Spectroelectrochemical Exploration of Biogenic Substrates for Electrosynthesis

Nils Kurig and Regina Palkovits*

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Spectroelectrochemistry, especially ATR-SEIRAS, is an emerging method to identify key descriptors for optimizing reaction systems in organic electrosynthesis. Here, the upgrading of biogenic acids via Kolbe electrolysis and reductive transformations was studied. The findings affirm acid group adsorption on electrodes, consistent with existing literature. The effectiveness of Kolbe reaction in suppressing the parasitic ethanol oxidation reaction was observed, whereas it faces stiff competition from the methanol oxidation reaction. Parallel reduction and reductive amination of levulinic acid were uncovered, both relying on adsorbed organic species rather than molecular H_2. Intriguingly, the electrode's polarization influences the bond strength, enabling discrimination between acid and ketone species within levulinic acid.

Keywords: ATR-SEIRAS, Biomass, Electrocatalysis, Electrosynthesis, In situ spectroscopy

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1 Introduction

In the realm of sustainable energy and eco-friendly chemical production, organic electrochemistry emerges as a pivotal research frontier. By leveraging a profound understanding of catalyst materials and reaction mechanisms, researchers can unlock pathways to more efficient and environmentally benign processes, thereby catalyzing progress toward cleaner, energy-efficient technologies. When optimizing synthesis routes and processes in the established research field of organic electrosynthesis, there are a large number of mechanistic questions to address. These have been and are being elucidated not only by electroanalytical tools but also increasingly by spectroelectrochemistry (SEC), which nominally combines spectroscopic and electrochemical methods and is becoming a key player in the knowledge-driven development in the field.

Since in situ (Latin "in place") or in operando (Latin "in operation") methods are usually meant, SEC describes the electrochemical processes in solutions or at electrode surfaces in a time-resolved manner [1–4]. In thermo-catalysis, in situ and in operando spectroscopic methodologies are well established and systematic development has enabled studies at close to real reaction conditions [5–9]. In electrochemistry, the gap between an ideal reaction environment to gain mechanistic insights in spectroscopic analyses and the experimental setups to study systems under relevant reaction conditions has just started to close. As two methods based on electromagnetic fields are used simultaneously, the measurements often interfere. To keep this interference small enough so that the individual measurements are still meaningful, various measures must be taken. In in situ nuclear magnetic resonance (NMR) SEC, for example, complex shielding and fine-tuning of the NMR parameters are necessary [10]. In in situ attenuated total reflectance (ATR) surface-enhanced infrared absorption spectroscopy (SEIRAS), there are strong shifts of the baselines and the signals are shifted compared to ex situ measurements [11, 12]. Additionally, as with other in situ methods, there is the difficulty to perform a background or reference measurement without losing information.

In the early 1960s, ATR was introduced as a variant of infrared (IR) spectroscopy. If an IR beam falls at a certain angle on a dielectric with a large refractive index, it is reflected several times and an evanescent wave is formed. This reaches just far enough above the so-called ATR

[1,2]Dr. Nils Kurig https://orcid.org/0000-0003-0717-1964,
[2,3]Prof. Regina Palkovits
https://orcid.org/0000-0002-4970-2957
(palkovits@itmc.rwth-aachen.de)
[1]Department of Chemistry, Scripps Research, La Jolla, CA 92037, USA.
[2]RWTH Aachen University, Institute of Technical and Macromolecular Chemistry, Worringerweg 2, 52074 Aachen, Germany.
[3]Institute for a Sustainable Hydrogen Economy, Forschungszentrum Jülich, Am Brainenergy Park, 42428 Jülich, Germany.

element (often made of silicon, germanium, zinc selenide, or diamond) to penetrate a sample placed on it by a few micrometers. If this sample absorbs IR radiation, a spectrum with high intensity and good contrast is obtained [13, 14]. Detailed presentations of the ATR principle are nowadays an integral part of any spectroscopic textbook. It became clear that this method for studying chemical thin films and adsorbates can become an important tool in interfacial sciences such as heterogeneous catalysis and electrochemistry. Initially, optically transparent materials such as glass coated with tin oxide or the germanium ATR element itself were used as electrodes [15, 16]. Later, studies on thin metal films on ATR elements followed [17], which were eventually used as electrodes [18, 19]. In parallel, a surface enhancement effect of adsorbed molecules on certain metal surfaces was discovered in ATR spectroscopy [20, 21]. Thus, ATR-SEIRAS has become a standard method in SEC [22, 23]. Several commercial experimental setups are available (e.g., from Bruker, Billerica, USA or Jackfish SEC, Saskatoon, Canada) and there are probably numerous in-house setups by other research groups [24–28]. While the Burgess group investigated how different pyridine derivatives adsorb to different gold surfaces [29, 30], they further developed the Jackfish SEC cell. As a result, silicon wafers have been developed as alternative substrates for metal films, which are superior to conventional ATR elements, particularly due to their reduced cost [31]. The diversity and usefulness of ATR-SEIRAS will be illustrated in the following with selected examples of current research.

In particular, ATR-SEIRAS is used to study the oxidation of small molecules such as methanol and ethanol on platinum or gold to elucidate the reaction mechanism. In a study that does not explicitly address the surface enhancement effect, although nanostructured platinum electrodes are used, the fast scan method of IR spectroscopy was used to obtain time-resolved information. This showed that bridging adsorbed carbon monoxide (CO) already blocks the electrode from the starting potential of the methanol oxidation reaction (MOR), while linearly bound CO only appears at the peak potential [25]. This poisoning process of the electrode with CO in MOR [32, 33] was additionally investigated with in situ IR spectroscopy in the ethanol oxidation reaction (EOR) [34].

ATR-SEIRAS has been used in the electrochemistry of small molecules such as methanol [25, 32, 33], ethanol [34], or acetate [35, 36], and very large biomolecules [37]. However, few studies of medium-sized molecules as relevant in organic electrosynthesis or biomass upgrading can be found, so far [38–41]. With platinum [32, 33], gold [30, 36], copper [42, 43], and silver [35], many common electrode materials can be used in ATR-SEIRAS. In addition, even alloys [44] and supported electrocatalysts [45] have been applied, but unfortunately the experimental procedure has not been extensively described. Thus, there are interesting opportunities for further research.

This study gives a tutorial to facilely collect spectroelectrochemical data about popular reactions of biomass conversion and deepens the understanding of reaction mechanisms. First, Kolbe electrolysis is considered in aqueous as well as organic solutions, unveiling the nature of surface adsorption of carboxylic acid groups for decarboxylation. Then, competitive electroreductive pathways of levulinic acid are studied to elucidate whether they proceed via an inner-sphere surface mechanism or via bulk H_2 produced in the hydrogen evolution reaction (HER), and to draw conclusions on the selectivity of the reaction.

2 Results

2.1 (Non-)Kolbe Electrolysis

In 1847, Herrmann Kolbe laid the foundation for organic electrochemistry, reporting the decarboxylative dimerization of valeric acid to form *n*-octane [46]. The search for adaptive energy storage technologies and the necessity to close carbon cycles revived this area of research in the last years. In past years, researchers have followed several approaches to emphasize the popularity of (non-)Kolbe electrolysis and increase the mechanistic understanding [47–57]. There is consensus in the literature that, in the first step of Kolbe electrolysis, carboxyl groups adsorb to the anode and are oxidized there to form radicals [48]. On the contrary, it is still under discussion whether these radicals desorb and exist in solution [58, 59] or are bound to the surface [60, 61] prior to recombination or further oxidation. Recently, the mechanism of a novel Kolbe reaction of biogenic dicarboxylic acids was studied by our group. During the research of biogenic Kolbe electrolysis value chains, a so far undescribed reaction pathway was discovered [53]. Molecules containing two carboxylic acid groups are more abundant in biomass [62]. The refinement of linear dicarboxylic acids was discussed in numerous publications [54, 63–69]. It is noticeable that usually one of the acid groups is protected to control the reactivity. However, if the radical mechanism of Kolbe electrolysis is considered for dicarboxylic acids, it should be possible to contain cyclic and unsaturated products by double decarboxylation. Contrary to the prevailing opinion in the literature [70–75], this was shown in a mechanistic study [53]. However, it remained unclear whether this was a consecutive reaction in which the bi-radical recombines (or cyclizes) as soon as it is released, or whether the entire reaction occurs at the surface. The adsorption of dicarboxylic acids on a platinum surface is therefore studied using in situ ATR-SEIRAS (please see the Supporting Information for a detailed description of the experiments). As can be seen in Fig. 1, the baseline of the IR spectra was shifted and distorted by the polarization of the electrode. However, in order to leave the spectroscopic information as pristine as possible, the spectra were not

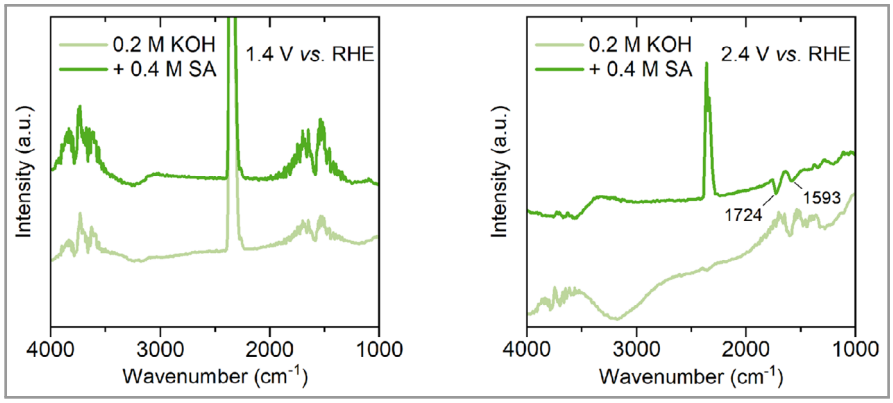

Figure 1. IR spectra of the pure electrolyte solution of aqueous 0.2 M KOH compared with a solution containing an additional 0.4 M succinic acid (SA) at two different potentials. Here, 1.4 V vs. RHE is below the starting potential of Kolbe electrolysis and 2.4 V vs. RHE is above it.

normalized or referenced to a single spectrum in this work. Therefore, the intensities of the spectra cannot be compared with each other and are presented without units.

Succinic acid, which is the chemically simplest substrate for the bi-radical mechanism, was chosen as the model substrate. To identify which signals belong to an adsorbed substrate, spectra above and below the critical potential for Kolbe electrolysis were compared. In addition, the spectrum of the pure electrolyte was recorded at the same potentials.

In the left graph of Fig. 1, it is clear that below the potential for Kolbe electrolysis at 1.4 V vs. RHE (reversible hydrogen electrode) there is no difference between the pure electrolyte solution and a solution with additional substrate. In the ranges of 1300–1800 cm^{-1} and 3500–3800 cm^{-1}, signals due to adsorbed water can be identified. The discussion of water signals in electrochemical ATR-SEIRAS is not complete, as well as very specific to the actual electrode and system. Therefore, only uniquely identifiable signals from the substrates are discussed in this work. For a more detailed consideration of water adsorption, a study by the group of Osawa [76] can be used as a starting point. In addition, a distinct CO_2 signal around 2360 cm^{-1} is apparent due to the measurement setup, which cannot be sealed off from ambient air. At 2.4 V vs. RHE, both spectra show a shift of the baseline to higher values for smaller wavenumbers. Such shifts are seen for all spectra recorded in the following and are influenced by the polarization of the surface [20, 21]. In addition, the polarized electrode with pure electrolyte shows a broadened signal at 3200 cm^{-1}, which is attributed to strongly bound water [35, 36]. In the measurement with substrate, hardly any water signals are seen at 2.4 V vs. RHE, with a carbonyl band showing up at 1724 cm^{-1}. If it is taken into account that IR bands shift due to the solvent and measurement conditions (especially in the case of SEC), this is in agreement with the literature value of 1691 cm^{-1} for the acid group of succinic acid [77]. However, at the same time, it shows that a mixture of several carboxylic acids would probably be difficult to evaluate. In addition, a second band at 1593 cm^{-1} is indicated. This can be assigned to the COO^- stretching vibration, which confirms the carboxylate already at the present pH 5 [78].

The absorption behavior of succinic acid was compared with that of succinic acid monomethyl ester. In this way, it is checked whether the dicarboxylic acid binds differently to the electrode than its mono-esterified derivative. From this, conclusions will be drawn about the novel Kolbe reaction pathway of the dicarboxylic acid. The corresponding spectra are shown in Fig. 2.

The spectra show no significant differences. On the one hand, this may mean that both succinic acid and its mono-esterified derivative bind to the electrode with only one acid group. In this case, the bi-radical mechanism would proceed consecutively. On the other hand, it is possible that the signal of succinic acid describes both acid groups since they are chemically identical. Even asymmetric dicarboxylic acids such as methylsuccinic acid often show only one carbonyl signal [79]. Moreover, in the given measurement setup, the critical current strength favoring the bi-radical mechanism could not be reached. In future studies, carboxylic acids with additional functional groups should be considered to obtain resolved acid signals. However, these may not react along the Kolbe bi-radical reaction pathway and are not present in the dicarboxylic acids considered so far [53]. First, however,

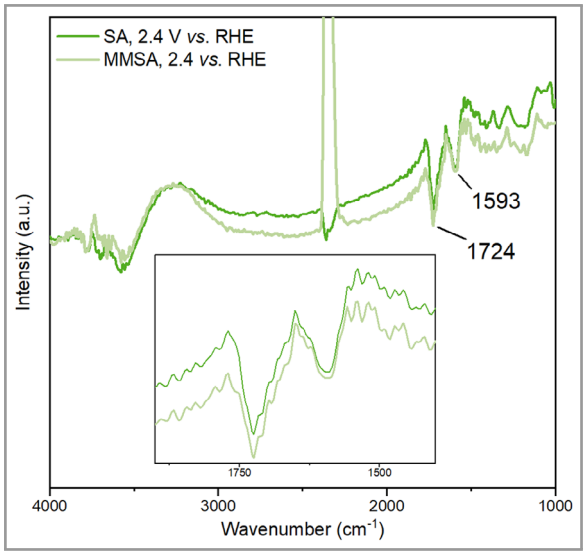

Figure 2. Comparison of the spectra of 0.4 M succinic acid (SA) and 0.4 M succinic acid monomethyl ester (MMSA) in 0.2 M aqueous KOH above the starting potential of Kolbe electrolysis at 2.4 V vs. RHE. Inset: Zoom on the carbonyl region.

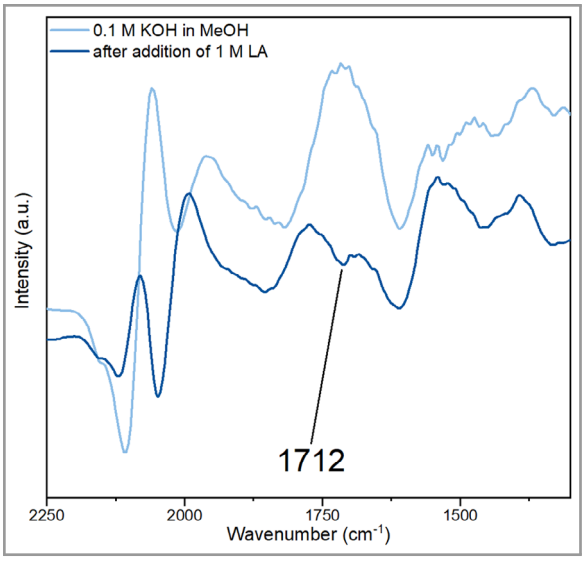

Figure 3. IR spectra of Kolbe electrolysis of levulinic acid (LA) in methanol compared with the pure electrolyte of 0.1 M KOH in methanol at 0.5 V vs. pseudo-reference.

the measurement conditions will be changed to investigate whether this affects the adsorption behavior.

Methanol is the most established solvent in Kolbe electrolysis and was also used for the bi-radical mechanism [53]. Therefore, it was tested whether the solvent could be exchanged for the spectroelectrochemical study. However, the measurements in the presented model system did not show meaningful spectra due to the distinct signals of solvent oxidation (see Supporting Information Figure 7.12). Therefore, the extensively studied model substrate levulinic acid was considered and the concentration was increased to 1.0 M, which is not possible with dicarboxylic acids due to low solubility. The spectra in Fig. 3 were recorded at a potential above the critical value for Kolbe electrolysis, determined by cyclic voltammetry versus a pseudo-reference.

The spectrum of the pure electrolyte is dominated by the signal of carbon monoxide (CO), which originates from solvent decomposition. At 2060 cm^{-1}, a split signal from adsorbed CO is found, as is the signal at 1800 cm^{-1} [33]. In contrast, the signals at 1550 and 1000 cm^{-1} are attributable to methanol [80]. Upon addition of levulinic acid, the CO signal at 2060 cm^{-1} shifts and distorts slightly, suggesting that Kolbe electrolysis is competitive with solvent oxidation. The most obvious difference after substrate addition is a signal at 1712 cm^{-1}, which is intense enough to compensate for the negative amplitude of the spectrum of the pure electrolyte. The vibrational frequency is attributed to the carboxylic acid of levulinic acid, which is reported in the literature to be around 1705 cm^{-1} [81, 82].

Overall, the interpretation of the recorded infrared spectra proves to be challenging, especially in methanol. This is due in part to the fact that background measurements, which serve as references in spectroscopic experiments, have limited comparability with polarized electrode measurements. This effect is particularly pronounced because the electrode surface is poisoned by the adsorption of CO from solvent decomposition. Nevertheless, based on these initial experiments, a protocol could be established to obtain meaningful adsorption measurements, which was recorded in the experimental section (see the Supporting Information). It was shown that the acid groups adsorb to the platinum electrode as reactive groups. In doing so, they inhibit the adsorption of the solvent, especially in the aqueous medium. Kolbe electrolysis definitely offers room for further spectroelectrochemical studies. In particular, it would be interesting to know which intermediates adsorb to the electrode. The Kolbe electrolysis literature has always investigated the nature of electron transfer and bond cleavage, as well as the role of adsorbed versus free carbon radical species. However, to do this, lower wavenumbers must first be accessed by further developing ATR-SEIRAS methods and materials. In addition, the studies should be complemented by other spectroscopic techniques such as electron spin resonance, which are particularly suitable for studying radical species and understanding their role in the reaction mechanism.

2.2 Reduction of Levulinic Acid

In 2021, our group presented a study on electrochemical reductive amination focusing on levulinic acid conversion to 1,5-dimethyl-2-pyrrolidone [83]. Therein, also the direct reduction of levulinic acid with water to 4-hydroxypentanoic acid was discussed. Once an amine is in the system, these reactions proceed competitively. It was shown that the pyrrolidone yield is largely determined by the equilibrium between ketone and imine. A selective reduction of only the imine shifts the equilibrium away from the ketone and thus limits the production of 4-hydroxypentanoic acid, which is why the surface mechanism is of interest. It is also important whether the adsorbed substrate reacts or whether the electrons are transferred across the Helmholtz layer while only hydrogen adsorbs to it [84]. In situ ATR-SEIRAS shows which organic functional groups are adsorbed to the polarized surface. In the reaction system described, the imine with a C=N group and the carbonyl with C=O are of primary interest. However, it is also possible that the amine adsorbs as a co-substrate.

The present measurements were performed using an ATR wafer coated with silver, and 2 M levulinic acid in 0.5 M aqueous KH_2PO_4 solution was used. Since there is no discrete reduction potential for the reductive conversions of levulinic acid, potential ramps are considered in the following experiments. Fig. 4 shows the ATR-SEIRAS spectra at three different potentials applied during chronoamperometric measurements.

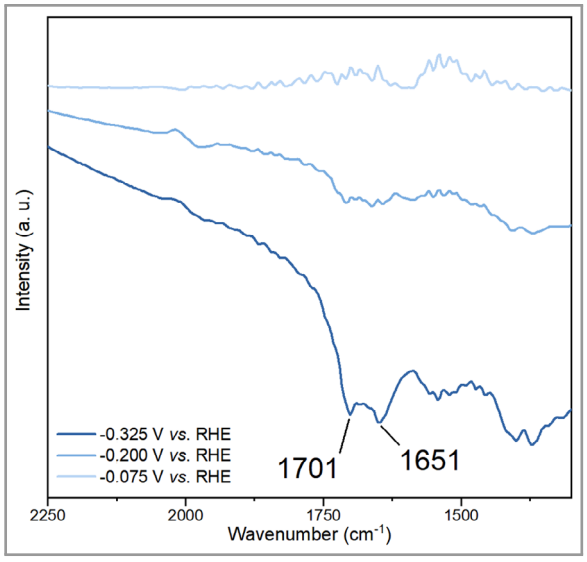

Figure 4. IR spectra of direct reduction of 2 M levulinic acid in aqueous electrolyte with 0.5 M KH_2PO_4 at different reductive potentials on a silver electrode.

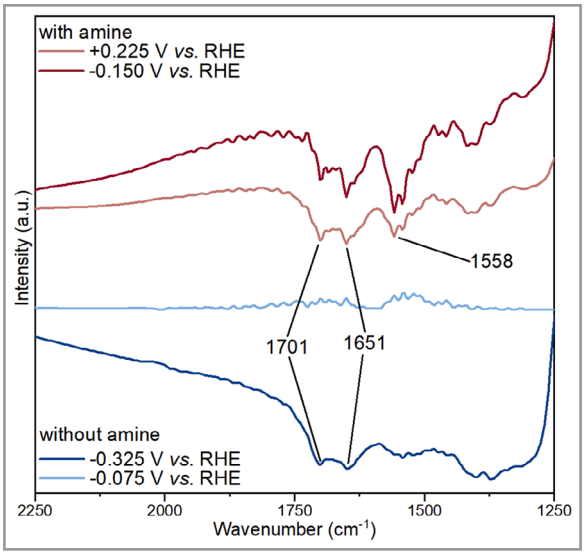

Figure 5. IR spectra of reductive amination of 2 M levulinic acid with 2.4 M methylamine in 0.5 M aqueous KH_2PO_4 at different reductive potentials on a silver electrode.

At –0.200 V vs. RHE, the adsorption of levulinic acid prevails over that of the electrolyte. If the potential is lowered further, the baseline shift increases and the adsorption signals become more distinct. The signal from the electrolyte solution also gains in intensity, especially in the region around 3200 cm^{-1}. At –0.575 V vs. RHE, both the water adsorption signals around 3600 cm^{-1} and the strongly bound water signal shifted from 3200 cm^{-1} to higher wavenumbers are prominent (see Supporting Information Fig. S2 for the full spectra) [35, 36]. The carbonyl signal of levulinic acid splits into two maxima at 1701 and 1651 cm^{-1}. Due to the negatively polarized electrode, the electron density is shifted to the carbonyl carbon and into the anti-bonding π^*-orbital of the carbonyl bond, respectively. This is weakened and its vibration is easier to excite, shifting the IR band to lower values as the wavenumber is proportional to the excitation energy. Since the acid group is predominantly deprotonated at the set pH of 12 and thus more difficult to polarize negatively, this occurs preferentially with the ketone. The signal at 1651 cm^{-1} can thus be assigned to the keto group. Overall, the values are shifted to lower values compared to literature spectra as for KBr pellets [82] or in cellulose hydrolysis [81], because the polarized electrode weakens both C=O bonds. While the reduction of the keto group is known under the given conditions [85–87], the reduction of the acid group has not yet been achieved electrochemically [88]. Usually, conclusions about the selectivity of the reduction can be drawn from the intensities. However, the baseline of the spectrum is overall too shifted and fluctuates during the chronoamperometric measurement, so that no quantitative statement is possible.

Direct reduction of levulinic acid yields 4-hydroxypentanoic acid as the product. If a primary amine, in this case 1.2 equivalents of methylamine, is added as a co-substrate of the reduction, levulinic acid and amine are present at equilibrium with an imine [83]. The corresponding ATR-SEIRAS spectrum is shown in Fig. 5.

An additional signal becomes detectable at 1558 cm^{-1}. Since the imine cannot be isolated, no direct literature comparison is possible. For other imines, it is known that the signal is shifted by about 60 cm^{-1} to smaller values compared to that of the corresponding ketone [89]. Accordingly, a signal in this range would be expected for the imine, but also for methylamine. Due to the free pair of electrons on the nitrogen atom, methylamine lacks the driving force to adsorb to a negatively polarized surface. This can be confirmed by an ATR-SEIRAS study of the electrolyte solution with the co-substrate. Although the spectrum (shown in Supporting Information Fig. S1) shows a signal at 1230 cm^{-1} in addition to the water signals already discussed, it does not show a signal around 1558 cm^{-1}.

In a solution of the electrolyte with levulinic acid, both carbonyl groups can be detected with a negatively polarized electrode. When the co-substrate methylamine is added, another signal is revealed, which is in the range of a C=N vibration [89]. The studies thus support the mechanism of imine formation in a chemical equilibrium and subsequent reduction at the cathode, as well as the competitive direct reduction of levulinic acid.

3 Conclusion

Kolbe electrolysis and electrochemical reductive amination represent interesting tools for biomass upgrading. This study aimed at using in situ ATR-SEIRAS to deepen the

understanding of the reaction mechanisms with the goal of optimizing electrolysis conditions. It was shown that Kolbe electrolysis suppresses solvent oxidation reactions like the OER or MOR. Inhibition of the OER is especially strong, making it an electron efficient and value-creating alternative anode reaction. On the other side of the electrolysis cell, it was confirmed that amination of levulinic acid to access green pyrrolidones proceeds via an inner-sphere reduction and not by molecular hydrogen from electrochemical hydrogen evolution. Competitive direct reduction of the ketone to the alcohol is likewise observed. In the future, spectroscopic insights into the reaction mechanisms will help to rationally design new selective electrocatalysts for those reactions.

Supporting Information

Supporting Information for this article can be found under DOI: https://doi.org/10.1002/cite.202300176.

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Abbreviations

ATR	attenuated total reflectance
EOR	ethanol oxidation reaction
IR	infrared
MOR	methanol oxidation reaction
NMR	nuclear magnetic resonance
OER	oxygen evolution reaction
RHE	reversible hydrogen electrode
SEC	spectroelectrochemistry
SEIRAS	surface-enhanced infrared absorption spectroscopy

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