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DOI

[10.1002/celec.201900734](https://doi.org/10.1002/celec.201900734)

Publication date

2019

Document Version

Final published version

Published in

ChemElectroChem

Citation (APA)

Bisselink, R. J. M., Crockatt, M., Zijlstra, M., Bakker, I. J., Goetheer, E., Slaghek, T. M., & van Es, D. S. (2019). Identification of More Benign Cathode Materials for the Electrochemical Reduction of Levulinic Acid to Valeric Acid. *ChemElectroChem*, 6(13), 3285-3290. <https://doi.org/10.1002/celec.201900734>

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Identification of More Benign Cathode Materials for the Electrochemical Reduction of Levulinic Acid to Valeric Acid

Roel J. M. Bisselink,^{*[a]} Marc Crockatt,^[b] Martin Zijlstra,^[a] Ivan J. Bakker,^[b] Earl Goetheer,^[b, c] Ted M. Slaghek,^[a] and Daan S. van Es^[a]

The electrochemical production of valeric acid from the renewable bio-based feedstock levulinic acid has the potential to replace the oxo-process, which uses fossil-based feedstock 1-butylene. The electrochemical reduction of the ketone functionality in levulinic acid using lead or mercury cathodes has already been known for over 100 years. However, large-scale electrochemical production of valeric acid might be limited, owing to the toxicity of these materials. In this study, we identified three additional cathode materials, cadmium, indium,

and zinc, which selectively and efficiently produce valeric acid. Of these materials, indium and zinc are considered more benign. More specifically, at indium there is no formation of the side product γ -valerolactone, thus resulting in the highest selectivity towards valeric acid. For the electrochemical reduction, a reaction mechanism involving the formation of an organometallic compound is proposed. Furthermore, a possible processing strategy is outlined to enable the continuous electrochemical production of valeric acid on a large scale.

1. Introduction

The depletion of fossil resources and related climate change due to its usage drives the transition of a fossil-based economy to a bio-based economy for the production of chemicals and fuels^[1] on one side and a new world energy economy, based on renewable energy production using wind, solar, biomass and hydropower on the other side.^[2] Organic electrosynthesis is a method which utilizes inherently pollutant-free electrons for chemical reactions and is in line with the principles of green chemistry.^[3] Whilst more commonly used for the synthesis of complex molecules, such as natural product synthesis and pharmaceuticals, it finds increasingly more applications in converting biomass and biomass derived chemicals to biofuels, solvents and monomers amongst others.^[4] The field of organic electrosynthesis started in 1849 by Hermann Kolbe^[5] and many organic products were synthesized electrochemically in the early 20th century, however, the growth of the petrochemical industry sharply curtailed electrochemical industrialization.^[6]

Levulinic acid (LA) is an interesting bio-based difunctional short chain fatty acid. LA (or the ester thereof) is a major by-product formed during the conversion of D-fructose (or D-glucose) to 5-hydroxymethylfurfural (HMF), an important

emerging bio-based platform chemical (see Scheme 1).^[7a-d] LA can also be prepared intentionally from mono- or polysaccharides.^[7b,e-f] Because of its ease of preparation and the presence of 2 functional groups (carboxylic acid and ketone group), LA has been the subject of many investigations directed at developing new compounds with novel applications.^[7b,d-f,g] While several initiatives for industrial production and valorization of LA are slowly emerging, there is still a significant interest in viable industrial products and processes based on LA.

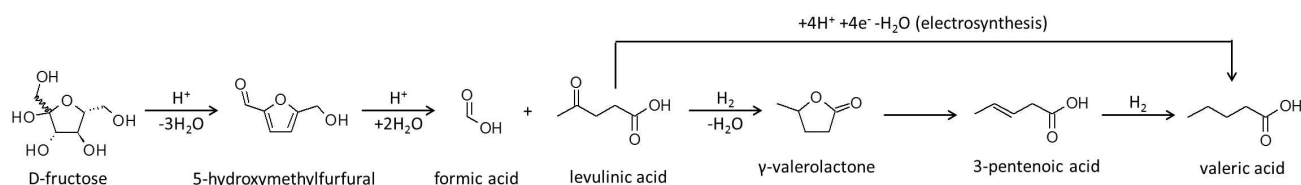
The rediscovery of the electrochemical reduction of LA to valeric acid (VA) is part of the recent renaissance of organic electrochemistry as it was already discovered in 1911 by Tafel and Emmert^[8a] and used in 1955 for the synthesis of 2-octanone.^[8b] This electro-organic reaction was revisited in 1983 by Chum and co-workers^[8c,d] and more recently by other research groups.^[8e-i] Advantages of the electro-organic approach are the ambient reaction conditions and one-step approach. In contrast, the chemo-catalytic approach involves hydrogenation and dehydration of LA to γ -valerolactone (gVL), followed by acid-catalyzed ring-opening to 3-pentenoic acid and hydrogenation to VA. This multiple step reaction of LA to VA is typically performed at high temperatures, high pressures, uses catalysts based on precious metals such as Pt, Ru and Pd or on metal embedded zeolites and can also be performed in a one-pot approach.^[9] However, the catalyst suffers from deactivation due to leaching or coke-formation.^[9c,d] VA is produced industrially via hydroformylation (oxo-process) of fossil-based 1-butylene and subsequent oxidation of valeraldehyde.^[10] VA is mainly used as intermediate in the production of lubricants. Other applications of VA are intermediates including the production of flavors and fragrances, animal feed and pharmaceuticals amongst others. Furthermore, new applications include the usage of VA in biofuels.^[9a-c] The high selectivity for the electrosynthesis of VA is attributed to the high (over) potential of lead (Pb).^[8f-h] It is also known that the reduction of

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Supporting information for this article is available on the WWW under <https://doi.org/10.1002/celc.201900734>



Scheme 1. Conversion of D-fructose to LA via HMF and subsequent production of VA via gVL (chemo-catalytic) or directly using electro-synthesis.

the carbonyl (C=O) functionality can yield a methylene (CH₂), olefin, pinacol, alcohol or organometallic functionality, which depends on the substrate, solvent, nature of the electrode material, potential and pH.^[9] Materials such as Hg, Pb, Cd, Sn, Zn, Al and Cu can be used to reduce the ketone or aldehyde to a methylene group in acid,^[9d] this led us to hypothesize their potential usage for the reduction of LA to VA. The possible applicability of other non-precious, and in most cases less toxic, metals stimulated us to explore the performance of various materials. Herein, we demonstrate the use of more environmentally benign cathode materials to produce VA from the renewable bio-based feedstock LA. The possible mechanism involved is discussed and we show that the promising cathode materials are quite stable. In addition, a possible processing strategy for VA on a larger scale is suggested.

2. Results and Discussion

Xin *et al.* and Dos Santos *et al.* previously showed that electrochemical reduction of LA using C, Cu, Fe or Ni cathodes gave low LA conversions and low selectivity towards VA compared to Pb.^[8f,h] In our study we focused on assessing various other materials known to yield the methylene group or with a similar overpotential. The conditions of the work of Chum *et al.*,^[8c,d] i.e. 150 mA/cm² at 50 °C, were applied, which is in line with the goal of at least 100 mA/cm² for an industrial electrochemical process.^[12] At 97% conversion the current efficiency (CE) was approx. 51%.^[8f] It was therefore decided to supply twice the theoretical amount of charge to enable full conversion. The obtained results of LA electrolysis with various cathode materials are shown in Table 1.

The selectivity towards VA at Pb is similar to those reported in other studies,^[8] although in our case a near to complete conversion (i.e. 99%) was achieved, which is 2% higher than reported up till now.^[8f] However, achieving complete conversion is difficult in a divided cell as 78% of the remaining LA is present in the anolyte due to diffusion of LA through the Nafion membrane. Almost complete conversion of LA was also achieved with Cd closely followed by In, then by Zn and to a lesser extent by Al and Ni. Metals at which lower LA conversions were obtained are accompanied with initially more intensive evolution of hydrogen gas. Especially the identification of In and Zn as cathode material is very promising as these are considered less toxic than Pb, Cd and Hg and in the case of In, higher selectivity towards VA and no formation of gVL. Moreover, the use of In has, to the best of our knowledge, not been

Table 1. Electrochemical reduction of LA at various cathodes in a divided cell configuration, 150 mL 1 M H₂SO₄ + 0.5 M substrate as catholyte, Nafion 117 separator, 150 mL 1 M H₂SO₄ as anolyte, IrO_x anode, temperature 50 °C and 8 F/mol.

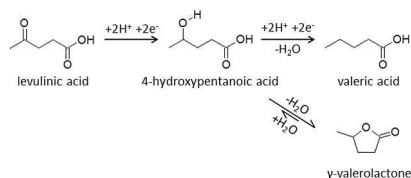
Cathode	Substrate	Conversion ^[a] [%]	Selectivity ^[a] [%]		Current efficiency ^[b] [%]
			VA	gVL	
Pb	LA	98.6 ± 0.1	94.0 ± 2.5	2.5 ± 0.4	46.1 ± 0.6
Cd	LA	98.0 ± 0.5	91.9 ± 4.1	3.0 ± 1.1	44.8 ± 0.1
In	LA	88.4 ± 1.8	99.1 ± 0.6	0.0 ± 0.0	43.6 ± 2.3
Zn	LA	65.1 ± 12.8	95.5 ± 0.2	2.1 ± 0.5	30.8 ± 5.0
Al	LA	14	74	21	5.6
Ni	LA	7.3	71	22	2.7
Ga	LA	0	–	–	0
Ag	LA	0	–	–	0
Ti ^[c]	LA	0	–	–	0
Sn	LA	0	–	–	0
Pb	gVL	1	0	–	0
Ni	gVL	0	–	–	0

[a] Conversion and selectivity are based on HPLC analysis. [b] Related to VA and based on HPLC analysis. [c] 4 F/mol charge supplied.

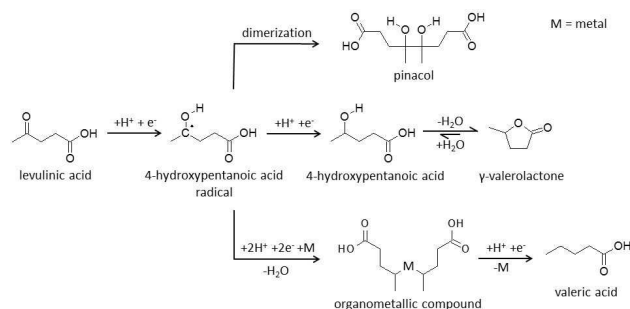
reported for this type of reaction. The total selectivity towards VA and gVL being below 100% is attributed to experimental errors as no indications of other by-products, such as the pinacol product, were found by HPLC and ¹H NMR analysis.

The near to full conversion of LA resulted in a CE close to the theoretic maximum of 50% at 8 F/mol for Pb, Cd and In, which is similar as obtained with Pb at conversions above 90%.^[8f,g] The electrode potential, however, shows a rapid decrease at ~2.7 F/mol (~95 min.) for Pb and Cd (see Supporting Information, Figure S1). This shift in potential is attributed to the depletion of LA resulting in the formation of H₂ at a lower potential. This indicates that the high current efficiency of ~90% obtained at 30% conversion^[8c,d] can be expanded to 61% conversion (~2.7 F/mol @ 90% CE) and is possibly related to the positive influence of an increased temperature for this type of electrochemical reduction reaction.^[11e,g] The electrode materials made of Ga, Ag, Sn and Ti, having a similar overpotential to Zn,^[13] are unable to reduce LA. 2-pentanone, which lacks the carboxylic acid functional group compared to levulinic acid, follows a different order of cathode reactivity towards the methylene group: (Cd > Zn > Pb > Hg > Sn ≈ Fe > Al > Ni > Cu).^[11c] Acetone, being a smaller ketone compared to 2-pentanone, follows again a different order.^[11h] In addition, the potential during electrolysis had the following order: Al < Ga < Pb ≈ Cd < In < Zn < Ti < Sn < Ag < Ni (see also Supporting Information, Figure S1). These findings indicate that LA reduction is not solely controlled by the electrode potential, but also by the nature of the cathode material and substrate. The nature of the

cathode material influences the product distribution,^[11h] and resulted in our case to increased selectivity towards gVL at Ni and Al. Toshiro *et al.* obtained an even higher selectivity towards gVL during electrocatalytic hydrogenation (ECH) of LA under alkaline conditions at Raney Nickel.^[14] ECH under acidic conditions was also proposed as mechanism for gVL and VA formation,^[8f-i] which differs from the reduction mechanism of a carbonyl to a methylene group.^[11b,h,k] The carbonyl reduction mechanism does not involve chemisorbed hydrogen and is probably similar to the Clemmensen reduction.^[15] The ECH mechanism of LA (Scheme 1) involves the two-electron reduction to 4-hydroxypentanoic acid (4-HPA), which readily lactonizes to gVL or is reduced further to VA. The simplified adaptation of the carbonyl reduction mechanism for LA (Scheme 2) involves protonation of LA, followed by the one-electron reduction to the 4-hydroxypentanoic acid radical, from which it can form 1) the pinacol by dimerization; 2) gVL via a subsequent one-electron reduction to 4-HPA; 3) an organometallic compound which can hydrolyze to form 4) VA. Possible formation of an olefinic compound, viz. pentenoic acid, is not taken into account, however possible with the hydrolysis of an organometallic compound.^[11h] The lactonization of 4-HPA is an equilibrium reaction of which approx. 3% is present as 4-HPA in 1 M H₂SO₄.^[16] According to the ECH mechanism conversion of gVL to VA should be feasible, which is not the case for the carbonyl reduction mechanism. We therefore electrolyzed gVL in our system to assess the (partial) involvement of ECH. Ni was used as being a well-known ECH catalyst and Pb because of the suggested involvement of ECH. The obtained results of gVL electrolysis at Pb and Ni are shown in Table 1 and clearly show that there was virtually no gVL conversion and moreover VA was not detected. The involvement of ECH for the electrosynthesis of VA from 4-HPO is therefore unlikely and the carbonyl reduction mechanism outlined in Scheme 3 more plausible. For



Scheme 2. Electrocatalytic hydrogenation of LA to gVL and VA.^[8f]



Scheme 3. Adapted reduction mechanism for LA to VA, gVL and pinacol based on the generic carbonyl reduction mechanism.^[11h,k]

Table 2. Dissolved metals after electrolysis of 0.5 M LA.

Cathode	Catholyte [mg/L]	Anolyte [mg/L]	%M dissolved [%]	Ratio VA:M [mol/mol]
Pb	27.8 (9.2) ^[a]	0.3	0.07	3.4 · 10 ³
Cd	18.7	0.1	0.06	2.7 · 10 ³
In	107	0.4	0.40	4.8 · 10 ²
Zn	61.1	< 1.3	0.23	2.9 · 10 ²
Al	1924	22.5	20	0.77
Ni	6.5	< 0.1	0.02	2.4 · 10 ²
Ga	96.0	1.8	0.04	–
Ag	0.12	< 0.1	0.00	–
Ti ^[a]	0.14	< 0.1	0.00	–
Sn	2.1 ^[b]	0.5	0.01	–

[a] Total Pb concentration incl. precipitates, between brackets Pb as precipitate. [b] Some precipitates noticed in solution and not taken into account.

the formation of gVL however, ECH might still be involved. The validity of the carbonyl reduction mechanism is also supported by findings of Tafel and Emmert, who reported the formation of an organomercury compound^[8a] and Chum, who reports the formation of a dimeric compound from LA ester.^[8c] The mechanism involves hydrolysis of an organometallic compound to yield VA, however, dissolution of (un)stable organometallic compounds or metal ions is possible,^[11h] which can have a detrimental effect on the cathode stability. Catholyte and anolyte obtained after electrolysis were therefore analyzed on metal content, which are shown in Table 2 together with the derived molar ratio between formed VA and dissolved metal (ratio VA:M). A relatively low amount of metals was obtained in the electrolytes, except for Al of which a large amount was dissolved. Corrosion of the cathode, resulting in dissolution of metals prior and after electrolysis is possible,^[4i] together with the elevated temperature of 50 °C this might result to somewhat higher Pb concentrations in the catholyte than reported elsewhere, although a similar amount of Pb being dissolved from the cathode, i.e. 0.1%.^[4f,j] Of the materials at which LA is not converted, corrosion of Ga and Sn is more pronounced than Ag and Ti, which is expected based on their Pourbaix diagrams.^[17] Therefore, the contribution of organometallic compounds to the dissolution of metals of the other cathode materials is unknown. Nevertheless, dissolution of organometallic compounds appear limited, except for Al, as indicated by the high ratio VA:M in Table 2. Interestingly, trials with leaded bronze (an alloy of Pb, Cu and Sn) exhibited visible cathodic corrosion (see Supporting information, Figure S2). The obtained high LA conversion and VA selectivity and limited metal dissolution outlines a positive prospect for the development of an industrial electrochemical process. This prospect can be strengthened by a facile isolation procedure to recover the pure product.^[12] Only product isolation involving extraction using ether and distillation to obtain pure VA is reported.^[8a,b] Another suggested strategy involves product separation due to the reduced solubility of VA in water at room temperature.^[8h] Formation of a second liquid phase was also observed during electrolysis at 50 °C using Pb, Cd and In, however, the composition of this phase is unknown. We therefore briefly address product isolation to strengthen the outlook of a

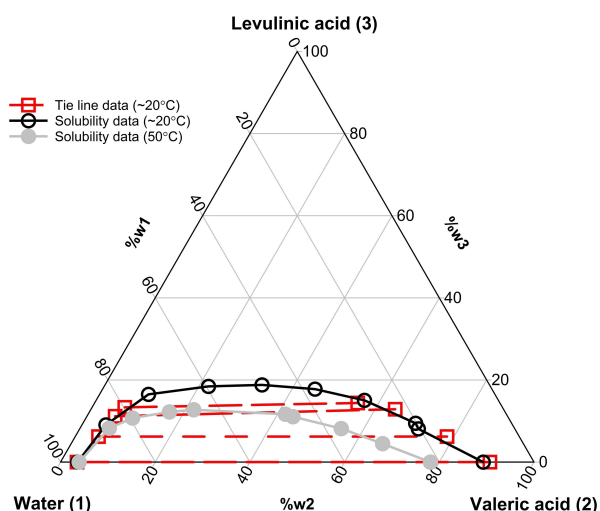


Figure 1. Ternary diagram for LLE of the water (1) – valeric acid (2) – levulinic acid (3) system determined at room temperature ($\sim 20^\circ\text{C}$) and 50°C .

continuous electrochemical process. The influence of LA on the solubility of VA at room temperature ($\sim 20^\circ\text{C}$) and 50°C is illustrated by the ternary diagram for the LLE of the H_2O – VA – LA system (Figure 1). The solubility of VA in water, 3.6% at 20°C and 3.9% at 50°C , and the solubility of water in VA, 11% at 20°C and 22% at 50°C is in good agreement with literature data.^[18] Introducing LA increases the mutual solubility until no phase separation occurs ($\sim 19\%$ LA at 20°C and $\sim 13\%$ LA at 50°C). Thus, depending on the LA conversion degree and temperature, the VA-rich phase contains $\geq 10\%$ water and LA next to VA. In addition, sulfuric acid is also present in the VA-rich phase. Additional processing is therefore required to obtain pure VA. Separating VA from a sulfuric acid solution by for example thermal methods might prove to be problematic on an industrial scale due to the corrosive nature of sulfuric acid. We therefore revisited the extraction methodology of Tafel and Emmert, including various other organic solvents using model solutions to assess the extraction of individual compounds. The results of the extraction are shown in Table 3 and show that the highest VA extraction efficiency is obtained using fatty alcohols and diethyl ether, however LA is co-extracted. The extraction efficiency for LA and VA is decreased when using toluene and hexane, however a superior separation for VA/LA is obtained. More specifically, almost no extraction of LA with the aliphatic extractant hexane was detected, making it a promising candidate to recycle the electrolyte including unreacted LA back to the electrolyzer, while continuously removing formed VA.

Further processing of recovered VA might involve thermal techniques due to the differences in vapor pressure of hexane, gVL and VA. The promising extraction results are used to outline an outlook of a continuous electrochemical process to obtain pure VA by utilizing indium as cathode and a facile down-stream processing approach as illustrated in Figure 2.

Table 3. Extraction of VA, gVL and LA from aqueous solutions (2 g/L) using various organic solvents, a 1:1 volume ratio at 20°C and 2 hours contact time.

Extractant	LA Extraction [%]	gVL Extraction [%]	VA Extraction [%]
1-Octanol	18.4 ± 2.4	32.3 ± 1.5	92.6 ± 2.1
1-Decanol	15.1 ± 0.5	27.8 ± 0.7	94.0 ± 0.4
Diethyl ether	16.2 ± 0.4	32.2 ± 4.0	94.1 ± 0.3
Toluene	0.5 ± 0.1	48.9 ± 2.5	62.3 ± 0.6
Hexane	0.1 ± 0.2	3.7 ± 0.5	36.4 ± 0.8

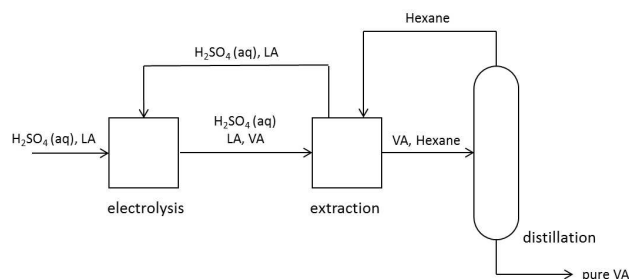


Figure 2. Envisioned continuous electrochemical process for the conversion of LA to VA.

3. Conclusions

In our study we have identified Cd, In and Zn as cathode materials for the electrochemical reduction of levulinic acid to valeric acid. Low conversions were obtained with Al and Ni, whereas Ga, Ag, Ti and Sn showed no activity towards valeric acid. More benign materials resulted in superior (99% at In) or similar (96% at Zn) selectivity, compared to Cd (92%) and already known Pb (94%). Remarkably, electrochemical reduction of levulinic acid at In showed no formation of the side-product γ -valerolactone and to the best of our knowledge this is the first time this material is used for this type of electrochemical reduction. Regarding the formation of valeric acid and γ -valerolactone from levulinic acid, we propose a reaction mechanism involving the formation of an organometallic intermediate. Selective conversion of LA to VA, good cathode stability and facile down-stream processing approach based on extraction and distillation outlines a promising outlook for a continuous electrochemical process.

Experimental Section

All chemicals used were of analytical grade and deionized water was used in all experiments. The metals were of $\geq 99.99\%$ purity, except for gallium (99.9%). Concentrations of LA, VA and gVL were determined by 1) HPLC (Waters Alliance) using a Waters Xbridge C18 column ($5\ \mu\text{m}$, $2.1\ \text{mm} \times 50\ \text{mm}$) eluting on a gradient with $0.5\ \text{mL} \cdot \text{min}^{-1}$ MeCN/Water/Formic acid and a Photodiode Array (200–500 nm) detector and 2) HPLC (Agilent 1100) using a BioRad Aminex HPX-87H column ($300\ \text{mm} \times 7.8\ \text{mm}$) at 35°C , eluting with $0.5\ \text{mL} \cdot \text{min}^{-1}$ with 5 mM H_2SO_4 in water and a refractive-index (Agilent 1260 G1362 A) detector.

Samples of the obtained catholyte solutions were 1:1 dissolved with D₂O, ¹H NMR spectra were recorded of these D₂O mixtures on a Bruker Advance III spectrometer operating at 400.17 MHz to verify formed VA and gVL (see Supporting information, Figure S3). Concentrations of various dissolved metals were determined by the Element XR High Resolution Inductively Coupled Plasma Mass Spectrometer (HR-ICP-MS; Thermo, Bremen, Germany). All data acquisitions are carried out in several resolution modes, to avoid the influence of spectral interferences on the results. The quantification is carried out by external two-point-calibration according to ISO 17294–2006. The stock solutions are diluted to relevant concentration levels.

Preparative Electrolysis

Preparative electrolysis was performed in a custom designed double-walled divided electrochemical cell in a three-electrode configuration under galvanostatic conditions (150 mA/cm²) using a potentiostat (Ivium Technologies, the Netherlands). The electrochemical cell contained 150 mL catholyte (1 M H₂SO₄ and 0.5 M reagent), 150 mL anolyte (1 M H₂SO₄), was divided by a NafionTM 117 membrane and operated at 50 °C. The three-electrode configuration consisted of an IrO_x-based DSA type anode (DeNora, Germany), SCE reference electrode (Radiometer Analytical REF401) via a Luggin' capillary, and various metal wires of 1 mm diameter, except gallium which was used as liquid pool. Insulated titanium wire was used as electrical connection to the gallium pool. All metal wires were of 70 cm length, except titanium being 22 cm, and were spirally wound to fit into the electrochemical cell. Approx. 4 mL of the catholyte was used to fill the Luggin' capillary and reservoir into which the SCE reference electrode was placed. Electrolysis was performed until twice the theoretical amount for conversion of LA to VA was supplied to the system, i.e. 8 F/mol for LA electrolysis (~300 min.). The anolyte and catholyte solutions were collected separately after electrolysis, the chambers were rinsed twice with approx. 100 mL water and combined with the corresponding anolyte and catholyte solutions. LA conversion, selectivity towards VA and gVL and the current efficiency were calculated using the following equations [Eqs. (1)–(3)]:

$$\text{Conversion LA (\%)} = X_{\text{LA}} = \frac{\text{moles of LA consumed}}{\text{moles of LA initial}} \times 100 \% \quad (1)$$

$$\text{Selectivity } i \text{ (\%)} = S_i = \frac{\text{moles of } i \text{ formed}}{\text{moles of LA consumed}} \times 100 \% \quad (2)$$

$$\text{Current efficiency (\%)} = \text{moles of VA formed} \times \frac{n \cdot F}{I \cdot t} \times 100 \% \quad (3)$$

Where *I* is the electrical current (A), *t* the electrolysis time (s), *n* the stoichiometric constant (for VA this is 4) and *F*, which is the constant of Faraday (96485 C/mol). The LA conversion, VA and gVL selectivity and current efficiency are based on measurements of catholyte and anolyte samples, because VA is transported preferentially through the Nafion membrane.^[8d] Duplicate preparative electrolysis experiments were performed of the systems showing promising results, i.e. systems with In, Zn, Cd and Pb as cathode material. The results with these cathodes are reported as the mean ± standard deviation (SD). The results of each experiment are shown in Table S1.

Liquid-Liquid Equilibrium (LLE)

The binodal curve for the water+levulinic acid+valeric acid ternary system was determined by the cloud-point titration method at room temperature, which was approx. 20 °C and 50 °C. Water+levulinic acid and valeric acid+levulinic acid mixtures of known compositions were stirred in a glass beaker or double walled reactor. The third component was added until the transition from a homogeneous to a heterogeneous phase was visually observed. Tie-lines were determined at room temperature by using a mixture of the three components which composition lies within the immiscibility region. The mixture was shaken vigorously for 1 hour and after a period of at least 48 hours, allowing sufficient phase separation, samples were removed from both phases using a syringe. The densities of both phases together with the levulinic acid and valeric acid concentrations were measured to determine their compositions.

Extraction

The extraction of LA, VA and gVL was determined by mixing aqueous solutions containing 2 g/L of either LA, VA and gVL with 1-octanol, 1-decanol, diethyl ether, toluene or hexane at room temperature. Experiments were performed in at least 4-fold and reported as the mean ± SD, the results of each experiment are shown in Table S2. The ratio between the aqueous and organic phase was one by using 10 mL for each phase. After a contact time of approx. 2 hours the phases were separated and the aqueous phase analyzed on LA, VA and gVL and compared with the initial concentration. The extraction efficiency was calculated using the following equation [Eq. (4)]:

$$\text{Extraction } i \text{ (\%)} = \frac{\text{moles of } i \text{ after extraction (aq)}}{\text{moles of } i \text{ initial (aq)}} \times 100 \% \quad (4)$$

Acknowledgements

This work is financially supported by the 'topsector Chemie' via the Dutch Ministry of Economic Affairs. The authors greatly acknowledge Kees Miermans (TNO, Utrecht) for the ICP analysis and the Waldvogel group in Mainz for supplying the leaded bronze materials.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: sustainable chemistry · deoxygenation · electrocatalysis · renewable resources · Clemmensen reduction

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Manuscript received: May 15, 2019

Accepted manuscript online: May 29, 2019