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Electrochemistry for the generation of renewable chemicals: electrochemical conversion of levulinic acid†

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The oxidative and reductive electrochemical conversion of levulinic acid to its primary products valeric acid, γ-valerolactone, 2,7-octanedione, 4-hydroxy-2-butanone and 3-buten-2-one is studied in detail. The reactions were performed in aqueous solutions and at ambient temperature, following the principles of green chemistry. The obtained primary reaction products were studied with respect to the oxidative and reductive electrochemical formation of secondary products, such as *n*-octane, 1-butanol and 1,3-butanediol. It is shown that the choice of electrolyte composition, educt concentration and the nature of the electrode material has a strong influence on the selectivity of product formation. For instance it is demonstrated that in alkaline solutions γ-valerolactone can be gained from levulinic acid at iron electrodes with similar Coulombic efficiency (~20%) but higher selectivity ($S = 70\%$) than on lead ($S = 50\%$). Furthermore, for the first time the electrochemical two-step reaction of levulinic acid to 1-butanol *via* 4-hydroxy-2-butanone is reported. For some of the reaction pathways the main product is water insoluble, which allows a direct separation of the product and the potential electrolyte reuse in a semi-continuous process. Especially the use of the electrocatalytic hydrogenation may provide a path for the storage of electricity into liquid organic fuels as shown by a basic energetic assessment of all electrochemical conversions.

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1. Introduction

Levulinic acid (LA), produced from lignocellulosic biomass, is considered to be an important precursor for renewable chemicals and liquid biofuels.[1–3] The synthesis of levulinic acid from saccharose was reported already in 1840 [4] and since then has been studied from different perspectives. Generally, LA can be produced in high yields from carbohydrates and from lignocelluloses by acid catalyzed hydrolysis.[5–15] The review by Rackemann and Doherty[16] outlines the chemistry of levulinic acid synthesis and discusses current and potential technologies for producing levulinic acid from lignocellulosics biomass. Its molecular structure, comprising two functional groups (a keto and a carboxyl group), makes levulinic acid an ideal platform chemical. Thus, the lab-scale synthesis of bio-chemicals, polymers, pharmaceuticals, flavor agents, solvents, antifreeze agents, biofuels, plasticisers, and herbicides from LA has been reported.[2,17–23] The respective syntheses are generally based on homogeneous and heterogeneous catalysis, whereas electrochemical conversions of LA are only rarely described. The electrochemical formation of γ-valerolactone (gVL) from LA was described by Tafel, when he studied the electrochemical reduction of levulinic acid in alkaline solution at a lead cathode.[24–26] Further examples are the oxidative formation of 5-acetyl-2,9-decanedione in a methanol/water solution[27] and recently the works of Xin *et al.* and Qiu *et al.* reporting on electrocatalytic processing of levulinic acid to produce biofuels.[25,28]

By means of an electrochemical hydrogenation coupled with a Kolbe reaction for the conversion of levulinic acid to *n*-octane, with valeric acid (VA) as intermediate product, we recently proposed the use of electrochemistry for the production of liquid biofuels (also denominated as "electrofuels"). The high selectivity (>95%) of the electrochemical hydrogenation of levulinic acid to valeric acid achieved in this study in batch-reactions was recently confirmed by Xin *et al.* for a flow cell process, yielding 90% valeric acid and 5% γ-valerolactone.[25]

In this work we investigate promising primary as well as secondary electrochemical conversion processes of levulinic acid, comprising oxidative as well as reductive pathways (Scheme 1). This study considerably expands the portfolio of chemicals that can be obtained from the electrochemical

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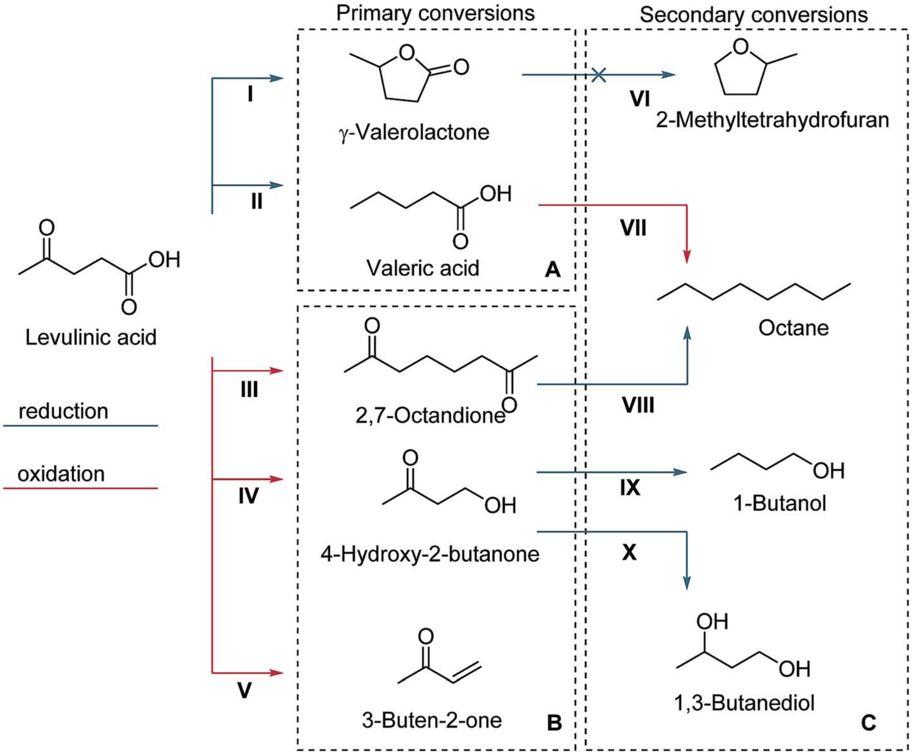


Scheme 1 Schematic illustration of the pathways for the primary and secondary electrochemical conversion of levulinic acid. (A) Electrochemical reduction of levulinic acid to: (I) γ-valerolactone or (II) valeric acid, (B) electrochemical oxidation from levulinic acid to: (III) 2,7-octanedione, (IV) 4-hydroxy-2-butanone or (V) 3-buten-2-one and (C) electrochemical conversion of the primary reaction products to: (VI) 2-methyltetrahydrofuran (electrochemical conversion was not reproducibly possible) (VII and VIII) *n*-octane, (IX) 1-butanol or (X) 1,3-butanediol.

conversion of LA,[29] as it introduces the electrochemical synthesis of not only valeric acid, and *n*-octane but also γ-valerolactone, 2,7-octanedione, 4-hydroxy-2-butanone and 3-buten-2-one (also known as methyl-vinyl-ketone) as well as *n*-octane, 1-butanol, 1,3-butanediol and methyl-tetrahydrofuran.

Scheme 1 summarizes the primary and secondary oxidation as well as reduction reactions investigated in this study. The derived products may either find direct application as fuels or solvents or may serve as intermediates for further processes – which are summarized in Table 1.

As Table 1 also shows, most of the conventional synthesis routes for the conversion of levulinic acid are high-temperature and high-pressure processes. Electrochemical synthesis may provide an alternative route, as the respective reactions can be carried out in aqueous solutions and at room temperature and thus fulfill major criteria of green chemistry.[30]

Additionally to the interesting product spectrum and its exploitation for (bio)chemical synthesis, the direct use of electric current for chemical conversions may even allow the storage of energy from renewable resources like wind power and photovoltaic in the form of chemical potential energy into compounds with higher energy density. For serving as a high energy density fuel molecule, oxygen functionalities have to be removed from LA, for which new processes are needed. For some of the conversions from LA to a (more reduced and thus higher energy dense) target molecule consecutive reactions, *i.e.* an oxidation followed by a reduction or *vice versa*, are necessary. Such a combined oxidation and reduction can, in principle, be achieved in one electrochemical cell.

As demonstrated in a principle energetic assessment of the described transformation routes, the electrochemical conversion of levulinic acid provides a promising platform.

With the results in the present manuscript, we aim to demonstrate that some well-known electrochemical reactions like the Kolbe and non-Kolbe reaction and the electrocatalytic hydrogenation, are well suitable for the conversion and generation of green platform chemicals.

2. Experimental section

2.1 Chemicals

All chemicals used in this study were of analytical grade. For qualitative and quantitative analysis, reference materials and solvents were used as purchased, without purification. 2,7-octanedione was produced by Kolbe-electrolysis and was purified by re-crystallization in heptane and its purity was confirmed by in-house NMR (^{1}H and ^{13}C) measurements.

2.2 Electrode materials

As anode or cathode material were used: graphite foil (chemPUR, Germany), polycrystalline graphite sheet (SGL Carbon GmbH, Germany), graphite felt (SGL Carbon GmbH, Germany),

Table 1 Relevance of the compounds potentially derived from levulinic acid *via* electrochemical conversion: applications and conventional production methods

Products	Applications	Production methods
Valeric acid (VA)	Intermediate to valeric fuels and additives	For example by catalytic hydrogenation of levulinic acid to valeric acid, typically performed in a two-step reaction at 150–350 °C, under hydrogen pressure of 10–40 bar and at platinum metal based catalysts[3,31,32]
γ-Valerolactone (gVL)	Intermediate for butene, valeric acid, and 5-nonanone production. gVL can be used as renewable solvent	Catalytic hydrogenation using different transition metal based catalysis at high temperature (70–265 °C), under hydrogen atmosphere (5–150 bar)[33–45]
2,7-Octanedione (2,7-OD)	The occurring 2,7-octanedione can be used in a intramolecular aldol reaction[46,47] or intramolecular pinacol coupling[48]	Usually achieved by complex catalytic routes, *e.g.*, based on Au catalyzed reactions of the di-acetylene at 120 °C,[49] Ir-complex-catalyzed addition of water to 1,7-octadiyne at 70 °C (ref. 50) or the Pd catalyzed Wacker oxidation of olefins at 80 °C under oxygen (6 atm) in DMA[51]
4-Hydroxy-2-butanone (4H2B)	4-Hydroxy-2-butanone is used as a platform chemical for further syntheses, like the dehydration to 3-buten-2-one[52] and the reduction to 1,3 butanediol[53] or to 1-butanol (electrochemical path shown below)	4-Hydroxy-2-butanone is industrially produced by the coupling of fossil source based propanone and formaldehyde in basic media.[54] The Wacker-type oxidation of 3-buten-1-ol,[55] selective catalytic dehydrogenation of 1,3-butanediol,[56–58] selective heterogeneous catalytic oxidation of 1,3-butanediol with H_2O_2 in CH_3CN,[59,60] and reduction of a dicarbony (1,3-butanone) at 130 °C over metallocene complexes[61] are examples for the complex formation of 4-hydroxy-2-butanone[62]
3-Buten-2-one (MVK)	Used in the production of gas-tight plastics, a intermediate in the production of pharmaceutical, fungicides,[63] vitamin A and vitamin E.[64] Important compound in Michael-additions, Robinson-annulations, Diels–Alder-reactions, Baylis–Hillman-reactions, radical additions heterocycle-synthesis; often found in natural material synthesis (polyketides, macrolactone, terpenes, pheromones and alkaloids)[63]	Technically, 3-buten-2-one is built from acetone with formaldehyde and diethylamine hydrochloride (Mannich-reaction) or by aldol-condensation of acetone and formaldehyde.[63] The catalytic oxidation of levulinic acid over CuO/CeO_2 and CuO/Al_2O_3 gives 2-buten-3-one in 15.5% yield at 175 °C (ref. 65) or 67.5% at 300 °C over CuO_2,[66] it is also patent-registered[67]
1,3-Butanediol (1,3-BDO)	Polyester plasticizers, humectants	
n-Octane	*n*-Octane is used as solvent, cleaning agent, fuel additive or as reaction agent like oxidation by cobalt[68] aromatization[69] is described also	Fractional distillation and refining of petroleum or the selective electrolytic reductive homocoupling of alkyl iodides at Ag–Pd cathodes in dipolar solvents[70]
Methyl-tetrahydrofuran (MTHF)	2-Methyltetrahydrofuran is mainly used as a higher boiling substitute for tetrahydrofuran as specialty solvent. 2-Methyltetrahydrofuran can also be used in the electrolyte formulation for secondary lithium electrodes and as a component of alternative fuels[71,72]	2-Methyltetrahydrofuran is produced by Ni-catalyzed hydrogenation of 2-methylfuran. This reaction can be performed in the liquid phase under H_2 pressures of 2 MPa or in the vapor phase at atmospheric pressure with common supported Ni catalysts[73]

lead sheet (99.999%, chemPUR, Germany), copper-sheet (99.999%, chemPUR, Germany), iron sheet (99.5%, chemPUR, Germany), nickel sheet (99.5% PHYWE Systeme GmbH & Co. KG, Germany), and platinum sheet (99.9%, chemPUR, Germany).

A pretreatment procedure was applied to remove contaminants from the electrode surfaces. The lead electrodes were rinsed in 25% HNO_3, treated with sand paper (grain size 8000) and washed with deionized water. Graphite felt electrodes were washed with deionized water and used directly. Platinum electrodes were pretreated by flame annealing and washed with deionized water. All the other electrodes were washed in HCl, treated with sand paper (grain size 8000) and washed with deionized water.

2.3 Electrochemical procedures

All electrochemical reactions were conducted under potentiostatic control using a potentiostat/galvanostat (AMEL 7050 (Amel srl, Milano, Italy) or a SP50 potentiostat (Bio-Logic SAS, Claix, France)). A three electrode configuration is used with E_{WE} standing for the potential applied at the working electrode and

E_{CE} for potential measured at the counter electrode *versus* reference electrode, for which Ag/AgCl sat. KCl electrodes (SE11, Sensortechnik Meinsberg, Germany, 0.195 V *vs.* standard hydrogen electrode (SHE)) were used throughout the study. All electrode potentials in this study are reported *versus* Ag/AgCl sat. KCl, but normalized to standard hydrogen electrode for energetic calculations.

As electrochemical cells for batch reaction one chamber undivided glass cells with 50 mL reaction volume and two-chamber H-type electrochemical glass cells with 40 mL anode and cathode chambers, separated *via* a cation exchange membrane (fumasep® FKE, Fumatech, Germany), were used, with a geometric electrode area varying from 5 to 24 cm^2. All reported current densities are normalized to the geometric surface area of the working electrode.

The electrochemical flow cells were a custom-made Plexiglas® cell with 21 mL reaction volume and 11 cm^2 anode and cathode area and a micro flow cell (Micro Flow Cell, ElectroCell, Denmark) with 10 mL volume and 10 cm^2 for anode and cathode. The cells were operated in single-pass or recirculation mode at flow rates between 0.36 and 10 mL min^{-1} (thus the hydraulic residence time varies from 6 to 3600 s).

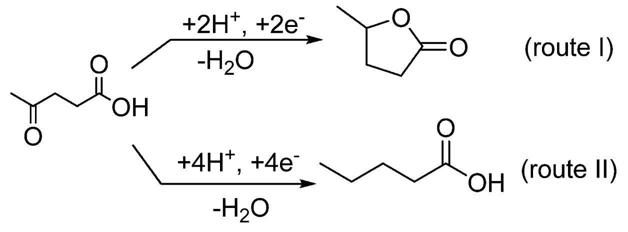
The duration of the electrolysis experiments varied according with initial concentration and achieved current. A detailed overview on all performed reactions is shown in the Tables SI 1 to SI 3 in the ESI.†

2.4 Analysis

Qualitative and quantitative analysis was carried out using gas chromatography-mass spectrometry (GC-MS) (Trace GC Ultra, DSQ II, Thermo Scientific, Germany) equipped with a TR-5MS (30 m × 0.25 mm ID × 0.25 μm film GC column Thermo Scientific, Germany) or TR-Wax MS (30 m × 0.25 mm ID × 0.25 mm film GC column, Thermo Scientific, Germany).

Quantitative analysis was further carried out by gas chromatography (GC) with flame ionization detection (FID) (Hewlett Packard Series II 5890, Hewlett Packard, USA) equipped with a DB-5 (30 m × 0.25 mm ID × 0.25 mm film GC Column from Agilent JW Scientific, USA).

External calibration curves with different concentration levels in a range from 0 to 600 ng μL^{-1} were used for quantification.



Scheme 2 Reaction pathways of the electrochemical reduction of levulinic acid to (I) γ-valerolactone and (II) valeric acid (part A of Scheme 1).

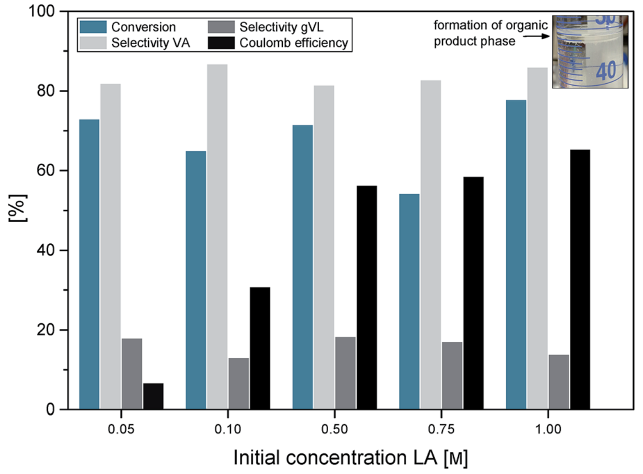


Fig. 1 Electrocatalytic hydrogenation of levulinic acid at Pb-electrode in a divided H-Cell at different initial concentration of levulinic acid after 4–8 hours electrolysis at a potential of −1.8 V. The formation of the organic product phase is shown in the inset picture. Details of all reactions can be found in Table SI 1† entry 1 to 17.

Routine substance quantification was obtained by high performance liquid chromatography (HPLC), by means of a refractive index (RI) detector (Spectra system P4000, Finnigan Surveyor RI Plus Detector, Fisher Scientific) equipped with a HyperREZ XP Carbohydrate H + 8 μm (S/N: 026/H/012-227) column. Sulfuric acid (0.005 N, flow rate 0.5 mL min^{-1}) served as the eluent. The column was operated at different temperatures depending on samples composition; the refractory index detector was operated at 40 °C.

Quantitative analysis was further realized with a HPLC-UV/VIS system (Hewlett Packard Series 1050, Hewlett Packard, United States of America) with a diode array detector (DAD) and equipped with a HyperREZ XP Carbohydrate H + 8 μm (S/N: 026/H/012-227). Phosphoric acid (0.05%, flow rate 0.5 mL min^{-1}) served as the eluent. The column was kept at room temperature. Educt and product concentrations were determined using calibration curves in a range from 0 to 0.2 M.

For details on raw data (SI 1 for primary and SI 2 for secondary reactions) as well as calculations of Coulombic efficiency (CE) and selectivity (*S*) (SI 3) see ESI.†

3. Results and discussion

3.1 Primary reductive reactions: reduction of levulinic acid to valeric acid and γ-valerolactone

Scheme 2 shows the electrochemical reduction pathways of LA. Selected conditions have already been investigated by several authors, *e.g.*, Xin *et al.*[25] In the present study, we systematically studied the impact of a variety of electrode materials, the electrolyte composition and the educt concentration on the LA reduction.

Fig. 1 summarizes the results of the levulinic acid reduction as a function of initial educt concentration. Changing the educt concentration does not affect the selectivity of the product formation: at a Pb electrode in 0.5 M H_2SO_4 electrolyte solution, and an applied working electrode potential of −1.8 V, valeric

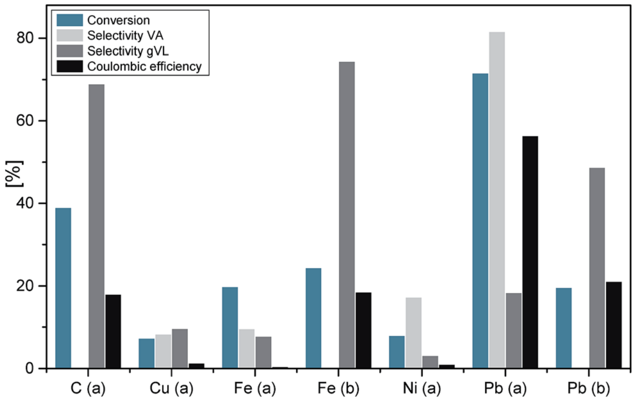
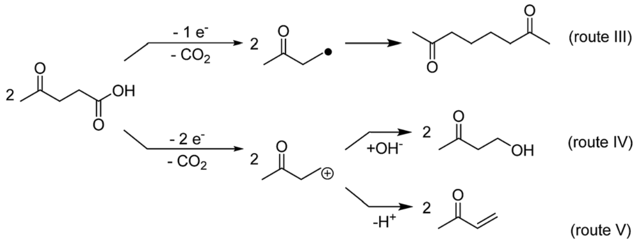


Fig. 2 Electrocatalytic hydrogenation of levulinic acid in a divided H-Cell as a function of the nature of electrode material and electrolyte: (a) 0.5 M H_2SO_4 and (b) 1 M NaOH. The data are based on 2–4 hours electrolysis at an electrode potential of −1.8 V; the initial LA concentration was 0.5 M.



Scheme 3 Reaction pathways of the electrochemical oxidation of levulinic acid.

acid is always the main product. The increase of the initial educt concentration has, as expected, a positive impact to the Coulombic efficiency (CE) (see ESI S3† for definition). At sufficiently high levulinic acid concentration the hydrogenation process is the dominating reaction; whereas at low educt concentrations hydrogen evolution *via* water electrolysis as the main side reaction prevails, leading to low Coulombic efficiency and LA hydrogenation rate. Consequently, when using a LA starting concentration of 0.5 M instead of 0.05 M, the average conversion rate increases from 3.3 mg cm^{-2} h^{-1} to 29.5 mg cm^{-2} h^{-1} and the achieved Coulombic efficiency increases from 6% to 60%. A LA concentration of 0.5 M represents an optimum value, since a further increase of the starting concentration does not lead to a further significant increase of conversion rate and CE.

Beside the Coulombic efficiency aspect, it is of special interest to achieve high product concentrations for the conversion of levulinic acid to valeric acid (Scheme 2 – route II), since spontaneous product separation can be achieved when the saturation concentration of valeric acid of 0.39 M is exceeded (see inset picture in Fig. 1).

Electrochemical conversions are heterogeneous processes, and as such, their mechanisms are decisively determined by the nature of the electrode material. Fig. 2 summarizes major parameters of the levulinic acid reduction as a function of the used electrode material and nature of electrolyte. In 0.5 M sulfuric acid, lead stands out clearly over the other electrodes in terms of educt conversion to valeric acid and Coulombic efficiency. This performance may be explained by the higher overpotential of the hydrogen evolution reaction at Pb-cathodes, since at Cu, Fe and Ni the water electrolysis commences already at an electrode potential of −1.0 V.

When switching the cathode material from lead to carbon in acidic electrolyte, the hydrogenation of levulinic acid leads almost exclusively to the formation of γ-valerolactone (gVL). A conversion of 40% was obtained, which represents a ten-fold improvement as compared to the previous work by Xin *et al.*[25] The selectivity of the gVL formation is 68%. Whereas gVL is formed in sulfuric acid solutions at Cu and Ni electrodes, no formation of valeric acid was observed in alkaline solution at this electrode materials. In alkaline solution gVL is the major product only when Pb and Fe electrodes are used. For the electrochemical conversion of LA to gVL at Pb electrodes a Coulombic efficiency of 21% can be achieved, whereas the use of Fe cathodes results in a slightly lower Coulombic efficiency (18%), but a higher selectivity. For this reason, and especially with regard to the sustainability of the process, Fe and C are very promising alternatives as electrode material for further investigations. It is very likely, that the Coulombic efficiency can be enhanced when using higher initial educt concentrations or when operating in a continuous system.

In summary, VA and gVL can both be obtained from LA with good selectivity and acceptable Coulombic efficiency.

3.2 Primary oxidative reactions: oxidation of levulinic acid to 2,7-octanedione, 4-hydroxy-2-butanone and 3-buten-2-one

Whereas the reductive conversion of levulinic acid may potentially be directly used for energy storage processes (see also 3.4.), the oxidation of levulinic acid is of primary interest for chemical production. Levulinic acid can be oxidized either to a keto-alkyl radical (one electron oxidation) or to a carbenium ion (two-electron oxidation) (see Scheme 3). Thereby the Kolbe product[74–77] of LA, the dimer 2,7-octanedione, yields from the radical and its subsequent dimerization (route III).[29] The carbenium ion, product of the two-electron oxidation, on the other hand, may react further either with nucleophiles like hydroxide ions (non-Kolbe-reaction or Hofer–Moest-reaction[78–80]), yielding 4-hydroxy-2-butanone (route IV), or may undergo an elimination of H^+, forming 3-buten-2-one (route V).[81]

One-electron oxidation: formation of 2,7-octanedione (route III). In accordance with our previous study,[29] 2,7-octanedione can be gained with good selectivity and a good Coulombic efficiency at platinum electrodes in methanol solution. In the present work we show that water can also be used as an alternative solvent. A major disadvantage, however, is a decrease of the selectivity and a significant impact on the Coulombic efficiency – decreasing from 86% in methanol to 5% in aqueous solution (see ESI, Table SI 1,† entry 13 and 14). This was not unexpected, since in aqueous solution the current density was higher, promoting a stronger solvent decomposition. An increase of the initial levulinic acid concentration could not compensate this effect. Furthermore, aqueous solutions stabilize ionic species like the two-electron oxidation product carbenium ion, which leads to the formation of multiple side products. The formation of side products explains the lower selectivity (27%) in comparison to methanol (60%) even at higher conversion of levulinic acid (74%).

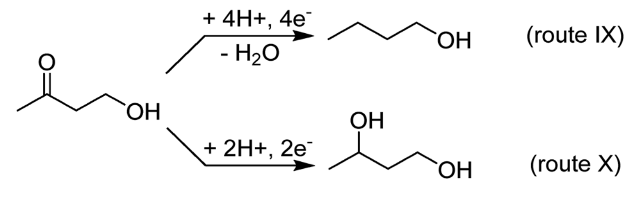
Two-electron oxidation: formation of 4-hydroxy-2-butanone (route IV) and formation 3-buten-2-one (route V). The formation of the carbenium ion by the two-electron oxidation of LA can be generally enhanced by the use of a graphite anode instead of platinum, as at Pt radical adsorption promotes dimerization.[74] The reactions were first conducted in a batch reactor in an aqueous 0.2 M NaOH electrolyte solution using a carbon sheet anode. In alkaline solution carbenium ions are captured by hydroxide ions, leading to the formation of 4-hydroxy-2-butanone (route IV). At an electrode potential of 6 V a selectivity of 20% and a Coulombic efficiency of 5% was obtained. Noteworthy, to our knowledge it is the first time that the direct production of this compound from levulinic acid is presented. In addition to this non-Kolbe product only minor amounts of side products including the Kolbe product (2,7-octanedione) and 2-butanone were identified. When the above reaction is performed in alcoholic solution,[82,83] alkoxide ions serve as nucleophile; thus the reaction product is the respective ether. We have confirmed the formation of 4-methoxy-2-butanone and 4-ethoxy-2-butanone in methanol or ethanol electrolyte solution (data not shown).

Interestingly, when performing the reaction in a membrane-separated flow cell, the major oxidation product is 3-buten-2-one (Scheme 3, route V). This finding (see Fig. S1†) can so far not be explained and has to be studied further.

3.3 Secondary electrochemical conversion steps

The products of the primary LA conversions can be used as educts for secondary electrochemical conversion steps (see Scheme 1 – secondary conversions). Some of these reactions, as the production of *n*-octane by the reduction of 2,7-octanedione and the Kolbe-coupling of valeric acid have been already reported.[29] The following section presents further details of the Kolbe and the non-Kolbe reaction of valeric acid. Further, the hydrogenation of γ-valerolactone (Scheme 1, route VI) is very appealing, but unfortunately could not be experimentally proven.

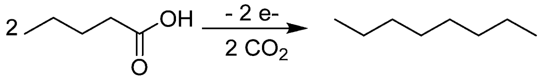
Electrochemical hydrogenation of 4-hydroxy-2-butanone (route IX and X). The electrocatalytic hydrogenation of 4-hydroxy-2-butanone (4H2B) was performed at Pb electrodes in aqueous 0.5 M sulfuric acid electrolyte solution. After 3.5 h of electrolysis, 85% conversion of 4-hydroxy-2-butanone was achieved and 1-butanol was gained with 84% selectivity. At 100% conversion 1-butanol is gained with 75% yield and with a Coulombic efficiency of 29%. 1,3-butanediol was found as the only side product. For the use of other electrode materials both conversion rate and Coulombic efficiency were lower (comparable to the results found for the hydrogenation of levulinic acid) and 1,3-butanediol was produced only with low selectivity (not higher than 10%).



Scheme 4 Reaction pathways for the electrochemical hydrogenation of 4-hydroxy-2-butanone.

Similar as for the hydrogenation of levulinic acid, the Coulombic efficiency of the 4H2B hydrogenation can be significantly improved by higher initial educt concentration. Thus, the Coulombic efficiency of 1-butanol formation increased from 13% for a 0.08 M solution to 52% using a 0.5 M 4-hydroxy-2-butanone solution.

In order to achieve a higher selectivity of 1,3-butanediol formation, the hydrogenation of 4H2B was studied using different electrolytes and different electrode materials. Here, the use of phosphate buffer solution (0.5 M, pH 7) and iron electrodes yielded the highest 1,3-butanediol selectivity of 34% (see ESI, Table SI 2,† entry 1 to 7) (Scheme 4).

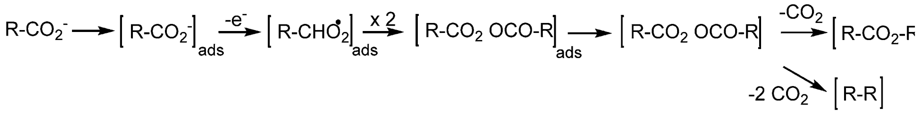


Scheme 5 Reaction pathway for the electrochemical oxidation of VA to *n*-octane.

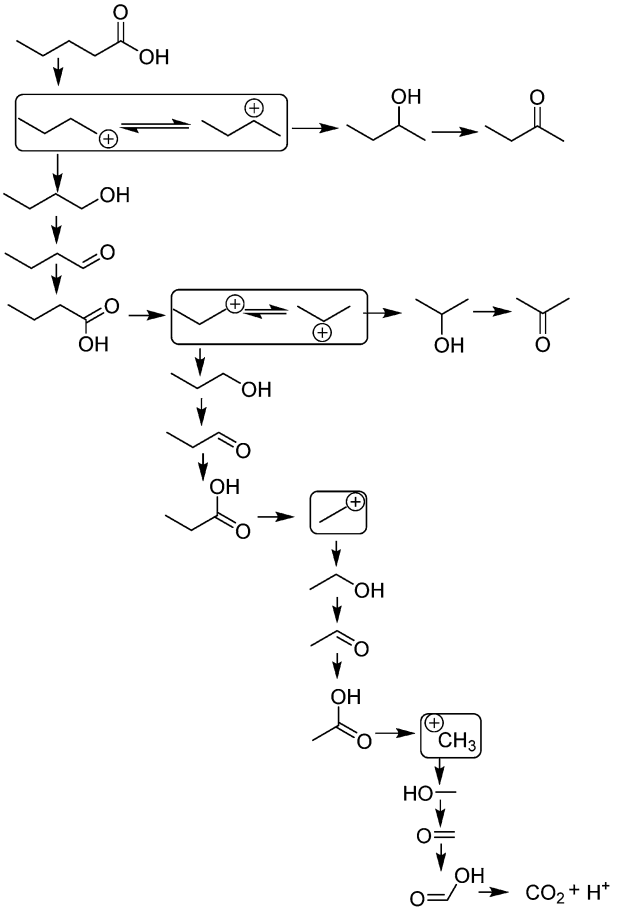
Oxidation of valeric acid to *n*-octane (route VII). The Kolbe electrolysis of valeric acid to *n*-octane was already presented in our previous work,[29] where the production of *n*-octane by the one-electron oxidation of valeric acid was performed in an undivided cell, at a Pt anode and in aqueous as well as methanolic solutions.

As known from literature, the Kolbe reaction proceeds preferably at high current density and high educt concentration – both factors promoting the formation of high keto alkyl radical concentrations at the electrode surface and thus to the production of the dimer – in this case *n*-octane (Scheme 5). Additional to *n*-octane, this organic phase contains the side products butyl-valerate and 1-butanol.[29] Wadhawan *et al.* proposed a possible mechanism for the production of esters during the Kolbe electrolysis in aqueous solution (Scheme 6).[84] Scheme 6 illustrates that butyl-valerate is formed, when only one CO_2 is cleaved, whereas the formation of *n*-octane requires the complete elimination of both CO_2.

The side product 1-butanol is generated *via* a Hofer–Moest reaction by a two electron oxidation of valeric acid and the formation of a carbenium ion that reacts with a hydroxide ion to form 1-butanol. The side product formation is dependent on the starting concentration of valeric acid and on the reactor configuration. In order to suppress this kind of side-reactions, experiments in a flow reactor were performed. Compared with our previous results for batch reactors, the Coulombic efficiency could not be improved with this setup, but even for a non-optimized system a CE of 50% was reached. A further improvement can be achieved, when using a flow reactor, as the



Scheme 6 Potential mechanism for the formation of *n*-octane and butyl-valerate during Kolbe electrolysis (derived from Wadhawan[84]).



Scheme 7 Anodic degradation of valeric acid at graphite electrodes.

selectivity of *n*-octane formation increases from 51 to 81%. The higher selectivity may result particularly from the lower residence time, which was for batch systems at least 4 hours, whereas a residence time not longer than 5 minutes, preventing further reactions, was realized in flow-through reactors.

Two-electron oxidation and the non-Kolbe-reaction of valeric acid. Within this investigation a non-Kolbe reaction based decomposition of valeric acid (Scheme 7) was studied and the difficulty to control the product formation is demonstrated.

When the electrochemical conversion of short chain fatty acids, like valeric acid, is performed at carbon instead of platinum electrodes, the reaction leads to the formation of carbenium cations *via* a two-electron oxidation. These cations can then be attacked by a respective nucleophile (in water the hydroxide ion). Thus, the electrolysis of valeric acid at a carbon anode in aqueous environment (0.5 M H_2SO_4, see ESI, Table SI 3, entry 2) leads to the formation of alcohols. Depending on the location of the positive charge at the carbenium ion the hydroxide ion can attack either at position 1 (to form 1-butanol) or at position 2 (to form 2-butanol). At the applied positive anode potential a further oxidation of these products takes place: 1-butanol is oxidized to butanal, 2-butanol is oxidized to 2-butanone. Whereas ketones are inert to further oxidation, the aldehyde can be oxidized to carboxylic acids – which again can be decarboxylated in a further oxidation cycle. Thus – as illustrated in Scheme 7 – a successive shortening of the carbon chain occurs, leading to carbon dioxide as the final product.

In order to control the reaction and to prevent the successive decomposition, a charge transfer from a primary to secondary carbenium ion is necessary. The secondary carbenium ions will react with hydroxide ion to a secondary alcohol and thus no further oxidation than to the ketone is possible. Such control of the reaction did not succeed in full extent and the use of large electrolyte ions, such as ClO_4^- and HCO_3^{2-}, as described in literature[79] did not lead to the desired success. This cannot be fully explained, but the effect was mainly described for Pt-electrodes, where anion can adsorb thus prevent dimerization. In our study, we used graphite, at which anion adsorption may not, or only to a minor extent, take place.

As depicted in Fig. 3, the proposed in Scheme 7 degradation can be experimentally confirmed. Depending on the reaction time (and thus the degree of valeric acid conversion), the major reaction products and intermediates could be found.

The experiment also confirms the accumulation of 2-butanone – the product of the secondary carbenium ion. Interestingly, no acetone was detected throughout the experiments,

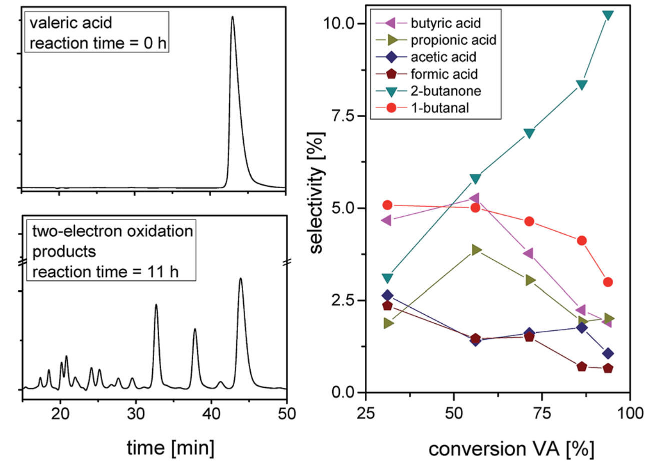


Fig. 3 HPLC – chromatograms and the quantitative product analysis of a valeric acid (50 mM) non-Kolbe electrolysis (performed at a graphite electrode in 50 mM NaOH solution, at a potential of 2.5 V and a current density of 2.5 mA cm^{-2}).

Table 2 Estimation of the energy storage efficiency based on heating values and the molar electric energy for reduction conversions and combination of the two-step reactions (details to reaction pathways at Scheme 1 and detailed data for oxidation reactions at Table SI 5)

Route			Energy density[a] (H_{LHV})/kJ mol^{-1}		Δ Molar heating values/kJ mol^{-1}	Achieved[b]					Theoretical maximum			
			Educt	Product		z[c]	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 efficiency/%
Reduction	I	Levulinic acid → γ-valerolactone	2420	2650	230	2	−1.5	20	1447	16	−1.3	100	251	92
	II	Levulinic acid → valeric acid	2420	2840	420	4	−1.5	60	965	44	−1.3	100	502	84
	VI	γ-Valerolactone → 2-methyl-THF	2751	2863	112	4	—	—	—	—	−1.3	100	502	22
	VIII	2,7-Octanedione → *n*-octane	4323	5047	724	8	−1.5	10	10 526	7	−1.3	100	1003	72
	IX	4-Hydroxy-2-Butanone → 1-butanol	2083	2446	363	4	−1.3	58	865	42	−1.3	100	502	72
	X	4-Hydroxy-2-butanone → 1,3-butanediol	2083	2273	190	2	−1.3	2	12 543	2	−1.3	100	251	76
Two steps	I + VI	Levulinic acid → 2-methyl-THF	2420	2863	443		—	—	—	—		100	753	59
	II + VII	Levulinic acid → *n*-octane	2420	5047	207				1795	11.53		100	743	28
	III + VIII	Levulinic acid → *n*-octane	2420	5047	391				11 071	3.53		100	1245	31
	IV + IX	Levulinic acid → 1-butanol	2420	2446	26				11 285	0.23		100	984	3
	IV + X	Levulinic acid → 1,3-butanediol	2420	2273	−147				22 963	−0.64		100	733	−20

[a] Estimated according to Boie.[86] [b] Achieved in this study. [c] Number of electrons.

which indicates that the primary propyl carbocation very quickly reacts to the primary alcohol, before the secondary carbenium ion is formed. The addition of other electrolyte species, however, did not have any significant impact on the course of the reaction (see Table SI 3†).

3.4 Energetic considerations for electrochemical levulinic acid conversions

Alternatively to their exploitation as platform chemicals (see Table 1) the electrochemical conversions of LA can be used for the storage of electric energy. The derived products may serve as alternative "green" fuels for combustion engines.[85] To be exploited as an alternative fuel two key properties of a chemical have to be considered: (i) its ignition properties and (ii) its calorific value. Both properties are strongly influenced by the oxygen content of a substance. Dependent on the nature of the functional group, oxygen can be removed either reductively (*via* electrocatalytic hydration), or oxidatively (*e.g.*, *via* Kolbe reaction). Certainly, a reduction reaction may represent a direct way to store electric energy into a chemical compound, whereas a (partial) oxidation lowers the absolute energy content with respect to the educt/starting material. Yet, the electrochemical oxidation reaction of levulinic acid (and its primary products) not only allows removing functional groups like carboxylic groups from a given educt (thus improving its ignition properties), but it also allows increasing the mass related energy density of the product by removing the oxygen containing functional groups. For instance the energy density of levulinic acid – a compound that is not suitable to be used in combustion engines due to the carboxylic group – of $H_{\mathrm{LHV}} = 20.8$ MJ kg^{-1} can be increased to that of 1-butanol ($H_{\mathrm{LHV}} = 36$ MJ kg^{-1}) and of *n*-octane ($H_{\mathrm{LHV}} = 44.4$ MJ kg^{-1}) by electrochemical oxidation (see Table SI 4†). (For the determination of the respective lower heating value, H_{LHV}, the method according to Boie[86] was used (see SI 3† for details)).

In order to assess the energy efficiency of the reactions shown in Scheme 1, a calculation of the "energy storage efficiency", *i.e.* the difference of the lower heating values of educt and product divided by the energy needed for the electrochemical reaction, for the different compounds and the input energy for the reaction is present in Table 2. Thereby the theoretical and experimentally required electric energy to drive the reaction(s) was compared to the increase in terms of energy density of the product molecules (see ESI S3† for details of definitions and all calculations.). Since in our study all reactions were performed in half-cell experiments, the energy calculation was based on the respective half-reaction, considering the needed average working electrode potential (*vs.* standard hydrogen electrode, SHE). The average working electrode potential for the reduction reactions was −1.8 or −1.5 V (*vs.* Ag/AgCl, corresponding respectively to a potential of −1.5 and −1.3 V *vs.* standard hydrogen electrode, SHE). For the oxidation reactions the applied working electrode potential varied from 2 to 10 V (*vs.* Ag/AgCl, corresponding respectively to a potential of 2.2 and 10.2 V *vs.* standard hydrogen electrode, SHE), please note that the higher oxidation potentials were only applied for systems using organic solvents.

Table 2 shows the maximum and so far achieved energy storage efficiencies. Regarding the one step reactions, only the reductions provide the possibility for energy storage (the values for the oxidations are shown in Table SI 5†). Most of the reduction reactions exhibit a potential for energy storage efficiency higher than 70%. Here, for the theoretically most favourable reduction of levulinic acid into γ-valerolactone, (with a maximum energy storage efficiency of 92%), only 16% are achieved in our experiments. However, clearly closer matches of the theoretical and achieved energy storage capacity are shown, *e.g.* for route II and route IX. For the two-step reactions the theoretical maximum values are lower and the achieved energy storage efficiencies are maximum *ca.* 10% (route II combined with route VII). These calculations show that electrochemical conversions, here of levulinic acid and its primary products, can provide an interesting and potentially energetically and thus economically competitive alternative not only for chemical production, but also for fuel generation and energy storage.

4. Conclusions

We have reported the electrochemical transformation of levulinic acid to its primary products valeric acid, γ-valerolactone, 2,7-octanedione, 4-hydroxy-2-butanol and 3-buten-2-one. In a secondary step, the obtained products were subjected to further electrochemical oxidations and reductions. The presented electrochemical approach represents an energetical and thus potentially economical alternative to the conventional catalytic processes. Thereby, the selectivity for the reaction products can be tailored by electrolyte composition, electrode material and current density. The use of aqueous electrolyte solutions, ambient pressure and room temperature allows obeying the rules of green chemistry. Therefore, the results demonstrate that renewable electricity could be used for the sustainable synthesis of a variety of renewable chemicals from levulinic acid and for the storage of electric energy in the form of organic compounds, partially being already suitable as drop-in biofuels.

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