Platinized Titanium as Alternative Cost-Effective Anode for Efficient Kolbe Electrolysis in Aqueous Electrolyte Solutions

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Five commercial materials were assessed for electrochemical conversion of n-hexanoic acid by Kolbe electrolysis. Platinized titanium performed best, achieving a coulombic efficiency (CE) of 93.1 ± 6.7% (n = 6) for the degradation of n-hexanoic acid and 48.3 ± 3.2% (n = 6) for the production of n-decane, which is close to the performance of pure platinum (89.7 ± 14.4 and 55.5 ± 3.5%; n = 6). 56.7 mL liquid fuel was produced per mole n-hexanoic acid, converting to an energy demand of 6.66 kWh and 1.22 € per L. Using optical profilometry and scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy, it was shown that the degree of coverage of the titanium surface with platinum played the most important role. An uncovered surface of as little as 1–3% already led to a deterioration of the CE of approximately 50%. Using platinized titanium requires >36 times less capital expenditure at only <10% increased operational expenditure; an electrode lifetime of 10000 h can be expected.

Among the plethora of electrochemical synthesis are, for instance, the chlorine-alkali electrolysis,[9] the conversion of muconic acid to diacid monomers,[10] and the CO₂ reduction to formate, CO, or hydrocarbons.[11] An electrochemical synthesis that was already discovered by Faraday in 1834[12] is the Kolbe electrolysis. Of special recent interest is the Kolbe electrolysis of medium-chain carboxylic acids (MCCA), which are carboxylic acids with a carbon chain length of 5 to 8 C-atoms (C₅₋₈). Urban et al. showed the conversion of corn beer and corn silage to a hydrocarbon mixture with fuel properties using the Kolbe electrolysis.[13] This was achieved by combining a biological step for converting the complex substrate into a MCCA mixture with the extraction of the MCCA and subsequent Kolbe electrolysis. The process line possessed an efficiency of 0.48 g chemical oxygen demand (COD) per 1 g COD of corn beer, where COD is a sum-parameter of oxidizable carbon equivalents, and the Kolbe electrolysis showed a coulombic efficiency (CE) >80% for MCCA oxidation.[14]

During Kolbe electrolysis MCCAs are either converted into longer-chain n-alkanes (Kolbe products) via an intermediate radical step or a carbocation is formed from the radical intermediate, which further reacts to form n-alkenes, alcohols, or esters (non-Kolbe products, see Scheme 1). Thereby, the pathways, yields, and side reactions strongly depend on the reaction conditions.

Detailed studies on the Kolbe electrolysis of MCCA are scarce (see Table 1), and different MCCA in aqueous solution have been used. Among others, the influence of the electrode material, the electrode potential, and the type and concentration of the supporting electrolyte were examined. For the latter, we previously demonstrated that Na₂SO₄ as supporting electrolyte different to KNO₃ has no effect on the CE of the Kolbe electrolysis of n-valeric acid, but a higher a concentration of Na₂SO₄ increases the rate of acid degradation.[15] Additionally, we also proved that due to local pH shifts n-octanoic acid/n-octanoate forms agglomerates in aqueous solutions during Kolbe electrolysis, leading to a deterioration of the

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In summary, supporting electrolyte species and concentration, pH, as well as the nature of the MCCAs have an influence on the Kolbe electrolysis performance and therefore have to be well balanced. Concerning the electrode material most work was performed using (monolithic) pure platinum (Pt). Using pure Pt anodes, it is the current density \(j\) rather than the potential that determines the efficiency of the Kolbe electrolysis as shown in Table 1. To date only few other mostly self-made electrode materials such as thin film Pt, RuO\(_2\), IrO\(_2\), or boron-doped diamond have been examined.\(^{[16,17]}\) However, these are not commercially available, hardly scalable, and do not have a CE and selectivity comparable to that of pure Pt.

Furthermore, most of the studies only investigate acid degradation and thus CE values are only reported for this process. However, when considering the diversity of products that can be gained (Scheme 1), this only provides an insufficient picture. Yet, comparable data like CE, yield, and selectivity for the production of Kolbe and specific non-Kolbe products resulting from Kolbe electrolysis of MCCAs are almost completely missing.

To propel the development of Kolbe electrolysis of MCCAs, in this study we screened different commercially available electrode materials using pure Pt as benchmark. Therefore, the conversion of \(n\)-hexanoic acid \((\text{C}_6\)\) to \(n\)-decane \((\text{C}_{10}\)\) in aqueous solution served as model reaction (see Scheme 1). In addition to the CE for the acid degradation, we also report the CE for the produced by-products as well as the selectivity and the yield based on the Kolbe product \(n\)-decane.

### Results and Discussion

**Validation of the electrochemical cell**

In order to validate the experimental setup, Kolbe electrolysis was performed in one- and two-chamber electrochemical cells using a Pt anode. As Table 1 shows, Pt is the most common anode material used for Kolbe electrolysis of MCCAs. CE values based on the degradation of the MCCAs used as substrate of around 90\% are reported. This was confirmed for both one- and two-chamber setups, with a CE\(_{\text{hexanoic acid}}\) of 94.1 \(\pm\) 17.4\% \((n = 6)\) and 89.7 \(\pm\) 14.4\% \((n = 6)\), respectively. Noteworthy, when considering the CE\(_{\text{decane}}\) based on the formation of the Kolbe product \(n\)-decane (see Figure S1), a significant difference for the two configurations of the electrochemical cell is observed. CE\(_{\text{decane}}\) is significantly higher in the two-chamber setup (CE\(_{\text{decane}}\) = 55.5 \(\pm\) 3.5\% \((n = 6)\) than in the one-chamber system (CE\(_{\text{decane}}\) = 41.9 \(\pm\) 3.4\% \((n = 6)\); see also Figure S2).

This might be explained by the prevention of side reactions by separation of anode and cathode chamber. Since the two-chamber system has an increased internal resistance due to the presence of the membrane, the cell voltage \((E_{\text{cell}})\) was 25.4 \(\pm\) 2.1 V at the start of the experiment and decreased during the 4 h of electrolysis to 12.5 \(\pm\) 1.7 V due to the pH-shift (see below). In contrast to this, \(E_{\text{cell}}\) was only 6.5 \(\pm\) 0.1 to 6.2 \(\pm\) 0.2 V in the one-chamber setup. Also, the pH of the reaction solutions differed. In the two-chamber setup the pH in the anode chamber dropped from 7.05 \(\pm\) 0.06 to 6.09 \(\pm\) 0.20 during the duration of the experiment due to the fact that \(\text{H}^+\) from the converted \(n\)-hexanoic acid remained in the reaction solution, while the pH in the cathode chamber increased due to the accumulation of \(\text{OH}^-\) ions from water splitting and \(\text{H}_2\) evolution. This can be expected as for pH neutral conditions other ions than \(\text{H}^+\) and \(\text{OH}^-\) are responsible for the charge-balancing ion transfer.\(^{[18]}\) In the one-chamber system both processes necessarily had to take place in the same reaction solution, so the pH increased from 7.00 \(\pm\) 0.08 to 8.33 \(\pm\) 0.07. Noteworthy, esters were only found in the product spectrum for the two-chamber setup. In conclusion, based on the higher CE\(_{\text{decane}}\) as well as the more confined experimental space, all follow-up experiments were performed using two-chamber electrochemical cells.

**Electrochemical characterization**

As mentioned above, the most common material used as anode for Kolbe electrolysis is pure monolithic Pt. Especially for the Kolbe electrolysis of MCCAs only a few other materials were investigated. For instance, RuO\(_2\) thin film, IrO\(_2\) thin film and Pt thin film based on Ti were assessed in comparison to pure Pt by...
| pH | Electrolyte | \( \text{CE} \) [%] | Y [mol cm\(^{-2}\) L \( \text{h} \)] | Specifications | Ref. |
|----|-------------|-----------------|-----------------|-----------------|------|
| 7.1 | Pt foil; Pt thin film on Ti foil | 7.1 | – | – | [18] |
| 8.3 | Pt foil | 8.3 | 15-20°C | 64.5 | [14] |
| 8.5 | Pt foil | 8.5 | 15-20°C | 66.5 | [12] |
| 110 | Pt thin film on Ti foil | 110 | – | – | [12] |
| 5 | K\(_2\)CO\(_3\) | 5 | – | – | [12] |
| 5.5 | pH 5.5 | 5.5 | – | – | [12] |

**Table 1. Literature overview for the performance of Kolbe electrolysis with MCCA in aqueous media.**

- **Specifications:**
  - \( \text{CE} \) [%]: Current efficiency of the reaction.
  - Y [mol cm\(^{-2}\) L \( \text{h} \)]: Yield of the product.
  - Specifications: Conditions for the electrolysis reaction.

- **Chemical Reagents:**
  - \( \text{pH} \): pH of the electrolyte.
  - Electrolyte: Chemicals used in the electrolyte.

- **Electrodes:**
  - Anode: Different anodes used in the electrolysis process.
  - Supporting electrolyte: The electrolyte used in the electrolysis process.

- **Other Information:**
  - \( \text{CE} \) [mol cm\(^{-2}\)]: Current efficiency of the reaction.
  - Y [mol cm\(^{-2}\) L \( \text{h} \)]: Yield of the product.
  - Specifications: Conditions for the electrolysis reaction.

- **Notes:**
  - Note 1: Additional information or notes related to the experiment.

- **References:**
  - [14]: Reference for the experimental setup.
  - [17]: Reference for the electrolyte composition.

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| C<sub>substrate</sub> | Anode | pH; supporting electrolyte | CE<sub>substrate</sub> [%] | CE<sub>dimer</sub> [%] | Yield [%] | Side products | r [mol cm<sup>2</sup> L<sup>-1</sup> h<sup>-1</sup>] | Specifications | Ref. |
|-------------------|-------|---------------------------|----------------|----------------|------------|--------------|----------------|----------------|-----|
| 0.69 M C<sub>7</sub> poly-crystal-line boron-doped diamond | pH 6.5 1 M NaOH | – | – | Y<sub>dimer</sub>; 0.35 A cm<sup>-2</sup>; 40 ± 5 | – | – | – | one-chamber electrochemical cell galvanostatic (0.35–0.70 A cm<sup>-2</sup>) 20 ± 3 ℃ 20 mL sono-emulsion (ultrasound) one-chamber electrochemical cell potentiostatic (3 V vs. Ag/AgCl sat. KCl) 3 h 50 mL | | [15] |
| 0.1 or 0.5 M C<sub>6</sub> pure Pt | pH 7.1–12.7 | 52 ± 1 to 90 ± 33 (n = 2) | – | – | – | – | – | sono-emulsion (ultrasound) one-chamber electrochemical cell potentiostatic (3 V vs. Ag/AgCl sat. KCl) 3 h 50 mL | | |
| | pH 6.5–12.6 0.06–0.5 M Na<sub>2</sub>SO<sub>4</sub> | 25 ± 1 to 70 ± 2 (n = 2) | – | – | – | – | – | | |
| | pH 6.6–7.7 0.05/0.5 M phosphate buffer | 22 ± 1 to 75 ± 5 (n = 2) | – | – | – | – | – | | |
| 0.5 M C<sub>6</sub> pure Pt | pH 7 0.25 M Na<sub>2</sub>SO<sub>4</sub> | 94.1 ± 17.4 (n = 6) | Y<sub>dimer</sub>; 46.2 ± 9.6 | C<sub>3</sub>–C<sub>12</sub> alkanes | r<sub>substrate</sub>; 0.0263 ± 0.0005 | r<sub>dimer</sub>; 0.0059 ± 0.0005 | one-chamber electrochemical cell galvanostatic (150 mA cm<sup>-2</sup>) room temperature 4 h 200 mL two-chamber electrochemical cell galvanostatic (150 mA cm<sup>-2</sup>) room temperature 4 h 200 mL | this study (Figure S2) | |
| 0.5 M C<sub>6</sub> pure Pt | pH 7 0.25 M Na<sub>2</sub>SO<sub>4</sub> | 89.7 ± 14.4 (n = 6) | Y<sub>dimer</sub>; 63.7 ± 12.4 | C<sub>3</sub>–C<sub>12</sub> alkanes | r<sub>substrate</sub>; 0.0251 ± 0.0004 | r<sub>dimer</sub>; 0.0078 ± 0.0005 | one-chamber electrochemical cell galvanostatic (150 mA cm<sup>-2</sup>) room temperature 4 h 200 mL | this study (Figure S2) | |

[a] CE<sub>substrate</sub> means the CE based on the substrate consumption and CE<sub>dimer</sub> means the CE based on the formation of the dimerized Kolbe product. For the substrate C<sub>n</sub>, the respective carboxylic acid with n C-atoms. All values are either stated in the references or derived from primary data thereof as described in the Experimental section.
Qi et al. for their decarboxylation efficiency of valeric acid, showing the highest CE of 91.2% using Pt foil as anode material while RuO₂ thin film as anode only showed a maximum CE of 49.7%.[16] However, all suitable materials other than pure Pt are by far not commercially available and their production is hardly scalable. In the aforementioned study, for example, the RuO₂ thin film electrode that showed the highest efficiency for electrolysis following pure Pt was prepared by pre-treatment of the Ti serving as current collector followed by stepwise dropping RuCl₃ precursor solution on Ti, thermal decomposition, and calcination at 470 °C for 3 h.[16] This procedure is time consuming and can only be applied to small electrode surfaces. However, cheaper electrode materials than pure Pt available at scale are needed to allow implementation of Kolbe electrolysis of MCCA at a technical scale (see also “Consequences for implementation”). Therefore, different already commercially available electrode materials were tested for conversion of n-hexanoic acid to n-decane by Kolbe electrolysis using the validated two-chamber electrochemical cell.

Figure 1 summarizes the achieved CE. It is remarkable that when using platinized Ti Type B as anode a CEₙ-hexanoic acid of 93.1 ± 6.7% is reached that is not significantly different than the CEₙ-hexanoic acid for pure Pt (89.7 ± 14.4%). All other electrode materials show a CEₙ-hexanoic acid in the range from 28.3 to 67.5%, including the second material that is based on platinized Ti (Type A, CEₙ-hexanoic acid = 46.6 ± 9.9%). When considering the formation of the Kolbe product n-decane the CE also strongly differs. The highest CEₙ-decane is reached using pure Pt as anode material with 55.5 ± 3.5%, followed by platinized Ti Type B with CEₙ-decane = 48.3 ± 3.2% and the platinized Ti Type A with CEₙ-decane = 27.4 ± 15.2%. Using anodes based on Ru MMO and Ir MMO on Ti did not lead to the formation of n-decane, at all. The latter is of special interest when considering that often only the substrate consumption (here the degradation of n-hexanoic acid), but not the formation of the Kolbe product as well as of side products is analyzed (see Table 1).

Additionally, the selectivity and the yield for the production of n-decane were studied (see Table 2). The selectivity for the dimerization is at least 50%, even if the CEₙ-decane is only 10.3 ± 18.5% as for the Pt/Ir mixture on Ti. This clearly underlines that the reaction mechanism towards Kolbe or non-Kolbe products does not only depend on the electrode material but is also influenced by the reaction conditions such as pH, temperature, and current density.[16] Both platinized Ti electrodes have a similar yield of 52.3 ± 6.9% and 60.4 ± 43.0%, respectively, in terms of n-decane production as pure Pt (Yₙ-decane = 63.7 ± 12.4%) even if the CEₙ-hexanoic acid and CEₙ-decane are not comparable. Wadhawan et al. reported only a Yₙ-decane of 24 ± 3% to 45 ± 5% in a one-chamber electrochemical cell with a comparable current density converting n-hexanoic acid into n-decane.[10] The selectivity of the reaction for the dimerization to n-decane for both platinized materials and pure Pt is above 60%, meaning on a molar basis nearly two-thirds of the reaction products are n-decane. Selectivities (Sₙ-decane) for the dimerization

| Electrode material | Carbon balance | Yₙ-decane [%] | Sₙ-decane [%] |
|--------------------|----------------|--------------|--------------|
| pure Pt (n = 6)    | 74.6 ± 13.6    | 63.7 ± 12.4  | 69.9 ± 1.8   |
| platinized Ti Type A (n = 3) | 77.2 ± 51.4 | 60.4 ± 43.0  | 63.9 ± 2.3   |
| platinized Ti Type B (n = 6) | 65.0 ± 7.5   | 52.3 ± 6.9   | 66.9 ± 0.9   |
| Pt/Ir on Ti (n = 3) | 31.2 ± 67.6   | 21.2 ± 52.6  | 49.9 ± 17.5  |
| Ru MMO on Ti (n = 3) | 4.6 ± 1.1    | –            | –            |
| Ir MMO on Ti (n = 3) | 7.8 ± 4.2    | –            | –            |

[a] "n" provides number of replicates, "±" represents the 95% confidence interval, and "-" indicates that the values could not be calculated, as no n-decane was gained.
between 31.3 and nearly 60% are reported for Pt foil depending on the reaction conditions. Interestingly, the observed differences of the materials on the suitability for Kolbe reaction were already indicated by analysis using cyclic voltammetry (see Supporting Information, section 4).

Of special interest, however, is the difference of platinized Ti Type A and B that were subjected to surface analysis together with the benchmark material pure Pt.

Surface and corrosion analysis

Surface properties were studied at the mm- and μm-scale. Since only pure Pt as well as platinized Ti Type A and B showed a CE decane of at least 25%, the other materials were excluded from the physical-chemical examination. The materials were studied before (“as-received”) and after use for Kolbe electrolysis. Further, the loss of Pt to the electrolysis solution due to corrosion was examined.

At the mm-scale optical profilometry reveals a remarkable difference between the surfaces of the pure Pt electrodes and the two types of platinized Ti (see Figure 2; Figure S4). Whilst the surface of pure Pt is relatively smooth with regular longitudinal grooves, the platinized Ti electrodes possess a more regular surface structure consisting of spherical elevations (Figure 2 B, C). A closer look at the latter reveals further differences amongst the platinized Ti electrodes: The Type A electrode is very finely structured with small spherical elevations appearing like fine granules, which are attached to the surface, leading to an increased overall roughness. These, however, are much coarser on the Type B electrode. Surprisingly, on the mm-scale there are no significant differences between new and used electrodes (Figure 2). To quantify the physical surface properties, the roughness $R_\alpha$, which provides the arithmetical mean deviation of the surface profile, was calculated (Table 3). As can be seen, $R_\alpha$ of all three electrode materials is in the same order of magnitude, which does apparently not reflect the different visual perception of the surface structure discussed above. More important, however, it cannot conclusively explain their different electrochemical performances.

Subsequently, the surface was examined on the μm-scale using scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX) (Figure 3 with all pictures are shown in Figures S5 and S6). SEM micrographs acquired on smaller fields of view are partially in contrast to the profilometry data. For instance, the used pure Pt electrode, considered rough according to profilometry, appears smooth in the SEM image (Figure 3A). Also, the fine structure measured by profilometry on new, as received platinized Ti Type A electrodes appears cracked and shows many small indentations in the SEM image (Figure 3C). In contrast to this, the new platinized Ti Type B electrode (Figure 3G) is nearly as smooth as the pure Pt and there are only a few spots where small granules can be seen. Here, the surface looks like it consists of valleys and mountain ranges. Comparing the two platinized Ti electrodes after use, the surface of the Type B electrode has hardly changed (Figure 3I). Only some small cracks and brittle-looking areas appear after six times of use for 4 h each at 150 mA cm$^{-2}$. The surface of the platinized Ti Type A electrode, however, has deteriorated significantly. Larger areas exposing the underlying Ti serving as current collector formed due to detachment of the Pt coating during the electrolysis (Figure 3E). After the electrolysis, the detached Pt can be found in the aqueous phase of the reaction solution (see Table 5). For Type B, the SEM micrographs look more stable, as

| Electrode material                  | $R_\alpha$ [μm] |
|-------------------------------------|-----------------|
| pure Pt new                         | 1.531 ± 0.15    |
| pure Pt used                        | 5.174 ± 0.69    |
| platinized Ti Type A new            | 1.182 ± 0.16    |
| platinized Ti Type A used           | 1.099 ± 0.01    |
| platinized Ti Type B new            | 3.177 ± 0.81    |
| platinized Ti Type B used           | 2.820 ± 0.47    |

Table 3. Roughness $R_\alpha$ ± SD calculated from the profilometric height profiles of the different electrode materials. For each material two height profiles were taken.
here the surface is very similar to the surface of pure Pt before as well as after use.

To complement the assessment of the electrode surface structure using SEM, EDX analysis was carried out to examine the distribution of Pt and Ti on the surface (Figure 3, right column; Figures S5 and S6). In addition to the Pt signal only the background noise was recorded for the pure Pt electrode, likewise for 3 out of 4 recordings of the new platinized Ti Type B electrode and 2 out of 4 recordings of the used platinized Ti Type B electrode. This shows clearly that the entire surface of both electrodes was covered by Pt. The remaining recordings reveal clear differences as shown in Figure 3D,F,J with a high EDX-signal for Ti (red) and a high signal for Pt (green). Already for the new platinized Ti Type A electrode, many small, sharply defined spots of Ti are observed. This indicates that the Pt coating (on the Ti base material) possesses holes of 3–40 μm, and thus both Pt and Ti face the electrolyte solution. We reason that during electrolysis this leads to an increased occurrence of the competitive reaction to the Kolbe electrolysis, the evolution of oxygen from water electrolysis. This lowers the CE to 27.4 ± 15.2% for the platinized Ti Type A compared to CE = 55.5 ± 3.5% for pure Pt. On the other site the CE increases from 0.6 ± 0.6% for pure Pt to 16.7 ± 2.5% for the platinized Ti Type A. In contrast, EDX analysis of the new platinized Ti Type B electrode does not reveal any Ti on the electrode surface, which leads to the conclusion that the water electrolysis is suppressed, as it is for monolithic Pt electrodes. This is perfectly in line with the low CE of only 1.4 ± 0.9%. The EDX maps of the electrodes after electrolysis reveal that for the Type A electrode the exposed surface of Ti has increased significantly. There are many areas of Ti exposure of diameters ranging from 3–120 μm. Only for 2 out of the 4 recordings of the used Type B electrode Ti was detected, but only isolated and with a small diameter of 5–30 μm. In order to quantify the optical assessment of the surface coverage, the EDX recordings were analyzed, and the degree of coverage was calculated (Table 4). This shows that even for the platinized Ti Type A electrodes the Ti exposure is minor. Yet, together with the electrochemical performance (see “Electrochemical characterization”) it provides clear evidence that even a small proportion of 1–3% Ti exposed to the aqueous electrolyte solution has a strong influence on the CE.

To further investigate this corrosion, the loss of Pt to the aqueous electrolyte solution after electrolysis was analyzed by inductively coupled plasma mass spectrometry (ICP-MS). The results in Table 5 show that all electrodes lose Pt during the electrolysis. The Pt concentration in the aqueous phase after electrolysis with the platinized Ti Type B electrode as anode is

**Table 4.** Area% ± SD of Pt and Ti on the electrode surface. Per electrode material 4 technical replicates were done diagonally across the electrode.

| Electrode material | Ti area [%] ± SD | Transition area [%] ± SD | Pt area [%] ± SD |
|--------------------|----------------|--------------------------|----------------|
| pure Pt            | 0.00 ± 0.00    | 0.00 ± 0.00              | 100.00 ± 0.00  |
| platinized Ti Type A new | 0.98 ± 0.47 | 1.06 ± 1.08              | 98.02 ± 1.49  |
| platinized Ti Type A used | 2.63 ± 1.42 | 3.96 ± 2.34              | 93.49 ± 3.72  |
| platinized Ti Type B new | 0.15 ± 0.26 | 0.12 ± 0.21              | 99.74 ± 0.45  |
| platinized Ti Type B used | 0.54 ± 0.16 | 2.18 ± 2.15              | 97.41 ± 1.87  |

**Table 5.** Average concentration ± SD of Pt in the aqueous phase after each electrolysis run.[a]

| Electrode material | $c_{Pt}$ (ng mL$^{-1}$) |
|--------------------|--------------------------|
| pure Pt ($n = 3$)  | 24.63 ± 9.47              |
| platinized Ti Type A ($n = 3$) | 99.00 ± 10.03 |
| platinized Ti Type B ($n = 6$) | 25.85 ± 3.83 |
| control ($n = 3$)  | 0.13 ± 0.06               |

[a] For pure Pt, the platinized Ti Type A electrode and the control 3 samples each from independent experiments and 6 samples from independent experiments for the Type B electrode were measured.
with $25.85 \pm 3.83 \text{ ng mL}^{-1}$, comparable to the concentration when pure Pt is used as anode ($c_{\text{Pt}} = 24.63 \pm 9.47 \text{ ng mL}^{-1}$). However, the Type B electrode is only platinized, and here the loss of Pt leads to a loss of electrocatalytic surface area for the Kolbe electrolysis as discussed above. This problem does not occur with a pure monolithic Pt electrode that can be considered as infinite reservoir of electrocatalyst. The average Pt concentration for the platinized Ti Type A electrode is 99 ng mL$^{-1}$, which is almost 4 times higher than the concentration when using the Type B electrode or pure Pt, but still is highly suitable for Kolbe electrolysis. This increased corrosion of Pt has to be taken into account when considering the use of different electrode materials at technical scale with the platinized Ti Type A electrode wearing out significantly fast. Most likely the corrosion process is due to detached Pt particles caused by the gas evolution at the electrode surface.

Consequences for implementation

The transfer of Kolbe electrolysis from laboratory to industrial scale requires anodes with a low capital expenditure (capex). Although there is a great potential for process improvement in electrochemical reactor engineering,[21] for simplicity reasons we are now considering an volume-to-electrode ratio of 5 cm$^3$ L$^{-1}$ as used here. For a 100 L reactor a 500 cm$^2$ electrode would be required. A suitable monolithic pure Pt electrode of this size would cost at least 24 € cm$^{-2}$, being 12,000 €. The platinized Ti Type B that is just as suitable for Kolbe electrolysis as pure Pt costs only 330 € for 500 cm$^2$ (0.66 € cm$^{-2}$), about 36 times less than monolithic Pt (see Table S2). The platinized Ti Type B material thus offers the possibility of combining high performance with an acceptable capex when the Kolbe electrolysis is scaled up to a technical scale. This is further substantiated by the expected lifetime of the electrode of almost 10,000 h, more than one year (see Table S4). As this assumes constant operation, which is highly unlikely for Power-to-X aiming for the utilization of surplus electric energy from fluctuations from renewables,[23] an even longer lifetime can be expected. In this line a further decrease of capex can be expected when replacing Ti by equally corrosion-resistant materials that are also suitable for platinization using high-temperature electrolysis, with alloyed stainless steels being most promising.

The derived operational expenditures (opex) of 1 L of organic product mixture that may serve as model for drop-in fuel additive without the need of down-streaming[13] can be simplified as follows: Per 1 mol of converted n-hexanoic acid, 65.7 mL of liquid fuel mixture is produced with pure Pt, and 56.7 mL with platinized Ti Type B as anode (see the Supporting Information, section B). This means in order to produce 1 L of fuel mixture it is necessary to convert 15.2 mol of n-hexanoic acid using 6.22 kWh (pure Pt) or 17.6 mol of n-hexanoic acid using 6.66 kWh (platinized Ti Type B) (see Table S3). When considering the electric energy price this equals an opex of 1.14 € (1.38 US$; pure Pt) or 1.22 € (1.47 US$, platinized Ti Type B) per L fuel mixture. Although this opex does not consider, for example, the costs for agitation of the reaction solution, this calculation has two key messages: First, there is only a minor price increase in the opex of $<10\%$ when using platinized Ti as anode material, but a significant decrease in capex as shown above. Second, the costs of fuel by Kolbe electrolysis are within a reasonable range (albeit tax, etc. is not included), but at the same time a green premium might be worth considering.[23]

Conclusion

Based on a highly reproducible experimental setup this study shows that commercially available platinized Ti can be used as anode for the efficient galvanostatic conversion of n-hexanoic acid to n-decane in aqueous solution with a coulombic efficiency ($\text{CE}_{\text{n-hexanoic acid}}$) of 93.1 $\pm$ 6.7%. Thereby, the Kolbe product n-decane is produced with a selectivity of 66.9 $\pm$ 0.9% and a $\text{CE}_{\text{select}}$ of 48.3 $\pm$ 3.2%. This performance together with the economic consideration demonstrates that platinized Ti can fully replace pure Pt as anode material for the Kolbe electrolysis.

However, we have demonstrated that the surface properties of the platinized Ti strongly influence the CE and selectivity. Thus, apparently similar materials at similar capital expenditure show strongly deviating electrochemical suitability. Consequently, further studies need to address the structure–function relationships in more detail as it was done, for instance, for the fabrication of electrode materials for Li-ion batteries.[24,25] This will shed light on the impact of the different production procedures and steps on the electrode properties and hence their suitability to be used for the Kolbe electrolysis or other electro-organic synthesizes, such as hydrogenations.[26]

With this study the production of fuel additives by Kolbe electrolysis of medium-chain carboxylic acids (MCCAs) comes closer to application. Consequently, as follow-up the scaling not only of electrodes but of entire electrochemical cells and the operation of these devices needs to be addressed as well as the conversions of mixtures of MCCAs. Aspects to be considered include electrode topographies and geometries, like the use of foams or other 3D electrodes to increase the active electrode surface area, or the insertion of turbulence promoters inside flow channels to increase mass transfer.[27] Improvement of electrochemical synthesis can also be achieved by reactor engineering, such as the use of parallel plate flow cells,[21] microchannel reactors,[27] or pulsing techniques combined with artificial intelligence.[28] Finally, to show applicability, the operation at scale with different loads at different current densities, as it can be expected from fluctuations from renewable electric power, needs to be addressed.

Experimental Section

General remarks

All chemicals were of at least analytical grade or as stated. All solutions were prepared with bidistilled water (Milli-Q IQ 7000,
Merck KgaA, Darmstadt, Germany). If not stated otherwise all experimental potentials refer to Ag/AgCl (saturated KCl, 0.197 V vs. standard hydrogen electrode (SHE)). A list of all used symbols and abbreviations can be found in the Supporting Information.

**Chemicals**

Na$_2$SO$_4$ (anhydrous, ≥ 99%) was obtained from Carl Roth GmbH + Co. KG (Karlsruhe, Germany), H$_2$SO$_4$ (98%), NaOH (pellets), aceton, n-hexane for dilution series (for GC), dichloromethane (dried), acetic acid (p.A.), iso-butyric acid (for synthesis), ethanol (p.A.), 2-propanol (for liquid chromatography), 2-butanol (p.A.), 2-pentanol (for synthesis), 3-pentanol (for synthesis), 1-hexanol (for synthesis), 1-heptanol (for synthesis), 2-heptanol (for synthesis), 1-octanol (pure), n-pentane (for spectroscopy), and n-hexanoic acid-3-methylbutyl ester (for synthesis) were supplied by Merck KGaA (Darmstadt, Germany). 1-Propanol (analytical standard), 1-butanol (analytical standard), 1-pentanol (99%), n-propanoic acid (99%), n-butyric acid (99%), n-valeric acid (99%), n-hexanoic acid (99%), n-heptanoic acid (99%), n-octanoic acid (99%), n-nonanoic acid (99%), n-decanoic acid (99%), n-hexane as analytical standard (95%), n-heptane (99%), n-octane (99%), n-nonane (99%), n-decane (99%), n-undecane (99%), n-dodecane (99%), n-tridecane (99%), n-tetradecane (99%), n-pentadecane (99%), n-hexadecane (99%), n-heptadecane (99%), n-octadecane (99%), isobutyil hexanoate (98%), cyclohexanone (99.8%), and undecanoic acid methyl ester (analytical standard) were purchased from Sigma-Aldrich (St. Louis, USA). Iso-valeric acid (98%) was supplied by Fluka Chemie GmbH (Buchs, Switzerland) and 2-hexanol (98%) as well as 3-heptanol (98%) by abcr GmbH (Karlsruhe, Germany). The carrier gases helium and argon (99.999 vol% purity) and the calibration gases for level 1, 2, 5, and 6 (composition see Table S1) for GC as well as N$_2$ (> 99 vol%) were obtained from Air Products GmbH (Hattingen, Germany). The calibration gases for level 3 and 4 (composition see Table S1) for GC were derived from Air Liquid S.A. (Paris, France) and Praxair N.V. (Oevel, Belgium).

**Experimental setup**

Electrochemical decarboxylation of n-hexanoic acid by Kolbe electrolysis, as well as acidification after the electrolysis were performed in a three-neck 250 mL flask (Schott AG, Mainz, Germany, Figure 4). The central neck contained a butyl-rubber stopper equipped with the working electrode (WE), the counter electrode (CE), the reference electrode (RE), a tailor-made electrode holder, as well as two needle ports, one for gassing the reaction chamber and the conductivity were measured continuously during the experiment using a SevenExcellence S470 (Mettler-Toledo, Greifensee, Switzerland) with an InLab Micro Pro pH electrode and an InLab 710 conductivity electrode (both Mettler-Toledo, Greifensee, Switzerland). Both electrodes were calibrated with the commercial buffer solutions (Mettler-Toledo, Greifensee, Switzerland) directly before each experiment. After each electrolysis, the anode was cleaned with acetone and afterwards rinsed with water. All other inlet parts of the setup were also cleaned with water.

**Figure 4.** Scheme of electrochemical cell.
Kolbe electrolysis

To prepare the reaction solution 450 mL of water were introduced into a 500 mL flask and 33 mL of n-hexanoic acid was added. Thereafter, the flask was weighed in order to determine the exact amount of n-hexanoic acid used for each experiment. Subsequently, the pH of the solution was adjusted to pH = 7 using NaOH pellets and H$_2$SO$_4$. The conductivity was adjusted by adding Na$_2$SO$_4$ to a concentration of 0.25 mol L$^{-1}$. Afterwards, water was added to exactly 500 mL. The solution for the cathode chamber was prepared to a similar pH and conductivity by adding NaOH pellets, H$_2$SO$_4$ and Na$_2$SO$_4$.

The 500 mL n-hexanoic acid solution was divided into 200 mL for the electrolysis and 200 mL as blank solution (100 mL remained unused). The 200 mL for the electrolysis were filled into the electrochemical cell and the reactor was weighed. Thereafter, the cathode chamber was filled with 9 mL of the cathode chamber solution, and the complete experimental setup was assembled. The gas outlet was connected to a N$_2$-mass flow meter/controller (MFM; LOW-AP-FLOW F-101D, 60 mL min$^{-1}$, Bronkhorst High-Tech B.V., Ruurlo, Netherlands) controlled via a Flow-Bus (Bronkhorst High-Tech B.V., Ruurlo, Netherlands) with a microGC (3000 Micro GC, INFICON, Cologne, Germany) in by-pass in order to determine the composition and the volume of the produced gas. The electrolysis was carried out for 4 h with a constant current of 300 mA at room temperature and 1000 rpm stirring.

After the electrolysis, the system was kept gas tight. The N$_2$-mass flow meter/controller was changed to a CO$_2$-mass flow meter/controller (EL-FLOW Select F-201 CV, 500 mL min$^{-1}$, Bronkhorst High-Tech B.V., Ruurlo, Netherlands) also controlled via a Flow-Bus (Bronkhorst High-Tech B.V., Ruurlo, Netherlands). Through the needle port 50% H$_2$SO$_4$ was added to adjust to pH 2. Thereby, the dissolved CO$_2$ was gassed out and the volume of CO$_2$ was measured in order to allow calculation of the carbon balance. Also, the pH of the blank solution was adjusted to pH 2 with H$_2$SO$_4$. The conductivity was adjusted by adding Na$_2$SO$_4$ to pH = 2. Thereby, the pH of the solution was increased to 250°C. Carboxylic acids (CA), n-alkanes, alcohols, and esters were identified using retention times and mass spectra of pure compounds. CA (aqueous: C$_2$-C$_8$, and C$_{10}$-C$_{18}$; organic: C$_2$-C$_{12}$), n-alkanes (organic: C$_{12}$-C$_{16}$, C$_{18}$; each 4 levels), alcohols (aqueous: C$_2$-C$_8$, 3 levels; organic: C$_2$-C$_8$, 3 levels), and some esters (organic: C$_{14}$-C$_{18}$, 3 levels) were quantified using external standards. The concentration of esters that were not calibrated (a very minor share) was estimated using an average response factor of all calibrated esters.

Gas-phase analysis

During electrolysis, the gas composition was analyzed with a four-channel microGC equipped with a thermal conductivity detector, which was calibrated for the components to be analyzed (see Table 6). Measurements were carried out at the beginning of the electrolysis ($t_0$) and every 10 min during the first 90 min of the experiment. During the remaining 150 min of the experiment the gas composition was determined every 30 min.

From the mass flow controller (see section above), the measured volume $v_{\text{measured}}$ [mL] is gained and the mole fraction y of each individual gas component i [%] is obtained from the microGC-TCD measurement. Determined gaseous reaction products are shown in Figure S1 (green boxes).

Liquid-phase analysis

GC–MS for quantification of liquid electrolysis products: To quantify the amount of the reaction products (see Figure S1, orange boxes) in the liquid phase, first a phase separation was carried out in a separating funnel for both the reaction solution and the blank solution for at least 2 h. After phase separation both phases (aqueous and organic) were separately filled into flasks. The electrochemical reactor flask and the separation funnel were rinsed with acetone, which was added to the aqueous phase. The weight of both phases was determined. The density of the phases was determined by weighing 1 mL. The aqueous phase was diluted in acid water (water adjusted with H$_2$SO$_4$ to pH = 2) and the organic phase in n-hexane and parallel in dichloromethane. Dilutions of 1:10, 1:100, and 1:1000 were analyzed.

The dilution series of the aqueous phase as well as both dilutions series of the organic phase were analyzed via GC–MS (GC 7890 A and MSD 5975 C InertXL, Agilent, Santa Clara, USA), using a DB-FATWAX capillary column (30 m × 250 μm × 0.25 μm, Agilent, Santa Clara, USA) with helium as carrier gas, undecanoic acid methyl ester as internal standard for the organic phase, and cyclohexanone as internal standard for the aqueous phase. The initial temperature was 50°C (held for 2 min) and with a temperature ramp of 15 K min$^{-1}$ it increased to 250°C. Carboxylic acids (CA), n-alkanes, alcohols, and esters were identified using retention times and mass spectra of pure compounds. CA (aqueous: C$_2$-C$_8$, and C$_{10}$-C$_{18}$; organic: C$_{14}$-C$_{18}$, 4 levels), n-alkanes (organic: C$_{12}$-C$_{16}$, C$_{18}$; each 4 levels), alcohols (aqueous: C$_2$-C$_8$, 3 levels; organic: C$_2$-C$_8$, 3 levels), and some esters (organic: C$_{14}$-C$_{18}$, 3 levels) were quantified using external standards. The concentration of esters that were not calibrated (a very minor share) was estimated using an average response factor of all calibrated esters.

Determination of Pt concentration in aqueous phase: The loss of Pt from the surface of the electrode during electrolysis was determined using ICP-MS measurements (ELEMENT™ XR ICP-MS, Thermo Scientific, USA) of the aqueous phase after phase separation. Calibration was conducted with worked Pt standards (0.05–1 ng mL$^{-1}$, 5-point-calibration) at a mass of 195. Re was added as internal standard to the sample solution at a concentration of 3.5 ng mL$^{-1}$ and measured at a mass of 185. All samples were diluted 1:100 for the measurement. The limit of quantification was 0.065 ng mL$^{-1}$. For control the aqueous phase of an n-hexanoic acid solution (identically treated) was used.

| Column | Carrier gas | t column [°C] | t injection [μs] | p column [g/s] | Analyzed components |
|--------|-------------|---------------|-----------------|---------------|-------------------|
| 14 m molsieve with 2 mL Plot U pre-column, 1 μL backflush injector | argon | 100 | 0 | 25 | H$_2$, O$_2$, N$_2$ |
| 8 m Plot Q, variable volume injector | helium | 80 | 25 | 20 | CO$_2$, propylene, propane, 1-butene, butane |
| 8 m OV-1, 1.2 μm thick, variable volume injector | helium | 60 | 250 | 20 | propylene/propane, butene/butane, iso-pentene, 1-pentene, pentane, 2-methyl-2-butene, 2-cis-pentene, 2-trans-pentene, hexane |
| 10 m Stabilwax, variable volume injector | helium | 60 | 250 | 15 | - |

[a] For all columns: sample inlet temperature = 100°C; injector temperature = 100°C; running time = 420 s.
Electrode surface analysis

Profilometry: To determine the physical electrode surface properties an optical profilometer (Sensofar SNeox 3D, Sensofar Metrology, Terrassa, Spain) with green LED illumination and 10× objective was used to acquire topography maps of the electrode surfaces with a lateral resolution of approximately 1 μm. In order to determine the surface roughness two topography maps per electrode were acquired as 8-bit grey-scale images with the topography encoded in the pixel brightness. These were then further analyzed using the software Fiji (Fiji is just ImageJ), Version: ImageJ 1.52p, https://imagej.net/Fiji, in order to obtain a map showing the deviation of the topography from the average height level: First, the average grey value of all pixels was calculated and subtracted from the image. Second, the absolute value was calculated for each pixel. Subsequently, the average grey value of the obtained image was determined as before. This average grey value was then divided by 255, which is the maximum range of grey values of an 8 bit image, and multiplied by the highest altitude value on the scale bar in order to calculate the roughness \( R_m \). Thus, the arithmetic mean of the absolute deviation from the average height is defined as roughness \( R_m \) in this study.

SEM/EDX: To determine the physical and chemical properties of the surface at a microscopic level, SEM imaging in combination with EDX was used. For that a Zeiss Merlin VP Compact field-emitting scanning electron microscope (Carl Zeiss Microscopy, Oberkochen, Germany) with the software package SmartSEM was used to acquire four SEM images per electrode. Additionally, to visualize the elemental distribution on the electrode surface via EDX a Bruker Quantax FlatQuad spectrometer (Bruker Nanoanalytics, Berlin, Germany) with the Software Esprit was used. In order to excite the L-alpha line of Pt an electron acceleration voltage of 18 kV was chosen. The beam current amounted to approximate 250 pA throughout the experiments. The elemental distribution was mapped as a grey-scale image (white: high concentration of Ti on the surface; black: absence of Ti on the surface), which was then used for further processing with Fiji (Fiji is just ImageJ), Version: ImageJ 1.52p, https://imagej.net/Fiji. For convenience, the grey-scale image was subsequently inverted, so black refers to a high Ti concentration on the surface and white to the absence of Ti, which then shows the presence of Pt on the surface in this study. Afterwards, different threshold limits were set to determine the percentage of Pt, Ti, and the transition from one to the other element on the electrode surface. The percentage is calculated from the amount of pixels within a given threshold range divided by the amount of all pixels of the image. Within a threshold of 0–50 only Ti was considered being present on the surface, between a threshold of 50–100 it was considered as transition area, and with threshold from 100–255 only Pt was considered being present on the surface. For illustration purposes, the element map was also color coded, with green reflecting the presence of Pt on the electrode surface and red the presence of Ti (see Figure 3).

Data processing and calculations

Quantification of gas components: For quantification of individual components in gas mixtures data from the MFM and the microGC-TCD measurements were combined. This allowed to calculate the absolute amount of each gaseous component that was produced during electrolysis. First, the total molar norm volume of the gas mixture, \( V_{\text{norm}}^{\text{mix}} \), was calculated as the sum of the incremental molar norm volumes, \( \Delta V_{\text{norm}}^{\text{m}} \), as follows [Eq. (1)]:

\[
V_{\text{norm}}^{\text{mix}} = \sum \Delta V_{\text{norm}}^{\text{m}}
\]

with Equation (2):

\[
\Delta V_{\text{norm}}^{\text{m}} = \frac{y_i}{100\%} \cdot V_{\text{norm}}^{\text{m}} \quad \text{and} \quad \Delta V_{\text{norm}}^{\text{m}} = \frac{M_i}{\rho_i^{\text{norm}}}
\]

where \( M_i \) is the molecular weight of the gaseous component \( i \), \( \rho_i^{\text{norm}} \) is the gas density of the component \( i \) at norm conditions, and \( y_i \) the mole fraction [%] of each individual gas component \( i \) measured (see “Gas-phase analysis”). This and all following calculations were performed for each sampling point individually. Norm conditions are defined as \( T = 273.15 \, \text{K} \) and \( p = 1.01325 \, \text{bar} \) in this paper.

The volume fraction, \( q_i^{\text{norm}} \), is gained by Equation (3):

\[
q_i^{\text{norm}} = \frac{\Delta V_{\text{norm}}^{\text{m}}}{V_{\text{norm}}^{\text{mix}}} = \frac{C_i^{\text{calibrated}}}{C_i^{\text{calibrated}}}
\]

As each gaseous component shows a different response in the \( N_2 \)-calibrated MFM, the measured volume of the gas mixture is corrected by a conversion factor. The reciprocal conversion factor \( C_i^{\text{calibrated}} \) of the gas mixture is calculated as the sum of the reciprocal incremental conversion factors \( \Delta C_i^{-1} \) [Eq. (4)]:

\[
\frac{1}{C_{\text{mix}}} = \sum \frac{1}{\Delta C_i}
\]

with Equations (5) and (6):

\[
\Delta C_i = q_i^{\text{norm}} \cdot \frac{1}{C_i}
\]

\[
C_i = \frac{C_i^{\text{calibrated}}}{\rho_i^{\text{calibrated}}}
\]

where \( q_i^{\text{norm}} \) is either the gas density of component \( i \) or that of the calibration gas of the MFM at norm conditions, \( C_i \) is either the specific heat capacity of component \( i \) or that of the calibration gas, and \( q_i^{\text{norm}} \) is the calculated volume fraction of each gas component [see Eq. (3)].

The actual incremental gas volume \( \Delta V_{\text{norm}}^{\text{measured}} \) of the gas mixture is determined via the average of the conversion factors \( C_{\text{mix,2}} \) of two successive gas measurements denominated as \( t_{\text{end}} \) and \( t_{\text{start}} \), calculated with Equation (4), and the measured incremental gas volume \( \Delta V_{\text{norm,calculated}}^{\text{measured}} \) of the gas mixture between these two points in time [Eq. (7)]:

\[
\Delta V_{\text{norm,real}}^{\text{measured}} = \frac{C_{\text{mix,2}} - C_{\text{mix,1}}}{2} \times \Delta V_{\text{norm,measured}}
\]

Up to this point the calculation is based on norm conditions since these are the calibration conditions for the MFM. Therefore, a conversion to standard conditions (STP) is necessary [Eq. (8)]. Standard conditions are defined as \( T = 273.15 \, \text{K} \) and \( p = 1.00 \, \text{bar} \) according to the IUPAC definition.

\[
\Delta V_{\text{STP,real}}^{\text{measured}} = \frac{\Delta V_{\text{norm,calculated}}^{\text{measured}}}{p_{\text{STP}}} \rho_{\text{STP}}
\]

To calculate the absolute amount of substance of each component \( n_i \), the incremental amounts of substance \( \Delta n_i \) are summed up [Eq. (9)]:
where $n_i$ is the amount of each substance in mol, $z_i$ is the number of transferred electrons, and $F$ is the Faraday constant (96,485 C mol$^{-1}$). The carbon balance, yield, selectivity, and rates of the electrolysis were calculated according to Equation (19):
related to the amount of all products formed (excluding CO₂, H₂ and O₂) [Eq. (20)]:

\[ S_{\text{decane}} = \frac{n_{\text{decane}}}{\sum n_{\text{products}}} \times 100\% \]  

(20)

For determining the consumption rate \( (r_i) \) of \( n \)-hexanoic acid and the production rate of \( n \)-decane, the degraded or produced amount of respective substance \( (\Delta n_i) \) was divided by the electrode surface area \( (A_{\text{electrode surface}} = 2 \text{ cm}^2) \), the reaction volume \( (V = 0.2 \text{ L}) \) and the electrolysis time \( (t = 4 \text{ h}) \) [Eq. (21)]:

\[ r_i = \frac{\Delta n_i}{A_{\text{electrode surface}} \times V \times t} \]  

(21)

Statistical analysis: All experiments were done in at least three independent replicates \( (n \geq 3) \). In this regard independent replicates means that the \( n \)-hexanoic acid solution, the following electrolysis of the solution, and finally the sample preparation were performed fully independent for each single replicate. All values are given as the mean ± confidence interval \( (CI, \alpha = 0.05) \) if not stated otherwise.

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Conflict of Interest

The authors declare no conflict of interest.

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[1] D. Yue, F. You, S. W. Snyder, Comput. Chem. Eng. 2014, 66, 36–56.
[2] A. Reichel, M. De Schoenmakere, J. Gillabel, Circular Economy in Europe – Developing the Knowledge Base (European Environment Agency Report No 2/2016), 2016.
[3] European Commission, Communication from the Commission to the European Parliament, the European Council, the Council, the European Economic and Social Committee and the Committee of the Regions The European Green Deal 117 Final European Commission, 2019, https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:52019DC0640.
[4] B. R. de Vasconcelos, J. M. Lavoie, Front. Chem. 2019, 7, 392.
[5] F. Harnisch, U. Schröder, ChemElectroChem 2019, 6, 4126–4133.
[6] H. G. Cha, K. S. Choi, Nat. Chem. 2015, 7, 328–333.
[7] Y. Kwan, K. J. P. Schouten, J. C. Van Der Waal, E. De Jong, M. T. M. Koper, ACS Catal. 2016, 6, 6704–6717.
[8] F. Harnisch, C. Urban, Angew. Chem. Int. Ed. 2018, 57, 10016–10023; Angew. Chem. 2018, 130, 10168–10175.
[9] T. Brinkmann, G. Giner Santonja, F. Schorcht, S. Roudier, L. Delgado Sanchez, Ind. Emiss. Dir. 2010/75/EU (Integrated Pollut. Prev. Control EUR 26844. Luxemb. Publ. Off. Eur. Union. JRC91156 2014, DOI: 10.2791/13138.
[10] J. E. Matthesen, J. M. Carraher, M. Vasilii, D. A. Dixon, J. P. Tessonnier, ACS Sustainable Chem. Eng. 2016, 4, 3575–3585.
[11] Y. Hori, H. Wakebe, T. Tsukamoto, O. Koga, Electrochim. Acta 1994, 39, 1833–1839.
[12] F. Harnisch, U. Schröder, ChemSusChem 2016, 9, 50–60.
[13] C. Urban, J. Xu, H. Sträuber, T. R. Dos Santos Dantas, J. Mülhenberg, C. Härtig, L. T. Angelent, F. Harnisch, Energy Environ. Sci. 2017, 10, 2231–2244.
[14] C. Stang, F. Harnisch, ChemSusChem 2017, 10, 1378–1389.
[15] Y. Qiu, J. A. Lopez-Ruiz, U. Sanyal, E. Andrews, O. Y. Gutiérrez, J. D. Holladay, Appl. Catal. B 2020, 277, 119277.
[16] J. D. Wadhawan, F. J. Del Campo, R. G. Compton, J. S. Foord, F. Marken, S. D. Bull, S. D. Davies, O. J. Walton, S. Ryley, J. Electroanal. Chem. 2001, 507, 135–143.
[17] F. Harnisch, U. Schröder, F. Scholz, Environ. Sci. Technol. 2008, 42, 1740–1746.
[18] P. Nilges, T. R. Dos Santos, F. Harnisch, U. Schröder, Energy Environ. Sci. 2012, 5, 5231–5235.
[19] H.-J. Schäfer in Electrochemistry IV (Ed.: E. Steckhan), Springer-Verlag, Berlin, Heidelberg, 1990.
[20] L. F. Arenas, C. Ponce de León, F. C. Walsh, J. Electrochem. Soc. 2020, 167, 23504.
[21] M. R. Tabar, M. Anvari, G. Lohmann, D. Heinemann, M. Wächter, P. Milan, E. Lorenz, J. Peinke, Appl. Catal. B 2012, 116, 268–2684.
[22] M. R. Tabar, M. Anvari, G. Lohmann, D. Heinemann, M. Wächter, P. Milan, E. Lorenz, J. Peinke, Appl. Catal. B 2012, 116, 268–2684.
[23] B. Gates, “Introducing the Green Premiums,” can be found under https://www.gatesnotes.com/Introducing-the-Green-Premiums, 2020.
[24] N. Nitta, F. Wu, J. T. Lee, G. Yushin, Mater. Today 2015, 18, 252–264.
[25] Y. R. Ji, S. T. Weng, X. Y. Li, Q. H. Zhang, L. Gu, Rare Met. 2020, 39, 205–217.
[26] F. Harnisch, M. C. Morejón, Chem. Rec. 2021, tcr.202100034.
[27] S. Zheng, J. Yan, K. Wang, Engineering 2021, 7, 22–32.
[28] D. E. Blanco, B. Lee, M. A. Modestino, Proc. Natl. Acad. Sci. USA 2019, 116, 17683–17689.
[29] J. Schindelin, I. Arganda-Carreras, E. Frise, V. Kaynig, M. Longair, T. Pietzsch, S. Preibisch, C. Rueden, S. Saalfeld, B. Schmid, J. Y. Tinevez, D. J. White, V. Hartenstein, K. Elsberry, P. Tomancak, A. Cardona, Nat. Methods 2012, 9, 676–682.