SUPPORTING INFORMATION

Tuning the Selectivity of Electrochemical Levulinic Acid Reduction to 4-Hydroxyvaleric Acid: A Monomer for Biocompatible and Biodegradable Plastics

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1. Products Identification and Quantification

Products of electrolysis were identified and quantified by liquid chromatography (LC) and ^{1}H NMR. LC analyses were performed in an Advion 2000 HPLC equipped with a 300 mm x 6.5 mm sulfonated polystyrene gel column (Hi-Plex H, Agilent, which is well-suited for the analysis of biomass-derived oxygenated compounds), as well as a UV diode array detector (DAD) and Advion Expression Compact Mass Spectrometer (S Series). A Bruker AVANCE-III 400 MHz NMR spectrometer was used for ^{1}H NMR analyses.

a) LC method

An LC method was developed for the identification and quantification of levulinic acid (LA), valeric acid (VA), γ-valerolactone (GVL), and 4-hydroxyvaleric acid (HVA). The separation between VA, GVL, and HVA is the most challenging (as can be seen in Figure S1). Evaluating the effect of mobile phase pH, we could conclude that a good separation between GVL+HVA (together) and VA is reached at pH below 2.3. The addition of organic solvent (e.g., 2.5 vol.% acetonitrile, ACN) makes the separation worse, and the column temperature and flow rate just affect the retention time of these compounds (lower retention time for higher temperature or flow rate, as expected), not impacting the separation (e.g. Figure S1b). Thus, 12.5 mM H_2SO_4 was chosen as the optimized eluent, and the flow rate and column temperature were set to 0.4 mL min^{-1} (which is the maximum flow rate allowable for the MS detector and also gives reasonable retention times) and 60ºC (the highest operating temperature for the column). Based on the UV spectra of these compounds (Figure S1c), we selected a wavelength of 210 nm for quantification. At

these conditions, LA showed a retention time of ~16.8 min, while GVL + HVA was ~29.7 min, VA was 32.8 min, and the "dead-time" (supporting electrolyte retention time) was at about 7.5 min. While GVL and HVA could not be separated, independent evaluation of mixtures was performed by ^{1}H-NMR analyses and mass spectrometry (MS), as will be shown below. For neutral-to-alkaline conditions that reliably produced pure HVA, the LC method was deemed adequate for HVA quantification.

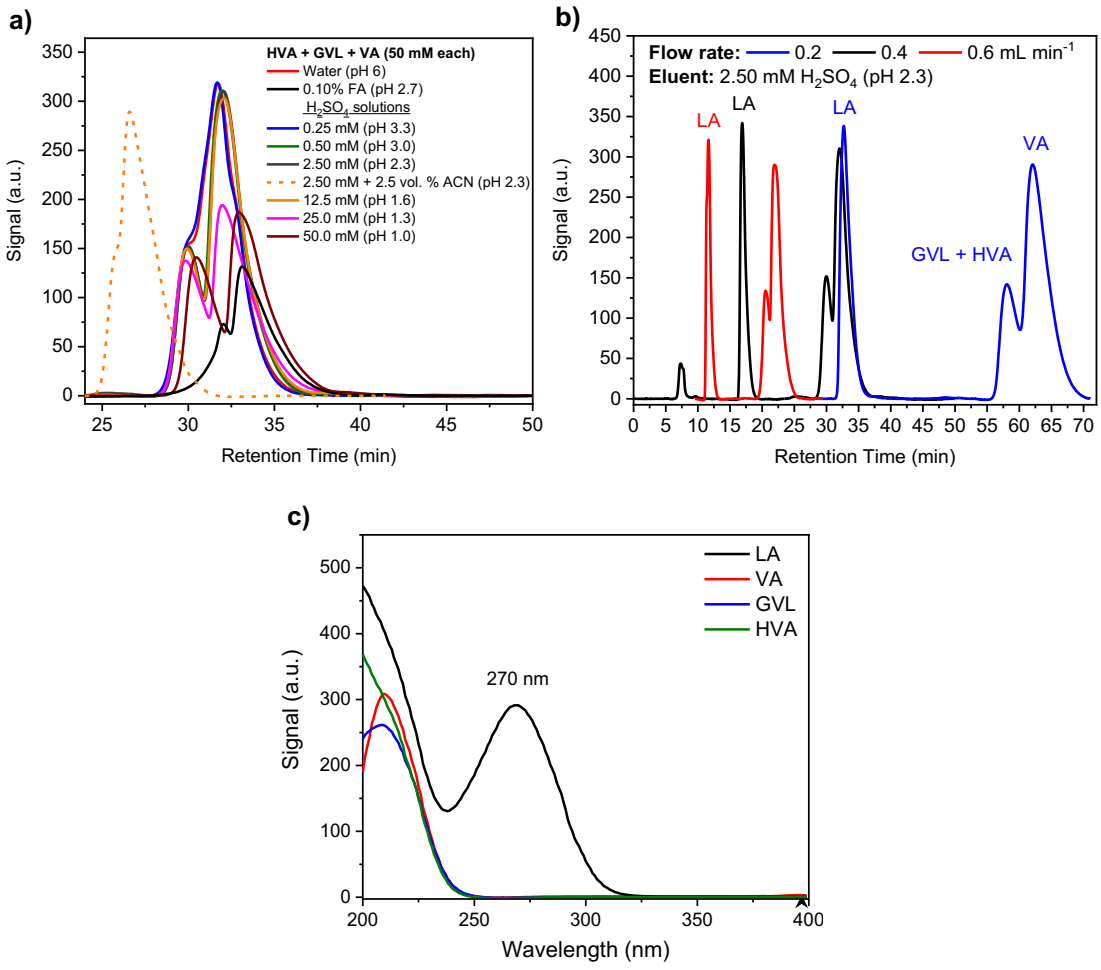


Figure S1. Chromatograms for a mixture of 50 mM LA, VA, GVL, and HVA, using UV detector at 210 nm and column temperature of 60 ºC. **a)** Eluent effect: flow rate of 0.4 mL min^{-1}and different eluents. **b)** Flow rate effect: 2.50 mM H_2SO_4 as eluent and flow rates of 0.2, 0.4, and 0.6 mL min^{-1}. **c)** UV-vis sprectra for LA, VA, GVL and HVA.

Using the developed LC method and ultrapure chemicals (with purity analyzed by ^{1}H-NMR), external calibration curves were made from standard solutions prepared in pure water, as can be seen in Figure S2b.

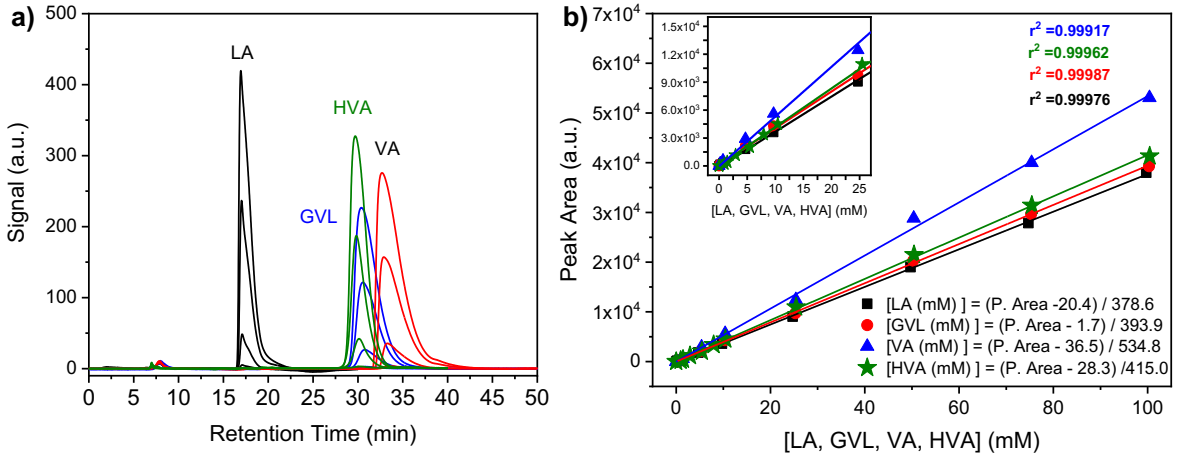


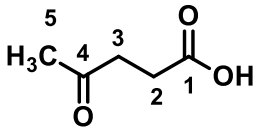
Figure S2. *a) Chromatograms for different concentrations of LA, VA, GVL, and HVA, using UV detector at 210 nm, column temperature of 60 ºC, flow rate of 0.4 mL min^{-1}, and 12.5 mM H_2SO_4 as eluent. b) Calibration curves.*

Sample preparation for LC analyses: 2 mL aliquots were collected from the electrolyte at the end of electrolyses and filtered through a 0.2 µm hydrophilic PTFE membrane (Millipore) into amber LC-vials. When using the MS detector, the eluent was diverted for the first 15 min of the run to avoid the introduction of supporting electrolyte salts to the ion source. Before analyses, this detector was calibrated with an ESI tuning mixture (Agilent Technologies). The molecular mass (molecular ion) of the compounds was identified using positive electrospray ionization (ESI+), with a capillary temperature and voltage of 250 ºC and 120 V, respectively, ESI voltage of 3500 V, and ultrapure N_2 at a flow rate of 4 L/min as ion/gas source.

a) NMR method

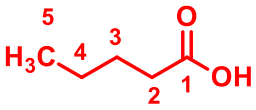
The chemical and analytical distinction between GVL and HVA (and also VA and LA) was based on chemical shift signature and mass fragmentation of their ^{1}H NMR and mass spectra, respectively. As can be seen in Figure S3, HVA and GVL have very distinct NMR signatures. At the top part of this figure, we can see the chemical structures of LA, VA, GVL, and HVA; the carbon atoms were numbered to help the correlation with their NMR spectrum, and respective exact masses are also shown.

LA ^{1}H NMR spectrum (400 MHz, H_2O + 10 w. % D_2O, water suppression): *δ* 2.87 (*t*, 2H), 2.60 (*t*, 2H), 2.23 (*s*, 3H) ppm. **VA** ^{1}H NMR spectrum (400 MHz, H_2O + 10 w. % D_2O, water suppression): *δ* 2.38 (t, 2H), 1.56 (*quintet*, 2H), 1.32 (*sextet*, 2H), 0.88 (*t*, 3H) ppm. **GVL** ^{1}H NMR spectrum (400 MHz, H_2O + 10 w. % D_2O, water suppression): *δ* 4.84 (*sextet*, 1H, suppressed under H_2O signal), 2.65 (*m*, 2H), 2.41 (*m*, 1H), 1.90 (*m*, 1H), 1.39 (*d*, 3H) ppm. **HVA** ^{1}H NMR spectrum (400 MHz, H_2O + 10 w. % D_2O, water suppression): *δ* 3.82 (*sextet*, 1H), 2.25 (*m*, 2H), 1.90 (*m*, 2H), 1.39 (*d*, 3H) ppm.



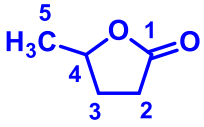
Exact Mass: 116.05

LA



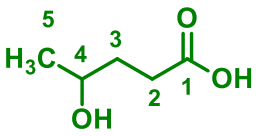
Exact Mass: 102.07

VA



Exact Mass: 100.05

GVL



Exact Mass: 118.06

HVA

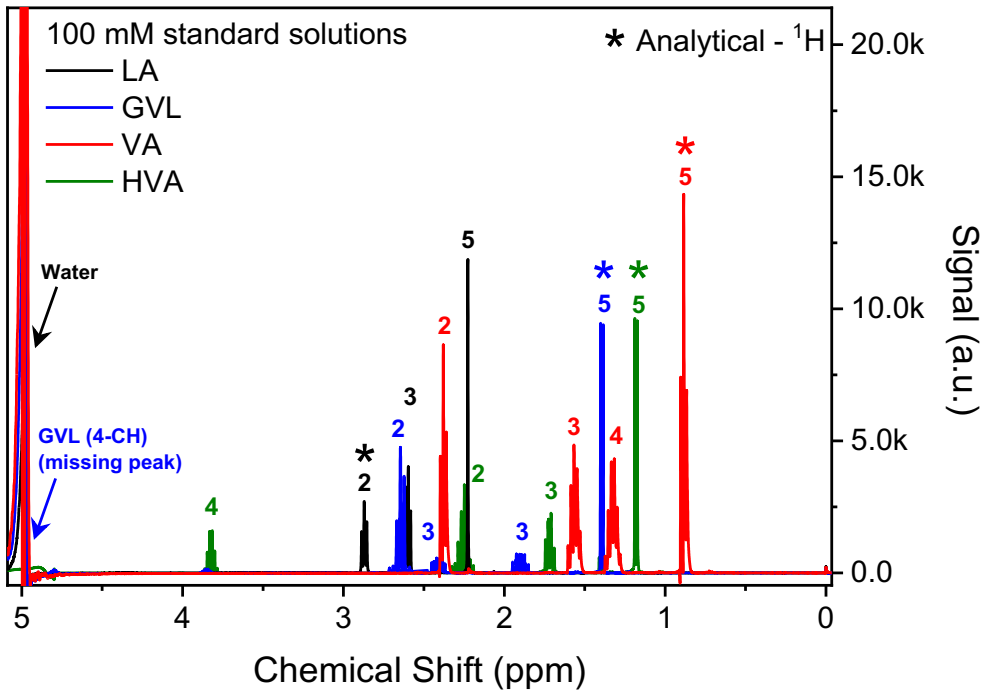


Figure S3. Top: Chemical structures of levulinic acid (LA), valeric acid (VA), γ-valerolactone (GVL), and 4-hydroxyvaleric acid (HVA), and their respective exact masses. Bottom: ^{1}H-NMR spectra for these compounds. The "*" peaks represent those used for the analytical quantification of these compounds in a mixture.

Sample preparation for NMR analyses: 450 µL aliquots were collected from the electrolyte and mixed with 50 µL of D_2O (with 0.05 wt.% TMSP, used as internal reference and standard for quantification).

2. Defining Equations for Selectivity, FE, and Conversion

Because LA is a viscous liquid compound, the correspondent quantity of compound used for each electrolyses was weighed (instead of volumetrically measured), and the total charge used for each electrolysis was calculated based on the following equation:

$$Q_T(C) = \frac{n_p \cdot m_{LA} \cdot F}{MW_{LA}} \therefore Q_T(C) = n \cdot F \,/\, mol\ of\ LA \ (eq.S1)$$

where, n_p is the number of electrons used for the reduction of LA to VA ($4e^-$), GVL ($2e^-$), or HVA ($2e^-$), m_{LA} the exact mass (in grams) of LA dissolved in the cathodic supporting electrolyte, F the Faraday constant (96485 C mol^{-1}), and MW_{LA} the LA molecular weight (116.12 g mol^{-1}). The faradaic efficiency (FE) for each product was then calculated as:

$$FE(\%)_{VA,\ GVL,\ or\ HVA} = \frac{n_p \cdot C_P \cdot V_{S.E.} \cdot F}{Q_T} \ (eq.S2)$$

where, in addition to previous notation, C_P its concentration (mol L^{-1}) of the individual product, and $V_{S.E.}$ is the volume of supporting electrolyte (0.01 L).

Since most of electrolyses showed close to 100% mass balance and 1 mol of LA can produce 1 mol of VA, GVL, and/or HVA, LA conversion (X%) was computed as: $X(\%) = \frac{(C_{VA}+C_{GVL}+C_{HVA})\cdot 100}{C_{LA-initial}} \cong \frac{C_{LA-final}\cdot 100}{C_{LA-initial}} (eq.S3)$

where, $C_{LA\text{-}initial}$ *and* $C_{LA\text{-}final}$ are the initial and final concentrations of LA, respectively, and C_{VA}, C_{GVL}, and C_{HVA} are the concentrations of VA, GVL, and HVA, respectively.

Thus, using equations S1-S3, the selectivity for individual products can be calculated with the equation:

$$S(\%)_{VA,\ GVL,\ or\ HVA} = \frac{C_{VA,\ GVL,\ or\ HVA}\cdot 100}{C_{VA}+C_{GVL}+C_{HVA}} = \frac{(FE_{VA}\ or\ 2\cdot FE_{GVL}\ or\ 2\cdot FE_{HVA})}{FE_{VA}+2\cdot FE_{GVL}+2\cdot FE_{HVL}} (eq.S4)$$

3. Supporting Figures and Discussion for Section 3.1

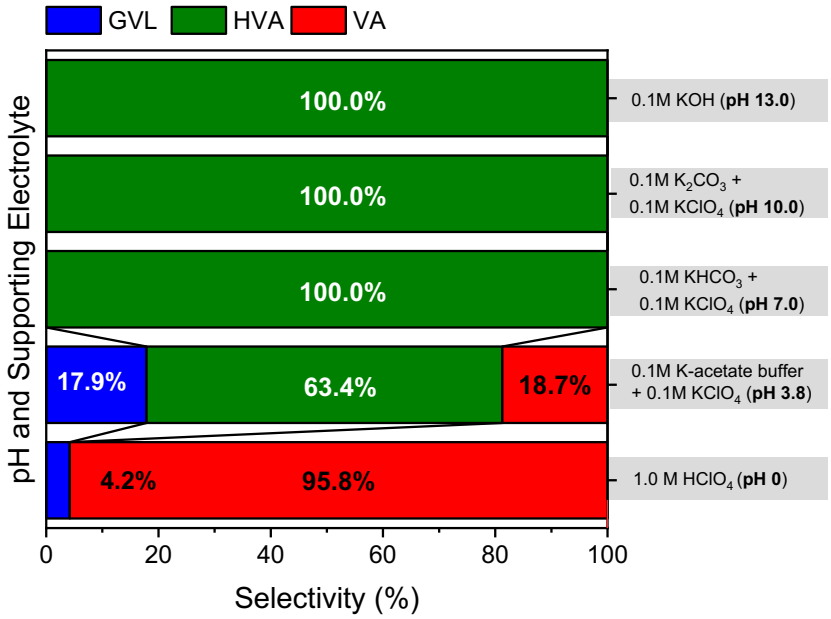


Figure S4. pH and supporting electrolyte effect on selectivities for electrolyses performed with 0.1 mol L^{-1} LA, at -1.9 V vs. RHE, for 4 F/mol of LA. VA: valeric acid, HVA: 4-hydroxyvaleric acid, GVL: γ-valerolactone, and FA: formic acid.

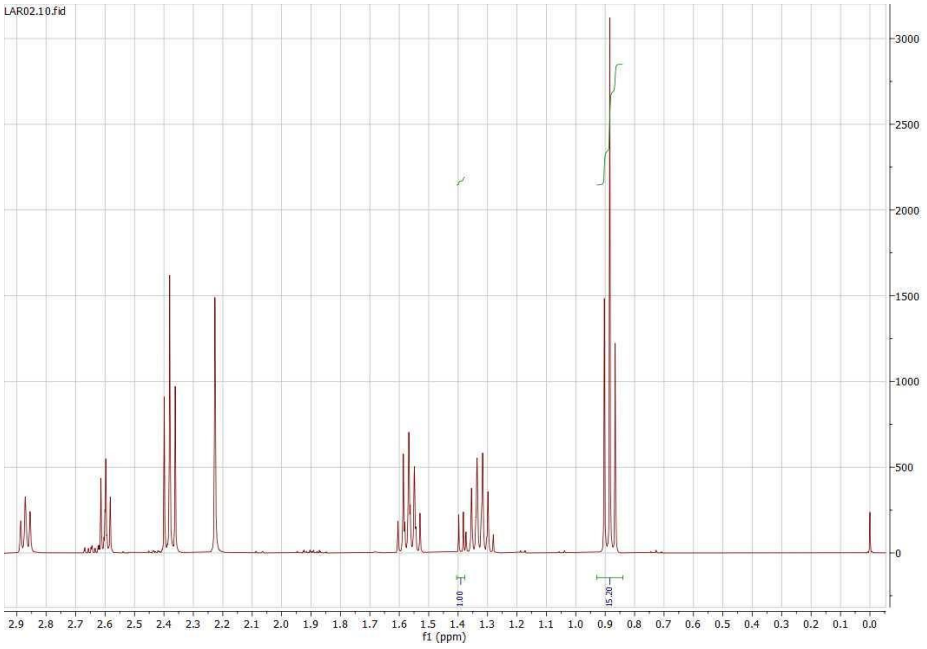


Figure S5. ^{1}H NMR spectrum for electrolysis performed in 0.5 M H_2SO_4 at -1.9 V vs. RHE, for 4 F/mol of LA.

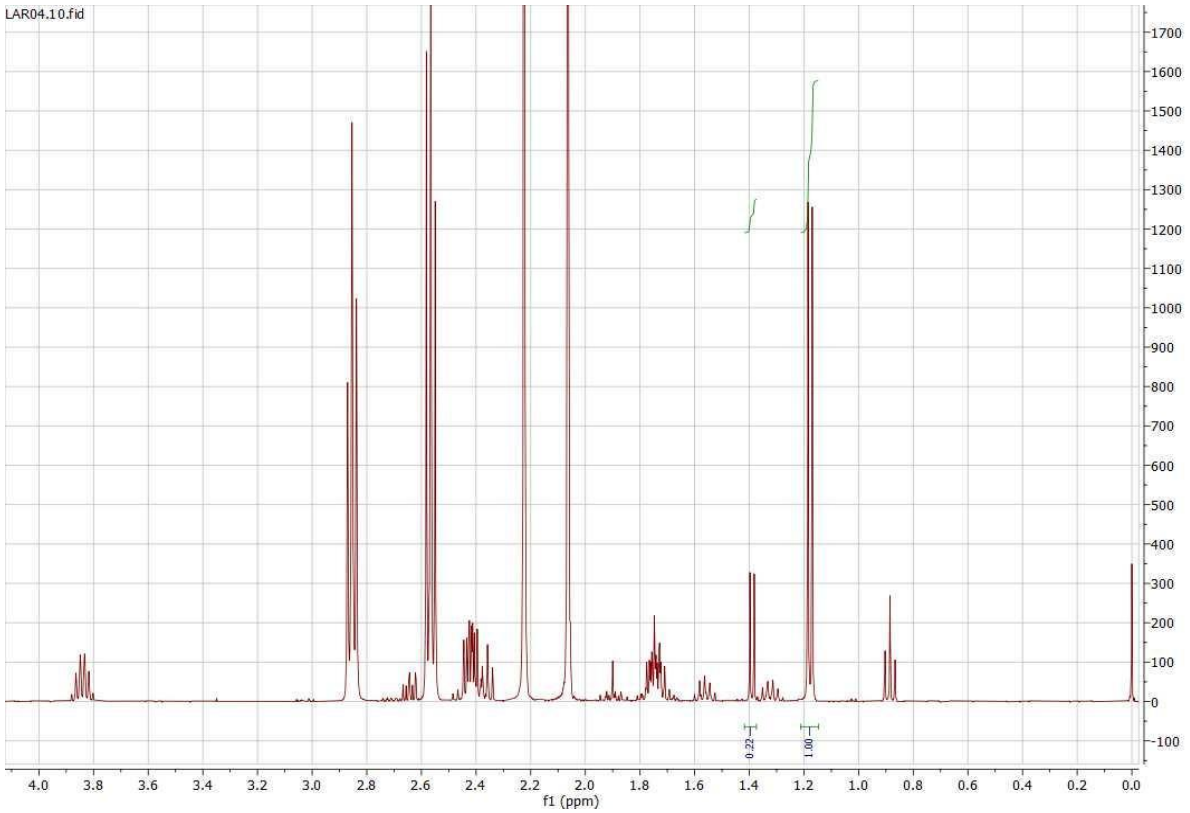


Figure S6. ^{1}H NMR spectrum for electrolysis performed in 0.1 M acetate buffer + 0.1 M $KClO_4$ at -1.9 V vs. RHE, for 4 F/mol of LA.

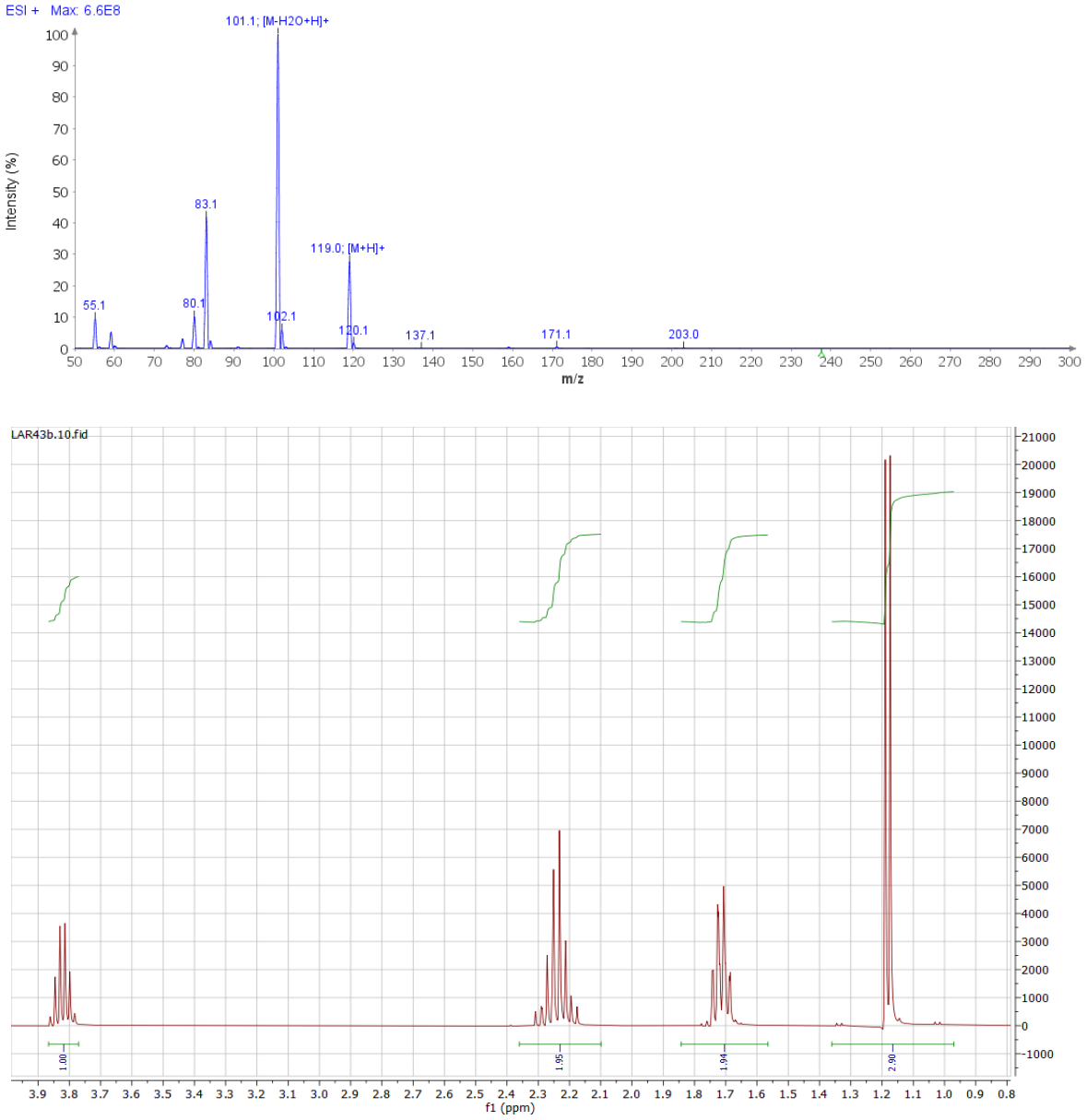


Figure S7. *Top:* ESI+ MS and *Bottom:* ^{1}H NMR spectra of HVA obtained from the electrolysis of 0.4 M LA at optimized conditions. The molecular ion, [HVA+H+], found was 119.0 m/z (while the calculated value is 119.1 m/z, <0.1% error), and the integration of hydrogens in ^{1}H-NMR spectrum showed only 3% error compared to the values expected. These results also exclude the presence of HVA dimer (Pinacol-HVA, which has double mass and does not have hydrogen at δ 3.82 ppm (1H NMR, 400 MHz, H2O + 10 w. % D2O, water suppression).

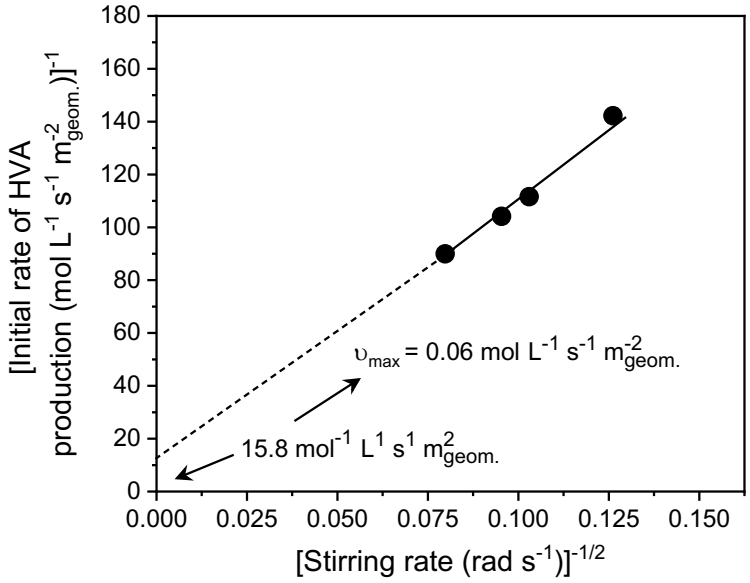


Figure S8. The inverse of initial rates of HVA production as a function of the inverse of the square-root of stirring rate for electrolyses carried out with 0.5 F / mol of LA (< 25% conversion), in 0.1 M $KHCO_3$ + 0.1 M $KClO_4$ and $[LA]_{initial}$ = 0.1 mol L^{-1}, at -1.3 V vs. RHE. and 20ºC. In addition to the general observation that rates always increased with faster stirring (up to experimental limits), the scaling with inverse square root of stirring rate suggests formation of a typical mass-transfer boundary layer across the electrode surface and predominance of diffusion control. (To a rough approximation, the boundary layer thickness for flow over a plate scales with Reynolds number as $Re^{-1/2}$, and $Re \propto \omega$ in a stirred tank). Contributions from migration of organic ions are not completely negligible (the transference number for LA^- is estimated to be ~10% under the optimized electrolysis conditions), and the extrapolated kinetic current cannot be considered quantitatively, but this nonetheless shows a predominance of diffusion resistance. Inherently, mass transfer control should remain in effect at more negative potentials (higher overpotentials) and higher temperatures.

4. Supporting Figures for Section 3.2

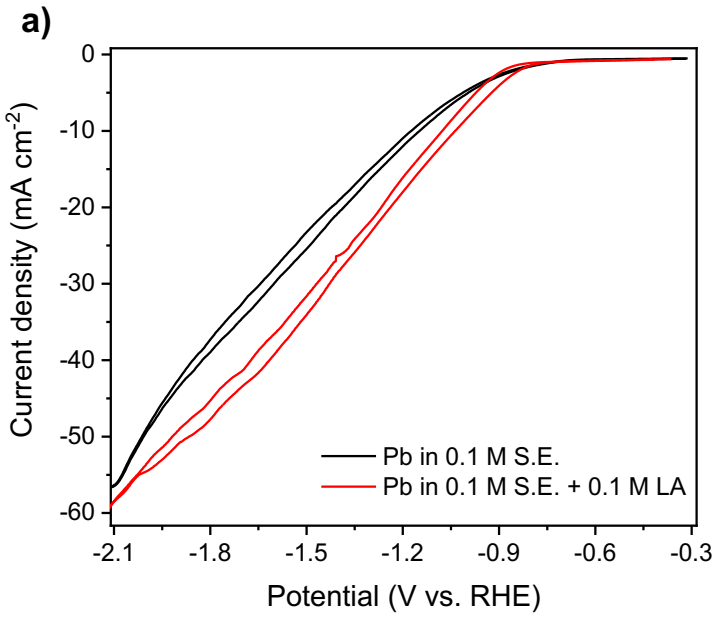


Figure S9. *Cyclic voltammograms of Pb electrode in 0.1 M $KHCO_3$ + 0.1 M $KClO_4$ (pH 7), with and without 100 mM levulinic acid at a scan rate of 50 mV s^{-1} and 20ºC.*

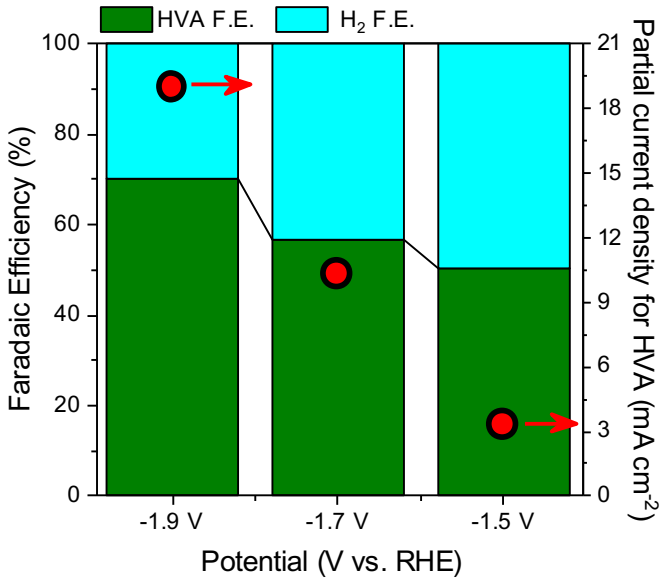


Figure S10. Potential effect for electrolyses carried out at 50 ºC, with 2 F/mol of LA in 0.1 M $KHCO_3$ + 0.1 M $KClO_4$.

5. Homogeneous hydrolysis of GVL

Extra non-electrochemical control experiments were used to verify if GVL can be hydrolyzed to HVA under experimental conditions used for these electrolyses. For this study, 0.1 mol L^{-1} GVL solutions in different supporting electrolytes [0.5 mol L^{-1} H_2SO_4 (pH 0), pure H_2O (pH 7), 0.1 mol L^{-1} $KHCO_3$ + 0.1 mol L^{-1} $KClO_4$ (pH 7), and in 0.1 mol L^{-1} KOH (pH 13)], kept at 50ºC for 3h (higher temperature and longer time than those used in any of the electrolyses), and afterward analyzed by ^1H NMR, are shown in Figure S7. Conversion rates of 2.5, 0.0, 3.8, and 6.7 x 10^{-3} mol L^{-1} h^{-1} (i.e. 7.4, 0.0, 11.5, and 20.0 mol % in 3h) were observed for hydrolysis of GVL to HVA in these different solutions, respectively. Given the low formation rate of HVA relative to electrolysis, it can be concluded that HVA is not formed from homogenous hydrolysis of GVL.

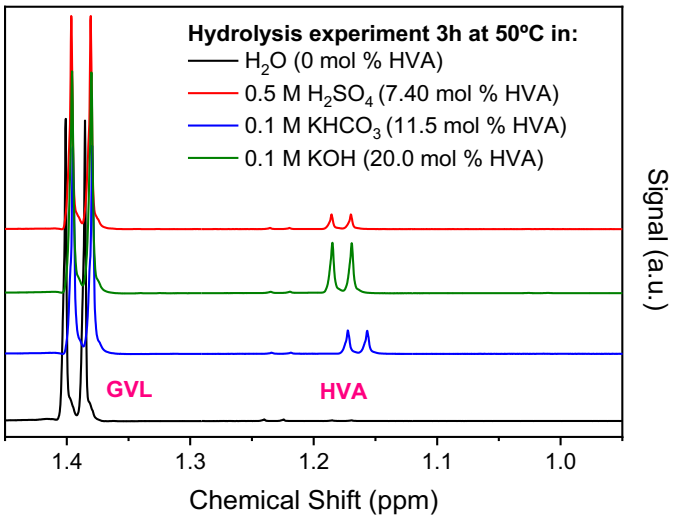


Figure S11. ^1H-NMR spectra for hydrolysis experiment: 0.1 mol L^{-1} GVL solutions were prepared in different supporting electrolytes [0.5 mol L^{-1} H_2SO_4 (pH 0), pure H_2O (pH 7), 0.1 mol L^{-1} $KHCO_3$ + 0.1 mol L^{-1} $KClO_4$ (pH 7), and in 0.1 mol L^{-1} KOH (pH 13)], kept at 50ºC for 3h.

6. In-line *Operando* Quantification of LA Conversion

LA conversion into products can be followed by in-line UV-vis, since only LA absorbs at the region around 270 nm (cf. Figure S1). For this proof-of-concept experiment, electrolysis of LA (carried out in 0.1 M $KHCO_3$ + 0.1 M $KClO_4$ at 50 ºC, -1.9 V vs. RHE, and for $[LA]_{initial}$ = 0.1 mol L^{-1}) was followed by recirculating the electrolyte from/to the electrochemical cell through the micro-cell of the UV-vis detector (from HPLC system, Advion 2000 HPLC, optical path 10 mm and volume of 0.1 mL), at a flow rate of 1.0 mL min^{-1}, and collecting UV-vis spectra of the electrolyte (Figure S13a). A calibration curve for this experiment was obtained by recirculating known amounts of LA dissolved in supporting electrolyte and correlating the LA concentration ([LA]) with the peak intensity at 270 nm (as can be seen at the top part of Figure S13a). Thus, [LA] as a function of time was obtained (Figure S13b), and these results agree with those obtained from the chromatography (Figure 4)

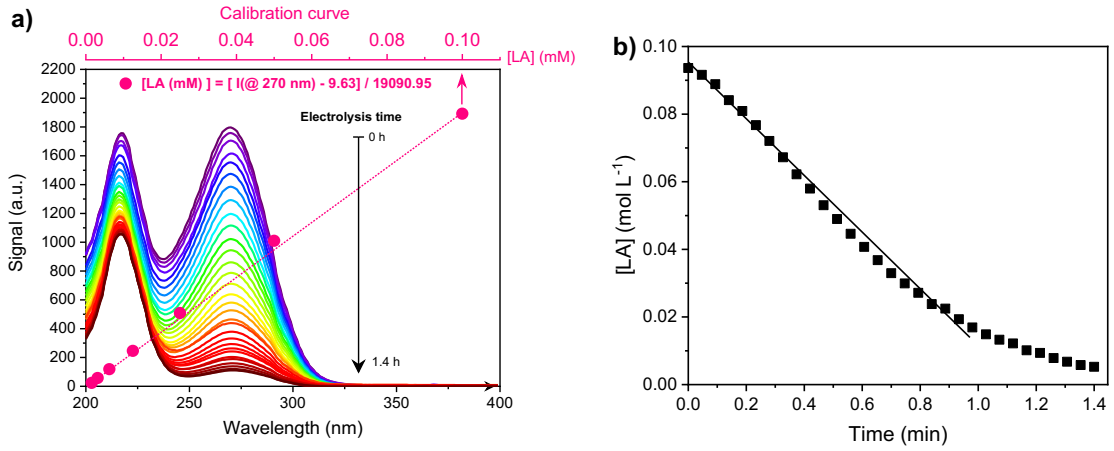


Figure S12. **a)** *Top scale*: Calibration curve for LA using the peak signal intensity at 270 nm. *Bottom scale*: UV-vis spectra, at different electrolysis times, for electrolyte recirculated from the electrochemical cell under *operando* electrolysis (carried out in 0.1 M $KHCO_3$ + 0.1 M $KClO_4$ at 50 ºC, -1.9 V vs. RHE, and for $[LA]_{initial}$ = 0.1 mol L^{-1}) through the UV-vis cell at 1 mL min^{-1}. **b)** Concentration of LA (LA) as a function of electrolysis time obtained from spectra of Panel **a**.

7. One-pot conversion of HVA into GVL

The conversion of HVA to GVL can be easily carried out *via* an acid-catalyzed intramolecular esterification reaction. As a proof-of-concept, 300 µL of H_2SO_4 was added to 10 mL of 0.39 mol L^{-1} HVA solution obtained from electrochemical reduction of LA carried out from 0.4 mol L^{-1} LA, with 3F / mol_{LA} at -1.9 V vs. RHE (which gives 97% conversion, FE of 65%, and HVA production rate of ~32 g L^{-1} h^{-1}). The acid was added immediately after the electrolysis was completed, and the solution was kept stirring at the same temperature (50 ºC) for 15 min, before being neutralized with 0.55 M K_2CO_3 for ^{1}H-NMR analysis. A sample was collected before the addition of acid. As can be seen in ^{1}H-NMR spectra shown in Figure S14, 96% of HVA was converted into GVL with >99.9% selectivity, illustrating this as a promising one-pot electrochemical-chemical method of upgrading LA into GVL.

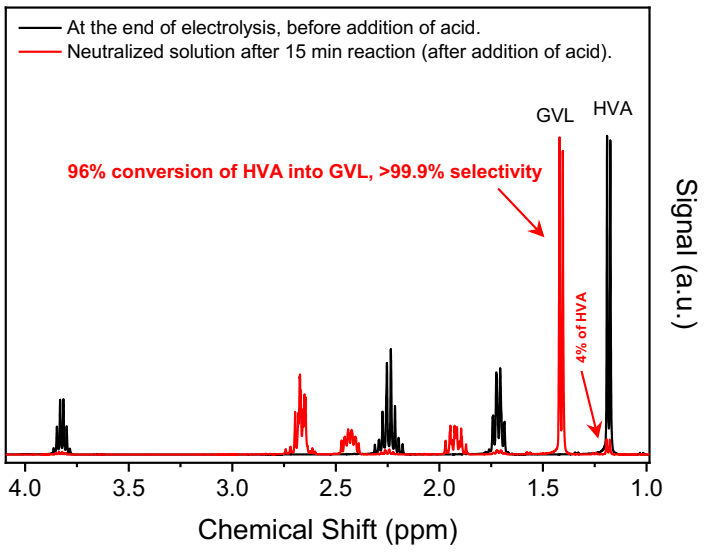


Figure S13. ^{1}H NMR spectra for conversion of 0.39 mol L^{-1} HVA (obtained from the electrochemical reduction of 0.4 mol L^{-1} LA at optimized conditions) into GVL via an acid-catalyzed intramolecular esterification reaction.

8. Table of All Electrolyses

Table S1. Electrolysis conditions, faradaic efficiency, LAR selectivity, average partial current for LAR, and total current for experiments discussed in the paper.

Entry	Conditions	Faradaic Efficiecy (%)	LAR selectivity (%)	Conversion (%)	Average partial current density for LAR (mA cm^{-2})	Total current density (mA cm^{-2})	Electrolysis Time (min)
			pH effect				
1[a]	SE: 0.5 M H_2SO_4 (pH ~0)	VA: 71.3 / GVL: 2.3 / HVA: 0 / H_2: 24.9	VA: 93.8 / GVL: 6.16 / HVA: 0	75.9	143.7	195.2	16.5
2[a]	SE: 0.5 M H_2SO_4 + 0.1M $KClO_4$ (pH ~0)	VA: 71.1 / GVL: 3.1 / HVA: 0 / H_2: 25.5	VA: 92.0 / GVL: 8.0 / HVA: 0	77.3	144.9	195.3	16.5
3[a]	SE: 1.0 M $HClO_4$ (pH ~0)	VA: 69.8 ± 0.1 / GVL: 1.5 ± 0.1 / HVA: 0 / H_2: 23.3 ± 1.2	VA: 95.8 ± 0.2 / GVL: 4.20 ± 0.1 / HVA: 0	72.9	145.6 ± 1.2	204.2 ± 1.7	15.8 ± 0.1
4[a]	SE: 0.1 M potassium acetate buffer + 0.1 M $KClO_4$ (pH 3.8)	VA: 7.5 / GVL: 3.6 / HVA: 12.7 / H_2: 75.9	VA: 18.7 / GVL: 18.0 / HVA: 63.4	40.1	12.3	51.7	62.2
5[a]	SE: 0.1 M $KHCO_3$ + 0.1 M $KClO_4$ (pH 7)	HVA: 47.1 / H_2: 51.8	HVA: 100	94.2	7.8	16.6	193.7
6[a]	SE: 0.1 M $KHCO_3$ (pH 7)	HVA: 38.7 / H_2: 58.8	HVA: 100	77.4	5.0	12.9	249.3
7[a]	SE: 0.1 M $KClO_4$ ($pH_{initial}$ = 7, pH_{final} = 10)	HVA: 32.2 / H_2: 65.8	HVA: 100	76.4	6.4	19.9	161.6

8[a]	SE: 0.1 M K_2CO_3 + 0.1 M $KClO_4$ (pH 10)	HVA: 31.9 / H_2: 66.0	HVA: 100	63.8	7.4	23.2	138.6
9[a]	SE: 0.1 M KOH (pH 13)	HVA: 16.6 / H_2: 75.9	HVA: 100	33.2	2.6	15.7	204.9
10[a]	SE: 0.1 M KOH + 0.1 M $KClO_4$ (pH 13)	Disintegration (cathodic corrosion of electrode)					
Potential and temperature effects							
11[b]	E: -1.9 V vs. RHE	HVA: 56.7 ± 2.1 / H_2: 41.6 ± 2.5	HVA: 100	56.7	8.1 ± 0.3	14.3 ± 0.5	112.5 ± 3.9
12[b]	E: -1.7 V vs. RHE	HVA: 49.1 / H_2: 47.8	HVA: 100	49.1	5.9	12.0	134.0
13[b]	E: -1.5 V vs. RHE	HVA: 34.0 / H_2: 59.4	HVA: 100	34.0	4.3	12.6	127.6
14[b]	E: -1.3 V vs. RHE	HVA: 22.2 / H_2: 66.9	HVA: 100	22.2	2.7	12.2	131.8
15[b]	E: -1.1 V vs. RHE	HVA: 9.4 / H_2: 72.4	HVA: 100	9.4	0.4	4.2	382.9
16[c]	E: -1.9 V vs. RHE	HVA: 70.3 ± 2.5 / H_2: 29.7±2.2	HVA: 100	70.3	19.0 ± 0.2	27.0 ± 0.3	59.6 ± 0.7
17[c]	E: -1.7 V vs. RHE	HVA: 56.5 / H_2: 40.0	HVA: 100	56.5	10.3	18.2	88.4
18[c]	E: -1.5 V vs. RHE	HVA: 50.6 / H_2: 41.6	HVA: 100	50.6	3.3	6.52	246.6
Cation effect							

19[c]	SE: 0.1 M $LiHCO_3$ + 0.1 M $LiClO_4$	HVA: 64.3 ± 2.8 / H_2: 35.7 ± 3.5	HVA: 100	64.3	17.7 ± 0.3	27.5 ± 0.5	58.5 ± 1.1
20[c]	SE: 0.1 M $NaHCO_3$ + 0.1 M $NaClO_4$	HVA: 70.0 ± 2.6 / H_2: 29.0 ± 2.9	HVA: 100	70	18.4 ± 0.2	26.3 ± 0.3	61.1 ± 0.7
21[c]	SE: 0.1 M $CsHCO_3$ + 0.1 M $CsClO_4$	HVA: 62.6 ± 2.4 / H_2: 34.0 ± 2.5	HVA: 100	62.6	19.3 ± 0.4	30.8 ± 0.6	52.2 ± 1.0
Concentration effect							
22[c]	$[LA]_{Initial}$ = 0.1 M, Q: 0.5 F/mol_{LA}	HVA: 78.3	HVA: 100	78.3	21.1	26.9	59.8
23[c]	$[LA]_{Initial}$ = 0.1 M, Q: 1.0 F/mol_{LA}	HVA: 73.5	HVA: 100	73.5	19.7	26.8	60.0
24[c]	$[LA]_{Initial}$ = 0.1 M, Q: 1.5 F/mol_{LA}	HVA: 72.4	HVA: 100	72.4	19.6	27.1	59.3
25[c]	$[LA]_{Initial}$ = 0.1 M, Q: 2.0 F/mol_{LA}	HVA: 70.3 ± 2.5 / H_2: 29.7±2.2	HVA: 100	70.3	19.0 ± 0.2	27.0 ± 0.3	59.6 ± 0.7
26[c]	$[LA]_{Initial}$ = 0.1 M, Q: 2.5 F/mol_{LA}	HVA: 64.8	HVA: 100	64.8	17.5	27.0	59.6
27[c]	$[LA]_{Initial}$ = 0.1 M, Q: 3.0 F/mol_{LA}	HVA: 56.3	HVA: 100	56.3	15.2	27.0	59.6
28[c]	$[LA]_{Initial}$ = 0.2 M, Q: 0.5 F/mol_{LA}	HVA: 87.4	HVA: 100	87.4	79.9	91.4	17.6
29[c]	$[LA]_{Initial}$ = 0.2 M, Q: 1.0 F/mol_{LA}	HVA: 85.9	HVA: 100	85.9	78.5	91.4	17.6
30[c]	$[LA]_{Initial}$ = 0.2 M, Q: 1.5 F/mol_{LA}	HVA: 84.8	HVA: 100	84.8	77.5	91.4	17.6

31[c]	$[LA]_{Initial}$ = 0.2 M, Q: 2.0 F/mol_{LA}	HVA: 80.0	HVA: 100	80.0	73.1	91.4	17.6
32[c]	$[LA]_{Initial}$ = 0.2 M, Q: 2.5 F/mol_{LA}	HVA: 74.5	HVA: 100	74.5	68.1	91.4	17.6
33[c]	$[LA]_{Initial}$ = 0.2 M, Q: 3.0 F/mol_{LA}	HVA: 63.6	HVA: 100	63.6	58.1	91.3	17.6
34[c]	$[LA]_{Initial}$ = 0.4 M, Q: 0.5 F/mol_{LA}	HVA: 97.4	HVA: 100	97.4	108.1	111.0	14.5
35[c]	$[LA]_{Initial}$ = 0.4 M, Q: 1.0 F/mol_{LA}	HVA: 93.4	HVA: 100	93.4	103.7	111.0	14.5
36[c]	$[LA]_{Initial}$ = 0.4 M, Q: 1.5 F/mol_{LA}	HVA: 89.9	HVA: 100	89.9	99.8	111.0	14.5
37[c]	$[LA]_{Initial}$ = 0.4 M, Q: 2.0 F/mol_{LA}	HVA: 84.6	HVA: 100	84.6	93.9	111.0	14.5
38[c]	$[LA]_{Initial}$ = 0.4 M, Q: 2.5 F/mol_{LA}	HVA: 75.9	HVA: 100	75.9	84.2	111.0	14.5
39[c]	$[LA]_{Initial}$ = 0.4 M, Q: 3.0 F/mol_{LA}	HVA: 64.7	HVA: 100	64.7	71.8	111.0	14.5

a. Q: 4F /mol_{LA}, E: -1.9 V vs. RHE, T: 20ºC, and $[LA]_{Initial}$ = 0.1 M. **b.** Q: 2F / mol_{LA}, T: 20ºC, $[LA]_{Initial}$ = 0.1 M, and SE: 0.1 M $KHCO_3$ + 0.1 M $KClO_4$ (pH 7). **c.** Same as “b”, but T: 50°C.

Supporting references

(1) Huang, B.; Myint, K. H.; Wang, Y.; Zhang, Y.; Rao, R. R.; Sun, J.; Muy, S.; Katayama, Y.; Corchado Garcia, J.; Fraggedakis, D.; et al. Cation-Dependent Interfacial Structures and Kinetics for Outer-Sphere Electron-Transfer Reactions. *J. Phys. Chem. C* **2021**, acs.jpcc.0c10492. https://doi.org/10.1021/acs.jpcc.0c10492.

(2) Zebardast, H. R.; Rogak, S.; Asselin, E. Potential of Zero Charge of Glassy Carbon at Elevated Temperatures. *J. Electroanal. Chem.* **2014**, *724*, 36–42. https://doi.org/10.1016/j.jelechem.2014.03.030.

(3) Miyake, H.; Ye, S.; Osawa, M. Electroless Deposition of Gold Thin Films on Silicon for Surface-Enhanced Infrared Spectroelectrochemistry. *Electrochem. commun.* **2002**, *4* (12), 973–977. https://doi.org/10.1016/S1388-2481(02)00510-6.