# Supporting Information for "Electrochemistry for generation of renewable chemicals: Electrochemical conversion of levulinic acid"

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## S1. Results for primary reductive and oxidative conversions: Reduction of levulinic acid to valeric acid and γ-valerolactone and oxidation of levulinic acid to 2,7-octanedione, 4-hydroxy-2-butanone and 3-buten-2-one.

**Table SI 1:** Reactions conditions and main results for primary reductive and oxidative conversions.

| Entry | Route | Educt concentration [M] LA | Electrode material | $E_{WE}$ [V] | t [h] | Electrolyte solution | Conversion [%] LA | Selectivity [%] gVL | Selectivity [%] VA | | Coulombic efficiency [%] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **I, II** | 0.05 | Pb | -1.8 | 4 | 0.5 M $H_2SO_4$ | 73.0 | 18.0 | 82.0 | | 6.8 |
| 2 | **I, II** | 0.10 | Pb | -1.8 | 4 | $KH_2PO_4/K_2HPO_4$ | -- | -- | -- | | -- |
| 3 | **I, II** | 0.10 | Pb | -1.8 | 4 | 0.5 M $H_2SO_4$ | 65.1 | 13.1 | 86.9 | | 30.9 |
| 4 | **I, II** | 0.50 | Pb | -1.8 | 4 | 0.5 M $H_2SO_4$ | 71.6 | 18.4 | 81.6 | | 56.4 |
| 5 | **I, II** | 0.75 | Pb | -1.8 | 8 | 0.5 M $H_2SO_4$ | 54.3 | 17.2 | 82.8 | | 58.6 |
| 6 | **I, II** | 1.00 | Pb | -1.8 | 4 | 0.5 M $H_2SO_4$ | 77.9 | 13.9 | 86.1 | | 65.4 |
| 7 | **I, II** | 0.50 | Cu | -1.8 | 4 | 0.5 M $H_2SO_4$ | 7.3 | 9.6 | 8.3 | | 1.3 |
| 8 | **I, II** | 0.50 | Fe | -1.8 | 4 | 0.5 M $H_2SO_4$ | 19.9 | 7.8 | 9.6 | | 0.5 |
| 9 | **I, II** | 0.50 | Ni | -1.8 | 4 | 0.5 M $H_2SO_4$ | 8.0 | 3.2 | 17.3 | | 1.1 |
| 10 | **I, II** | 0.50 | C | -1.8 | 4 | 0.5 M $H_2SO_4$ | 39.0 | 69.0 | 0.0 | | 18.0 |
| 11 | **I, II** | 0.50 | Pb | -1.8 | 4 | 1.0 M NaOH | 19.6 | 48.7 | 0.0 | | 21.1 |
| 12 | **I, II** | 0.50 | Fe | -1.8 | 4 | 1.0 M NaOH | 24.5 | 74.5 | 0.0 | | 18.5 |
| | | **LA** | | | | | | **2,7-OD** | **4H2B** | **MVK** | |
| 13 | **III** | 1.00 | Pt | 5.0 | 7 | Methanol, pH 5.5 | 60.0 | 47.0 | -- | -- | 86.2 |
| 14 | **III** | 1.00 | Pt | 5.0 | 7 | $H_2O$, pH 5.5 | 74.0 | 27.0 | -- | -- | 5.0 |
| 15 | **IV** | 0.10 | C | 6.0 | 5 | $H_2O$, 0.2 M NaOH | 57.0 | -- | 20.0 | -- | 5.0 |
| 16 | **IV** | 0.10 | C | 1-3 | 5 | $H_2O$, 0.1M NaOH | 74.0 | -- | -- | 45.0 | 24.0 |
| 17 | **V** | 0.10 | C | 2-3 | 6.5 | $H_2O$, 0.1 M $H_2SO_4$ | 42.0 | -- | -- | 18.0 | 8.0 |

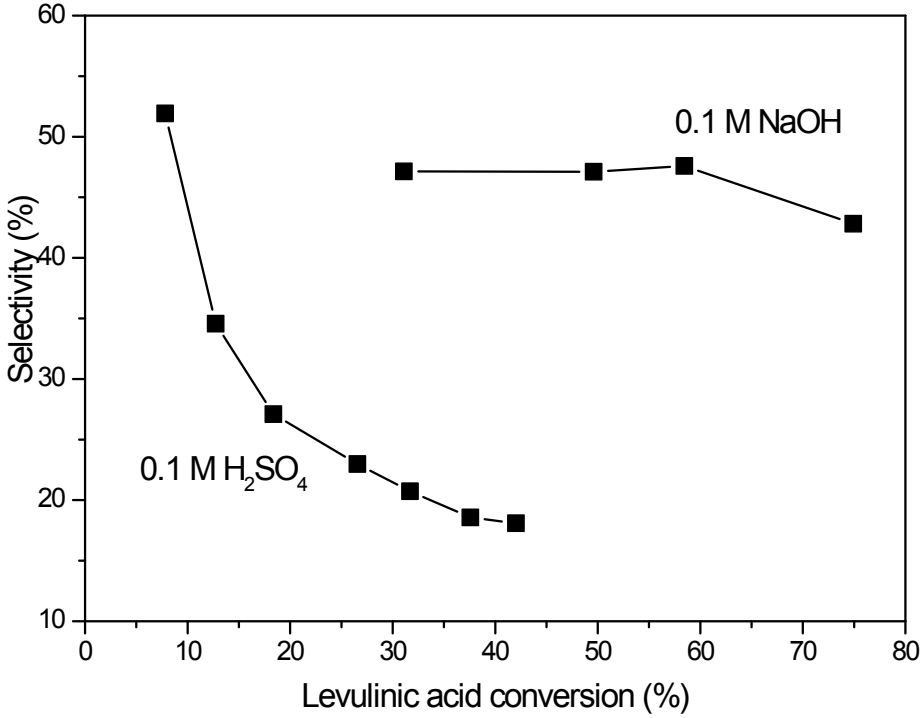


**Figure S1:** Selectivity of the 3-buten-2-one formation as a function of the degree of levulinic acid conversion and of the used electrolyte at a carbon anode at $E_{WE}$ = 3 V.

## S2. Results for secondary electrochemical conversion steps: Electrochemical hydrogenation of 4-hydroxy-2-butanone to 1-butanol and oxidation of valeric acid.

**Table SI 2:** Reactions conditions and main results for secondary reductive conversions.

| Entry | Route | Educt concentration [M] 4H2B | Electrode material | $E_{WE}$ [V] | t [h] | Electrolyte solution | Conversion [%] 4H2B | Selectivity [%] 1-BuOH | 1,3BDO | Coulombic efficiency [%] |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **IX, X** | 0.08 | Pb | -1.3 | 3.5 | 0.5 M $H_2SO_4$ | 17.8 | 15.9 | 0.4 | 16.8 |
| 2 | **IX, X** | 0.08 | Pb | -1.5 | 3.5 | 0.5 M $H_2SO_4$ | 65.1 | 71.5 | 2.6 | 12.7 |
| 3 | **IX, X** | 0.08 | Pb | -1.8 | 3.5 | 0.5 M $H_2SO_4$ | 68.8 | 55.6 | 1.7 | 8.0 |
| 4 | **IX, X** | 1.00 | Pb | -1.5 | 3.5 | 0.5 M $H_2SO_4$ | 19.2 | 58.0 | 2.5 | 59.5 |
| 5 | **IX, X** | 0.08 | Fe | -1.5 | 4 | $KH_2PO_4/K_2HPO_4$ | 23.9 | 0.0 | 23.1 | 2.1 |
| 6 | **IX, X** | 0.08 | Fe | -1.8 | 4 | $KH_2PO_4/K_2HPO_4$ | 34.4 | 0.0 | 34.7 | 2.4 |
| 7 | **IX, X** | 0.08 | Pb | -1.8 | 4 | $KH_2PO_4/K_2HPO_4$ | 9.8 | 19.3 | 0.7 | 0.7 | 2.1 |

**Table SI 3:** Reactions conditions and main results for primary reductive and oxidative conversions of the anodic oxidation of valeric acid at different graphite electrodes

| Entry | Educt concentration [M] VA | Electrode material | $E_{WE}$ [V] | t [h] | Electrolyte solution | Current density [%] [mA/cm2] | Conversion [%] | Selectivity[a] [%] | Coulombic efficiency [%] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.21 | $C_{sheet}$ | 2.5 | 6 | Water | 10 | 90 | 12 | |
| 2 | 0.22 | $C_{sheet}$ | 2.5 | 6 | $H_2SO_4$ 0.5M | 10 | 98 | 19 | |
| 3 | 0.23 | $C_{sheet}$ | 2.5 | 6 | NaOH 0.25 M | 10 | 98 | 18 | |
| 4 | 0.25 | $C_{sheet}$ | 2.5 | 10 | NaOH 0.25 M | 5 | 56 | 18 | |
| 5 | 0.24 | $C_{sheet}$ | 2.5 | 19 | NaOH 0.25 M | 1 | 35 | 22 | |
| 6 | 0.25 | $C_{sheet}$ | 2.5 | 10 | NaOH 0.75M | 25 | 79 | 18 | |
| 7 | 0.25 | $C_{sheet}$ | 2.5 | 10 | NaOH 0.75M | 10 | 52 | 4 | |
| 8 | 0.25 | $C_{sheet}$ | 2.5 | 10 | NaOH 0.75M<br>$NaHCO_3$ 0.75M | 10 | 53 | 4 | |
| 9 | 0.20 | $C_{sheet}$ | 2.5 | 11 | NaOH 0.75M<br>$NaHCO_3$ 0.25M | 25 | 64 | 13 | |
| 10 | 0.23 | $C_{sheet}$ | 2.5 | 7 | NaOH 0.75M<br>$NaHCO_3$ 0.25M | 45 | 78 | 26 | |
| 11 | 0.25 | $C_{sheet}$ | 2.5 | 13 | NaOH 0.75M<br>$NaHCO_3$ 0.10M | 45 | 95 | 16 | |

*Continuation of Table SI 3*

| Entry | Educt concentration [M] VA | Electrode material | $E_{WE}$ [V] | t [h] | Electrolyte solution | Current density [%] [mA/cm2] | Conversion [%] | Selectivity[a] [%] | Coulombic efficiency [%] |
|---|---|---|---|---|---|---|---|---|---|
| 12 | 0.22 | $C_{sheet}$ | 2.5 | 11 | NaOH 0.25 M<br>$NaClO_4$ 0.5 M | 7.5 | 83 | 13 | |
| 13 | 0.22 | $C_{sheet}$ | 2.5 | 11 | NaOH 0.25 M<br>$NaClO_4$ 0.5 M | 25 | 99 | 11 | |
| 14 | 0.22 | $C_{sheet}$ | 2.5 | 2 | NaOH 0.25 M<br>$NaClO_4$ 0.5 M | 45 | 77 | 7 | |
| 15 | 0.21 | $C_{sheet}$ | 2.5 | 2 | NaOH 0.25 M<br>$NaClO_4$ 1.0 M | 45 | 73 | 8 | |
| 16 | 0.22 | $C_{sheet}$ | 2.5 | 10 | NaOH 0.25 M<br>$Na_2SO_4$ 0.5M | 5 | 72 | 10 | |
| 17 | 0.22 | $C_{felt}$ | 2.5 | 2 | NaOH 0.25 M | 80 | 99 | 17 | |
| 18 | 0.22 | $C_{foil}$ | 2.5 | 2 | NaOH 0.25 M | 80 | 92 | 16 | |
| 19 | 0.25 | $C_{sheet}$ | 2.5 | 2 | NaOH 0.25 M | 80 | 98 | 16 | |
| 20 | 0.25 | $C_{sheet}$ | 2.5 | 10 | NaOH 0.35 M | 10-25 | 93 | 13 | |
| 21 | 0.25 | $C_{sheet}$ | 2.5 | 10 | NaOH 0.35 M | 2-5 | 55 | 15 | |
| 22 | 0.01 | $C_{sheet}$ | 2.5 | 8 | NaOH 10mM<br>$NaClO_4$ 0.1 M | 10 | 90 | 18 | |
| 23 | 0.04 | $C_{sheet}$ | 2.5 | 12 | NaOH 50mM<br>$NaClO_4$ 0.1 M | 10 | 95 | 21 | |
| 24 | 0.04 | $C_{sheet}$ | 2.5 | 7 | NaOH 50 mM | 2.5 | 94 | 28 | |
| 25 | 0.04 | $C_{sheet}$ | 2.5 | 7 | NaOH 50 mM | 10 | 99 | 26 | |

[a] selectivity considering only the products of secondary carbenium ion (mainly 2-butanol, 1-butanal and acetone)

## S3. Energetic considerations

i. Coulombic efficiency (*CE*) and Selectivity (*S*)

At the potential applied for the electrochemical decarboxylation reaction, side reactions like the solvent decomposition (e.g., the oxygen evolution or hydrogen evolution from water) take place, reducing the Coulombic efficiency of the (target) reactions.

$$Q_{applied} = n_{theoretical} \times z \times F \quad (1a)$$

$$Q_{applied} = i \times t \quad (1b)$$

$$n_{theoretical} = \frac{i \times t}{z \times F} \quad (2)$$

$n_{experimental}$ is obtained from analytical methods (HPLC and GC-MS).

$$CE = \frac{n_{experimental}}{n_{theoretical}} \quad (3)$$

$$S = \frac{n_{experimental\ of\ a\ \ prodcut}}{n_{theoretical\ of\ a\ product}} \quad (4)$$

ii. Energy for electrochemical upgrading:

The theoretically required electric energy to drive the reaction is defined as the product of cell voltage (*U*) and charge (*Q*): $E_{electric} = UQ$. The molar electric energy, $E_{electric,\ molar}$, can be calculated as $E_{electric,\ molar} = UzF$, with *F* being the Faraday constant and *z* being the number of transferred electron per molecule.

Since in our study all reactions were performed in half-cell experiments, the energy was calculated for the respective half-reaction considering the average working electrode potential *vs.* standard hydrogen electrode, SHE as *U*

Thus, the energy consumption in terms of molar energy can be calculated as depicted below:

$$Energy_{electrochemical\ upgrading} = \frac{z \times F \times U}{CE} \text{ (J mol}^{-1}\text{)} \quad (5a)$$

Considering the molar mass of products ($M_P$) the specific energy can be calculated.

$$Energy_{electrochemical\ upgrading} = \frac{z \times F \times U}{CE \times M_P} \text{ (J kg}^{-1}\text{)} \quad (5b)$$

iii. Energy storage efficiency :

$$Energy_{storage\ efficiency} = \frac{\Delta H_{LHV}}{Energy_{electrochemical\ upgrading}} \times 100 \text{ (\%)} \quad (6)$$

**Energy content of the products**

Table SI 4 shows the energy content of the respectively obtained products, according the method of Boie for calculate the lower heating value $H_{LHV}$:

$$H_{LHV} = 34.8\ \omega_C + 93.9\ \omega_H - 10.8\ \omega_O + 10.5\ \omega_S + 6.3\ \omega_N - 2.44\ \omega_{H2O} \quad (7);$$

(with the symbols representing the relative mass shares, $\omega$, of the elements and water)

**Table SI 4:** Summary of the energy density value for the different oxidation products derived from levulinic acid.

| | $H_{LHV}$ MJ kg-1 |
|---|---|
| levulinic acid | 20.8 |
| 2,7-octandione | 30.4 |
| 3-buten-2-one | 29.5 |
| 4-hydroxy-2-butanone | 23.6 |
| n-octane | 44.4 |
| 1-butanol | 36.0 |

| | |
|---|---|
| 1,3-butanediol | 25.2 |

**Table SI 5:** Summary of the energy density value for the different oxidation products derived from levulinic acid.

| | | | | | | | achieved [b] | | | | theoretical maximum | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | energy density [a] ($H_{LHV}$) / kJ mol$^{-1}$ | | Δ molar heating values / kJ mol$^{-1}$ | z [c] e | average electrode potential / V | *CE* / % | molar electric energy / kJ mol$^{-1}$ | energy storage efficiency / % | average electrode potential / V | CE / % | molar electric energy / kJ mol$^{-1}$ | energy storage efficienc / % |
| | | | educt | product | | | | | | | | | | |
| oxidation | III | levulinic acid → 2,7-octandione | 2328 | 4323 | -333 | 1 | 5.2 | 90 | 545 | -61.13 | 2.5 | 100 | 241 | -138 |
| | IV | levulinic acid → 4-hydroxy-2-butanone | 2328 | 2083 | -245 | 2 | 2.7 | 10 | 10420 | -2.35 | 2.5 | 100 | 482 | -51 |
| | V | levulinic acid → 3-buten-2-one | 2328 | 2067 | -261 | 2 | 2.7 | 20 | 2171 | -12.03 | 2.5 | 100 | 482 | -54 |
| | VII | Valeric acid → n-octane | 2691 | 5047 | -335 | 1 | 3.7 | 40 | 830 | -40.30 | 2.5 | 100 | 241 | -139 |

[a] estimated according to Boie [87], [b] achieved in this study, [c] number of electrons