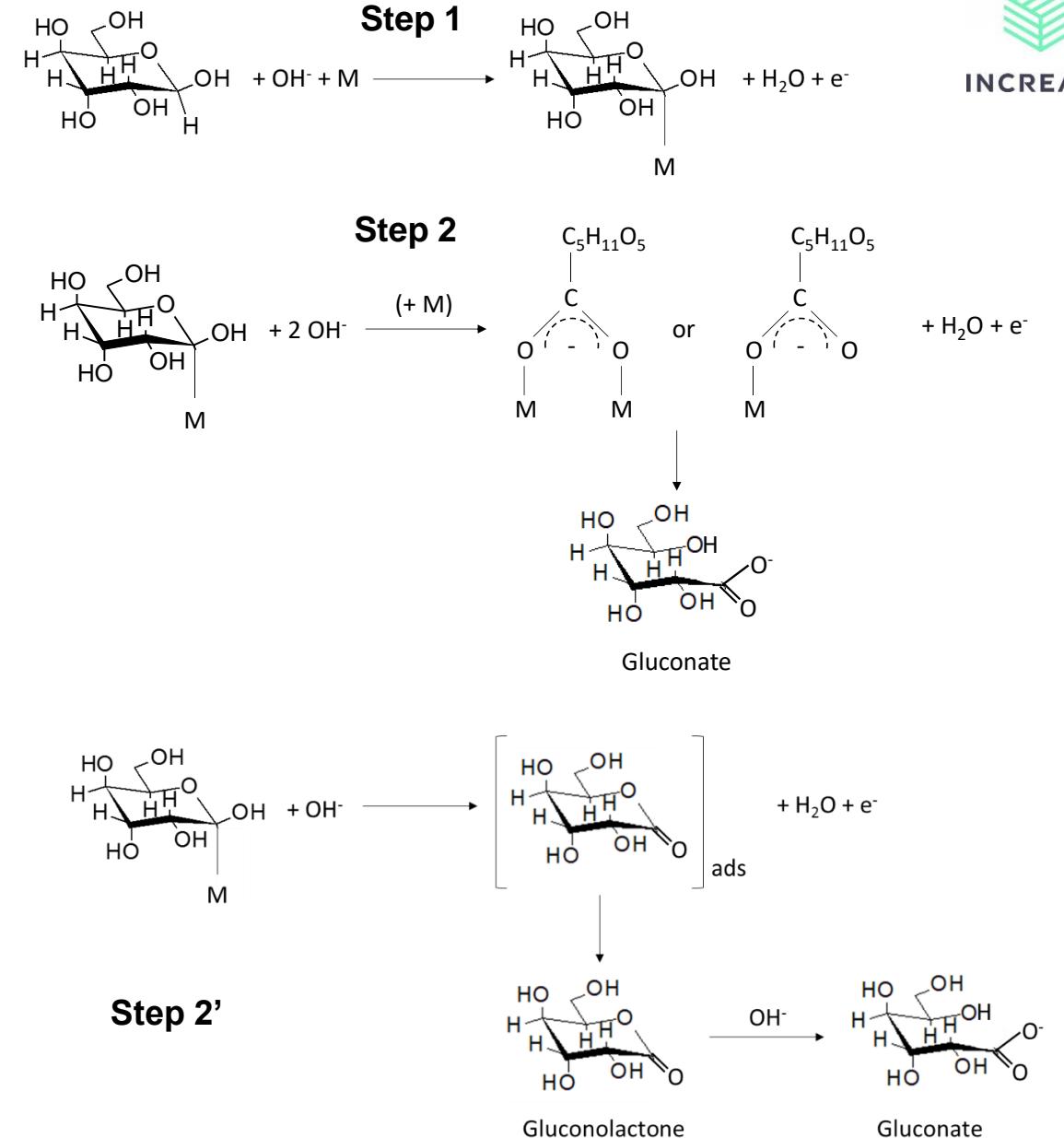
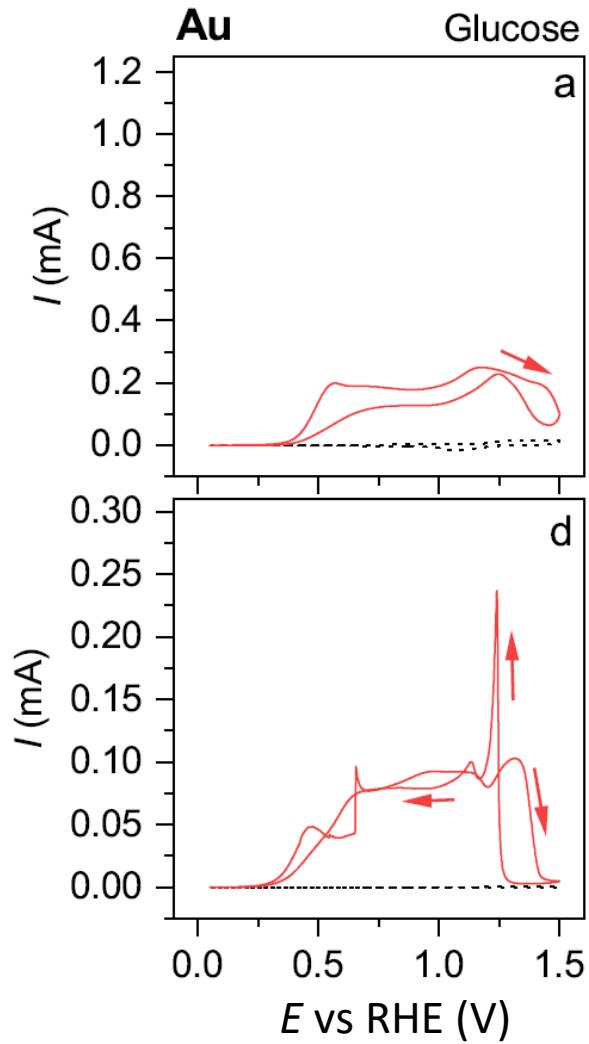




Cyclic voltammograms of bulk Pt and Au at 100 (upper panels) and 0.001 V.s<sup>-1</sup> (lower panels). Blank cyclic voltammograms measured in supporting electrolyte (10<sup>-1</sup> M NaOH) are reported in dotted (black) line, while cyclic voltammograms with 10<sup>-1</sup> M glucose in supporting electrolyte are reported in solid line.  $T = 293$  K

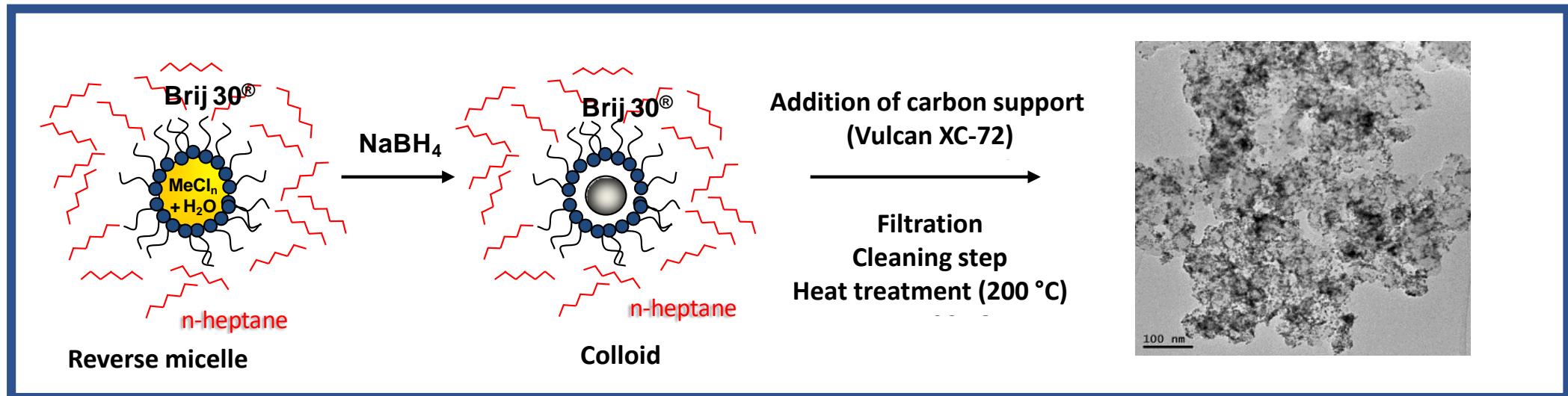
T. Faverge, B. Gilles, A. Bonnefont, F. Maillard, C. Coutanceau, M. Chatenet, *In situ investigation of D-glucose oxidation into value-added products on Au, Pt and Pd under alkaline conditions: a comparative study.* ACS Catal. 13 (2023) 2657–2669.

# Generally proposed mechanism on Au



B. Beden, F. Largeaud, K. B. Kokoh, C. Lamy, Fourier transform infrared reflectance spectroscopic investigation of the electrocatalytic oxidation of D-glucose: identification of reactive intermediates and reaction products, *Electrochim. Acta* 41, (1996) 701-709.

M. Pasta, F. La Mantia, Y. Cui, Mechanism of glucose electrochemical oxidation on gold surface, *Electrochim. Acta* 55 (2010) 5561-5568.



## Synthesis parameters:

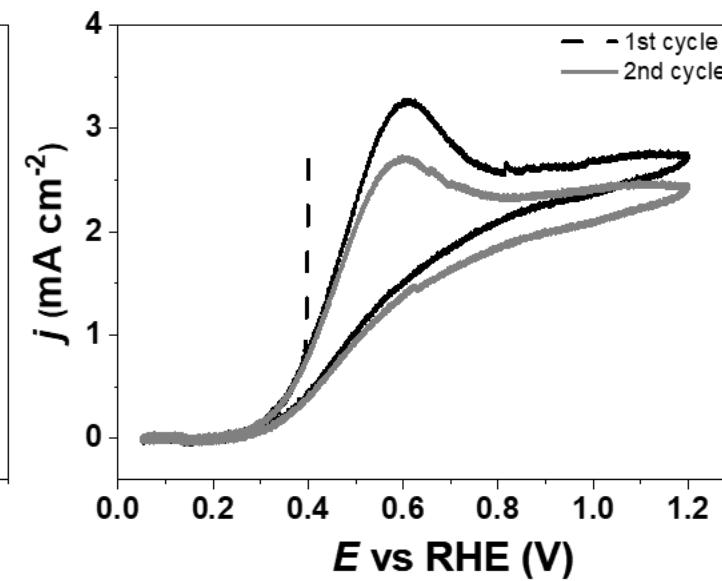
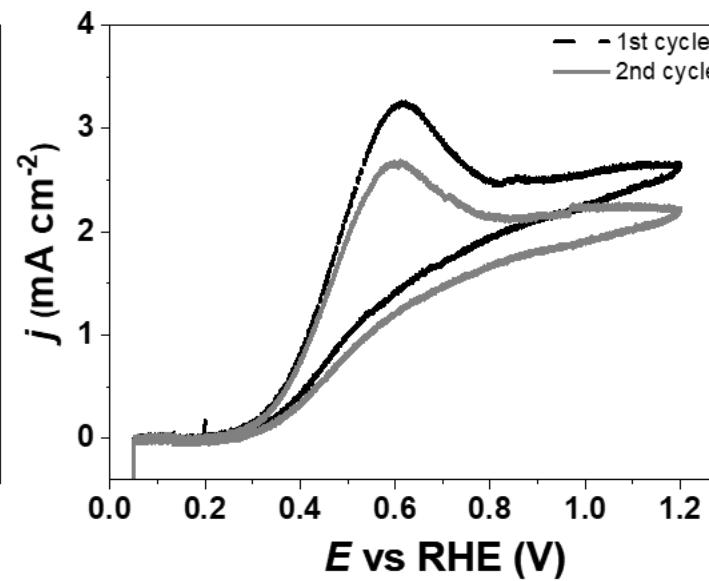
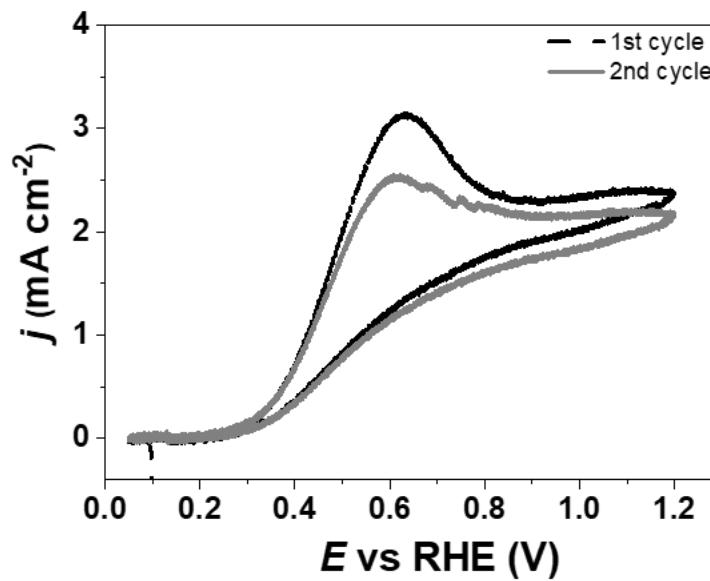
- HAuCl<sub>4</sub> • 3H<sub>2</sub>O
- Metal salt concentration: **0.1 mol L<sup>-1</sup>**
- Brij®30: **16.1 g**
- Heptane: **37 g**
- NaBH<sub>4</sub> : **100 mg (large excess)**
- Nominal metal loading: **40 wt%**

	<b>W / wt%</b> <b>(TGA)</b>	<b>a / Å</b> <b>(XRD)</b>	<b>L<sub>v</sub> / nm</b> <b>(XRD)</b>	<b>d<sub>TEM</sub></b> <b>(TEM)</b>	<b>ECSA / m<sup>2</sup> g<sup>-1</sup></b> <b>(CV*)</b>
<b>Au-NPs/C</b>	<b>35.4</b>	<b>4.047</b>	<b>4.4</b>	<b>6.8</b>	<b>14</b>

\* Reduction of AuO monolayer

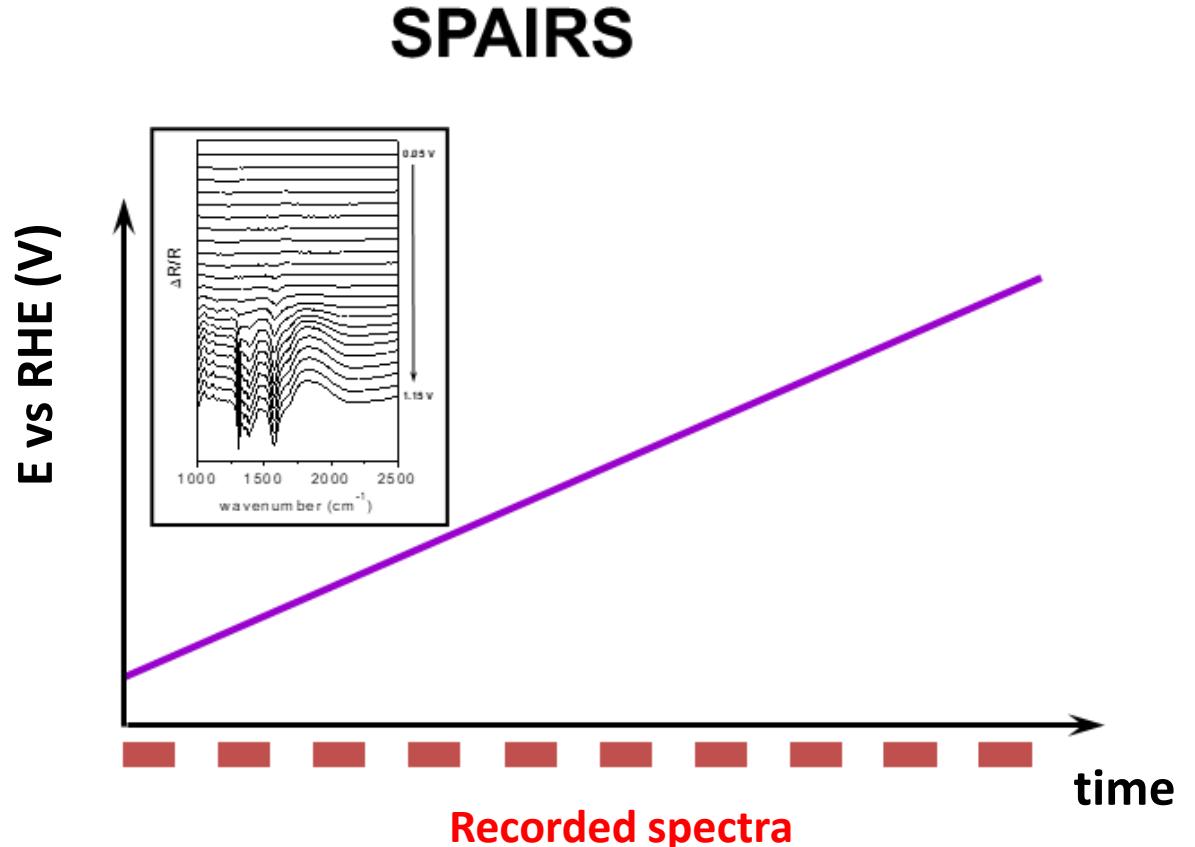
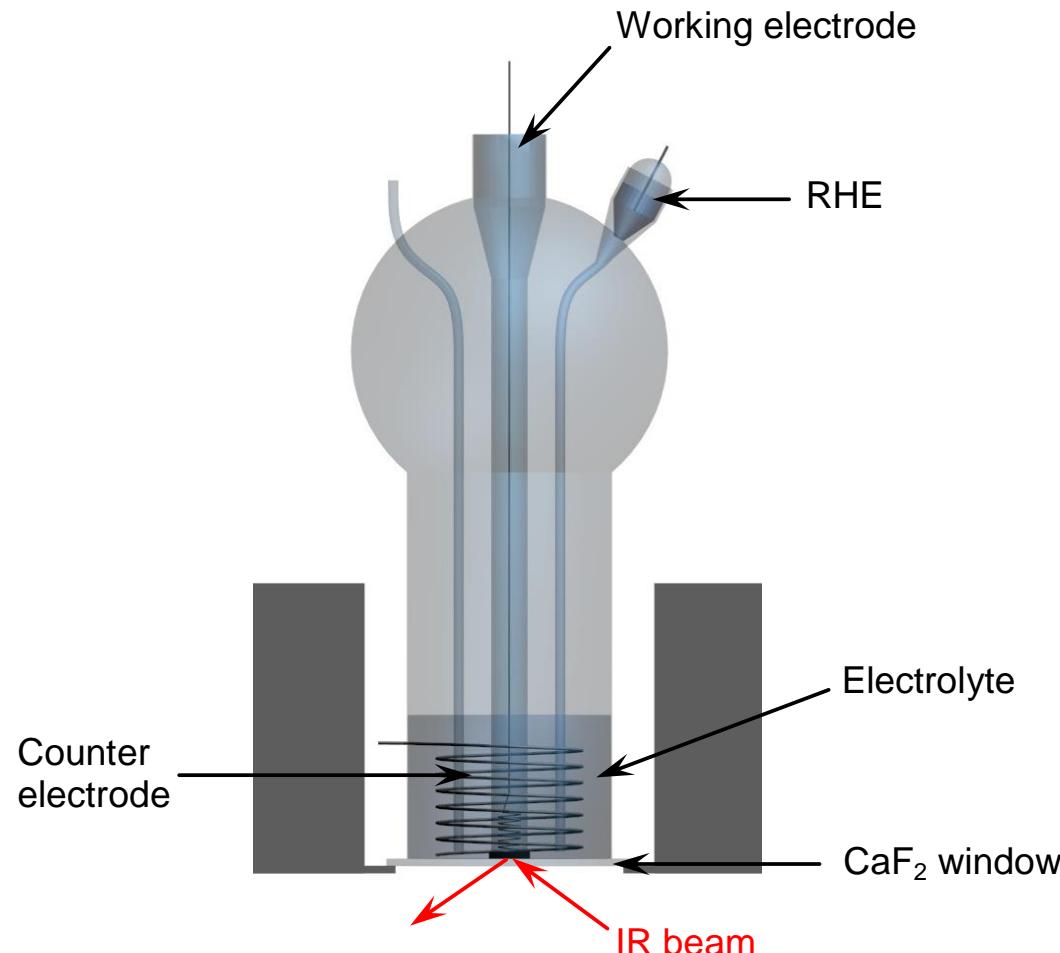
T. Rafaïdeen, S. Baranton, C. Coutanceau, Highly efficient and selective electrooxidation of glucose and xylose in alkaline medium at carbon supported alloyed PdAu nanocatalysts, *Appl. Catal. B: Env.* 243 (2019) 641-656.

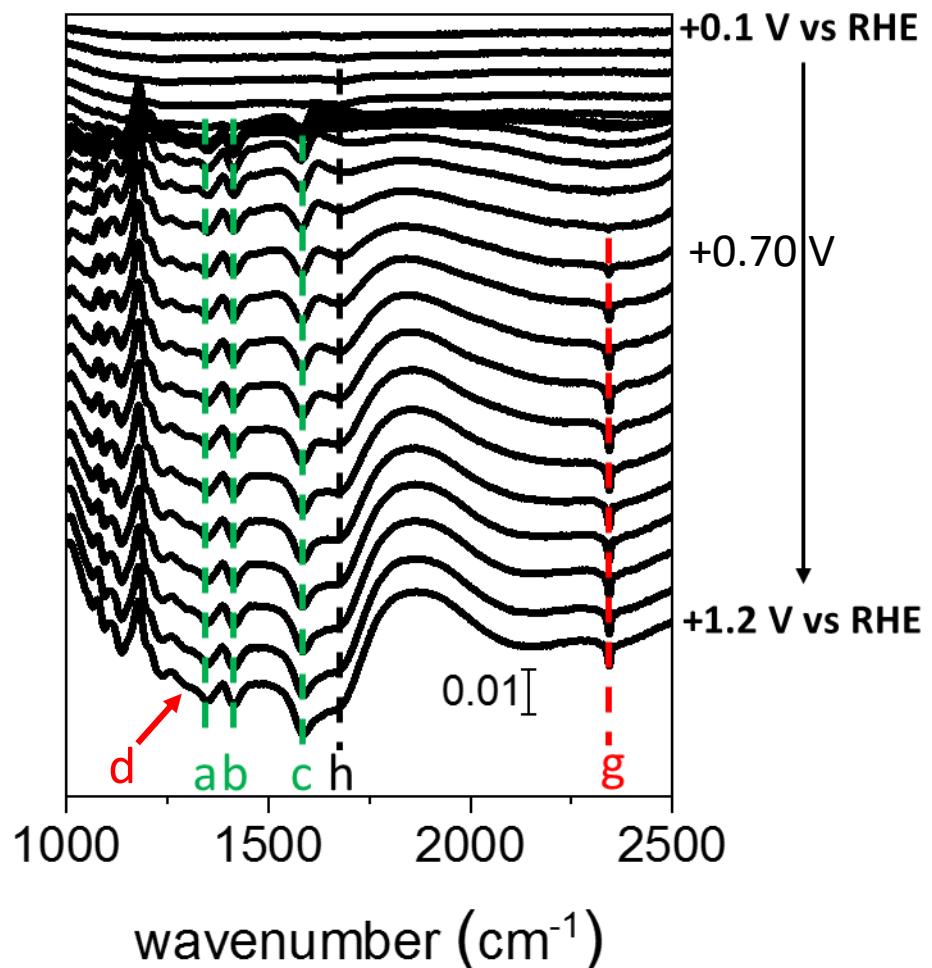
N. Neha, S. R. B. Kouamé, T. Rafaïdeen, S. Baranton, C. Coutanceau, Remarkably efficient carbon-supported nanostructured platinum-bismuth catalysts for the selective electrooxidation of glucose and methyl-glucoside, *Electrocatalysis* 12 (2021) 1-14.



Cyclic voltammograms recorded in N<sub>2</sub>-purged 0.10 mol L<sup>-1</sup> NaOH electrolyte at a (a) Pt-NPs/C electrode and (b) Au/C electrode in the absence (black plain line), and in the presence (dotted black line for the first cycle and plain grey line for the second one) of 0.10 mol L<sup>-1</sup> glucose after chronoamperometry.

Scan rate = 0.005 V s<sup>-1</sup>, T = 293 K

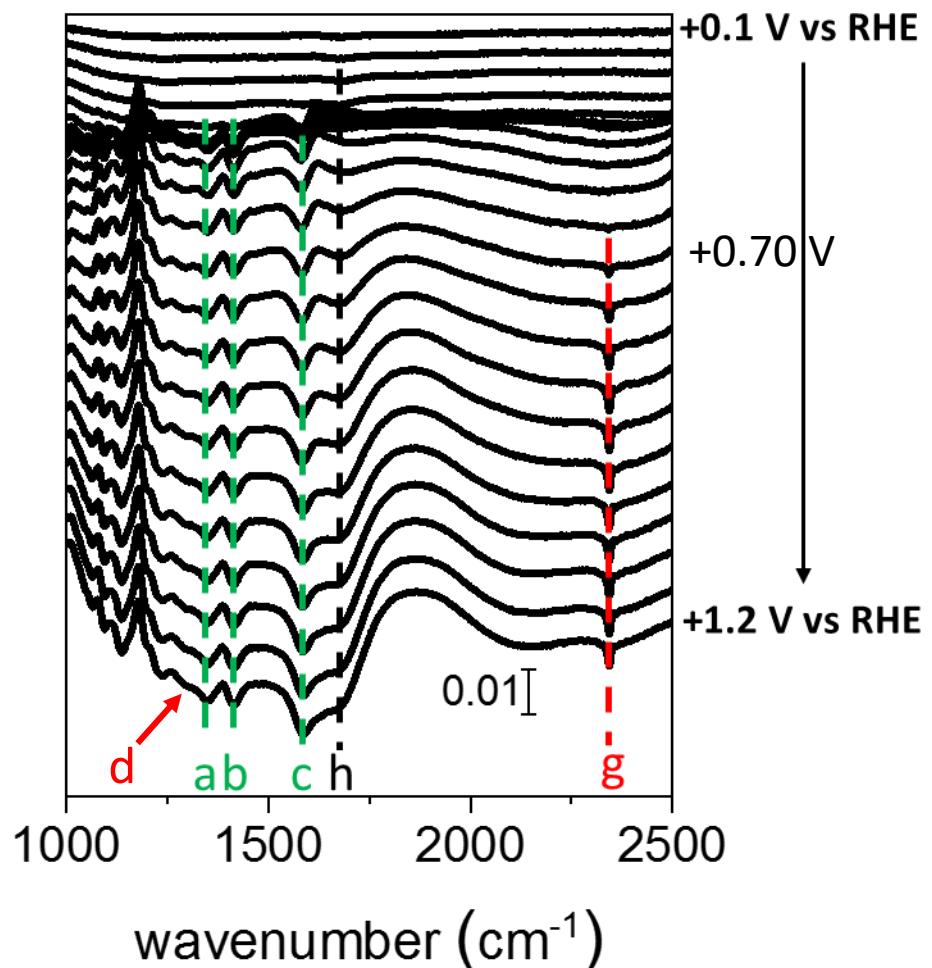




- a:  $1346 \text{ cm}^{-1} \Rightarrow \delta(\text{CH}_2)$  mode of gluconate or gluconolactone
- b:  $1415 \text{ cm}^{-1} \Rightarrow \nu_{\text{sym.}} (\text{O-C-O})$  of carboxylate
- c:  $1581 \text{ cm}^{-1} \Rightarrow \nu_{\text{sym.}} (\text{O-C-O})$  of carboxylate

B. Beden, F. Largeaud, K. B. Kokoh, C. Lamy, Fourier transform infrared reflectance spectroscopic investigation of the electrocatalytic oxidation of D-glucose: identification of reactive intermediates and reaction products, *Electrochim. Acta.* 41, (1996) 701-709.

IR spectra recorded every 0.050 V during 0.10 mol L<sup>-1</sup> glucose electrooxidation in 0.10 mol L<sup>-1</sup> NaOH electrolyte from +0.100 V to +1.200 V vs RHE on Au-NPs/C catalysts. Scan rate: 0.001 V s<sup>-1</sup>, resolution 4 cm<sup>-1</sup>, T = 293 K. Vertical scale: ΔR/R



a:  $1346 \text{ cm}^{-1} \Rightarrow \delta(\text{CH}_2)$  mode of gluconate or gluconolactone

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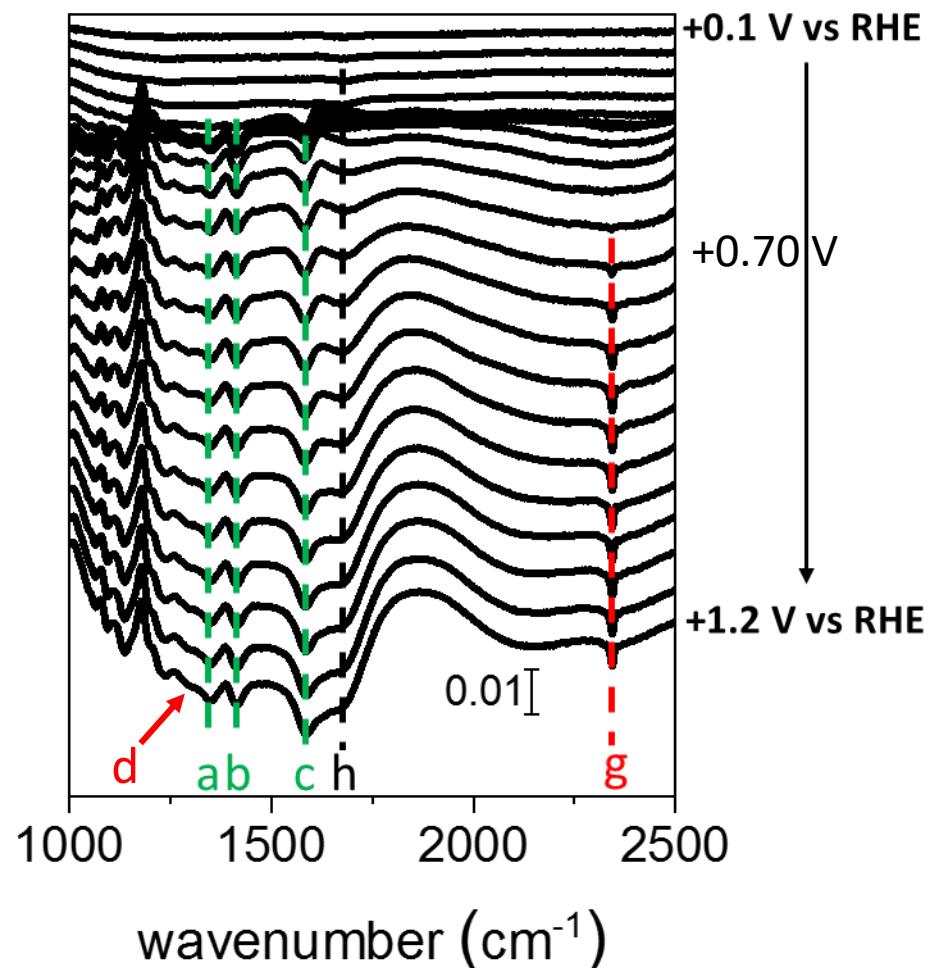
d:  $1304 \text{ cm}^{-1} \Rightarrow \text{HCO}_3^-$

g:  $2343 \text{ cm}^{-1} \Rightarrow$  interfacial  $\text{CO}_2$

C. Lafforgue, F. Maillard, V. Martin, L. Dubau, M. Chatenet, Degradation of carbon-supported platinum-group-metal electrocatalysts in alkaline media studied by in situ Fourier transform infrared spectroscopy and identical-location transmission electron microscopy, *ACS Catal.* 9 (2019) 5613–5622.

L. Dubau, F. Hahn, C. Coutanceau, J.-M. Léger, C. Lamy, On the structure effects of bimetallic PtRu electrocatalysts towards methanol oxidation, *J. Electroanal. Chem.* 554/555 (2003) 407-415.

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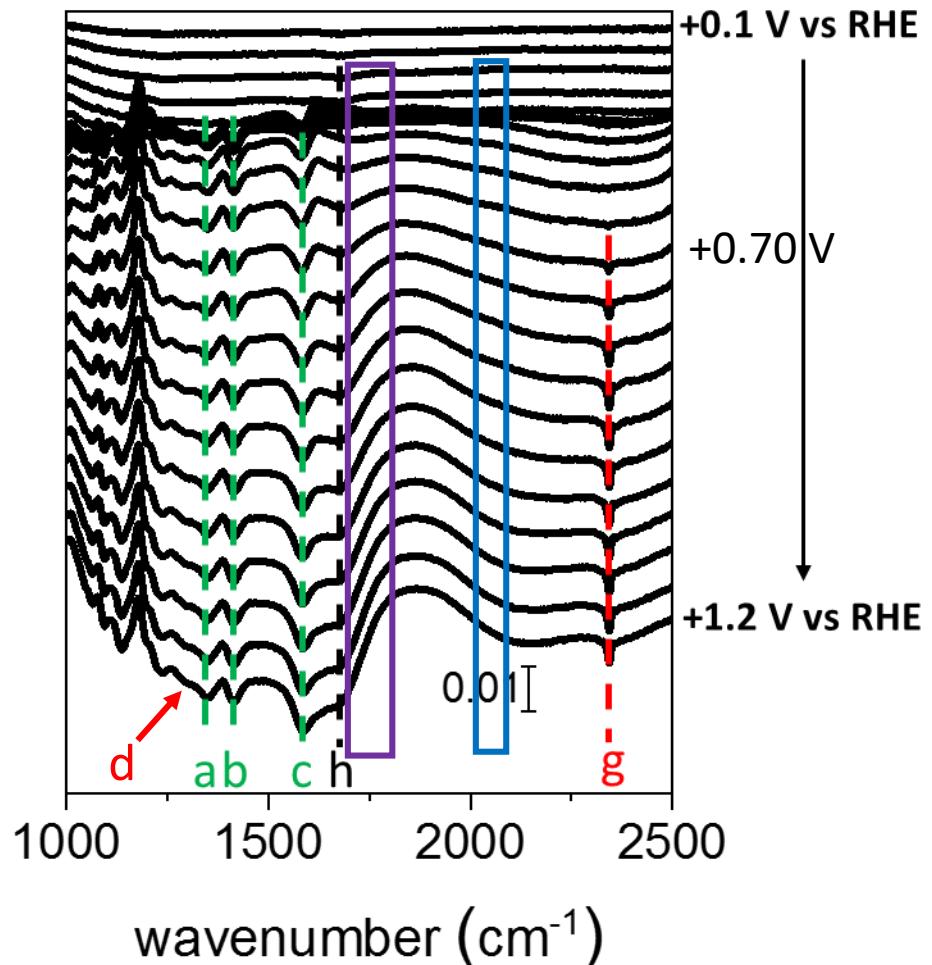
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h:  $1680 \text{ cm}^{-1} \Rightarrow$  any possible assignation to carbonyl species, pseudo-band related to the interfacial water band at  $1640 \text{ cm}^{-1}$

A. Rodes, E. Pastor, T. Iwasita, An FTIR study on the adsorption of acetate at the basal planes of platinum single-crystal electrodes, *J. Electroanal. Chem.* 376 (1994) 109-118.

IR spectra recorded every 0.050 V during  $0.10 \text{ mol L}^{-1}$  glucose electrooxidation in  $0.10 \text{ mol L}^{-1}$  NaOH electrolyte from +0.100 V to +1.200 V vs RHE on Au-NPs/C catalysts. Scan rate:  $0.001 \text{ V s}^{-1}$ , resolution  $4 \text{ cm}^{-1}$ ,  $T = 293 \text{ K}$ . Vertical scale:  $\Delta R/R$



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Missing bands:

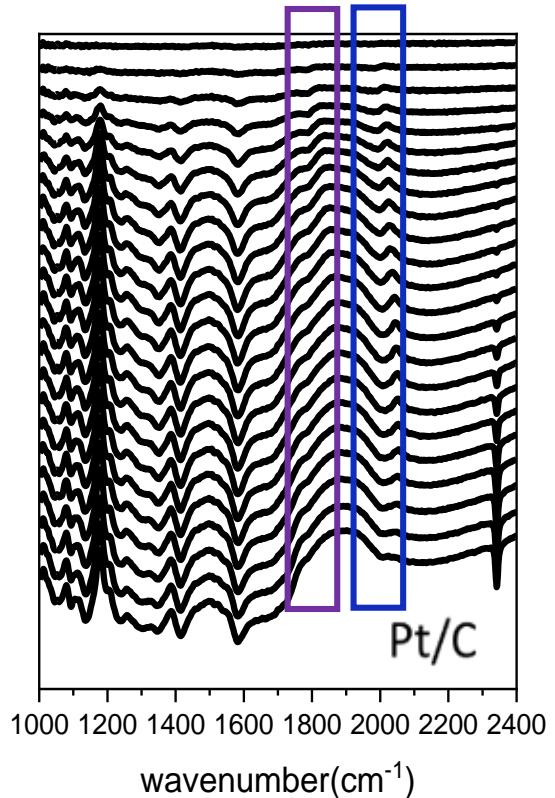
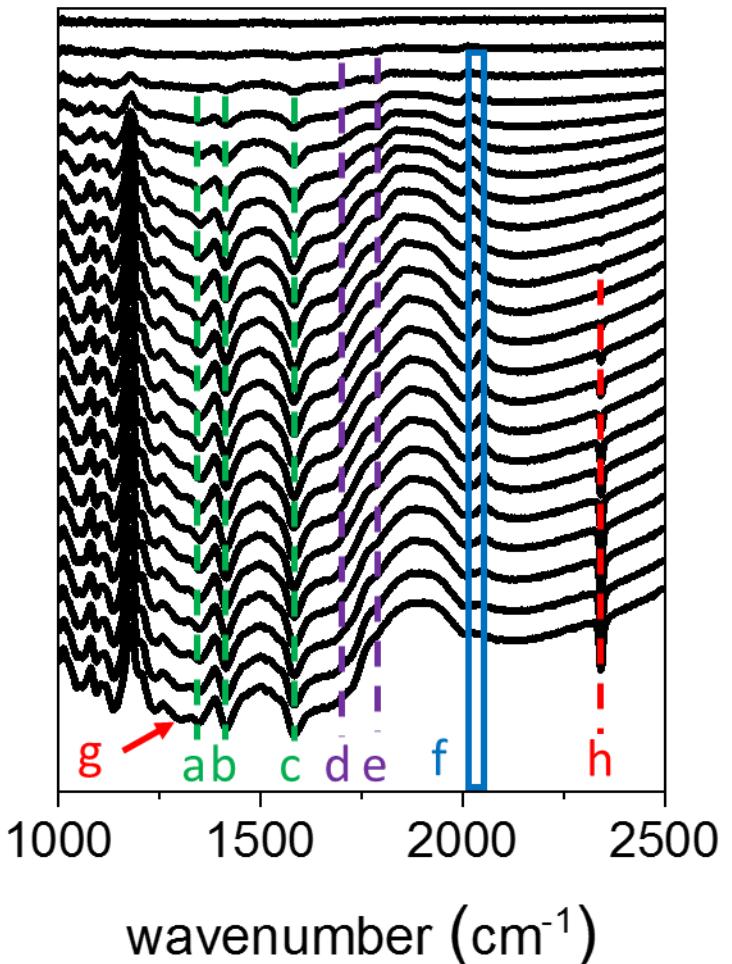
$1720 \text{ cm}^{-1} \Rightarrow \nu(\text{C=O})$  of  $\delta$ -gluconolactone

$1785 \text{ cm}^{-1} \Rightarrow \nu(\text{C=O})$  of  $\gamma$ -gluconolactone

B. Beden, F. Largeaud, K. B. Kokoh, C. Lamy, Fourier transform infrared reflectance spectroscopic investigation of the electrocatalytic oxidation of D-glucose: identification of reactive intermediates and reaction products, *Electrochim. Acta.* 41, (1996) 701-709.

$2050 \text{ cm}^{-1} \Rightarrow$  linearly adsorbed CO species

A. Couto, A. Rincon, M. C. Perez, C. Gutierrez, Adsorption and electrooxidation of carbon monoxide on polycrystalline platinum at pH 0.3–13, *Electrochim. Acta* 46 (2001) 1285–1296.



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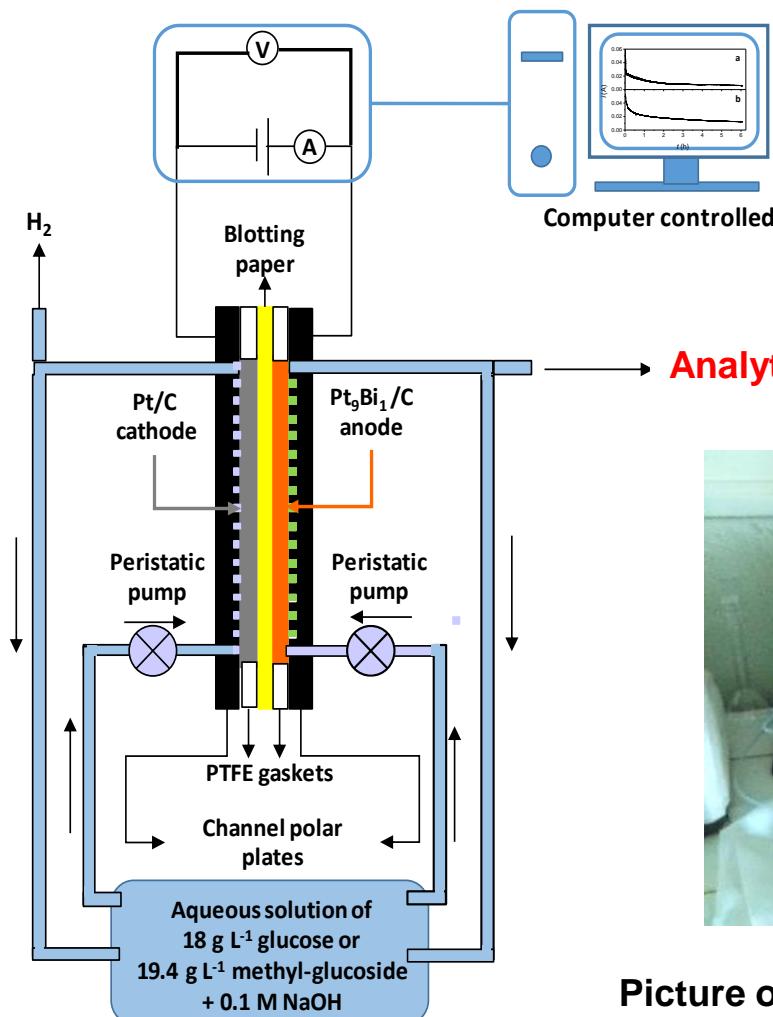
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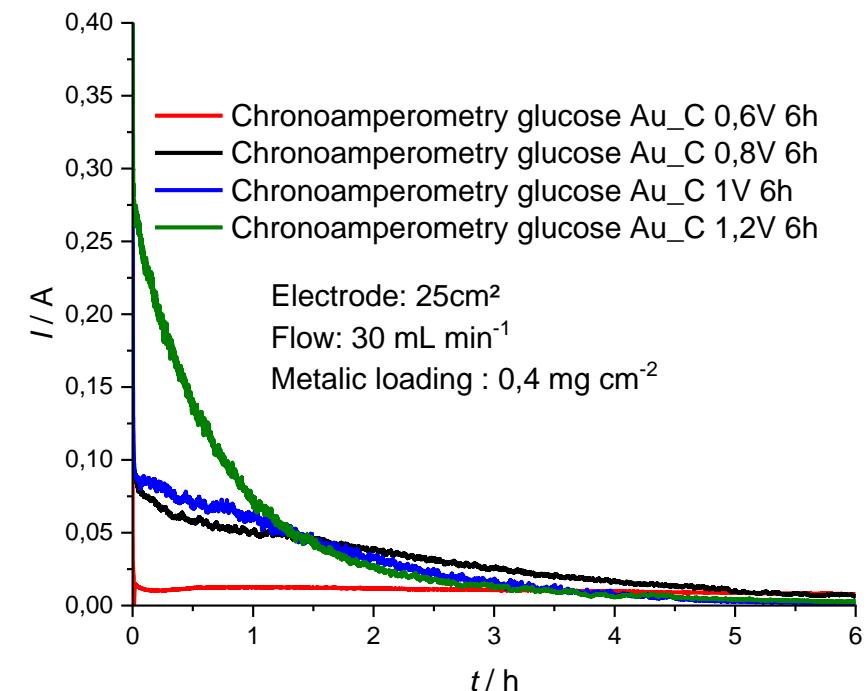
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## Scheme of principle for CA measurements



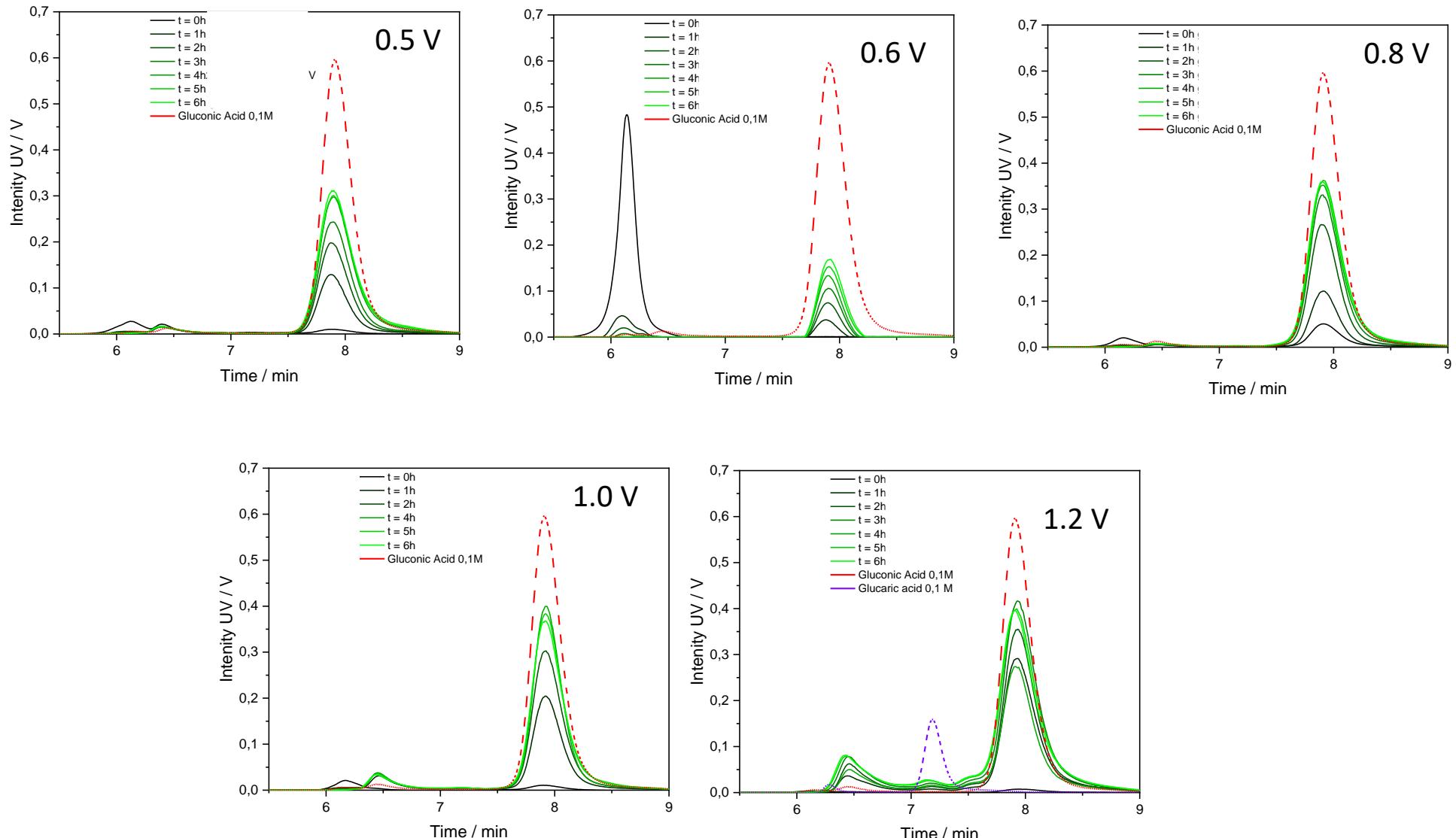
## Chronoamperometry curves



Picture of the experimental set-up

Anode: Au/C at  $0.5\text{ mg}_{\text{Au}}\text{ cm}^{-2}$   
Cathode: Pt/C cathode at  $0.5\text{ mg}_{\text{Pt}}\text{ cm}^{-2}$   
Solution: 30 mL of  $0.10\text{ mol L}^{-1}$  NaOH with  $18.0\text{ g L}^{-1}$  glucose ( $0.1\text{ mmol L}^{-1}$ )  
 $T = 20^\circ\text{C}$

# Electrooxidation of glucose at Au/C



From CA followed by CVs experiments: the first step of glucose adsorption is evidenced

From in-situ infrared spectroscopy: no CO<sub>ads</sub> and no lactone detected by IR

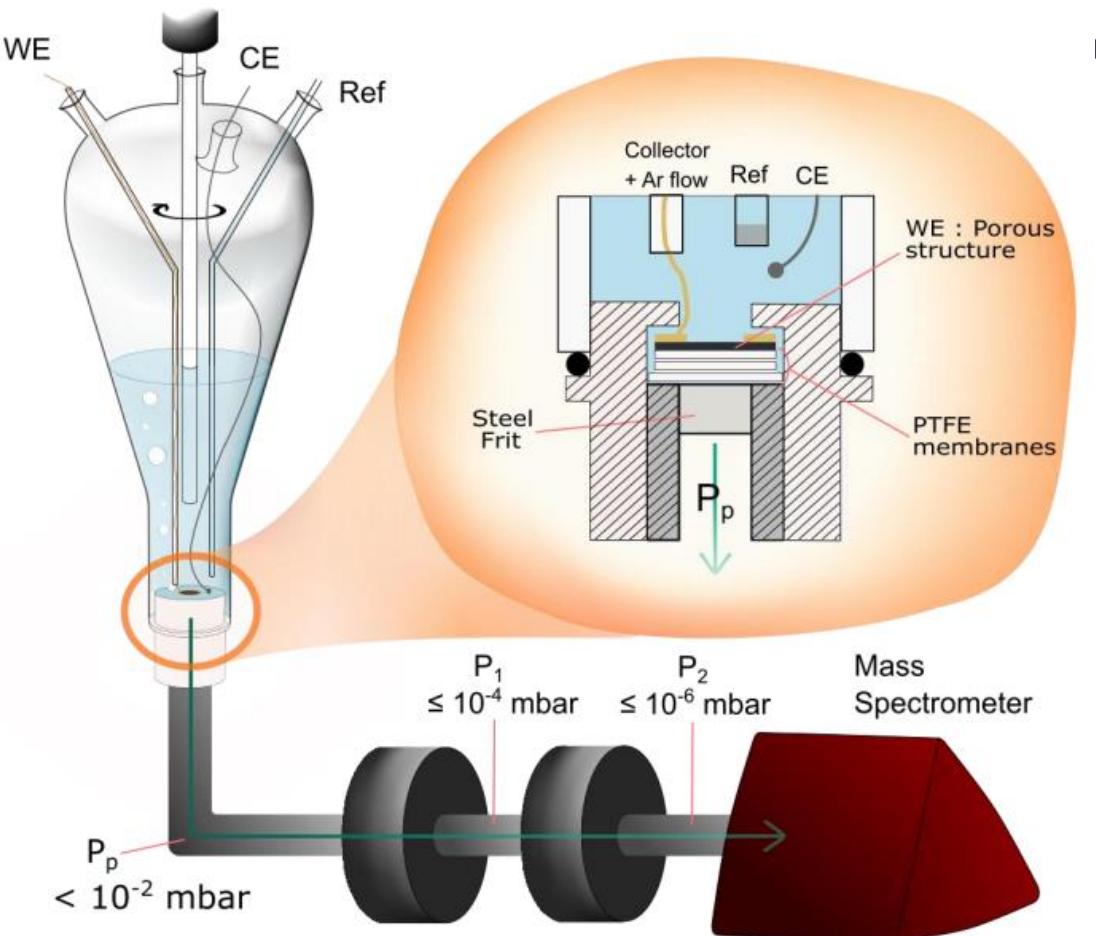
- => adsorbed gluconate species from very low potentials
- => CO<sub>2</sub> only detected from ca. 0.700 V vs RHE
  
- => gluconate as main reaction product at low potentials
- => gluconate + overoxidized compounds + degradation products + CO<sub>2</sub> at high potentials

Confirmed by CA and HPLC measurement of reaction products

Detection of gases and volatile species by the mass spectrometer during cyclinc volatmmetry

Detection of hydrogen ( $\text{H}_2$ ,  $m/z = 2$ )

Detection of carbon dioxyde ( $\text{CO}_2$ ,  $m/z = 44$ )



Guillaume Braesch : « Electrocatalyseurs pour la Réaction d'Oxydation des Borohydrures : des surfaces modèles aux électrodes non-nobles de piles à combustible », Grenoble, 2020

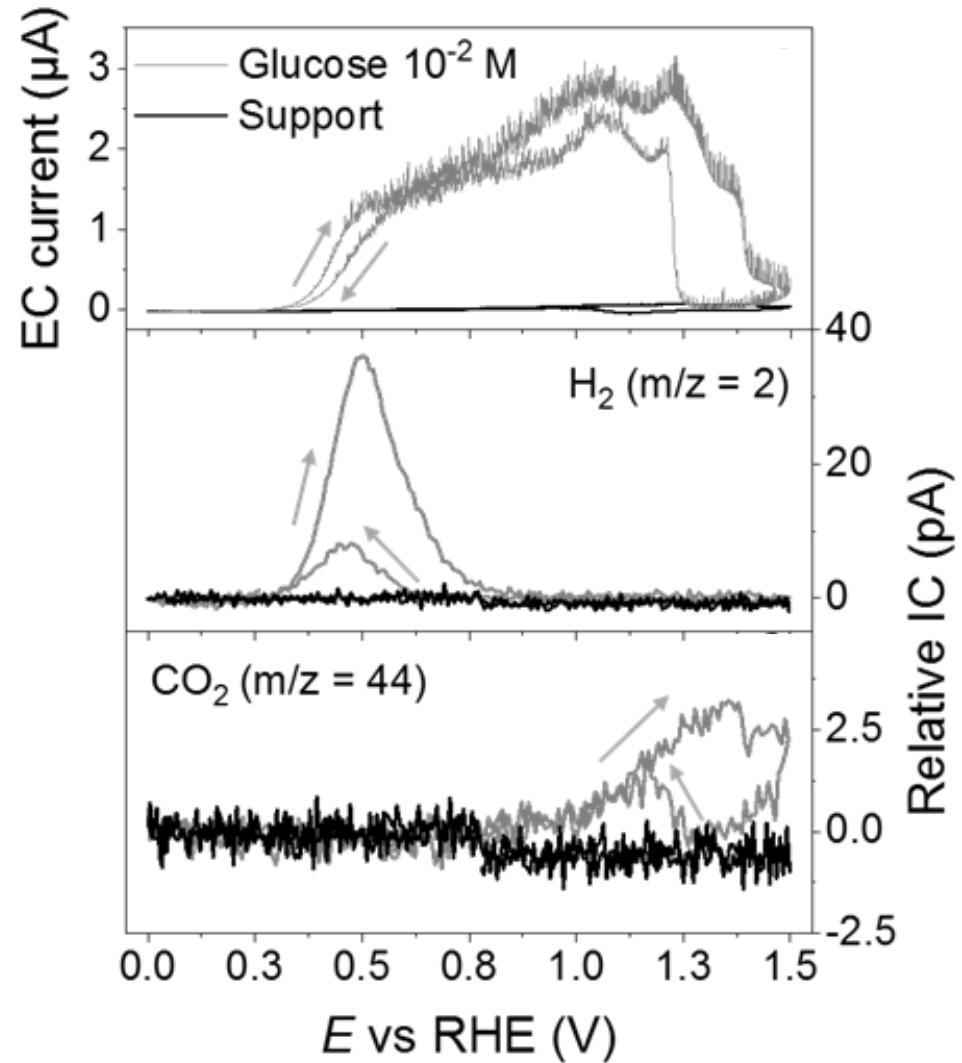
To avoid any possible signal perturbation due to carbon support oxidation into  $\text{CO}_2$  (potentials  $> 0.207 \text{ V vs RHE}$ )

=> DEMS experiments carried out on unsupported sputtered Pt-NPs and Au-NPs

Working electrodes: Pt or Au nanoporous layer by sputtering onto the porous PTFE membrane (pore size  $0.02 \mu\text{m}$ , thickness  $20 \mu\text{m}$ , Cobetter filtration®), which serves as interface between the electrochemical cell and the high vacuum chamber of the mass spectrometer.

=>  $0.28 \text{ cm}^2$  area,  $50 \text{ nm} \pm 10 \text{ nm}$  average thickness

=> AFM: small grains of  $5\text{-}10 \text{ nm}$  with  $1\text{-}2 \text{ nm}$  root means square of profile height deviation from the mean line



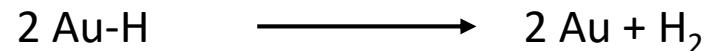
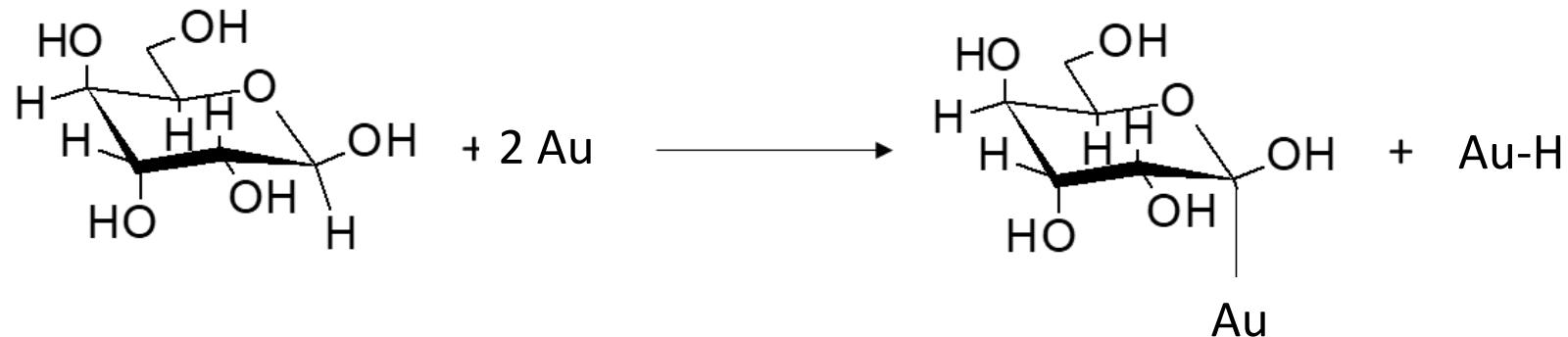
CVs of 10<sup>-2</sup> M glucose oxidation in 10<sup>-1</sup> mol L<sup>-1</sup> NaOH electrolyte on sputtered Au-NPs.  
Scan rate: 0.010 V s<sup>-1</sup>,  $T = 293$  K.

DEMS measurement performed at m/z = 2 for the electrooxidation of 0.010 mol L<sup>-1</sup> glucose oxidation in 0.10 mol L<sup>-1</sup> NaOH electrolyte on sputtered Au-NPs;

DEMS measurement performed at m/z = 44 for the electrooxidation of 0.010 mol L<sup>-1</sup> glucose oxidation in 0.10 mol L<sup>-1</sup> NaOH electrolyte on sputtered Au-NPs.

# Proposed mechanism on Au-NPs

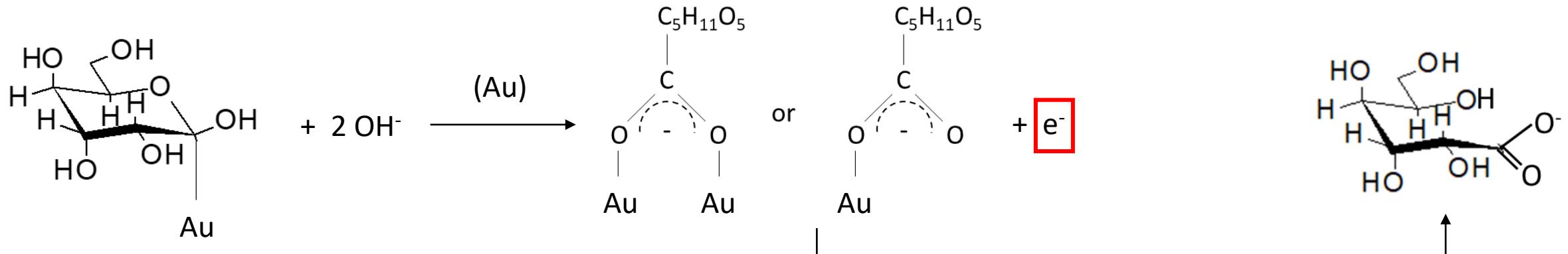
**Step 1 (Au)**



N. Arjona, G. Trejo, J. Ledesma-García, L. G. Arriaga, M. Guerra-Balcázar, An electrokinetic-combined electrochemical study of the glucose electrooxidation reaction: effect of gold surface energy, RSC Adv. 6 (2016) 15630–15638.

S. A. C. Carabineiro, B. E. Nieuwenhuys, Adsorption of small molecules on gold single crystal surfaces, Gold Bull. 42 (2009) 288-301.

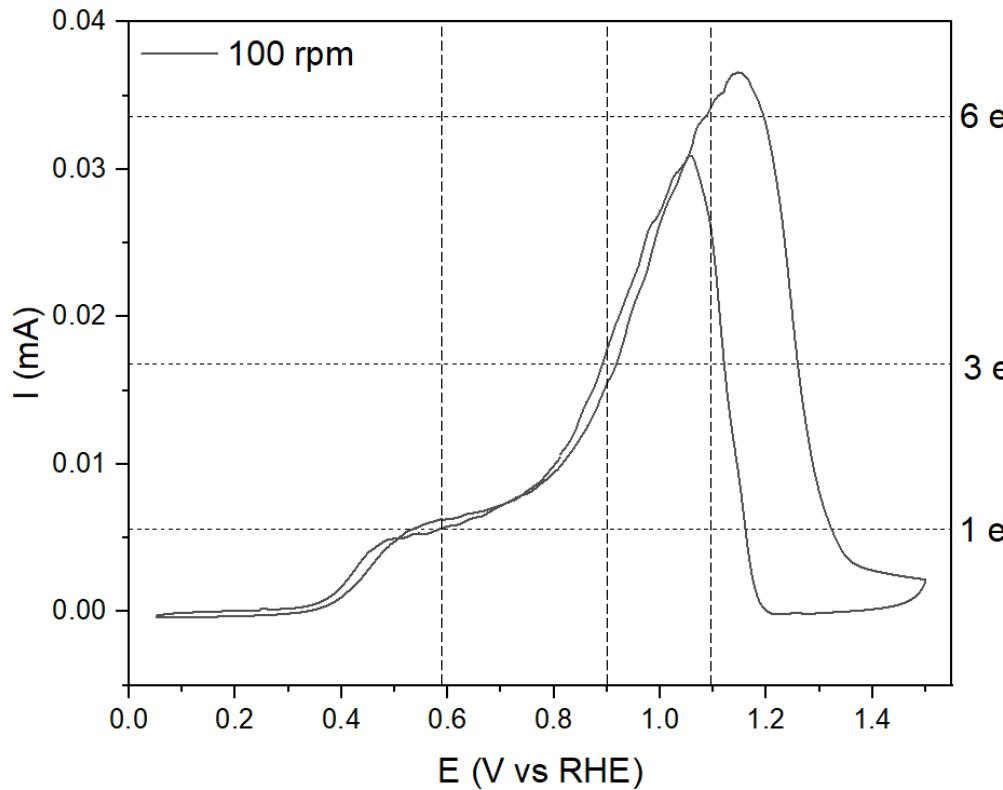
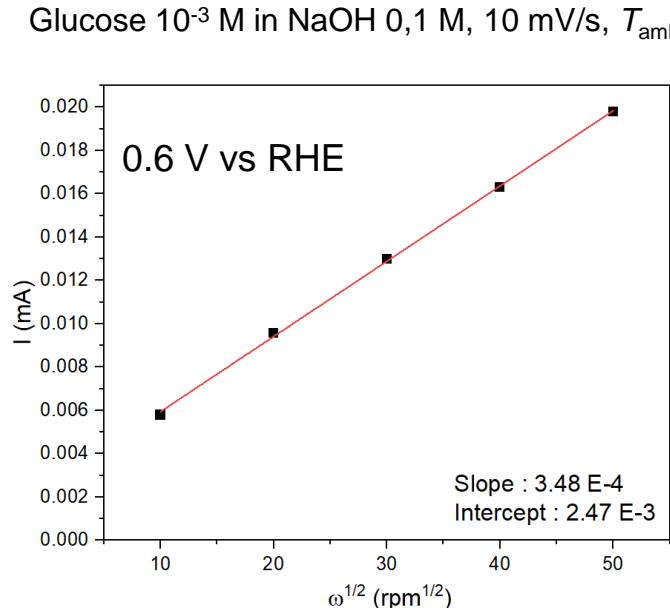
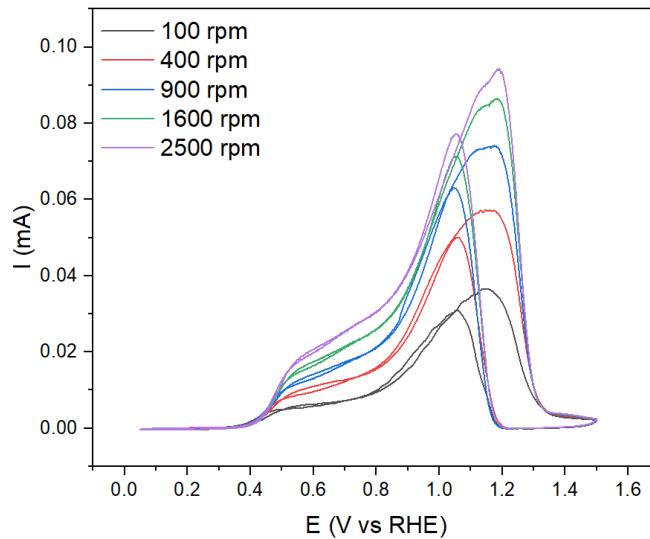
W. Watkins, Y. Borensztein, Mechanism of hydrogen adsorption on gold nanoparticles and charge transfer probed by anisotropic surface plasmon resonance, Phys. Chem. Chem. Phys. 19 (2017) 27397 - 27405.



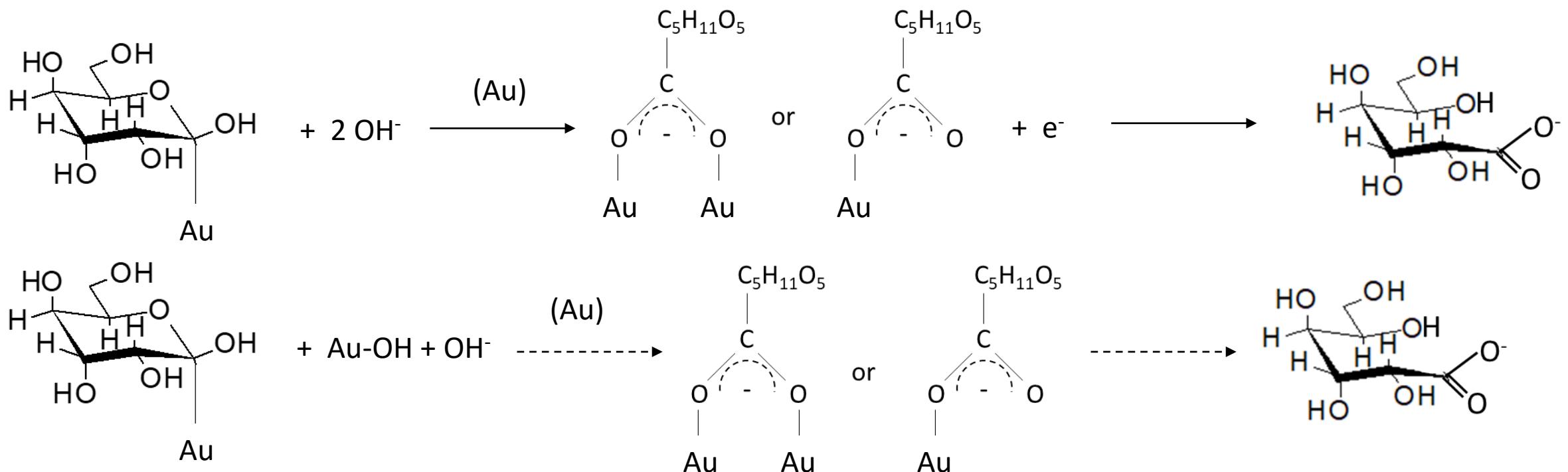
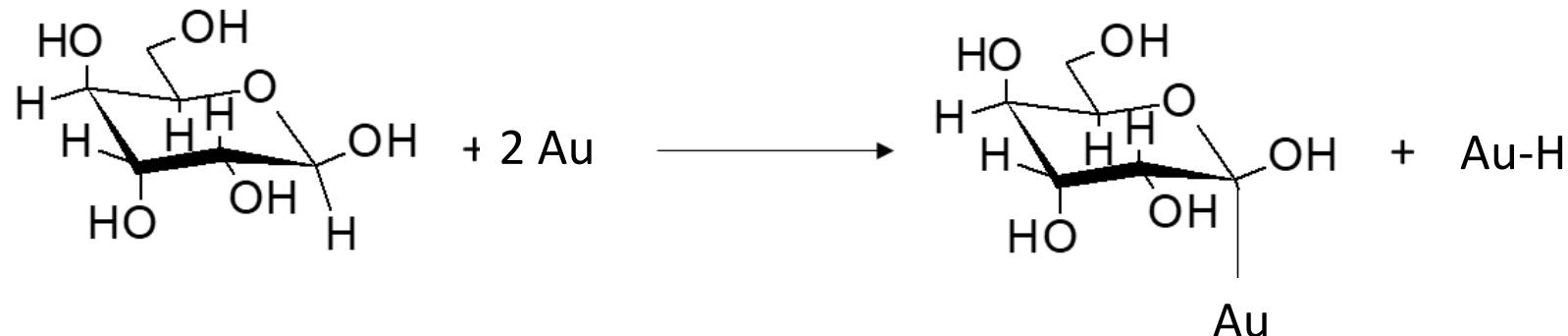
# Number of exchanged electrons by Levich study

→ Caution : not purely mass transport limited conditions

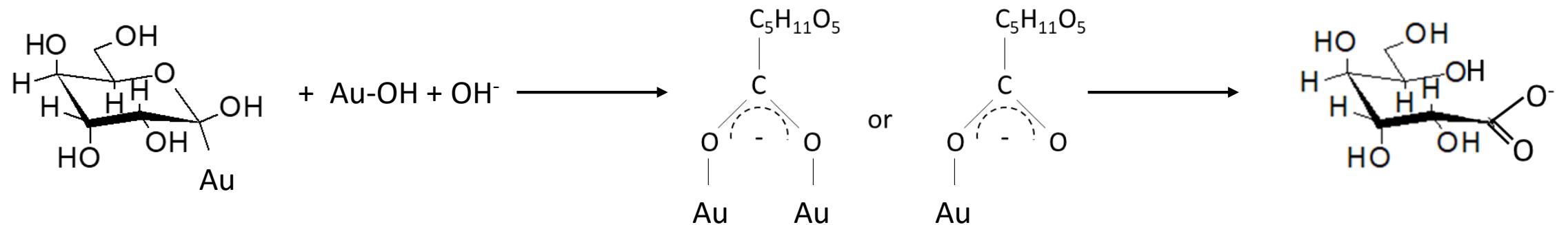
Levich equation:  $I_L = 0.620 n F A D^{\frac{2}{3}} v^{\frac{-1}{6}} C \omega^{\frac{1}{2}}$



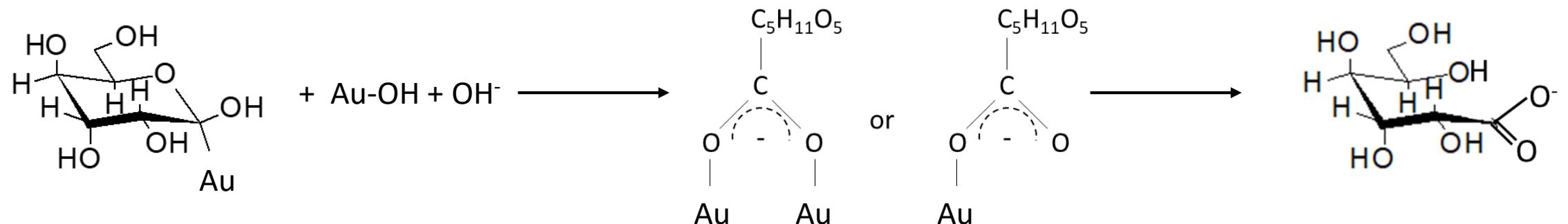
## Step 1 (Au)



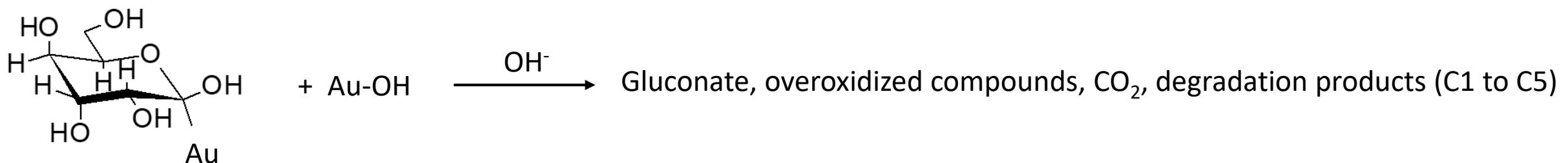
For  $0.500 \text{ V} < E < 0.850 \text{ V}$  vs RHE



For  $0.500 \text{ V} < E < 0.850 \text{ V}$  vs RHE



For  $0.850 \text{ V} < E < 1.500 \text{ V}$  vs RHE



- Au-NPs: high specificity, activity and selectivity towards gluconate for  $0.300 \text{ V} < E < 0.800 \text{ V}$  vs RHE
  - Gold appears as a good catalysts for the selective glucose electrooxidation
- H<sub>2</sub> evolution on gold over the same electrode potential range: bad or good news?
  - Alloying gold with another metal (Pt or Pd) allowing H oxidation
- Higher activity for  $U_{\text{cell}} = 0.5 \text{ V}$  than for  $U_{\text{cell}} = 0.6 \text{ V}$ 
  - Gold surface poisoning? Competitive reactions? Etc.?
- $U_{\text{cell}}$  higher than 0.8 V leads to overoxidized products in agreement with in-situ FTIRS and DEMS measurements

Special thanks to

Neha Neha (Post-doc IC2MP)

Thibault Rafaïdeen (Post-doc IC2MP)

Théo Favergé (PhD student IC2MP/LEPMI)

Marian Chatenet (Professor LePMI)

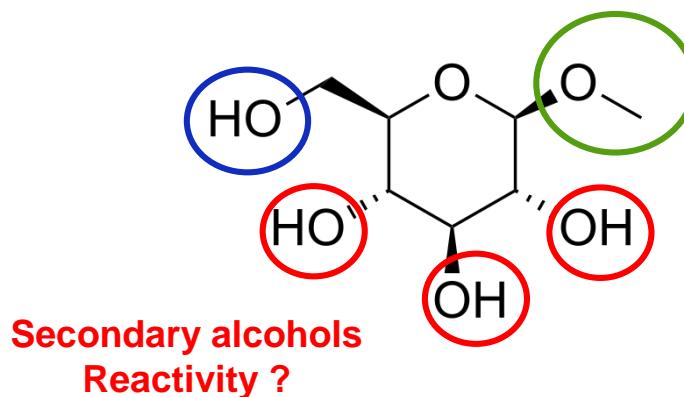
Frédéric Maillard (CNRS Research Director LePMI)

C6 : Primary alcohol

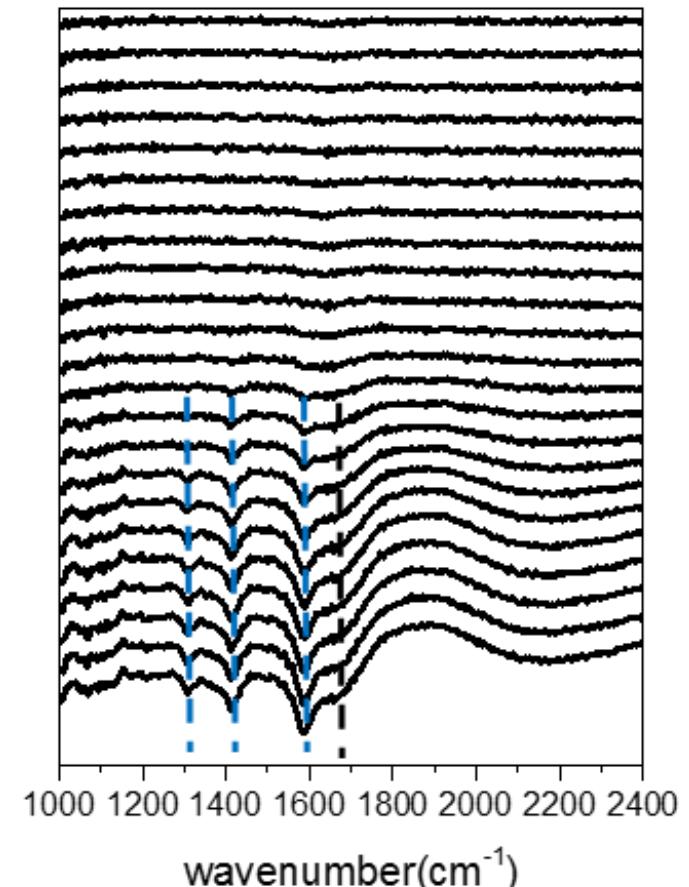
Thermodynamically hard to oxidize

C1 : Protected anomeric function

Not oxidizable



$\beta$ -D-Methylglucoside



+0.1 V vs RHE

+1.2 V vs RHE



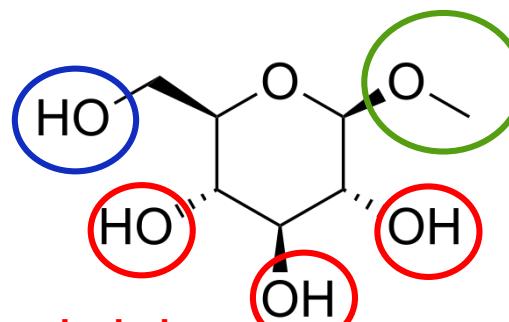
INCREASE

C6 : Primary alcohol

Thermodynamically hard to oxidize

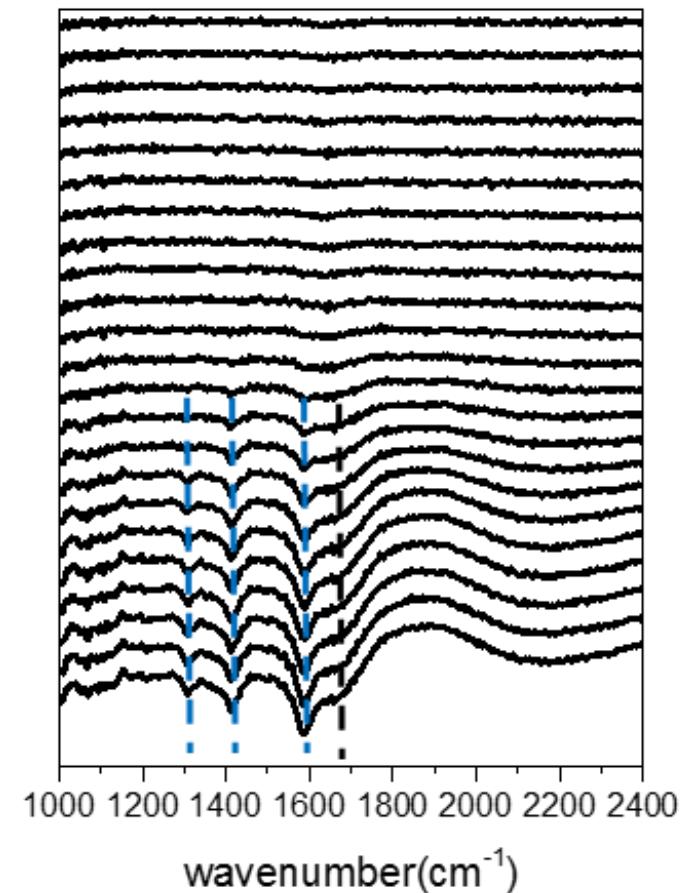
C1 : Protected anomeric function

Not oxidizable



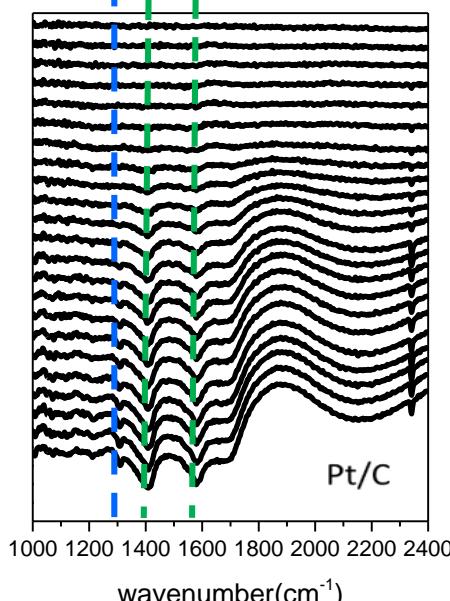
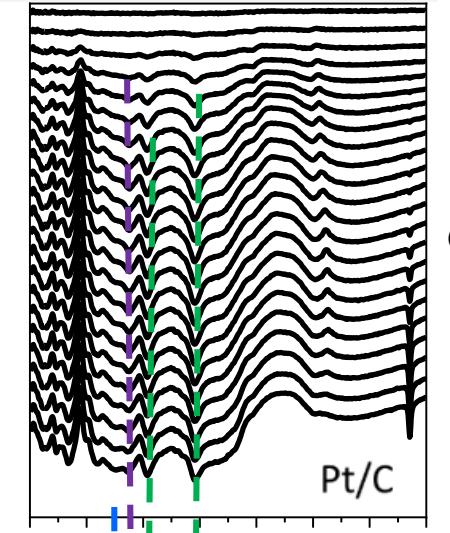
Secondary alcohols  
Reactivity ?

$\beta$ -D-Methylglucoside



+0.1 V vs RHE

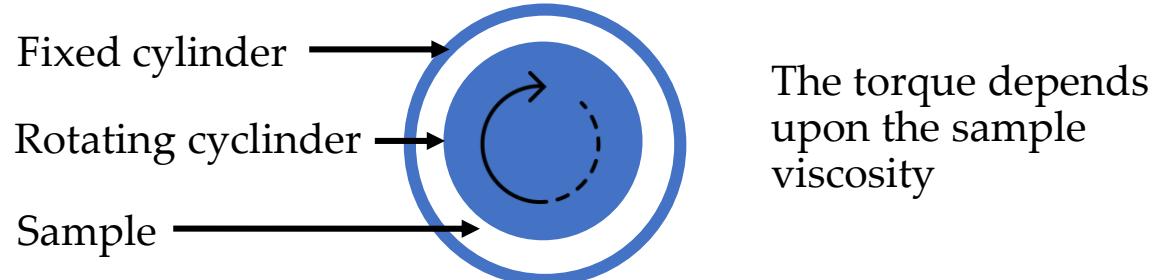
+1.2 V vs RHE



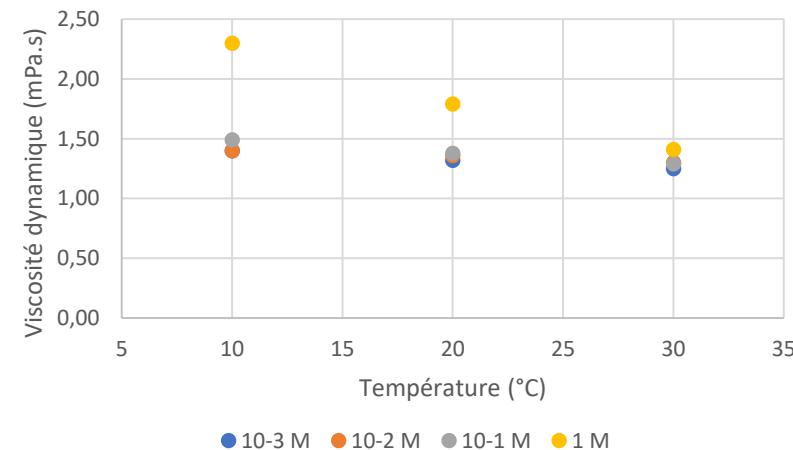
Glucose

$\beta$ -D-Methylglucoside

## Dynamic viscosity ( $\eta$ ) measurement – glucose in NaOH 0,1 M



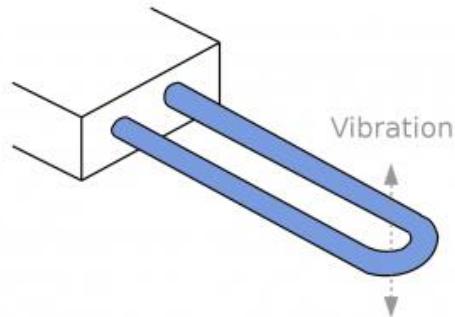
Dynamic viscosity, $\eta$ (mPa.s)	Temperature			
	10°C	20°C	30°C	
Glucose concentration	$10^{-3}$ M	1,40	1,32	1,25
	$10^{-2}$ M	1,40	1,36	1,30
	$10^{-1}$ M	1,49	1,38	1,29
	1 M	2,30	1,79	1,41



→ Density measurement missing to calculate kinematic viscosity ( $\nu$ )

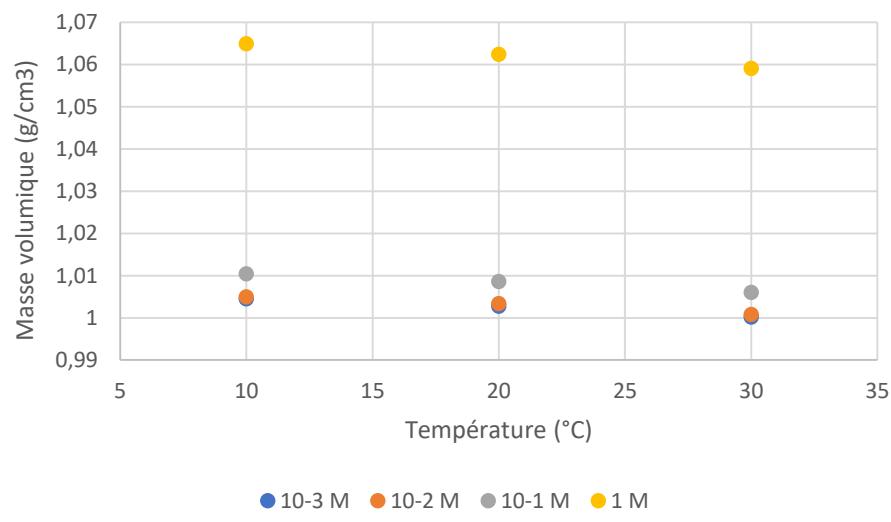
## Density measurement – glucose in NaOH 0,1 M

Vibrating U tube filled with the sample



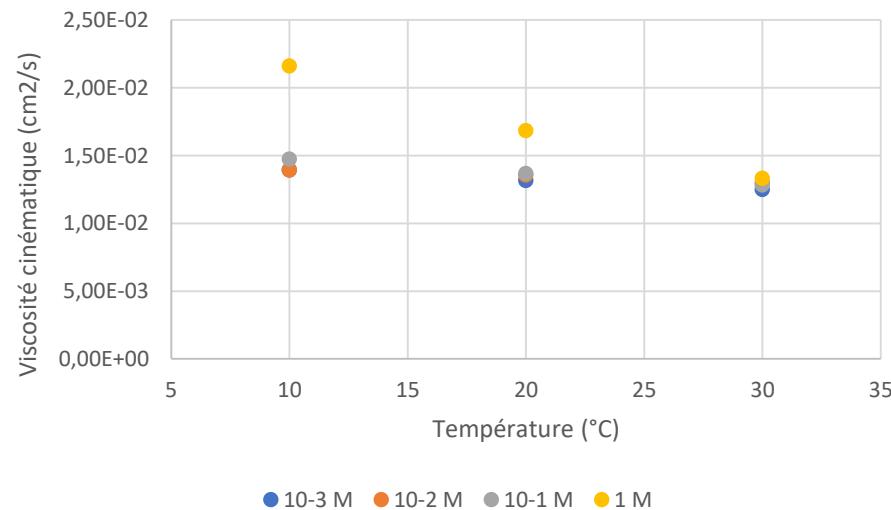
The vibration frequency depends upon the sample mass (and so its density)

Volumetric mass, $\rho$ (g/cm <sup>3</sup> )		Temperature		
		10°C	20°C	30°C
Glucose concentration	10 <sup>-3</sup> M	1,0045	1,0028	1,0002
	10 <sup>-2</sup> M	1,005	1,0034	1,0008
	10 <sup>-1</sup> M	1,0104	1,0086	1,006
	1 M	1,0649	1,0624	1,0591

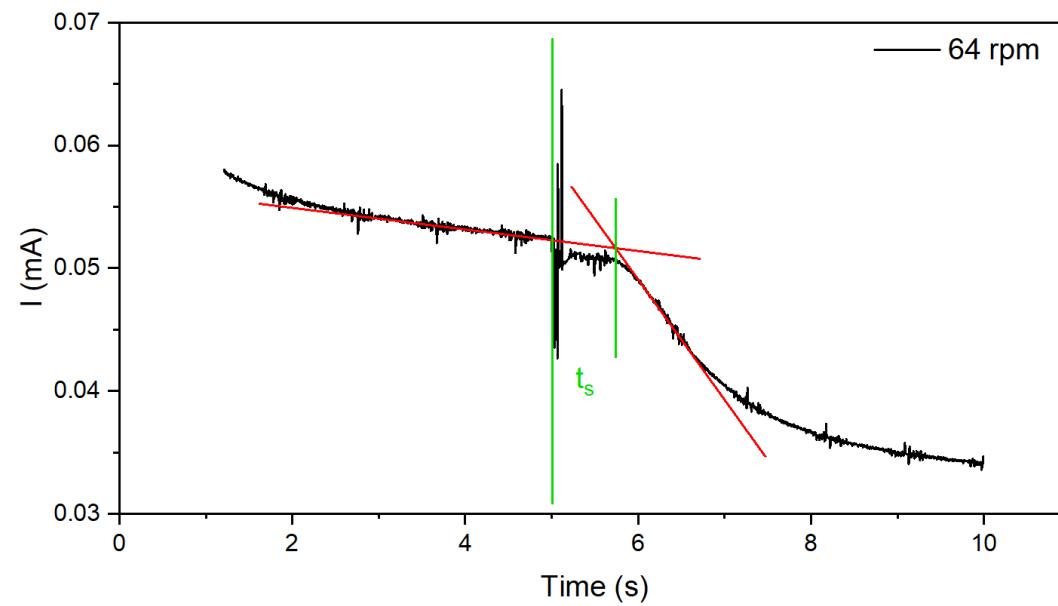
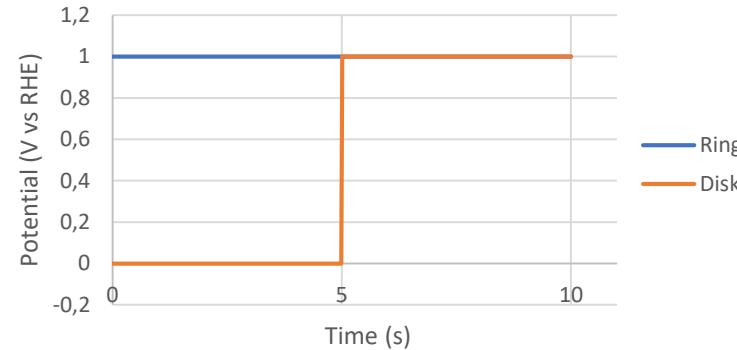
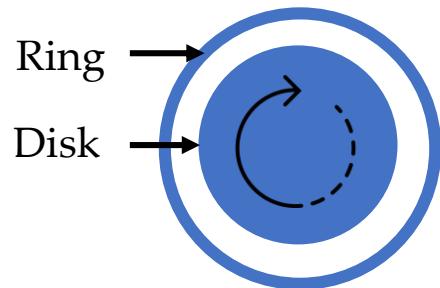


Kinematic viscosity ( $\nu$ ) calculation :  $\nu = \eta / \rho$

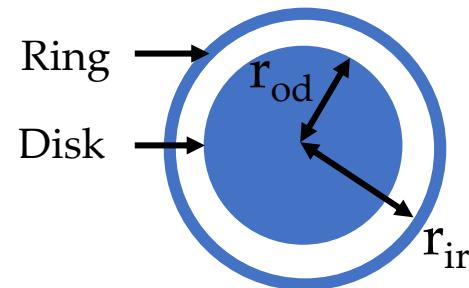
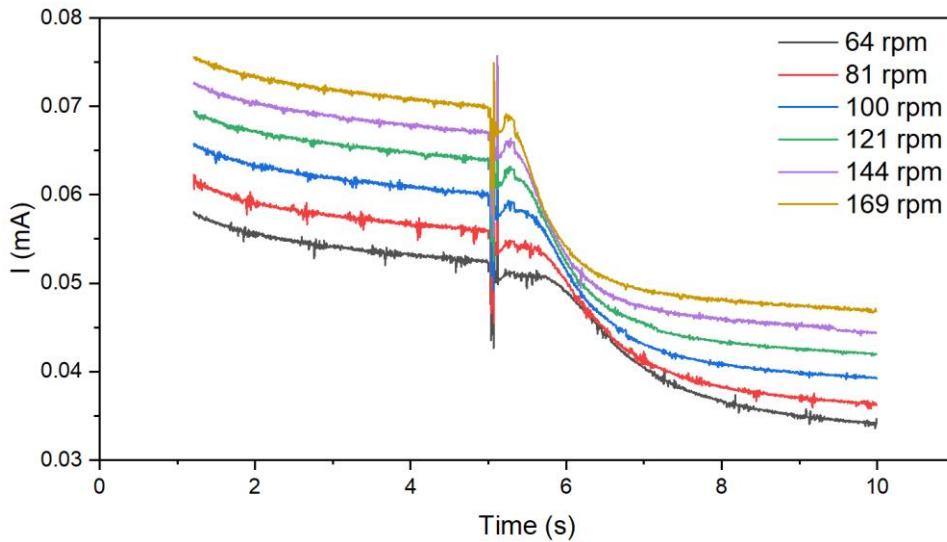
Kinematic viscosity, $\nu$ ( $10^{-2}$ cm $^2$ /s)	Temperature			
	10°C	20°C	30°C	
Glucose concentration	10 <sup>-3</sup> M	1,39	1,32	1,25
	10 <sup>-2</sup> M	1,39	1,36	1,30
	10 <sup>-1</sup> M	1,47	1,37	1,28
	1 M	2,16	1,68	1,33



## Diffusion coefficient measurement – RRDE transit time method



## Diffusion coefficient measurement – RRDE transit time method



$$t_s = K \left(\frac{v}{D}\right)^{\frac{1}{3}} \omega^{-1}$$

where

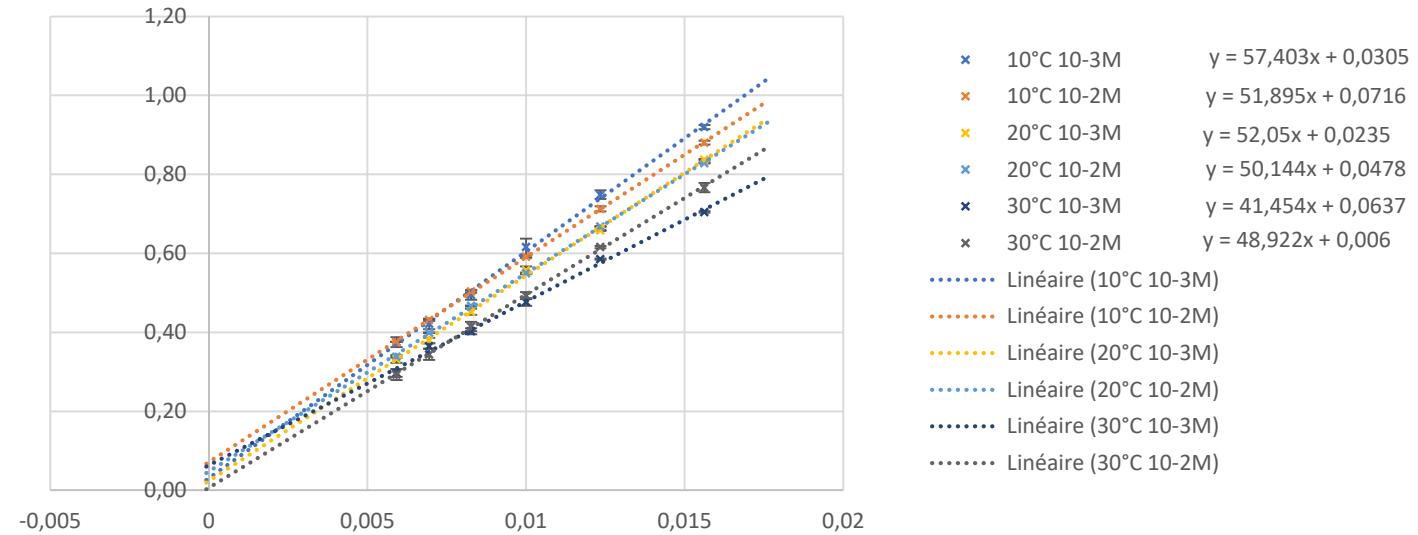
$$K = 43,1 \left(\log \frac{r_{ir}}{r_{od}}\right)^{\frac{2}{3}}$$

and

$r_{ir}$  = ring inner radius

$r_{od}$  = disk outer radius

Chatenet, M., Molina-Concha, M. B., El-Kissi, N., Parrour, G. & Diard, J. P. Direct rotating ring-disk measurement of the sodium borohydride diffusion coefficient in sodium hydroxide solutions. *Electrochim. Acta* **54**, 4426–4435 (2009)

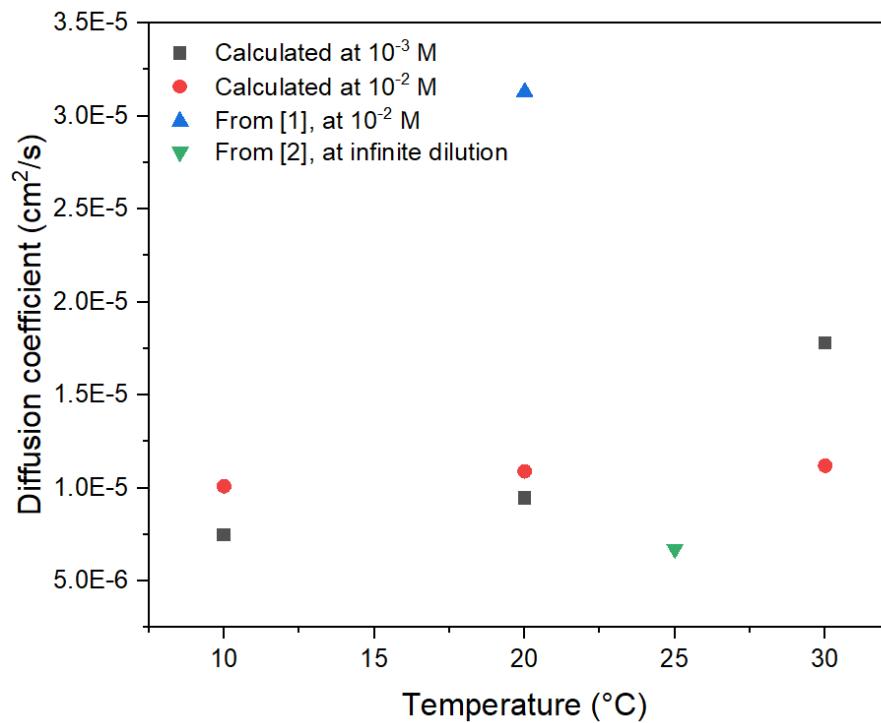


3 replicates per concentration, temperature and rotation rate

## Diffusion coefficient measurement – RRDE transit time method

Here,  $r_{ir} = 4,96 \text{ mm}$  &  $r_{od} = 4,57 \text{ mm} \rightarrow K = 4,661$

Diffusion coefficient, D ( $\text{cm}^2/\text{s}$ )		Temperature		
		10°C	20°C	30°C
Glucose concentration	$10^{-3} \text{ M}$	7,46E-06	9,45E-06	1,78E-05
	$10^{-2} \text{ M}$	1,01E-05	1,09E-05	1,12E-05
	$10^{-1} \text{ M}$	Inoperable data		
	1 M	No data		



[1] Karim Hassaninejad-Darzi, S. & Yousefi, F. Electrocatalytic oxidation of glucose on the modified carbon paste electrode with sodalite nanozeolite for fuel cell. *Iran. J. Hydrot. Fuel Cell* **1**, 47–58 (2015).

[2] David R. Lide, ed., CRC Handbook of Chemistry and Physics, Internet Version 2005, <<http://www.hbcpnetbase.com>>, CRC Press, Boca Raton, FL, 2005