Supplementary Information

Electrochemical depolymerisation of polylactic acid

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1 Experimental

1.1 Materials

All commercially acquired materials used in this work are listed in the table below. The stated purities correspond to the manufacturer's specifications. All substances are used without any further purification. Rac-lactide was prepared by equally mixing L-lactide PURALACT®L polymer type (water < 0.01%, free acid = 0.54 meq kg^{-1}) and D-lactide PURALACT®D polymer type (water < 0.01%, free acid = 0.55 meq kg^{-1}). The rac-lactide was stored at -35 °C in a glovebox filled with nitrogen and was donated by Total Corbion PLA.

Table S1 Materials used in this work.

Chemical	Supplier	Purity
1,4-Dioxane	Sigma Aldrich	99.8 %
Acetonitrile-d3	Sigma Aldrich	99.8 %
DL-Lactic acid	Sigma Aldrich	90 %
Ethanol absolute	Supelco. Merck	> 99.9 %
Graphite foil 0.4 mm	Alfa Aesar	99.8 %
Lithiumperchlorate	Sigma Aldrich	> 95 %
L-(+)-Lactic acid	Sigma Aldrich	> 99.9 %
Mesitylene	Alfa Aesar	> 98 %

1.2 Electrolysis

The standard electrochemical cell for the conducted experiments, was a two electrode setup in an undivided cell, assembled from a 20 mL glass vial (Figure S1). To hold the electrodes in place, a custom cap was designed and 3D-printed. The cap separates the two electrodes and assures repeatability in their immersion depth (12 mm). The standard setup used two platinum electrodes (5 x 1 cm, active surface: 1.2 cm^2), but steel, titanium, and graphite were also tested as cathode materials. A magnetic stirrer was used for agitation of the reaction mixture. A water bath controlled the reaction temperature to 60°C. Current densities from 10 to 40 mA/cm^2 were used for transferring 10 to 1000 C.

Figure S1: Electrochemical setup for batch electrolysis in an undivided cell using a glass vial with a 3D printed cap.

The standard reaction mixture with a volume of 7 mL consisted of dioxane with 10v% water, 5 mg/mL PLA and 0.25 M $LiClO_4$. Dioxane was combined with PLA first and stirred until dissolution. Then water and electrolyte were added. Based on the standard reaction mixture, variations of the parameters transferred charge, PLA concentration, molecular weight, and current density were investigated. HPLC, GPC, and NMR analysis were performed after the reaction.

To get first insights in the reaction mechanism, electrolysis was performed in a divided cell of a different custom-built set-up (Figure S2). The cell consists of a stacking construction of two modules with cylindrical recesses (r = 1 cm, h = 1 cm) in square manufactured parts. They are completed by a module for heating and are screwed and fixed by plates from both sides. The modules are separated by two electrodes and a Nafion®N-324 membrane (0.15 mm thick, Teflon fabric reinforced). The electrode surface of each electrode amounts to 3 cm^2. The distance between the electrodes is 2 cm and each compartment holds a volume of 3 mL.
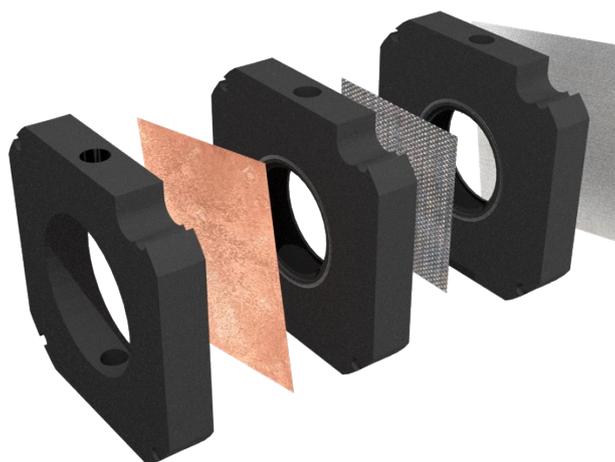
Figure S2: Electrochemical setup for batch electrolysis from left to right with heating module, anode, anode compartment, membrane, cathode compartment, and cathode.

1.3 HPLC analysis

Reaction solutions were analysed using high performance liquid chromatography (Shimadzu Prominence LC-20 system). 100 µL were taken from the reaction solution and diluted with 100 µL water to precipitate the polymer. The mixture was filtered through a Chromafil Xtra polyamid filter (25 mm, 0.45 µm) before analysis. The following method was used to quantify the lactic acid in the solution (Table S2).

Table S2 Parameter settings of the HPLC analysis.

Parameter	Values
Model	Cs Organic Acid Resin 8 x 250 mm
Pressure (bar)	66
Oven temperature (°C)	40
Flow (mL min^{-1})	1.0
Eluent	5 mmol L^{-1} sulfuric acid
Injection volume (µL)	5
Run time (min)	20

The yield was obtained by using the following equations:

$$c(LA) = \frac{A(LA)}{K_f}$$

$$Yield(LA) = \frac{2 * c(LA) * V(reaction) * M(rep.unit)}{M(LA) * m(PLA)}$$

c(LA): concentration of lactic acid in HPLC sample (mg/mL)

A(LA): area of lactic acid in chromatogram (-)

K_f: calibration factor (mL/mg)

V(reaction): reaction volume (mL)

M(rep.unit): molar mass of the repetition unit (72.08 g/mol)

M(LA): molar mass of lactic acid (90.08 g/mol)

m(PLA): weight of PLA (mg)

1.4 GPC

Molecular weights (M_n, M_w) and molecular weight distributions (M_w/M_n) were determined by gel permeation chromatography (GPC). Polymer residues of the reaction were precipitated by adding the reaction solution into 50 mL of cold ethanol (-18°C). The solid residues were filtered off and dried in air. For analysis a Viscotek GPCmax (Malvern Panalytical GmbH), equipped with a HPLC pump, a Viscotek VE3580 refractive index detector (Malvern Panalytical GmbH), a Viscotek 270 Dual detector viscosity detector (Malvern Panalytical GmbH) and two Viscotek T columns (Malvern Panalytical GmbH), based on porous styrene-divinylbenzene copolymer was used, with a maximum pore size of 500 Å and 5000 Å. As mobile phase, THF was used, at a flow rate of 1 mL/min. The samples concentration was set at 5 g/L. For the evaluation of the chromatographic results, a conventional calibration was performed. According to the literature, the Mark-Houwink correction factor of 0.58 was used for the molar mass of PLA in relation to polystyrene.[1,2]

1.5 NMR

^{1}H-NMR spectra were recorded at 300 MHz using a Bruker AV300 spectrometer. The measurements were performed at room temperature. Acetonitrile-d3 (D_3CCN) was used as NMR solvent, with mesitylene as an internal standard. The chemical shifts were referenced to the aromatic proton signal of the mesitylene at 6.28 ppm (^{1}H-NMR (300 MHz, D_3CCN) δ = 2.26(s), 6,28(s) ppm).

1.6 Preparation of PLA

For preparation, the *react*Raman reactor[3] was heated to 150°C under vacuum and flooded three times with argon. The preparation of the respective samples was performed in the nitrogen filled glovebox. Rac-Lactide (8.00 g, 55.5 mmol) and the catalyst [Zn{(R,R)DMEG$_2$(1,2)ch}$_2$](OTf)$_2$ THF in the appropriate [M]/[I] ratio were weighed and homogenized in an agate mortar. The reaction mixture was removed from the glovebox in a sealed glass vial. The lactide-catalyst mixture was transferred to the heated reactor in argon countercurrent, the stirrer (260 rpm) was turned on. Depending on the [M]/[I] ratio, the reaction time was adjusted. If benzyl alcohol (BnOH) was used as a co-initiator, it was added to the reaction mixtures in the reactor. After the polymerization was terminated, the polymer was removed from the reactor. The polymer was dissolved in DCM (approximately 4 mL), precipitated in ethanol (200 mL) at room temperature, and dried. By GPC, the molar mass of the dried polymer was determined.

Table S3 Polymerization details of the lactide polymerization in the *react*Raman reactor (150°C, 260 rpm).

Lactide (g/ mmol/ eq.)	Catalyst (mg/ mmol/ eq.)	Coinitiator (mg/ mmol/ eq.)	t min	M_n(PLA) g mol^{-1}
8/ 55.5/ 500	116.4/ 0.111/ 1	-	3	40900
8/ 55.5/ 1000	58.2/ 0.056/ 1	120/ 1.11/ 20	3	7700

2 Supporting results

2.1 Estimation of experimental error

The experimental error was estimated by repeating an electrolysis with medium conversion three times (n = 3). Therefore, a Pt cathode and anode were used for a current density of 40 mA/cm^2. The standard reaction conditions using a dioxane/water mixture (vol. 9:1) with 0.25 M LiClO$_4$ and 5 mg/mL PLA (48300 g mol^{-1}) at 60°C were applied. The standard deviation (STD) was calculated from the HPLC yields (x) using the following equation:

$$STD = \sqrt{\frac{\sum(x - \bar{x})^2}{n}}$$

A standard deviation of 2.6% was found for the averaged HPLC yield of 35.7% of this experiment.

2.2 Investigating product spectrum by NMR

To investigate the product spectrum of the reaction NMR spectra before and after the reaction are compared with a spectrum from a reference experiment without PLA (Figure S3). Acetonitrile (δ = 1.94(m) ppm), mesitylene (δ = 2.26(s), 6,28(s) ppm), and dioxane (δ = 3.62(s) ppm) are visible in all spectra. Protons belonging to the primary carbon (δ = 1.52(d)) and to the tertiary carbon (δ = 5.19(q)) of the repetition unit of PLA are detected before and after the reaction. Apart from some signals due to dioxane decomposition, which are also visible in the reference spectrum, only two signals belonging to lactic acid (δ = 1.32(d), δ = 4.45(q)) can be seen proving the high selectivity of the reaction.
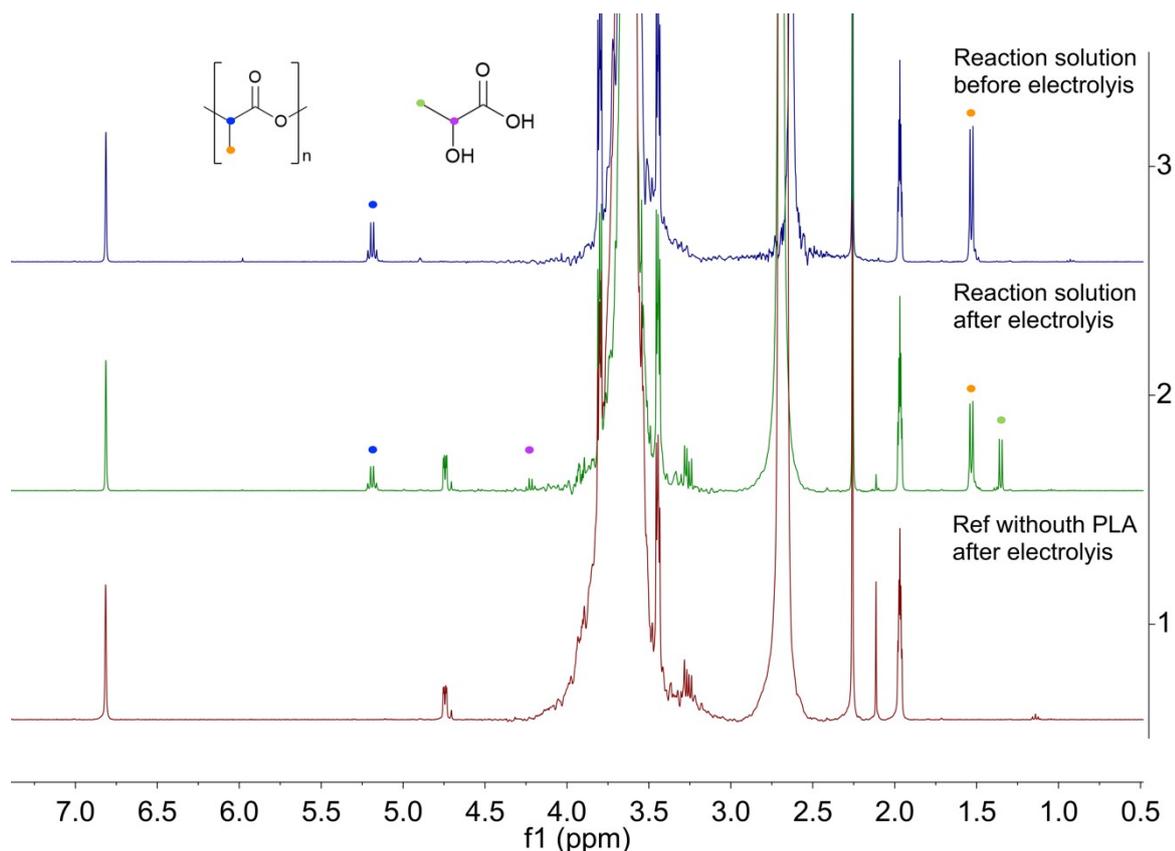

Figure S3: NMR spectra of reaction solution before and after the reaction and of a reference reaction without PLA (^{1}H-NMR (300 MHz, D$_3$CCN)).

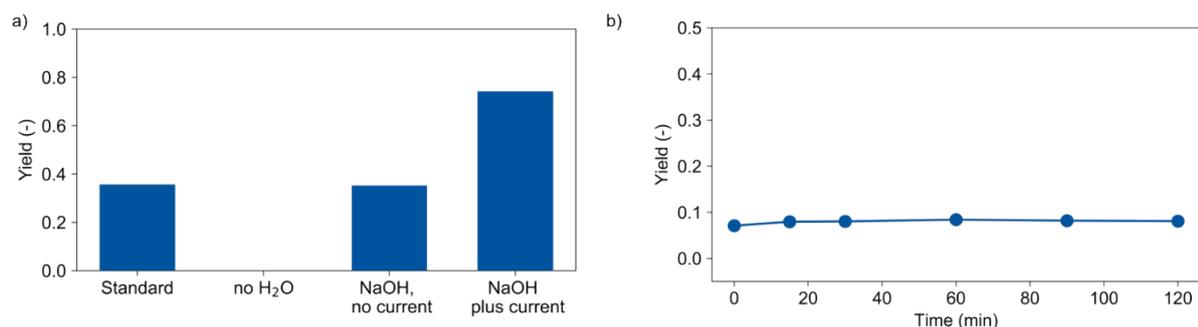## 2.3 Additional electrolysis experiments

Figure S4: Electrolysis experiments a) under standard conditions, without water in the electrolyte, and with additional NaOH (0.2 mol/L in reaction solution), and with NaOH plus current b) after a charge transfer of 50 C at 60°C (t = 0 min). Standard conditions: Pt cathode, Pt anode, 40 mA/cm^2, dioxane/water (vol. 9:1), 0.25 M LiClO$_4$, 60°C, 5 mg/mL PLA (48300 g mol^{-1}).
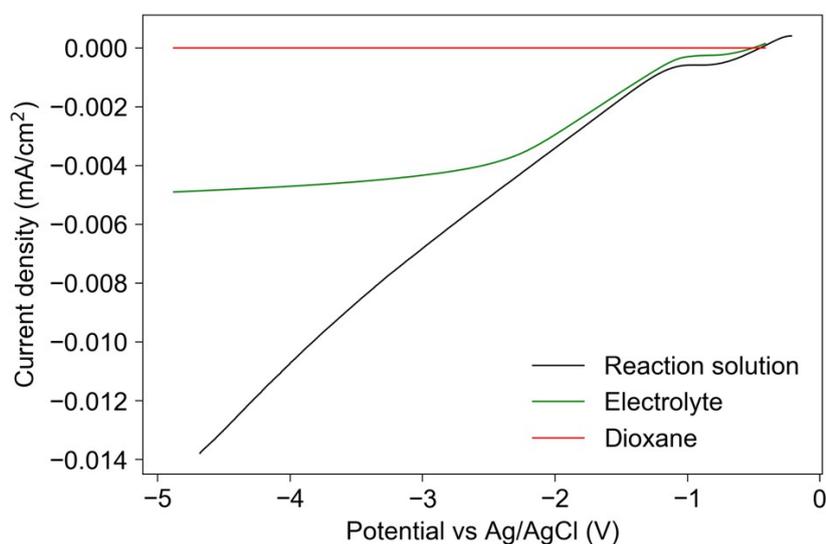
2.4 Cyclic voltammetry

Figure S5: Cyclic voltammogram of reaction solution with (black) and without (green) PLA and pure dioxane (red) with a scan rate of 50 mV/s.

2.5 Comment on greenhouse gas emissions

The GHG emissions during the presented recycling process are compared to the GHG emissions during biodegradation to address ecological issues by an educated guess. Two scenarios are discussed, one using the German electricity mix and one applying the Canadian one. The usage of German electricity leads to the emission of 40,100 g CO_2e/kg_{PLA} whereas for the canadian case the GHG emission are estimated with 170 g CO_2e/kg_{PLA}.[3,4] In comparison, biodegradation (85%) of PLA emits the inferior amount of 4.5 g CO_2e/kg_{PLA}.[5-8] However, it must be considered that the demonstrated recycling process is only lab-scale and GHG emissions for electricity generation are expected to decrease prospectively. Furthermore, lactic acid is directly obtained from the recycling process as valuable substrate for a renewable chemical industry whereas biodegradation finally only generates CO_2 and H_2O.

3 References

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