Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

TUNEABLE C3 PRODUCT SELECTIVITY OF GLYCEROL ELECTROOXIDATION ON CUBIC AND DENDRITIC Pt NANOCATALYSTS

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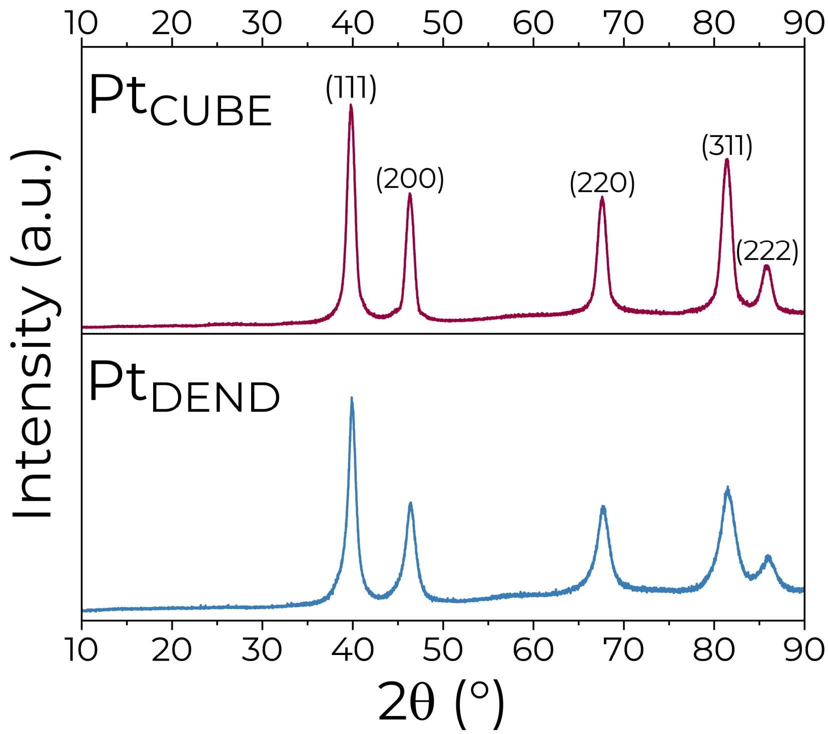


Fig. S1. PXRD diffractograms of Pt nanocatalysts.

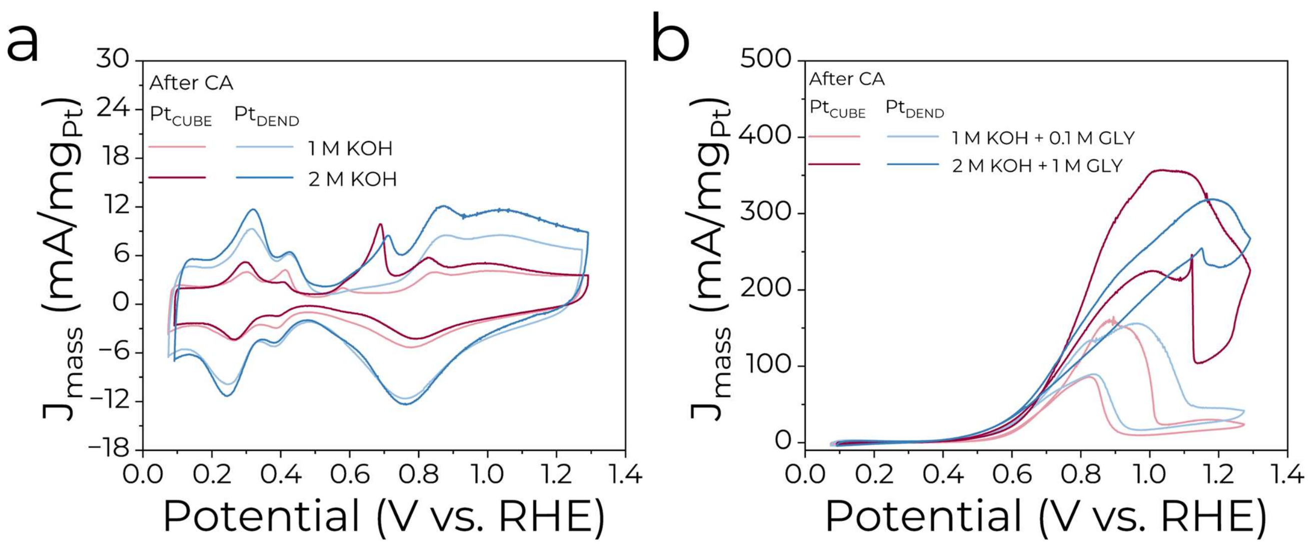


Fig. S2. CV profiles of Pt nanocatalysts in (a) 1 M KOH and 2 M KOH and (b) 1 M KOH + 0.1 M GLY and 2 M KOH + 1 M GLY solutions after potentiostatic measurements. The currents are normalised by the absolute Pt mass loading.

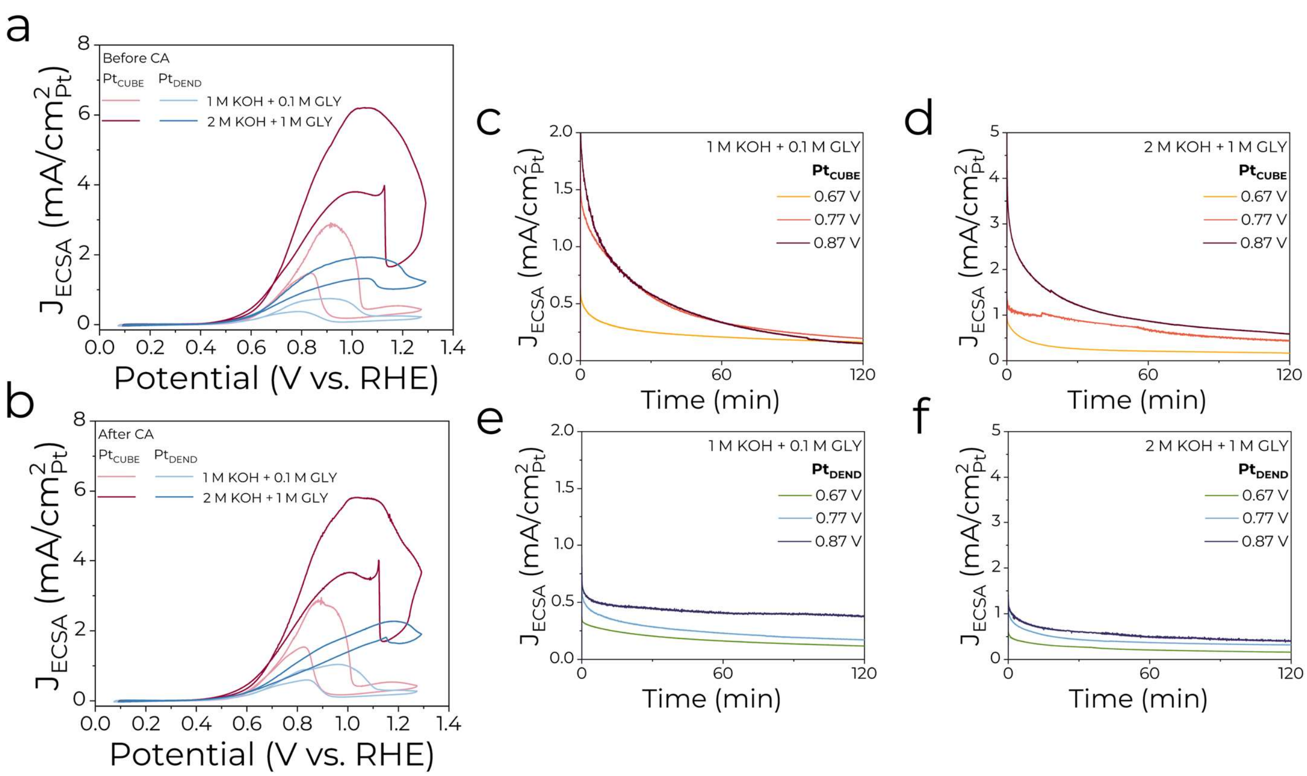


Fig. S3. CV profiles of Pt nanocatalysts in 1 M KOH + 0.1 M GLY and 2 M KOH + 1 M GLY solutions (a) before and (b) after the electrolysis. Potentiostatic electrolysis curves at 0.67, 0.77 and 0.87 V for (c–d) Pt_{CUBE} and (e–f) Pt_{DEND} in 1 M KOH + 0.1 M GLY and 2 M KOH + 1 M GLY solutions. The currents are normalised by the aECSA.

Product Analysis

The glycerol conversion, product selectivity, carbon balance and total Faradaic efficiency were calculated using **Eqs S1–4**. The results are presented in **Tables S1–2**.

Glycerol conversion:

$$\eta_{glycerol} = \frac{C_{0,glycerol} - C_{glycerol}}{C_{0,glycerol}} \cdot 100\% \qquad (\textbf{S1})$$

where $C_{0,glycerol}$ and $C_{glycerol}$ are the initial and final glycerol concentrations, mmol/l.

Product selectivity:

$$S_{product} = \frac{C_{product}}{\sum C_{all\ products}} \cdot 100\% \qquad (\textbf{S2})$$

where $C_{product}$ and $C_{all\ products}$ are the individual product and total products' concentrations, mmol/l.

Carbon balance:

$$CB = \frac{C_{glycerol} + C_{C3} + \frac{2}{3} \cdot C_{C2} + \frac{1}{3} \cdot C_{C1}}{C_{0,glycerol}} \cdot 100\% \qquad (\textbf{S3})$$

where C_{C3} is the concentration of the three-carbon products (dihydroxyacetone, glycerate, lactate, tartronate); C_{C2} is the concentration of the two-carbon products (glycolate, oxalate, glyoxylate); C_{C1} is the concentration of the one-carbon product (formate). All the concentrations are in mmol/l.

Faradaic efficiency:

Calculations of the total Faradaic efficiency (FE) of the GEOR are based on the following half-reactions:

Dihydroxyacetone: $CH_2OH\text{-}CHOH\text{-}CH_2OH + 2OH^- \rightarrow CH_2OH\text{-}CO\text{-}CH_2OH + 2H_2O + 2e^-$

Glycerate: $CH_2OH\text{-}CHOH\text{-}CH_2OH + 5OH^- \rightarrow CH_2OH\text{-}CHOH\text{-}COO^- + 4H_2O + 4e^-$

Lactate: $CH_2OH\text{-}CHOH\text{-}CH_2OH + 3OH^- \rightarrow CH_3\text{-}CHOH\text{-}COO^- + 3H_2O + 2e^-$

Tartronate: $CH_2OH\text{-}CHOH\text{-}CH_2OH + 10OH^- \rightarrow {}^-OOC\text{-}CHOH\text{-}COO^- + 8H_2O + 8e^-$

Glycolate: $CH_2OH\text{-}CHOH\text{-}CH_2OH + 13/2OH^- \rightarrow 3/2CH_2OH\text{-}COO^- + 5H_2O + 5e^-$

Oxalate: $CH_2OH\text{-}CHOH\text{-}CH_2OH + 14OH^- \rightarrow 3/2{}^-OOC\text{-}COO^- + 11H_2O + 11e^-$

Glyoxylate: $CH_2OH\text{-}CHOH\text{-}CH_2OH + 19/2OH^- \rightarrow 3/2HCO\text{-}COO^- + 8H_2O + 8e^-$

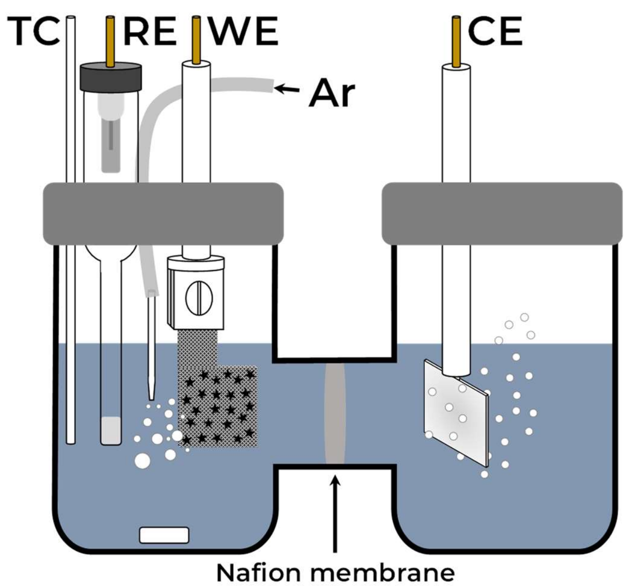
Formate: $CH_2OH\text{-}CHOH\text{-}CH_2OH + 11OH^- \rightarrow 3HCOO^- + 8H_2O + 8e^-$

$$FE = \frac{\sum z \cdot C_{product}}{Q} \cdot V \cdot F \cdot 100\% \quad \textbf{(S4)}$$

where z is the number of electrons transferred, V is the anolyte volume, 0.015 L; F is the Faraday constant, 96485 C/mol, and Q is the total charge passed during electrolysis, C.

The carbon balance and Faradaic efficiency were not normalised by the electrolyte evaporation and concentration effects during the electrolysis.

High values above 100% could be due to (i) concentration effects as a result of the electrolyte evaporation, (ii) heterogeneous GEOR on Pt nanocatalysts in addition to the electrochemical oxidation, and (iii) uncertainties in HPLC analysis.



Scheme S1. Electrochemical divided cell. WE—working electrode, RE—reference electrode, CE—counter electrode, TC—thermocouple, Ar—argon gas.

Table S1. GEOR products concentrations, carbon balance and total Faradaic efficiency of GEOR for Pt NCs in a 1 M KOH + 0.1 M GLY electrolyte at different potentials.

Catalyst	Potential (V)	Concentration (mM)								CB	FE
		DHA	GLE	LACT	TART	GLO	OXA	GLYOXA	FORM	%	
Pt_{CUBE}	0.67	0.0	7.7	7.5	1.0	1.1	0.4	0.4	0.7	103.7	83.3
	0.77	0.0	12.7	9.4	2.1	2.6	1.9	0.7	1.7	102.6	77.4
	0.87	0.0	13.3	7.2	2.9	3.1	3.3	0.4	2.9	97.8	96.9
	Average									**101.4**	**85.9**
Pt_{DEND}	0.67	0.0	9.1	6.2	1.8	1.6	1.3	0.2	1.1	104.9	77.1
	0.77	0.0	7.2	4.0	3.1	2.5	4.0	0.0	2.1	98.7	67.6
	0.87	0.0	12.8	4.8	6.6	5.5	9.6	0.2	4.6	103.8	82.6
	Average									**102.5**	**75.7**

Table S2. GEOR products concentrations, carbon balance and total Faradaic efficiency of GEOR for Pt NCs in a 2 M KOH + 1 M GLY electrolyte at different potentials.

Catalyst	Potential (V)	Concentration (mM)								CB	FE
		DHA	GLE	LACT	TART	GLO	OXA	GLYOXA	FORM	%	
Pt_{CUBE}	0.67	0.0	6.9	21.9	0.6	0.4	0.0	1.5	0.9	99.9	109.3
	0.77	0.0	25.6	36.9	2.7	4.1	0.4	5.7	2.1	103.9	109.5
	0.87	0.0	38.7	35.7	5.8	5.7	3.4	5.0	3.6	105.8	107.7
	Average									**103.2**	**108.8**
Pt_{DEND}	0.67	0.0	19.9	28.1	1.4	1.5	0.0	3.9	1.9	104.2	127.2
	0.77	0.0	31.1	29.9	4.1	4.2	4.0	3.6	3.3	105.1	114.0
	0.87	1.9	44.5	31.5	5.9	6.3	2.2	5.5	5.0	105.6	105.4
	Average									**104.9**	**115.5**

Table S3. Comparison of recently reported Pt-based catalysts for the GEOR.

Ref.	Catalyst	T	v	Electrolyte	E_f	J_{mass} / J_{ECSA}	$E_{electrolysis}$	t	$S_{d.prod.}$
Present work	Pt nanocubes	20	50	1 KOH + 0.1 glycerol	0.92	178 mA/mg$_{Pt}$ 2.9 mA/cm$^2_{Pt}$	0.67 vs RHE −0.4 vs SCE	120	glycerate (41%) lactate (40%)
							0.77 vs RHE −0.3 vs SCE		glycerate (41%) lactate (30%)
							0.87 vs RHE −0.2 vs SCE		glycerate (40%) lactate (22%)
				2 KOH + 1 glycerol	1.05	397 mA/mg$_{Pt}$ 6.2 mA/cm$^2_{Pt}$	0.67 vs RHE −0.418 vs SCE		lactate (68%) glycerate (21%)
							0.77 vs RHE −0.318 vs SCE		lactate (48%) glycerate (33%)
							0.87 vs RHE −0.218 vs SCE		glycerate (40%) lactate (36%)
	Pt dendritic nanoparticles			1 KOH + 0.1 glycerol	0.91	93 mA/mg$_{Pt}$ 0.7 mA/cm$^2_{Pt}$	0.67 vs RHE −0.4 vs SCE		glycerate (43%) lactate (29%)
							0.77 vs RHE −0.3 vs SCE		glycerate (32%) lactate/oxalate (17%)
							0.87 vs RHE −0.2 vs SCE		glycerate (29%) oxalate (22%)
				2 KOH + 1 glycerol	1.05	237 mA/mg$_{Pt}$ 1.9 mA/cm$^2_{Pt}$	0.67 vs RHE −0.418 vs SCE		lactate (49%) glycerate (35%)
							0.77 vs RHE −0.318 vs SCE		glycerate (39%) lactate (37%)
							0.87 vs RHE −0.218 vs SCE		glycerate (43%) lactate (31%)
[18]	Pt@Pd nanocubes	RT*	50	0.5 KOH + 0.5 glycerol	~(−0.13) vs SCE**	3.2 mA/cm$^2_{Pd}$	−0.4 vs SCE	120	glyceraldehyde (40%) glycolate (30%)
							−0.1 vs SCE		glyceraldehyde (40%) glycolate (35%)
							0.2 vs SCE		glyceraldehyde (35%) glycolate (40%)
[20]	Pt catalyst with hierarchical pores	60	10	1 NaOH + 0.1 glycerol	~0.88	~310 mA/mg$_{Pt}$ 6.9 mA/cm$^2_{Pt}$	0.69	60	glycerate (59%) formate (18%)
	Pt catalyst with cubic pores				~0.86	~620 mA/mg$_{Pt}$ 3.3 mA/cm$^2_{Pt}$			glycerate (58%) formate/oxalate (14%)
	Pt catalyst with linear pores				~0.80	~255 mA/mg$_{Pt}$ 5.6 mA/cm$^2_{Pt}$			glycerate (60%) formate (17%)
[22]	Pt nanoflowers	RT*	50	1 KOH + 1 glycerol	~(−0.15) vs SCE	~1250 mA/mg$_{Pt}$	−0.25 vs SCE	60	N/A
	Pt_3Ru_1 nanoflowers				~(−0.18) vs SCE	~1750 mA/mg$_{Pt}$			

	Pt_1Ru_1 nanoflowers				~(−0.17) vs SCE	~2000 mA/mg$_{Pt}$			
	Pt_1Ru_3 nanoflowers				~(−0.16) vs SCE	2412 mA/mg$_{Pt}$			
	Pt_1Ru_5 nanoflowers				~(−0.2) vs SCE	~1100 mA/mg$_{Pt}$			
[27]	Pt/C	60	50	0.1 KOH + 0.1 glycerol	1.02** (RT*)	191 mA/mg$_{Pt}$ 0.3 mA/cm$^2_{Pt}$	1.0	N/A	glycerate (59%) lactate (17%)
				0.5 KOH + 0.1 glycerol					glycerate (58%) lactate (23%)
				1 KOH + 0.1 glycerol					glycerate (49%) lactate (37%)
	PtCu/C			0.1 KOH + 0.1 glycerol	1.01** (RT*)	200 mA/mg$_{Pt}$ 0.44 mA/cm$^2_{Pt}$		N/A	glycerate (62%) lactate (13%)
				0.5 KOH + 0.1 glycerol					glycerate (40%) lactate (23%)
				1 KOH + 0.1 glycerol					glycerate (45%) lactate (19%)
[28]	Pt/C	RT*	50	1 KOH + 0.5 glycerol	N/A	N/A	0.45	720	lactate (50%) glycerate (41%)
							0.6		lactate (31%) glycerate (35%)
							0.9		lactate (23%) glycerate (50%)
							1.05		lactate (19%) glycerate (50%)
	$Pt_{90\%surf}Au/C$						0.45		lactate (69%) glycerate (24%)
							0.6		lactate (54%) glycerate (36%)
							0.9		lactate (22%) glycerate (53%)
							1.05		lactate (27%) glycerate (47%)
	$Pt_{64\%surf}Au/C$						0.45		lactate (60%) glycerate (25%)
							0.6		lactate (43%) glycerate (42%)
							0.9		lactate (25%) glycerate (49%)
							1.05		lactate (31%) glycerate (41%)
	$Pt_{29\%surf}Au/C$						0.45		lactate (61%) glycerate (22%)
							0.6		lactate (55%) glycerate (32%)
							0.9		lactate (43%) glycerate (37%)
							1.05		lactate (29%) glycerate (37%)
	$Pt_{15\%surf}Au/C$						0.45		lactate (73%) glycerate (18%)
							0.6		lactate (61%) glycerate (27%)
							0.9		lactate (41%) glycerate (42%)

							1.05		glycolate (33%) lactate (27%)
[29]	Pt/GNS	RT*	50	0.5 KOH + 0.5 glycerol	−0.03 vs SCE**	0.3 mA/cm^2_{Pt}	−0.4 vs SCE	120	glycolate (36%) glyceraldehyde (32%)
							−0.1 vs SCE		glycolate (55%) glycerate (15%)
							0.2 vs SCE		glycolate (65%) glycerate (13%)
	PtNi/GNS				−0.13 vs SCE**	0.4 mA/cm^2_{Pt}	−0.4 vs SCE		glycolate (42%) glycerate (36%)
							−0.1 vs SCE		glycerate (48%) glycolate (33%)
							0.2 vs SCE		glyceraldehyde (30%) glycerate (28%)
	PtRu/GNS				−0.1 vs SCE**	0.4 mA/cm^2_{Pt}	−0.4 vs SCE		glyceraldehyde (31%) glycerate (31%)
							−0.1 vs SCE		glycerate (40%) glycolate (31%)
							0.2 vs SCE		glycolate (48%) glycerate (34%)
	PtRh/GNS				−0.16 vs SCE**	4.5 mA/cm^2_{Pt}	−0.4 vs SCE		glycolate (41%) oxalate (28%)
							−0.1 vs SCE		glycolate (40%) glyceraldehyde/glycerate (19%)
							0.2 vs SCE		glycolate (52%) glyceraldehyde/glycerate (14%)
	PtRuNi/GNS				−0.06 vs SCE**	0.4 mA/cm^2_{Pt}	−0.4 vs SCE		glycolate (54%) glycerate (26%)
							−0.1 vs SCE		glyceraldehyde/glycerate (33%)
							0.2 vs SCE		glyceraldehyde (39%) glycerate (15%)
	PtRhNi/GNS				−0.15 vs SCE**	5.6 mA/cm^2_{Pt}	−0.4 vs SCE		oxalate (38%) glyceraldehyde (31%)
							−0.1 vs SCE		glyceraldehyde (32%) oxalate (26%)
							0.2 vs SCE		glycolate (42%) glyceraldehyde (19%)

*room temperature, not specified in °C
**in 0.1 M KOH + 1 M glycerol electrolyte

T—temperature, °C; v—scan rate, mV/s; Electrolyte—electrolyte composition for the potentiostatic measurements, mol/l; E_f—forward peak potential, V vs RHE if not stated otherwise; J_{mass}—forward peak mass activity, $mA/mg_{catalyst}$; J_{ECSA}—forward peak specific activity, $mA/cm^2_{catalyst}$; $E_{electrolysis}$—applied potential, V; t—electrolysis time, min; $S_{d.prod.}$—selectivity of the two most dominant products, % (for some references, no exact numerical selectivity values were reported, so they were estimated from the reported GEOR products selectivity plots).

Catalyst supports: C—carbon; GNS—graphene nanosheets.

Reference electrodes: RHE—reversible hydrogen electrode; SCE—saturated calomel electrode (Hg/Hg_2Cl_2, sat. KCl).

All quantitative analyses of the GEOR products were performed using High-Pressure Liquid Chromatography (HPLC).

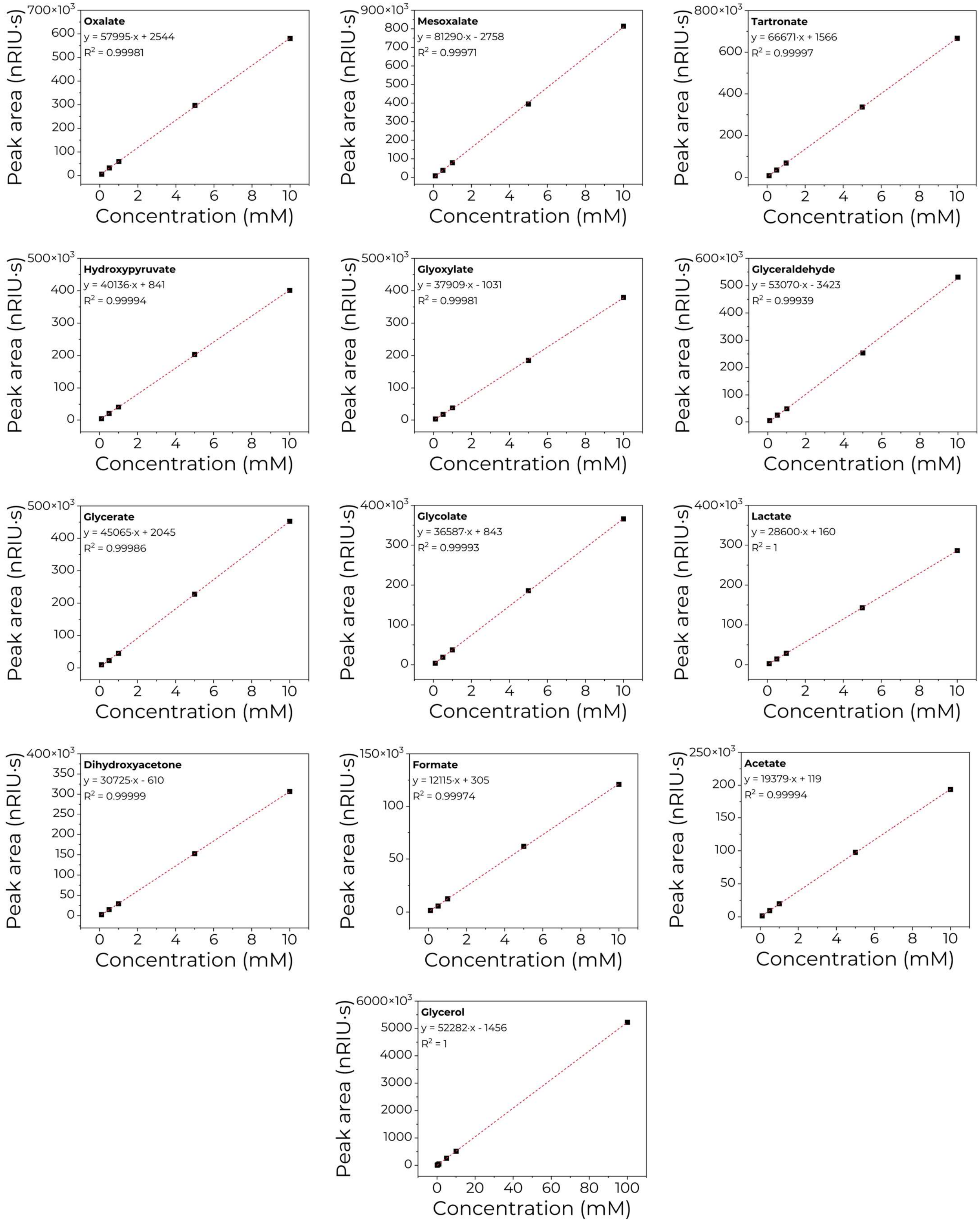


Fig. S4. Calibration curves of standard solutions of glycerol and possible GEOR products.

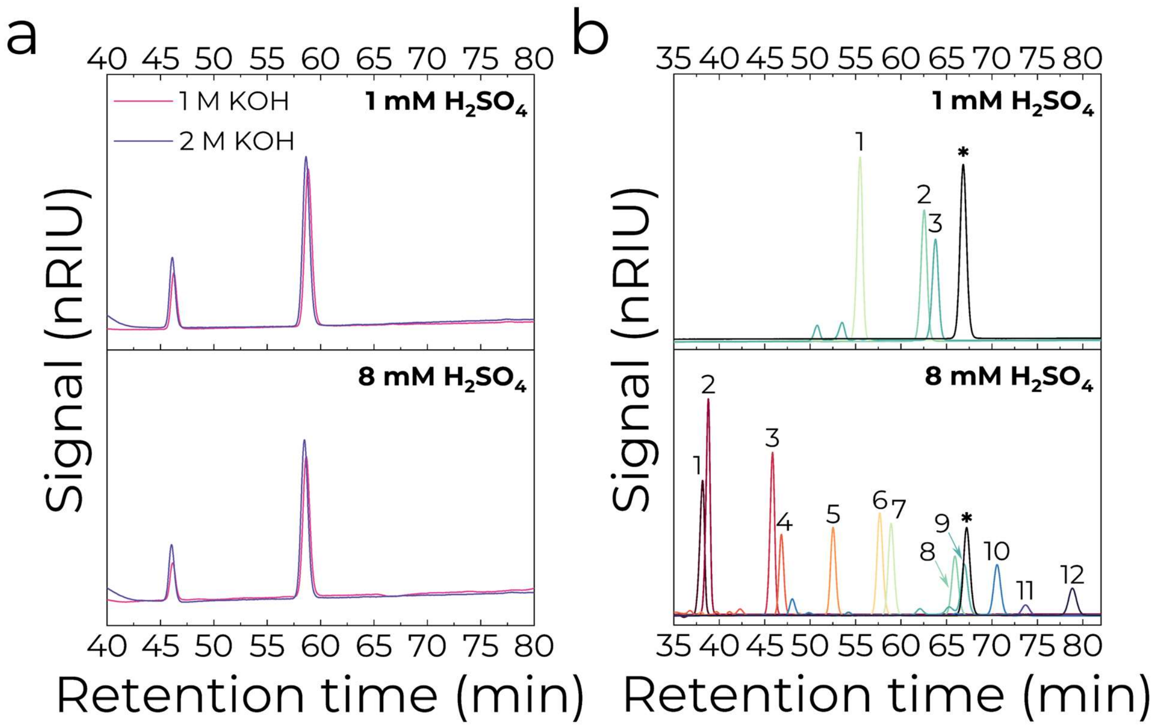


Fig. S5. HPLC chromatograms of a) 1 M and 2 M KOH solutions and b) 10 mM calibration solutions registered using 1 mM and 8 mM H_2SO_4 mobile phases.

(b, 1 mM H_2SO_4): 1—glycerate, 2—glycolate, 3—lactate, star—glycerol.

(b, 8 mM H_2SO_4): 1—oxalate, 2—mesoxalate, 3—tartronate, 4—hydroxypyruvate, 5—glyoxylate, 6—glyceraldehyde, 7—glycerate, 8—glycolate, 9—lactate, star—glycerol, 10—dihydroxyacetone, 11—formate, 12—acetate.

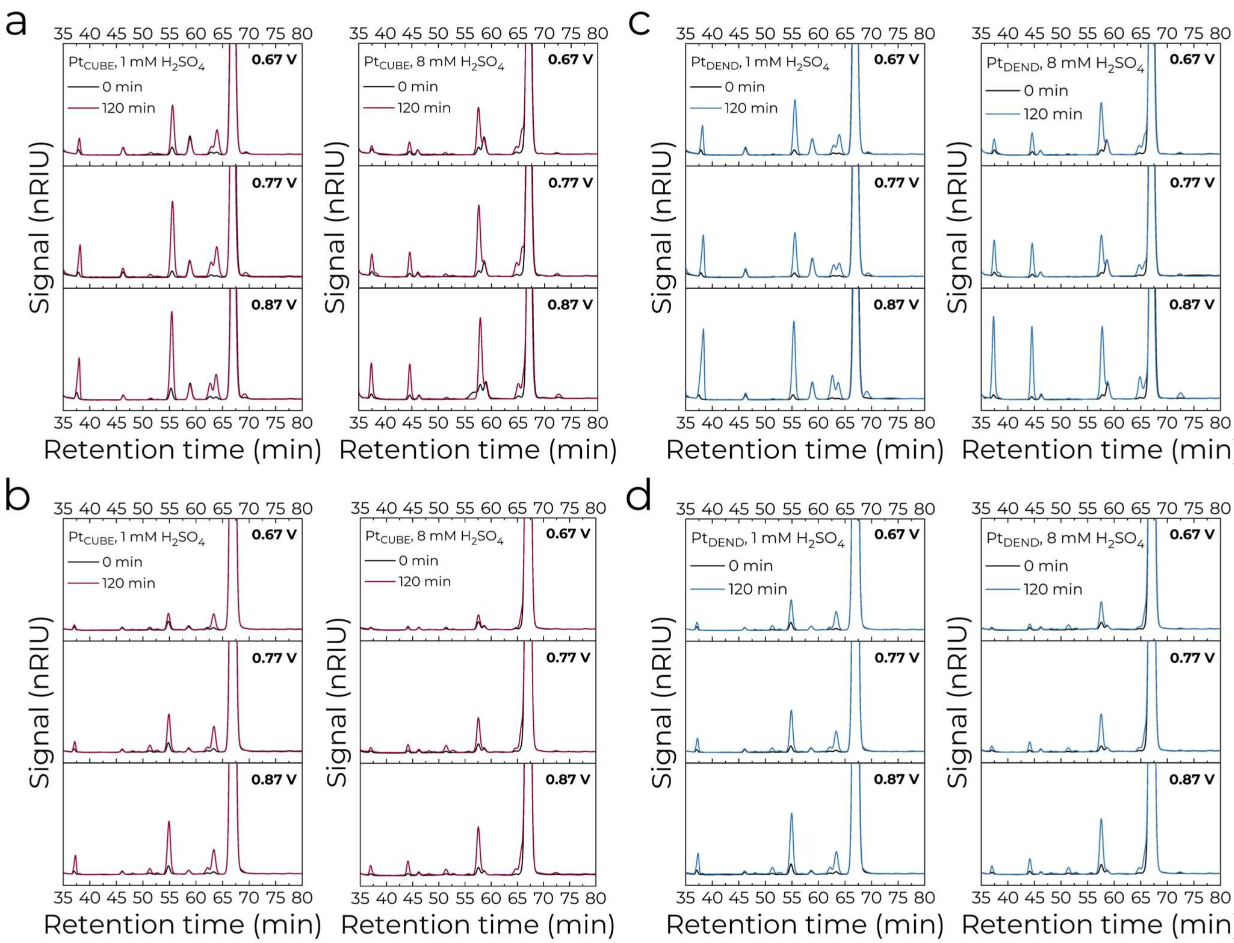


Fig. S6. HPLC chromatograms of samples collected from (a, c) 1 M KOH + 0.1 M GLY and (b, d) 2 M KOH + 1 M GLY electrolytes at different potentials for (a–b) Pt$_{CUBE}$ and (c–d) Pt$_{DEND}$ NPs using 1 mM H_2SO_4 and 8 mM H_2SO_4 as a mobile phase.

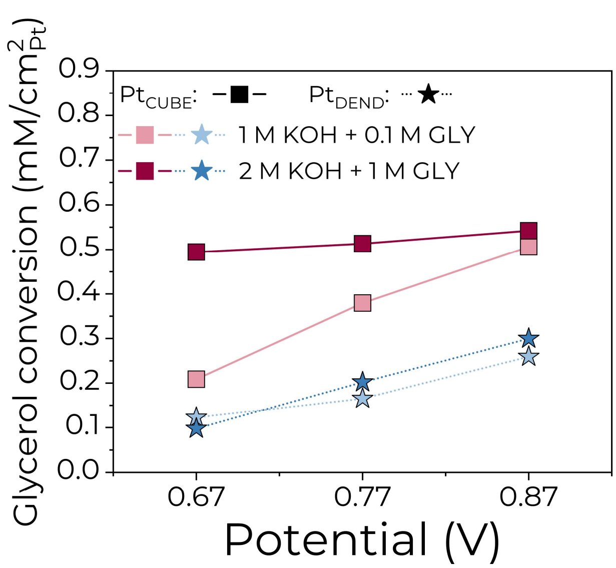


Fig. S7. Glycerol conversion for Pt$_{CUBE}$ and Pt$_{DEND}$ in 1 M KOH + 0.1 M GLY and 2 M KOH + 1 M GLY electrolytes. The converted glycerol concentration is normalised by the aECSA.

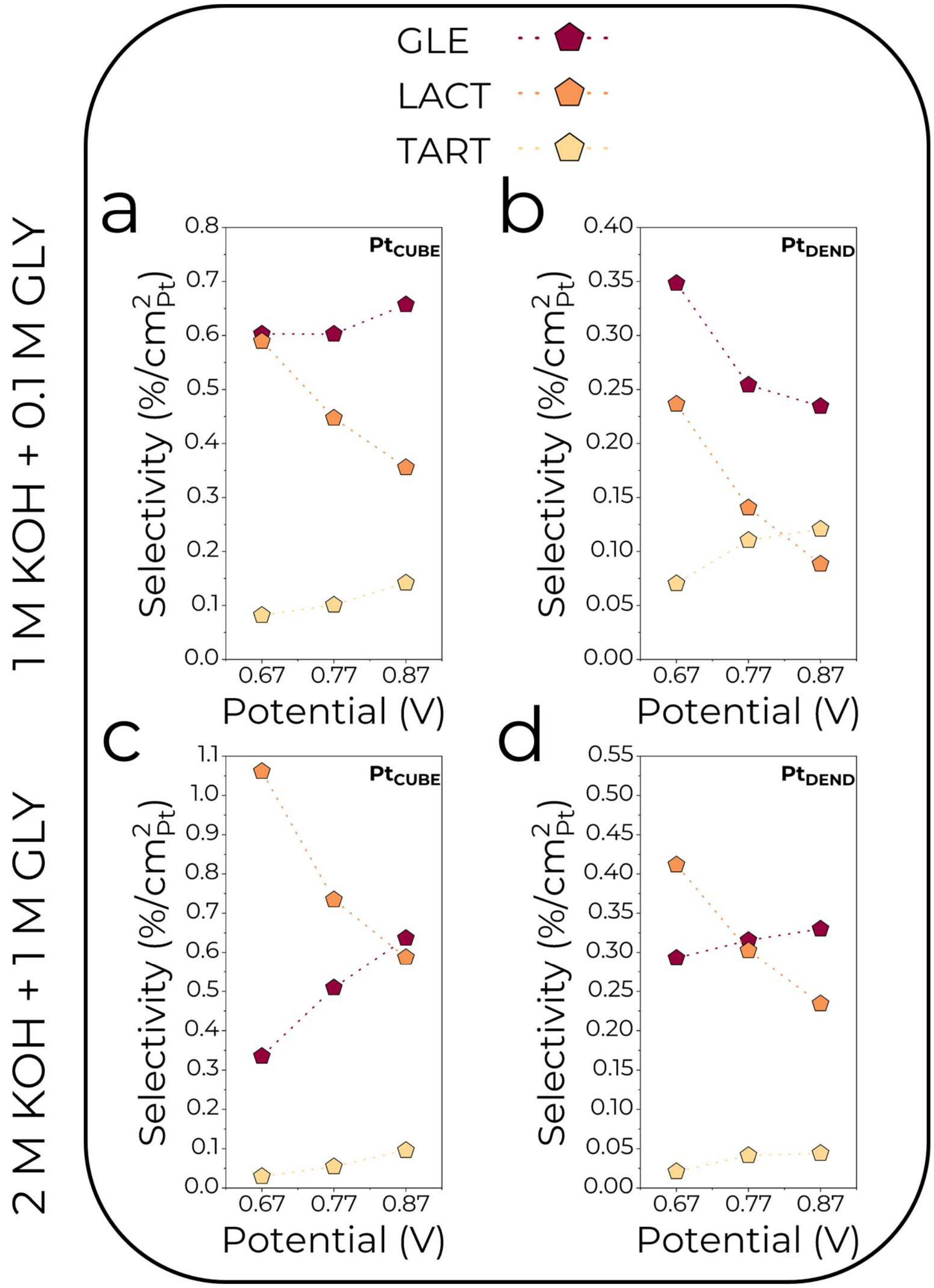


Fig. S8. Individual C3 products selectivity normalised by the aECSA as a function of the applied potential in (a–b) 1 M KOH + 0.1 M GLY and (c–d) 2 M KOH + 1 M GLY electrolytes. Note that all figures have different y-axis scales.