

Electrooxidation of the Glycerol Derivative Solketal over Cu–Co Hydroxycarbonates to Enable the Synthesis of Glyceric Acid

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The glycerol oxidation reaction (GOR) has high potential in substituting the oxygen evolution reaction (OER) in electrochemical water splitting, enabling the synthesis of value-added organic products. The Cu-rich Cu–Co hydroxycarbonates show high activity in GOR and promote formate production but undergo severe Cu leaching in the presence of deprotonated glycerol. In this work, the electrooxidation of solketal (SOR), acetal-protected glycerol, is explored over a series of Cu–Co hydroxycarbonates, to promote the formation of glycerol-

derived C3 products, such as glyceric acid, with faradaic efficiencies of around 70%, and to limit the Cu leaching from the catalyst. The competition between OER and SOR was evaluated using rotating disk electrodes and differential electrochemical mass spectrometry. Insights into the solketal deacetalization as a function of potential are obtained using in situ spectroscopic methods. The solketal/OH⁻ ratio influences the reaction selectivity, with oxalate production increasing when 7 M KOH is used instead of 1 M KOH.

Introduction

The electrochemical glycerol oxidation reaction (GOR) is seen as a possible reaction to substitute the oxygen evolution reaction (OER) in water splitting leading to an increased cost-efficiency for H₂ production via water electrolysis. Using GOR, valuable products can be synthesized at the anode by converting the triol, an abundant, inexpensive by-product from biodiesel production,^[1] to more valuable products than O₂, ideally at lower potentials. Various valuable products with one to three carbon atoms can be obtained by GOR, making GOR often referred to as a type of electroreforming, in which gaining

control over reaction selectivity becomes critically important.^[2,3] On non-noble metal-based electrocatalysts, glycerol usually undergoes C–C cleavage in an alkaline environment, which generates a mixture of C1, C2, and C3 products, with formic acid being the major product.^[4–11] Although there are reports of the preparation of non-formic acid products based on non-noble metal electrocatalysts, especially at near neutral pH,^[12–15] the formation of high yields of C3 products in the alkaline electrolyte, remains challenging. The synthesis of C3 products is of great interest due to their relatively high value. For example, glyceric acid has a market price of \$ 126 per kg in 2022,^[16] being more than a hundred times more valuable than formic acid (\$ 0.4–\$ 1.0 per kg in 2022^[17,18]) and provides a wide range of applications, especially in the field of medicine, in the synthesis of amino acids or the treatment of skin diseases.^[19,20]

To enable the synthesis of C3 products via GOR, C–C cleavage must be avoided, and to achieve this, different strategies were employed to protect the glycerol molecule.^[13,21] For example, Huang et al. found that adding borate ions to the alcohol-containing electrolyte allowed the coordination with glycerol, converting glycerol into a secondary alcohol and facilitating the synthesis of dihydroxyacetone with enhanced faradaic efficiency. We recently used solketal, a primary monoalcohol derived from glycerol by its ketalization with acetone, to promote glyceric acid formation over Ni-based electrocatalysts.^[21]

Cu and Co bimetallic catalysts emerged as potential GOR electrocatalysts in the last years, with studies conducted using Cu- and Co-based oxides,^[4,22–24] phosphides,^[25] and hydroxycarbonates.^[26] Han et al.^[4] showed that the combination of Co with Cu in a series of Co-based spinel oxides with different transition metals has the highest GOR activity, along with high selectivity for formic acid. In addition, Xie et al.^[25] proved that the mixed Co and Cu phosphide (CoP–Cu₃P) catalyst

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showed a higher GOR electrocatalytic activity than the monometallic CoP and Cu₃P. Using CoP-Cu₃P, only a potential of 1.13 V vs. RHE was required to reach the current density of 10 mA/cm², and formic acid and oxalic acid were the main products. Overall, the GOR electrocatalytic activity of the reported bimetallic Cu and Co catalysts was higher in strong alkaline electrolyte, compared to the monometallic ones.^[4,24–26] Still, several reports indicate a partial Co enrichment of the catalyst surface during the electrochemical experiments.^[25]

In previous studies, we explored Cu–Co hydroxycarbonates (Cu_{1-x}Co_x)₂CO₃(OH)₂ in the whole range of Cu–Co substitution (0 ≤ x ≤ 1) for the alcohol electrooxidation, including GOR and a full characterization of the fresh and spent catalysts.^[26] The Cu:Co ratio influenced the GOR activity, with the Cu:Co 80:20 hydroxycarbonate showing the highest initial electrocatalytic activity in the series, leading to formic acid as the predominant product. In addition, we observed that the Cu:Co 80:20 catalyst undergoes a fast deactivation in the presence of vicinal alcohols due to the formation of a stable complex^[27,28] between the deprotonated and bidentate alcohol in the alkaline environment and the Cu²⁺ ions present in the catalyst structure, resulting in the leaching of Cu²⁺ from the hydroxycarbonate structure.^[26] Thus, further insights about how the Cu–Co bimetallic catalyst's stability can be increased and if selectivity modulation towards C3 products is possible are required.

In this work, we studied the Cu–Co hydroxycarbonates as electrocatalysts for the solketal electrooxidation to enable the synthesis of C3 products while at the same time protecting the catalyst against the leaching of Cu²⁺. Rotating disk electrode measurements were initially used to assess the electrocatalytic activity, while the reaction selectivity was measured during prolonged electrolysis in a batch-type reactor under flow recirculation. In addition, the influence of the KOH concentration on the SOR selectivity was investigated in 7 M KOH. Differential electrochemical mass spectrometry (DEMS) and Otto attenuated total reflection–Fourier-transform infrared spectroscopy (Otto ATR-FTIR) measurements were performed to determine the contribution of oxygen evolution and key intermediates produced during the reaction, respectively.

Results and Discussion

To evaluate the activity of the Cu–Co hydroxycarbonate series towards the electrooxidation of solketal and to initially assess their stability, three consecutive cyclic voltammograms (CVs) were recorded using the rotating disk electrode (RDE) method (Figure 1). The recorded CVs show a different profile depending on the Cu:Co ratio of the hydroxycarbonates. While on the Cu-only hydroxycarbonate, very low currents were recorded, indicating no electrocatalytic activity neither for the OER nor the SOR, on the Co-only hydroxycarbonate, an exponential increase of the current is observed at potentials above ≈ 1.54 V vs. RHE, indicating OER as the main reaction (Figure 1b). For the mixed Cu–Co hydroxycarbonates, two regions can be identified, marked by an initial increase of the current at potentials ≈ 1.40–1.50 V vs. RHE, followed by an exponential increase of

the current at potentials higher than 1.55 V vs. RHE. The recorded currents and the slope registered in both regions strongly depend on the Cu:Co ratio, indicating that the hydroxycarbonate composition influences the competition between SOR and OER. Using the RDE method, the Cu–Co hydroxycarbonates with a Cu:Co ratio of 80:20 and 60:40 seem to be the most active SOR catalysts, with a current increase starting at ≈ 1.40 V vs. RHE. For the Cu:Co 80:20 catalyst, a stronger increase in the oxidation currents is observed at lower potentials than for the Cu:Co 60:40 catalyst, suggesting an earlier change in the reaction from SOR to OER once the potential reaches a value of ≈ 1.50 V vs. RHE. Interestingly, at potentials above 1.65 V vs. RHE, higher current densities were recorded for the Co-rich catalysts, as observed for Cu:Co 20:80 followed by Cu:Co 40:60 (Figure 1a), likely due to the higher activity of these catalysts in the competing OER.^[26]

By evaluating the evolution of the anodic current recorded at a defined potential of 1.50 V vs. RHE over the three consecutive CVs, we observed a slight increase of the activity with each CV for all compositions (Figure 1c), most pronounced for the Cu-rich ones (Cu:Co 80:20 to Cu:Co 50:50). The corresponding CVs are depicted in Figure S1. A similar trend of increasing activity was also observed during the ethanol oxidation reaction (EOR), which contrasts with our observations during the GOR on the Cu-rich compositions, for example, for Cu:Co 80:20, where the currents at 1.5 V vs. RHE decreased to a quarter within three CVs.^[26] The increased activity recorded over the three consecutive CVs in the SOR on the other hand indicates no catalyst deactivation and supports the initial assumption that solketal cannot leach out Cu²⁺ from the hydroxycarbonate structure. To test this conjecture, the hydroxycarbonate with a Cu:Co ratio of 80:20 was immersed in 1 M KOH and 0.1 M solketal and stirred at room temperature for 4 h, followed by inductively coupled plasma-optical emission spectrometry (ICP-OES) measurements of the recovered catalyst powder. As expected, the Cu:Co ratio remained constant before (Cu:Co 82:18) and after (Cu:Co 83:17) the leaching experiment. In contrast, we observed in the previous study that in the glycerol-containing 1 M KOH the Cu content decreased to 60 at.% using the otherwise same procedure.^[26] In an alkaline environment, the glycerol's vicinal alcohol groups are deprotonated, leading to the formation of a stable Cu polyalcohol complex^[28] and, thus to the Cu leaching from the catalyst structure. For monoalcohols, this is not the case since the formation of the complex requires the presence of deprotonated vicinal alcohols that can act as bidentate ligands. Therefore, also the use of monohydric solketal was not expected to leach Cu²⁺ ions from the hydroxycarbonate structure.

Figure 1d compares the first CVs on Cu:Co 60:40 for several alcohol-containing 1 M KOH solutions and with pure 1 M KOH. At potentials > 1.55 V vs. RHE, the currents recorded in 1 M KOH are higher than in the presence of any of the shown alcohols. Moreover, in the glycerol-containing electrolyte, the lowest current densities were recorded. Thus, we assume that the presence of solketal or ethanol cannot suppress OER to the same extent as glycerol. In addition, it can be noticed that the CV recorded in the presence of solketal follows a similar current

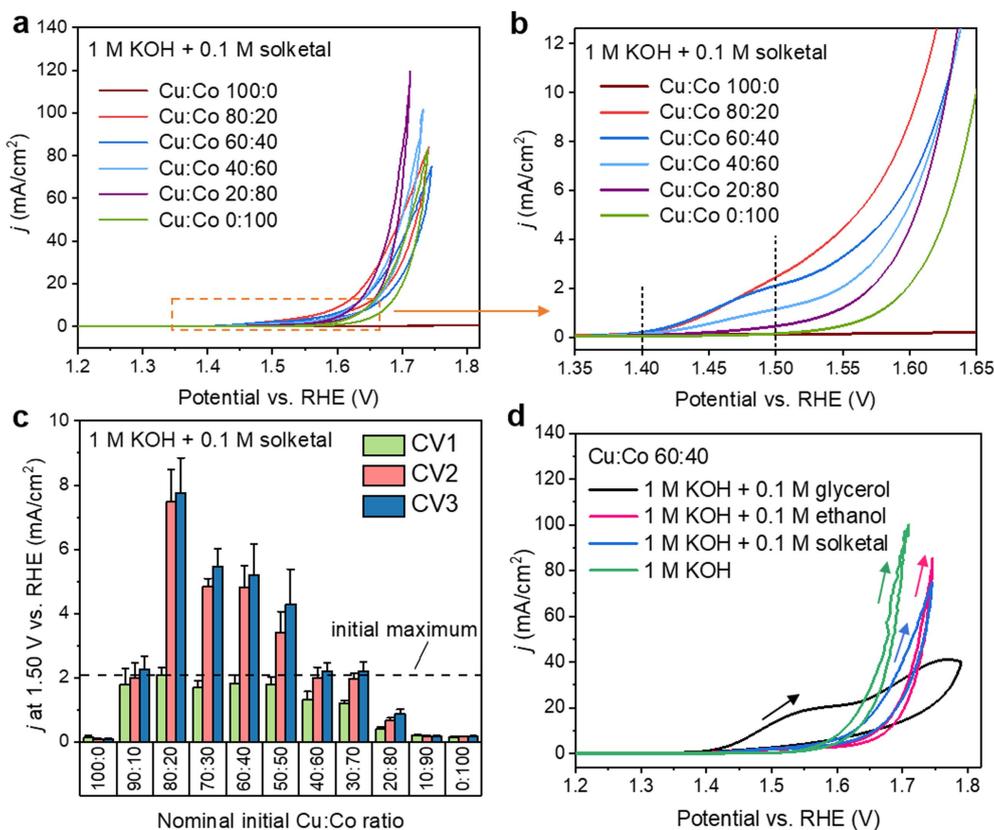


Figure 1. Cyclic voltammograms recorded during RDE measurements in 0.1 M solketal and 1 M KOH in the potential window from 1.0 V to 1.8 V vs. RHE (with iR-correction) with a scan rate of 5 mV/s at 1600 rpm for the Cu–Co hydroxycarbonate series. a) First CV cycle of the series from selected catalysts. b) Anodic scan of the first CV showing that the current starts at a potential 1.40 V vs. RHE and the Cu:Co 80:20 and 60:40 are the most active catalyst in the series at 1.50 V vs. RHE. c) Current density of three consecutive CVs recorded on RDE at the potential of 1.50 V vs. RHE as a function of the Cu:Co ratio in the Cu–Co hydroxycarbonate series. d) Comparison of the CVs recorded in 1 M KOH and 1 M KOH + 0.1 M alcohol (glycerol, ethanol or solketal) using Cu:Co 60:40. The data from 1 M KOH and 1 M KOH + 0.1 M glycerol and ethanol was reproduced from Ref [26]. Copyright (2022) ChemElectroChem published by Wiley-VCH GmbH.

profile as the one recorded in ethanol, which is also a primary monoalcohol, while significant differences are noticed compared with those recorded in the glycerol-containing electrolyte. These results further support that SOR follows a similar mechanism as EOR.

The contribution of OER to the currents recorded in the solketal containing electrolyte was further evaluated by DEMS in 1 M KOH and 0.1 M solketal, for the Cu:Co 60:40 and Cu:Co 80:20 hydroxycarbonates (Figure 2). These materials were selected since they show the highest SOR activity and have not only different Cu:Co ratios, but also different crystalline structures (malachite, Cu:Co 80:20 and kolwezite/rosasite, Cu:Co 60:40), respectively, as revealed in our previous study.^[26] The CVs recorded during the DEMS measurements show a similar behavior as those recorded during the RDE measurements (Figures 1a,b). A shift between the recorded current and the derived partial O₂ current from the *m/z* 32 signal can be observed in the potential range of ≈ 1.40 – 1.60 V vs. RHE, similar to the results obtained by RDE in the absence and presence of solketal. Based on this, it can be concluded that between ≈ 1.40 – 1.55 V vs. RHE, the SOR is the only reaction proceeding. At potentials higher than ≈ 1.65 V the recorded currents match the derived O₂ currents, indicating that OER becomes the

dominant reaction at high overpotentials, again showing a similar result compared with the oxidation of ethanol over Cu:Co 80:20.^[26]

The SOR selectivity over the two Cu–Co hydroxycarbonates was further investigated in a batch-type, two-compartment electrolyzer under continuous flow recirculation (abbreviated in the following as “flow cell”). The potential was set to 1.5 V vs. RHE for 4 h, and liquid samples, collected each hour from the anolyte and catholyte, were analyzed by high-performance liquid chromatography (HPLC). Representative chromatograms after the electrooxidation with Cu:Co 80:20 in 0.1 M solketal and 1 M KOH are presented in Figure S2. Before the HPLC analysis, the samples were acidified, inducing the hydrolysis of the acetal-protecting group from the unreacted solketal as well as of its derived oxidation products, releasing acetone and glycerol or glycerol-type derived products. This enables the detection of SOR products in the form of their conjugated acids, which therefore are referred to as such throughout this study. In 1 M KOH + 0.1 M solketal, higher currents are recorded for the Cu:Co 60:40 catalyst than for Cu:Co 80:20 (Figure 3a), but the currents decrease over the time of the experiment. On Cu:Co 80:20, a slight increase in the current can be noticed during the first hour of electrolysis followed by a stable current over

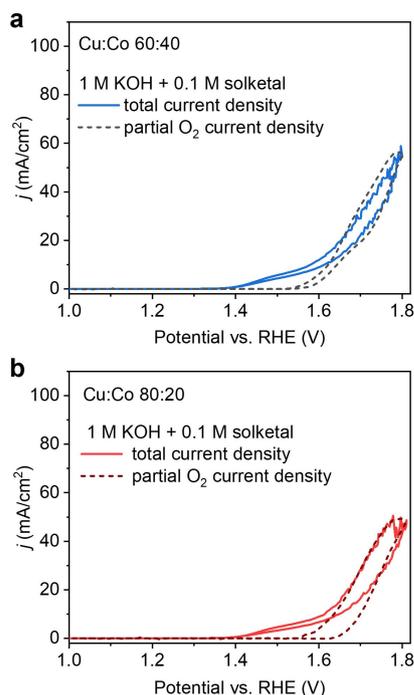


Figure 2. Differential electrochemical mass spectrometry (DEMS) measurements performed using a faraday cup detector in the potential window of 1.0 V to 1.8 V vs. RHE (without iR-correction) with the scan rate of 2 mV/s in 0.1 M solketal in 1 M KOH over Cu:Co 60:40 (a) and Cu:Co 80:20 (b). Electrochemical CVs (solid line) and the corresponding mass spectrometric CVs for the OER m/z 32 signal (dashed line) are shown.

the next 3 h. The decay observed for the Cu:Co 60:40 catalyst may be explained by the depletion of solketal, which undergoes almost 50% conversion during the 4 h electrolysis (Figure 3b). In contrast, the Cu:Co 80:20 catalyst only reaches a maximum of $\approx 25\%$ conversion after 4 h, which cannot explain the observed increase of the current (Figures 3a,b).

A possible explanation is that the Cu:Co 80:20 experiences a partial Cu leaching from its structure once solketal molecules get partially hydrolyzed under the local proton-enriched environment during the oxidation reaction at the anode, which in turn would activate the catalyst, as reported in our previous study.^[26] To verify possible leaching of Cu^{2+} during the electrolysis, we performed energy-dispersive X-ray spectroscopy (EDX) measurements on the spray-coated Cu:Co 80:20 and Cu:Co 60:40 electrodes before and after the electrolysis. While the Cu:Co ratios were close to the nominal Cu:Co ratios with Cu:Co 79:21 and 60:40 before the electrolysis, the corresponding Cu:Co ratios after the electrolysis changed significantly to Cu:Co 61:39 and 38:62, respectively, indicating leaching of Cu^{2+} during the electrochemical reaction. Still, the decrease in the Cu content is lower than the decrease recorded in glycerol-containing electrolyte.^[26]

The partial hydrolyzation of the solketal at 1.50 V vs. RHE may also be supported by the product distribution recorded over the two catalysts. On Cu:Co 80:20, the formation of formic acid, the main product of the glycerol electrooxidation, is observed with slightly higher efficiency than Cu:Co 60:40. Still, on both catalysts, glyceric acid is the main product with faradaic

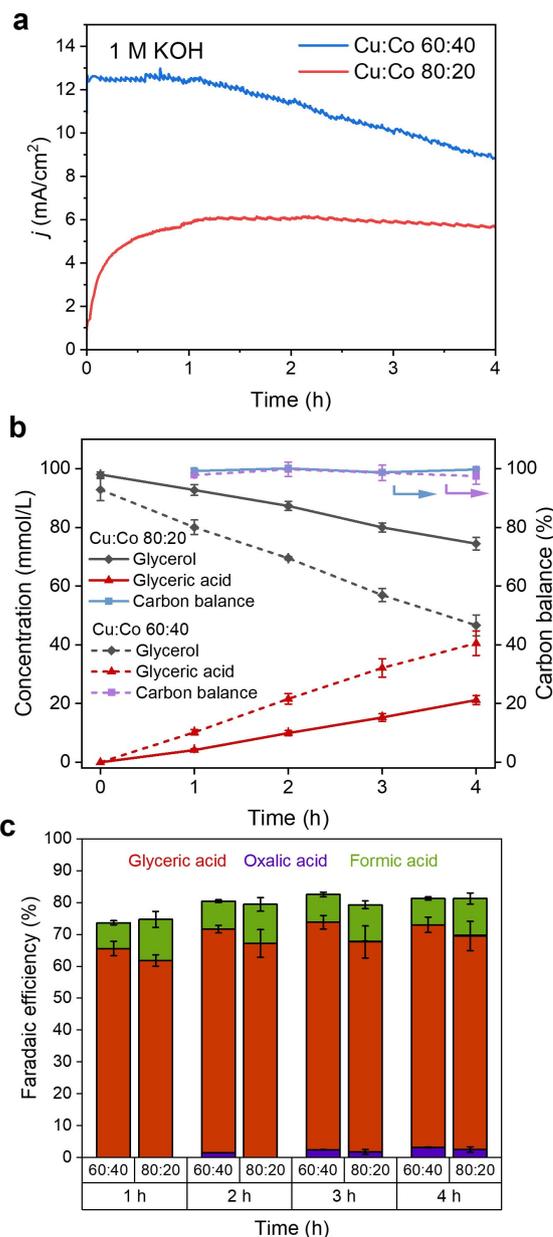


Figure 3. a) Chronoamperometric measurement performed with Cu:Co 80:20 and Cu:Co 60:40 in 1 M KOH and 0.1 M solketal for 4 h. b) Glycerol and glyceric acid concentration and the corresponding carbon balance during the time of the experiment. To enhance clarity, the contributions of minor products such as formic acid and oxalic acid are not shown. c) Faradaic efficiency of the different oxidative products from solketal conversion per hour interval.

efficiencies (FEs) of $\approx 70\%$. Besides formic acid and glyceric acid, oxalic acid is also detected in low amounts over the two catalysts, with a slight increase in oxalic acid production over prolonged electrolysis (Figure 3c).

To investigate intermediates prior to the acidic cleavage of solketal and the acetal-protecting group, Otto ATR-FTIR measurements were performed at 1.58 and 1.83 V vs. RHE in accordance with the procedure described beforehand by Cychy et al.^[21] (Figure 4). At 1.58 V vs. RHE, a current density of ca. 7 mA/cm² was obtained, only decreasing slowly over the course

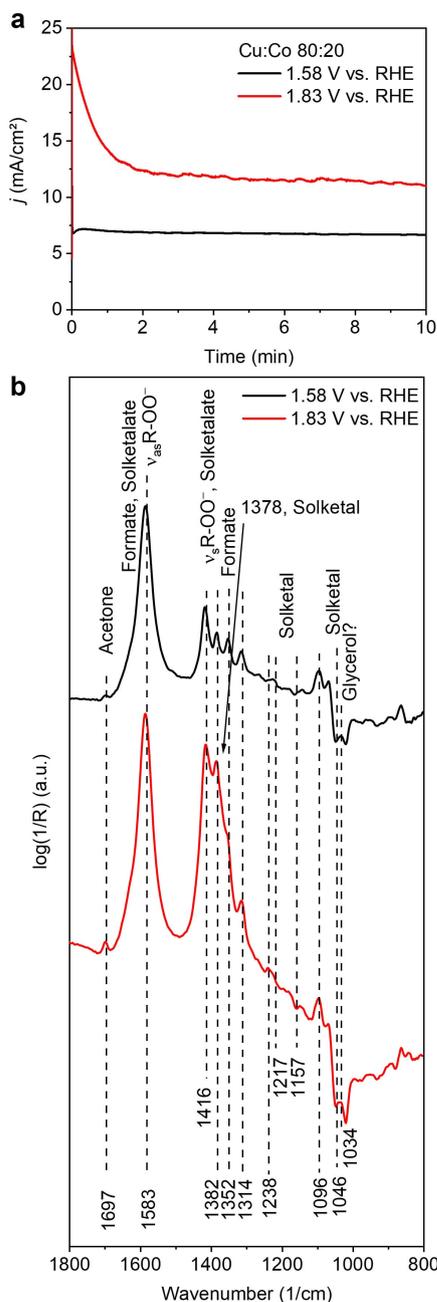


Figure 4. a) Chronoamperometric measurement performed on Cu:Co 80:20 in 1 M KOH and 0.1 M solketal in the spectroelectrochemical cell at $150 \mu\text{m}$ d_{TL} and an applied flow rate of $5 \mu\text{L}/\text{min}$ at 1.58 V and 1.83 V vs. RHE, respectively. b) Corresponding in situ ATR-FTIR spectra after 10 min electrolysis for both potentials.

of the experiment. In line with the experiment in Figure 3a, an initial increase of the activity is observable, which is less pronounced and shorter due to the restricted volume in the thin film cell and thus faster achievement of high conversions. However, when the potential is increased to 1.83 V vs. RHE the resulting current is much higher with $23 \text{ mA}/\text{cm}^2$ yet decreasing rapidly to $12 \text{ mA}/\text{cm}^2$ at 2 min. Afterwards, the deactivation kinetics are slower and overlaid with reactant depletion in the thin film. The current remains stable, but deactivation kinetics

are slightly faster than at the lower potential. At a potential of 1.58 V vs. RHE, a well-resolved spectrum is obtained showing negative (downwards pointing) bands indicating solketal depletion at 1217 , 1157 , and 1046 cm^{-1} . Solketal shows an adsorption band at 1378 cm^{-1} , but this overlaps with the bands of formate (1382 and 1352 cm^{-1}) and thus its depletion cannot be observed in this case. This shows that formate is already formed during electrolysis and does not or does not only form due to the acid treatment after the electrolysis (Figure 3c). The band at 1583 cm^{-1} is a superimposition of the formate, solketalate, and other possible $\nu_{\text{as}}(-\text{COO}^-)$ vibrations. The existence of solketalate is proven by the positive band at 1416 cm^{-1} . Upon oxidation of the solketal/solketalate, acetone is also observed at 1697 cm^{-1} , indicating a deprotection of the vicinal alcohol groups. This supports the hypothesis of activation of the catalyst Cu:Co 80:20 via Cu leaching since vicinal alcohols were shown to strongly promote this in an alkaline electrolyte. Additionally, the band at 1314 cm^{-1} also indicates oxalate formation. In principle, the spectrum recorded at a higher potential of 1.83 V looks quite similar, the differences are only due to higher conversion, i.e., higher intensity of the bands and changed selectivity towards a higher fraction of formate. The latter is evident in the more similar intensity of the solketalate band at 1416 cm^{-1} and the formate band at 1382 cm^{-1} .

Since alkaline water electrolysis runs in highly concentrated alkaline electrolyte, we evaluate the SOR also in 7 M KOH, the equivalent of the 30 wt.% KOH used in alkaline electrolyzers. Thus, the evaluation of activity and selectivity becomes relevant, especially since previous reports showed that the alcohol/ OH^- ratio can influence the alcohol oxidation reaction selectivity.^[11,29–31] The first CVs recorded during RDE measurements are shown in Figure S3 for the Cu:Co 80:20 and Cu:Co 60:40 catalysts. An increase of the recorded currents occurs at a lower potential of about 130 mV to 135 mV in the presence of solketal compared with the 7 M KOH only electrolyte, without significant changes in the shape of the CVs (Figures S3a,b). However, the Cu:Co 60:40 catalyst shows a higher activity than the Cu:Co 80:20 in 7 M and 0.1 M solketal, opposite to the trend observed in 1 M KOH and 0.1 M solketal (Figure S3c and Figure 1b). Additionally, the currents are higher in the 7 M electrolyte than in 1 M KOH (Figure S4). The influence of the solketal/ OH^- ratio on the SOR selectivity was further investigated for Cu:Co 80:20 and 60:40 in flow cell measurements. It can be observed that the Cu:Co 80:20 catalyst shows an activation in 7 M KOH and 0.1 M solketal within the first hour and even reached higher current densities than the Cu:Co 60:40 catalyst after 15 min (Figure 5a). The observed activation of Cu:Co 80:20 follow same trend as in 1 M KOH solution.^[26] In contrast, Cu:Co 60:40 shows a fast current decay at the beginning, followed by a constant decline of the currents (Figure 5a). While the fast current decay at the beginning may result from catalyst deactivation, the constant decline over the rest of the experiment can be attributed to continuous solketal depletion. Approximately 25% of solketal was converted over both catalysts.

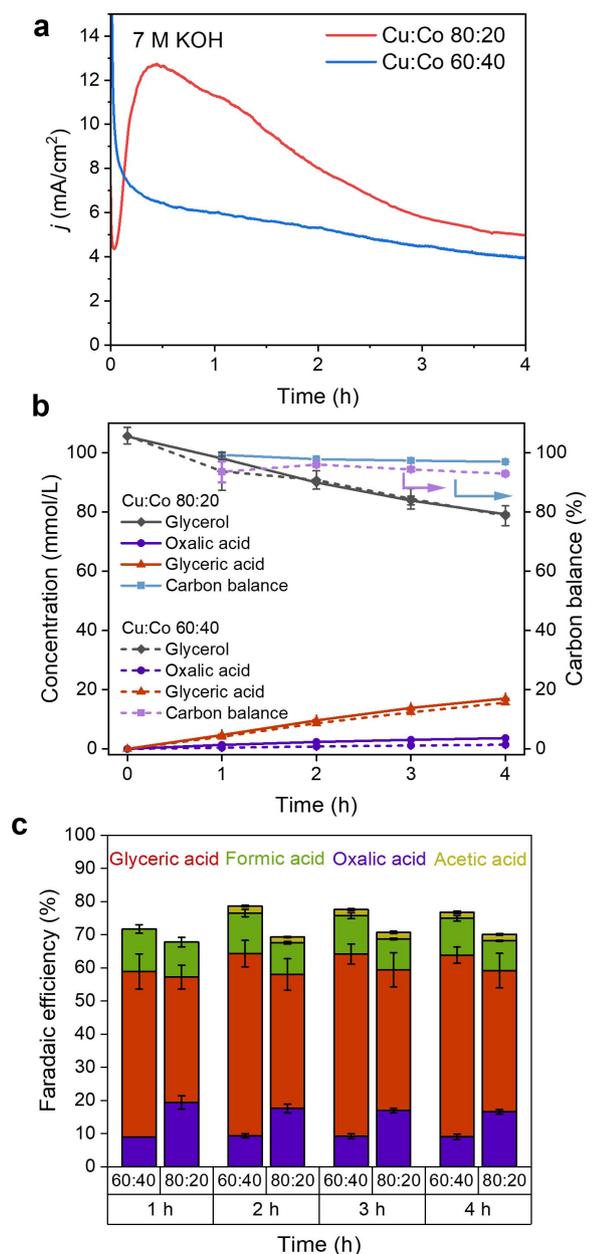


Figure 5. a) Chronoamperometric measurements performed with Cu:Co 80:20 and Cu:Co 60:40 in 0.1 M solketal and 7 M KOH for 4 h. b) Glycerol, oxalic acid, and glyceric acid concentration and the corresponding carbon balance during the time of the experiment. To enhance clarity, the contributions of minor products such as formic acid and acetic acid are not shown. c) Faradaic efficiency for the oxidative products from solketal conversion per hour interval.

Interestingly, a drastic change of the product selectivity is observed for 7 M KOH compared with 1 M KOH (Table 1). The FEs for the main product glyceric acid dropped to $43 \pm 5\%$ and $55 \pm 2\%$ for Cu:Co 80:20 and Cu:Co 60:40, respectively, while the FE towards the oxalic acid production increased significantly to $16.5 \pm 0.7\%$ for Cu:Co 80:20 and $9.0 \pm 0.8\%$ for Cu:Co 60:40. Furthermore, a decrease in the total FEs for Cu:Co 80:20 and 60:40 in 7 M KOH of up to 5–10% was observed, indicating that an increased KOH concentration may lead to a more pronounced formation of CO₂ or O₂. In addition, small amounts of acetic acid were formed. Due to the highly oxidative environment, the acetal moiety may be cleaved off, and the resulting intermediates and products can undergo C–C cleavage to form oxalic acid, acetic acid, formic acid, and CO₂ (carbonate in alkaline media), as previously described.^[21] Consequently, the increased amount of oxalic acid could result from the known cleavage of glyceric acid into formic acid and glycolic acid, which could be further oxidized to oxalic acid.^[4,7,32] We tested this hypothesis using Cu:Co 60:40 in 1 M KOH and 0.1 M glyceric acid and found oxalic acid and formic acid as the main products, while glycolic acid was only detected in small amounts, indicating that the electrooxidation of glyceric acid can indeed produce oxalic acid over the Cu:Co 60:40 hydroxycarbonate (Figure S5) under even milder conditions. The formation of oxalic acid with high concentrations has been reported before for NiO_x/MWCNTs–Ox. in 7 M KOH during glycerol oxidation reaction.^[11] However, no C3 product was obtained in that case. In contrast, during SOR in 7 M KOH the protective group can partly suppress the C–C cleavage and/or further oxidation of the C3 molecules and allows a higher selectivity towards glyceric acid even under the conditions of a highly alkaline industrial electrolyzer (Table 1).

Conclusion

A series of Cu–Co hydroxycarbonates was investigated as electrocatalyst materials for electrooxidation of solketal (SOR). The bimetallic catalysts with higher Cu contents show a higher electrocatalytic activity compared with the Co- and Cu-only electrocatalysts and the Co-rich hydroxycarbonates. By using solketal instead of glycerol, an increase of the electrocatalytic activity is observed when consecutive cyclic voltammograms are run, indicating that solketal is not promoting Cu leaching, as previously observed for glycerol. SOR performed with the Cu–Co hydroxycarbonates follows a similar trend as the ethanol electrooxidation and the differential electrochemical mass

Table 1. Solketal conversion and the faradaic efficiency observed for the formation of glyceric acid and oxalic acid after 4 h of electrolysis using the hydroxycarbonates with a Cu:Co ratio of 80:20 and 60:40.

Cu:Co ratio	Electrolyte	Solketal Conversion [%]	Faradaic efficiency after 4 h of electrolysis at 1.5 V vs. RHE [%]	
			Glyceric acid	Oxalic acid
80:20	1 M KOH + 0.1 M solketal	25 ± 1	67 ± 4	2.5 ± 0.8
60:40	1 M KOH + 0.1 M solketal	51 ± 5	70 ± 2	3.0 ± 0.1
80:20	7 M KOH + 0.1 M solketal	26 ± 0.8	43 ± 5	16.5 ± 0.7
60:40	7 M KOH + 0.1 M solketal	27 ± 1	55 ± 2	9.0 ± 0.8

spectrometry (DEMS) measurements confirm that, like ethanol, solketal has no hindering effect on the oxygen evolution reaction at high overpotentials, as previously observed for glycerol. Faradaic efficiencies of $67 \pm 4\%$ and $70 \pm 2\%$ for glyceric acid were obtained in 1 M KOH and 0.1 M solketal over the hydroxycarbonates with Cu:Co ratios of 80:20 and 60:40, respectively. Despite the high selectivity towards C3 products, formate is still obtained but with lower faradaic efficiencies (FEs) compared with glycerol oxidation reaction. Otto attenuated total reflection-FTIR measurements show the partial deacetalization of solketal or of its oxidation products under reaction conditions, which may explain the formation of formate during SOR. Mimicking the conditions in industrial alkaline electrolyzers, the electrooxidation of SOR was further evaluated using Cu:Co 80:20 and Cu:Co 60:40 also in 7 M KOH. While glyceric acid is still the major product with FEs of $43 \pm 5\%$ and $55 \pm 2\%$ after 4 h electrolysis on the Cu:Co 80:20 and Cu:Co 60:40, an increased production of the C2 product oxalic acid with $16.5 \pm 0.7\%$ and $9.0 \pm 0.8\%$, respectively, is observed.

Experimental Section

Materials and reagents

Solketal (Thermo Scientific, 97%), glycerol (Fisher Scientific, $\geq 99\%$), ethanol (VWR International, 99.97%), Nafion (Sigma-Aldrich, 5 wt.% in lower aliphatic alcohols and water), Ni foam (Goodfellow), sulfuric acid (Merck, 98%), ammonium formate (Sigma-Aldrich, $\geq 99\%$), glycolic acid (Sigma-Aldrich, 99%), calcium L(-)-glycerate dihydrate ($\geq 97\%$, Alfa Aesar) and oxalic acid (Fluorochem, 100%) were used as purchased without further purification. KOH solutions (Fisher Scientific, 86.8%) were purified by a Chelex 100 cation-exchange resin (Sigma-Aldrich, 50–100 mesh) to remove metal impurities. All solutions were prepared with ultrapure water.

The Cu–Co hydroxycarbonate series was synthesized by constant-pH co-precipitation and subsequent precipitate aging under hydrothermal condition as described in detail in our previous study. Further details on the synthesis and characterization of the series can also be found there.^[26] The catalyst series was taken as such for the measurements in this study.

Electrochemical, leaching, EDX, ATR-FTIR and DEMS experiments

Evaluation of the electrochemical activity. A rotating disk electrode (RDE) was used to evaluate the electrochemical activity of the Co–Cu hydroxycarbonates used for solketal oxidation reaction (SOR). Cyclic voltammograms (CVs) were recorded using a potentiostat/galvanostat (PGSTAT302 N) coupled with the RDE setup using a three-electrode configuration cell. A catalyst-coated glassy carbon electrode (GC) was used as the working electrode, while a Pt coil, separated by a porous glass frit from the bulk electrolyte, was used as a counter electrode. A double junction Ag/AgCl (3 M KCl) was used as a reference electrode. Ar saturated 1 M KOH and 0.1 M solketal in 1 M KOH was used as an electrolyte for the respective OER and SOR measurements. KOH was purified using a cation exchange resin (Chelex) to remove the metal impurities. The catalytic ink was prepared by adding 1 mg of catalyst in a 200 μ L mixture of ethanol, water, and Nafion (from a 5 wt.% resin solution) in the volume ratio (49:49:2), which was sonicated to obtain a homogeneous ink. The catalyst ink was drop-casted on the pre-

polished glassy carbon to achieve a mass loading of 0.21 mg/cm² and dried under ambient conditions.

Before recording the CV, electrochemical impedance spectroscopy (EIS), was recorded at the open-circuit potential (OCP) with an amplitude of 10 mV (RMS) by sweeping the frequency in the 100 kHz to 0.1 kHz range to determine the uncompensated resistance (R_u). For the activity measurements, three consecutive CVs were recorded on RDE in the potential window of 0 V to 0.8 V vs. Ag/AgCl (3 M KCl) with a scan rate of 5 mV/s at 1600 rpm over the Cu–Co hydroxycarbonate series.

The recorded potentials were converted from the Ag/AgCl (3 M KCl) scale to the reversible hydrogen electrode (RHE) scale using Equations (1) and (2).

$$E_{\text{RHE}} = E_{\text{measured}} + E_{\text{Ag/AgCl (3 M KCl)}}^0 + 0.059 \text{ pH} - i \cdot R_u \quad (1)$$

$$\text{pH} = 14 + \log([\text{OH}^-]) + \log(\gamma) \quad (2)$$

E_{RHE} is the working electrode potential with reference to RHE, E_{measured} is the measured potential at the working electrode with reference to Ag/AgCl (3 M KCl), $E_{\text{Ag/AgCl (3 M KCl)}}^0$ is the formal potential of Ag/AgCl (3 M KCl) vs. RHE (0.207 V at 25 °C), pH denotes the pH value of the electrolyte. The pH was obtained considering the OH⁻ concentration and using an average value of $\gamma = 0.766$ ^[33–35] and $\gamma = 1.298$ ^[11,36] in for the activity coefficient of 1 M KOH and 7 M KOH, respectively [Eq. (2)].

Investigation of SOR selectivity. Chronoamperometric (CA) measurements were performed for Cu: Co 80: 20 and 60: 40 in 0.1 M solketal in 1 M KOH and 7 M KOH at the potential of 1.5 V vs. RHE for 4 h, to check the product selectivity using a three-electrode, two-chambered flow cell using VSP-150 (Biologic) controlled by EC-lab software. An anion exchange membrane (FAA-3-PK-130) was used to separate the anodic and cathodic compartments of the cell. A spray-coated catalyst-modified carbon paper (H23, Freudenberg with exposed geometric area = 0.95 cm²) with mass loading 0.5 mg/cm² was used as a working electrode, whereas Ni foam and a leakless Ag/AgCl (3.4 M KCl) were used as the counter electrode and reference electrode, respectively. The flow cell was connected to the respective reservoirs for the catholyte and anolyte containing 7 mL of 1 M KOH (catholyte) and 1 M KOH + 0.1 M solketal (anolyte) or 7 M KOH (catholyte) and 7 M KOH + 0.1 M solketal (anolyte), respectively. The electrolyte was circulated through both chambers with the help of a peristaltic pump at the constant flow rate of ca. 7 mL/min. The electrochemical impedance was recorded in the frequency range of 100 kHz to 0.1 kHz at OCP and the chronoamperometric measurements were performed at 1.5 V for 4 h. During the measurements, the electrolyte samples were collected at regular per-hour time intervals and acidified immediately with sulfuric acid for the subsequent HPLC analysis. To prepare the catalyst-modified carbon paper, a catalytic ink of concentration 1.3 mg/mL was prepared in a solution of ethanol and 0.2 vol.% of Nafion which was spray coated onto the carbon paper using a spray coater from Sensolytics along with heating the carbon support at 125 °C.

ICP-OES. Measurements were performed on an Avio 200 ICP Optical Emission Spectrometer equipped with a PerkinElmer S23 Autosampler. Leaching experiments were performed by mixing 400 mg of the Cu:Co 80:20 with 50 mL of a solution consisting of 1 M KOH and 0.1 M of solketal. The resulting mixture was then stirred at room temperature for 4 h. After the experiment, the product was separated from the supernatant by centrifugation and washed with DI water before it was dried in a vacuum oven for 24 h at 333 K. For calibration, external calibration standards were created from a

Supelco ICP multi-element standard solution IV from Sigma Aldrich with a concentration of 1000 mg/L and trace metal grade nitric acid to the final elemental concentrations.

EDX. Measurements were performed using an Ultra Dry Silicon Drift detector on a SEM-EDX coupled system from Thermo Fisher Scientific. The spray-coated Cu:Co 80:20 and 60:40 electrodes were used to analyze the leaching of Cu^{2+} before and after electrolysis in presence of 0.1 M solketal in 1 M KOH at the potential of 1.5 V vs. RHE. The samples were prepared by placing the spray-coated electrodes on a sample carrier with electrically conductive carbon adhesive tape.

ATR-FTIR analysis. Detailed description of the setup can be found elsewhere.^[37] In brief, the glassy carbon ring of the borehole electrode was drop-casted with the same ink as for the CV-measurements described before. The catalyst was conditioned in 1 M KOH for 20 cycles from 0 V to 0.6 V vs. Ag/AgCl (3 M KCl) at a scan rate of 100 mV/s. Then, the electrode was immersed in the ATR-FTIR cell and a distance of 150 μm was set. A peristaltic pump was set to 5 $\mu\text{L}/\text{min}$ to constantly pump electrolyte through the thin liquid layer between the electrode and the Ge ATR internal reflection element. The desired potentials were applied at 0.55 and 0.8 V vs. Ag/AgCl (3 M KCl) for 10 min each. Shown spectra were recorded for 90 s overlying several individual scans started after 2 min of electrolysis time.

Product analysis. The analysis of the products resulted during SOR was done by an ion exclusion column (Eurokat H, Knauer) configured within an AZURA HPLC system (Knauer) using a refractive index detector (RID 2.1 L, Knauer) and a diode array detector (UV/VIS, DAD 2.1 L, Knauer) with 5 mM H_2SO_4 used as an eluent (mobile phase). The samples from 1 M KOH measurement were diluted with 0.5 M H_2SO_4 with a dilution factor of 2.2 and the samples from measurements in 7 M KOH were diluted with 3.5 M H_2SO_4 with a dilution factor of 2.08. The HPLC was operated at the flow rate of 0.6 mL/min at 70 °C temperature of the column oven. The samples were filtered using 0.2 μm pore size filters before running in the HPLC. The calibration for the respective products was performed using commercially available standard compounds. Products were quantified using the UV/Vis detector set at 220 nm, where glycerol is not detectable. Since glycerol and formic acid overlap in the refractive index detector (RID), glycerol concentrations were calculated by subtracting the peak area of formic acid, whose concentration was determined before at 220 nm and converted to RI scale using the respective calibration factors, from the whole peak area of glycerol and formic acid in the RID. Concentrations were converted to moles by using the anolyte and catholyte volumes corrected by the sampled volume. The Faradaic efficiency (FE) and the carbon balance were calculated using Equations (3) and (4).^[4,14]

Faradaic efficiency =

$$\frac{1}{\nu_p} \cdot \frac{(n_{t,\text{product}} - n_{i,\text{product}}) \cdot F \cdot n(e^-)}{Q_{\text{total}}} \cdot 100\% \quad (3)$$

ν_p	Stoichiometric factor,
$n_{t,\text{product}}$	Number of moles of the respective product at time t in mol,
$n_{i,\text{product}}$	Initial number of moles of the respective product in mol,
F	Faraday's constant 96485 C/mol,
$n(e^-)$	Number of electrons from the oxidation of 1 mol of glycerol into the respective product in mol,
Q_{total}	Total charge passed WE during electrolysis in C.

$$\text{Carbon balance} = \frac{C_{t,\text{total}}}{C_{i,\text{total}}} \cdot 100\% \quad (4)$$

$C_{t,\text{total}}$ Number of carbon atoms of both products and reactants obtained at time t in mol,

$C_{i,\text{total}}$ Number of carbon atoms of the reactant initially present at the beginning of the measurement in mol.

Differential electrochemical mass spectrometry (DEMS). This technique was used for in situ detection of oxygen during electrochemical experiments. Mass spectra were acquired by a Hiden HPR40 DEMS system (Hiden Analytical Ltd., UK). An electron energy of 70 eV was used for ionization, with an emission current of 500 μA . Ionized oxygen ($m/z=32$) was detected by a Faraday cup detector. DEMS electrochemical experiments were performed with a Biologic VSP-150 potentiostat. Cyclic voltammeteries were recorded from 1 to 1.8 V vs. RHE at a scan rate of 2 mV/s. The electrolyte was circulated through the cell in a continuous flow mode with a rate of 60 $\mu\text{L}/\text{min}$ by means of a syringe pump. The DEMS electrochemical cell was a single compartment thin-layer cell made of PEEK with a three-electrode configuration (supplied by HIDDEN Analytical Ltd.). The working electrode was a glassy carbon rod of 5 mm in diameter with the catalyst drop-coated on top, with a loading of 0.21 mg/cm^2 . The counter electrode was a Pt wire of 0.5 mm of diameter placed at the outlet of the electrolyte and the reference electrode was a leakless Ag/AgCl (3.4 M KCl) reference electrode (Innovative Instruments, Inc., USA). A 28 μm -thickness PTFE membrane with a pore size of 20 nm was located between the thin-layer cell and the mass spectrometer inlet port. DEMS signals were processed to minimize the influence of bubble noise on the recorded trends. The processing was performed by the adjacent averaging (over 3–5 points) of the software "Origin Pro 2022". Also, DEMS signals shown are background subtracted. In order to estimate the faradaic currents of OER from DEMS signals, the relationship between the m/z 32 DEMS signals and the corresponding O_2 faradaic currents was investigated by a proper calibration using a stable OER catalyst, Co-hydroxynitrate,^[38] in an alcohol-free 1 M KOH solution and the same conditions as the measurements, including the electrocatalyst film preparation. After that, the expression of Equation (5) was found for 1 M KOH and used to convert the obtained DEMS signals into the respective faradaic currents.

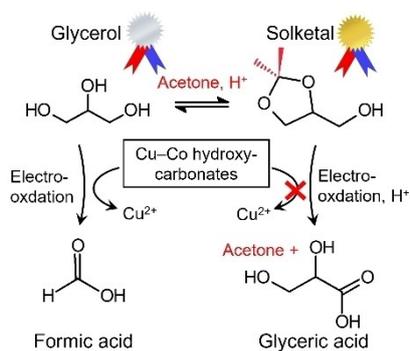
$$j_{\text{Oxygen}} \text{ (mA/cm}^2\text{)} = m/z \text{ 32 DEMS signal (Torr)} \cdot 1.706 \cdot 10^{11} \quad (5)$$

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RESEARCH ARTICLE

Electrochemical solketal (acetal-protected glycerol) oxidation reaction instead of the glycerol oxidation reaction on mixed Cu–Co hydroxycarbonates at the anode enables a product selectivity change from formic acid (C1 product) to the more valuable glyceric acid (C3 product), after removal of the acetal group, and protects the non-noble metal-based catalyst against Cu leaching.



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Electrooxidation of the Glycerol Derivative Solketal over Cu–Co Hydroxycarbonates to Enable the Synthesis of Glyceric Acid

