Electrochemistry Communications 172 (2025) 107880

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Investigation of the Electrocatalytic reduction of simple ketones in alkaline media

Axel Marth [a,b], Julia Piehler [a,b], Matthew Brodt [a], Maximilian Maier [a,b], Simon Thiele [a,b,*]

[a] Helmholtz-Institut Erlangen-Nürnberg for Renewable Energy (IET-2) Forschungszentrum Jülich GmbH, Cauerstr. 1, 91058 Erlangen, Germany
[b] Department of Chemical and Biological Engineering Friedrich-Alexander-Universität Erlangen Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany

ABSTRACT

Electrochemical energy storage in organic compounds has gained increasing interest recently. In particular, ketones and their secondary alcohols can serve as an electrochemical liquid organic hydrogen carrier (EC-LOHC) due to the possibility of selective oxidation of the hydrogen-rich counterpart. This study examines the possibility of hydrogenating ketones (acetone, 2-butanone, 2-pentanone) in alkaline media (KOH) and shows the influence of aliphatic side-chain length on the surface coverage of the polycrystalline platinum catalyst in an H-cell. This is done by performing linear sweep voltammetry (LSV) and cyclovoltammetry (CV). LSVs reveal similar onset potentials for the ketone reduction reaction, and the influence of onsetting hydrogen evolution reaction and its dependency on surface coverage in the voltage range below 0 V vs. RHE. Furthermore, it reports increased faradaic efficiency (FE) in alkaline media in comparison to acidic media.

1. Introduction

Climate change forces the world population to rethink how they produce, use, and store energy. Batteries are an option for short-term storage, but seasonal storage remains a challenge. One option for seasonal storage is the production and storage of H_2 [1]. A relevant approach to decrease storage cost of H_2 are liquid organic hydrogen carriers (LOHCs) [2–6]. LOHCs can be hydrogenated to store H_2 and dehydrogenated to release H_2 on demand. This cycle can be performed via catalysis. The most often and commercially available pathway is the usage of elevated temperature and thermocatalytic processes [7]. Nevertheless, low-temperature electrocatalysis is also feasible for these processes which lead to the term electrochemical LOHCs (EC-LOHCs). One such EC-LOHC is the acetone/2-propanol couple. Acetone (ACE) is a ketone, which is hydrogenated to a secondary alcohol (2-propanol). This secondary alcohol can be partially oxidized back to ACE, thus enabling a cycle [8–10]. The acetone reduction reaction (ARR) is a two-electron reaction and can be described in acidic media as:

$$2\,H^{+} + 2\,e^{-} + C_3H_6O \rightarrow C_3H_8O; E^0 = 0.118\ V\ vs.RHE \tag{1}$$

where E^0 is the standard potential. Other ketones, for example, 2-butanone (BON) and 2-pentanone (PON), and their corresponding alcohols are, in theory, also candidates for EC-LOHCs.

The ARR has been investigated in alkaline and acidic media [9–14]. For example, it was investigated in aqueous NaOH solution at 25 °C on Hg. These investigations were conducted at relatively large overpotentials, and it was concluded that pinacol was formed as a side product during hydrogenation, especially when the ACE concentration was increased [12]. Furthermore, the electrochemical hydrogenation of BON and 3-pentanone to their corresponding secondary alcohols has been performed in acidic media [13]. The authors conducted concentration experiments for both H^+ and ketone concentrations. They derived that the reaction mechanism differs between ACE and higher aliphatic ketones, where butanone and pentanone adsorb via their enol-tautomer and ACE either as its enol-tautomer or as a protonated ketone [13]. Furthermore, the electrochemical reduction of BON was performed in sulphuric acid solutions, which yielded butane as a product [15]. These studies showcase first approaches on this relevant topic of EC-LOHC hydrogenation.

This study investigates the reduction of ACE, BON, and PON on gas diffusion electrodes with polycrystalline nanoparticulate Pt/C in alkaline environment (KOH). Furthermore, we compare their surface coverage by comparing the hydrogen underpotential deposition (H_{upd}) region probed by cyclovoltammetry (CVs) for varying reactant concentrations. Both product analysis and electrochemical data prove the general feasibility of the electrochemical reduction of these ketones. Finally, comparing FEs for the ACE reduction in alkaline and acidic media demonstrates the elevated selectivity of the ARR in alkaline media.

---

[*] Corresponding author at: Helmholtz-Institut Erlangen-, Nürnberg, Germany
E-mail address: si.thiele@fz-juelich.de (S. Thiele).

https://doi.org/10.1016/j.elecom.2025.107880
Received 5 December 2024; Received in revised form 14 January 2025; Accepted 22 January 2025

2. Theory

The electrochemical reduction of ACE (ARR) is a two-electron reaction as described in eq. 1. The adjustment of standard potential for varying pH values can be performed as follows:

$$E_{pH=i} = E^0 - 0.059\ V{*}pH\ vs.SHE; E_{pH=14,ARR} = -0.708\ vs.SHE \tag{2}$$

The reaction of the ARR changes in alkaline media to:

$$2\,H_2O + 2\,e^- + C_3H_6O \rightarrow C_3H_8O + 2OH^- \tag{3}$$

for the reduction of BON and PON, the acetone/isopropanol molecules can be replaced with the corresponding ketone/secondary alcohol.

H_{upd} experiments can be performed to investigate the influence of ketone concentration on the surface coverage of adsorbed hydrogen on Pt. The mechanism for H_{upd} differs between alkaline (8) and acidic media (9) and can be described as [16]:

$$H_2O + e^- \rightleftharpoons H_{ad} + OH^- \tag{4}$$

$$H_3O^+ + e^- \rightleftharpoons H_2O + H_{ad} \tag{5}$$

Determining electrochemical surface area based on the measured charge can enable comparing different electrodes with similar loadings. This assumes that the mechanism on the same catalyst is identical, thus allowing a relative comparison between electrodes. This leads to the conclusion that comparing surface coverage between different ketones is possible based on the H_{upd} charge; when assuming a homogenous hydrogen monolayer on the catalyst, a surface coverage can be determined with the following equation:

$$\theta_{ketone} = \left(1 - \frac{q_{Hupd,ketone}}{q_{Hupd,blank}}\right){*}100\% \tag{6}$$

where θ_{ketone} is the surface coverage in %, $q_{Hupd,ketone}$ is the H_{upd} charge with ketone being present in the electrolyte in C, and $q_{Hupd,blank}$ is the charge of the blank measurement without any ketone being present in C.

Furthermore, the hydrogen evolution reaction (HER) exchange current density differs vastly between acidic and alkaline media [17]. This difference in exchange current density leads to the hypothesis that a ketone reduction below 0 V vs. RHE in alkaline media should provide higher faradaic efficiencies (FE) than in acidic media because the competitive HER is expected to be slower. In acidic media, a sharp decline in FE is reported for hydrogenation experiments below 0 V vs. RHE. [10,18] This is due to the onset of HER leading to a substantial current surge and H_2 formation.

3. Materials and methods

3.1. Materials and chemicals

A custom-built H-Cell made out of PTFE was used for this study. An SP-300 Potentiostat (Biologic, France) was used for electrochemical measurements. As a reference electrode (RE), a (RHE) mini-HydroFlex (Gaskatel GmbH, Germany) was used. The counter electrode (CE) was a graphite rod (Pine Instruments, USA), the WE a gas diffusion electrode with a Pt/C catalyst (40 wt% Pt) and a presoaked Nafion 117 membrane was used to separate the working electrode (WE), and CE chambers. For experiments in alkaline media, the membrane was soaked for at least 48 h in 1 M KOH to perform an ion exchange. The RE was placed inside a syringe filled with electrolyte, and a syringe filter (regenerated cellulose, 0.2 μm pore diameter, Sartorius, Germany) was used as a separator between WE-chamber and RE to prevent thermal hydrogenation of ketone on the RE. The electrolyte used for the investigation was 1 M KOH (Suprapur, Merck, Germany) and 1 M H_2SO_4 (Suprapur, Merck, Germany). The utilized ketones were ACE (EMSURE, Merck), BON (>99 %, Merck Germany), and PON (>99 %, Merck, Germany). Product analysis (50 μL sample size) was performed with a Clarus 590 with an FID detector using headspace GC (PerkinElmer, Inc., USA).

3.2. Experimental Protocol

For the surface coverage experiments, 90 mL of electrolyte was filled into the WE and CE chamber of the H-Cell. The electrolyte was degassed with 100 mL min^{-1} Ar (5.0, AirLiquide, France), and blanketed with a flow of 10 mL min^{-1} to maintain an O_2-free electrolyte. Afterwards, six CVs per sweep rate in the voltage range of 0.05 V vs. RHE to 0.65 V vs. RHE with a sweep rate of 10 mV s^{-1} and 25 mV s^{-1}, were performed. The last CV of each sweep rate was utilized for comparison and characterization. Then, linear sweep voltammetry (LSV) was performed from 0.35 V vs. RHE to −0.15 V vs. RHE with a sweep rate of 1 mV s^{-1}. For the ohmic drop compensation, a potentiostatic impedance spectroscopy (PEIS) measurement was conducted at 0.01 V vs. RHE in a frequency range of 2 MHz to 0.1 Hz, with 10 pts. per decade and a perturbation of 4 mV. Next, the ketone was added to the electrolyte to reach the concentration to be investigated. Solutions of 0 (blank), 0.01, 0.05, 0.10, 0.25, and 0.50 M were investigated for the concentration variation. After the addition of ketone, the same electrochemical measurement protocol was conducted.

A 0.5 M ACE electrolyte in either 1 M KOH or 1 M H_2SO_4 was prepared for the FE investigation. An impedance measurement with the same parameters as for the concentration variation was conducted, and afterward, a constant voltage of 0.01 V vs. RHE was held for two hours. After the two hours of constant voltage, 50 μL of the electrolyte in the WE chamber was taken and measured with headspace GC.

4. Results and discussion

4.1. Concentration Variation

A concentration variation was performed for each ketone to investigate the influence of varying concentrations. The results for the concentration variation of the investigated ketones are presented in Fig. 1.

The features observed in the voltage range between 0.5 V and 0.1 V can be correlated to the H_{upd}. While the features in the reductive current range correlate to the adsorption (Eq. 4 forward reaction), the features in the oxidative range correlate to the hydrogen desorption (Eq. 4 backward reaction). A decrease of H_{upd} with an increase in concentration can be observed for both the adsorption and desorption features. Through an increase in concentration, a progressing feature loss can be observed. This indicates a loss of surface sites available for H_{upd} and, thus, an increase in ketone surface coverage. Furthermore, when comparing ACE, BON, and PON, a correlation of aliphatic side-chain length and surface coverage can be derived. While for ACE, the H_{upd} features almost completely vanish, they remain more distinguishable with increasing side-chain length. Especially for PON, the H_{upd} feature remains visible even when concentrations increase. When comparing the H_{upd} charge for the different ketones, normalizing it to the blank measurement, and correlating it to the concentration for both the adsorption and desorption charge, the dependency becomes even more apparent. This behavior is depicted in Fig. 2.

This comparison underlines the influence of side-chain length on surface coverage for both the adsorption feature (Fig. 2a) and desorption feature (Fig. 2b). A general decrease in ketone surface coverage with an increase in the aliphatic side chain length can be observed. This is especially dominant for the PON experiments, which show fewer coverages than the other two ketones. BON and ACE are close to each other regarding surface coverage for the adsorption feature, with ACE demonstrating generally higher surface coverage. For the desorption features, the trend of lower aliphatic ketones showing higher surface coverages seems to be more distinct. These results support the general theory that a lower surface coverage with a longer aliphatic side chain is obtained. This could be due to the increased repulsion between the side

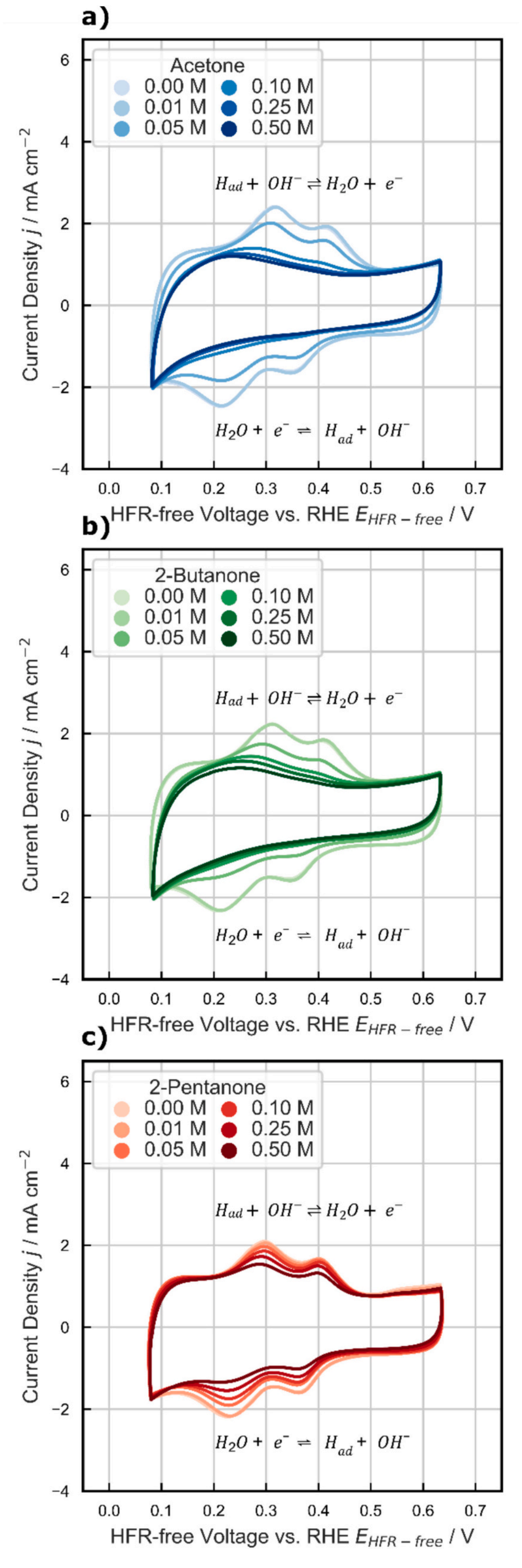

Fig. 1. CVs for the concentration variation of ACE (a), BON (b), and PON (c) at room temperature in 1 M KOH, recorded in the voltage range 0.05 V to 0.65 V vs. RHE with a sweep rate of 10 mV s^{-1}. The adsorption and desorption equations are given for reference.

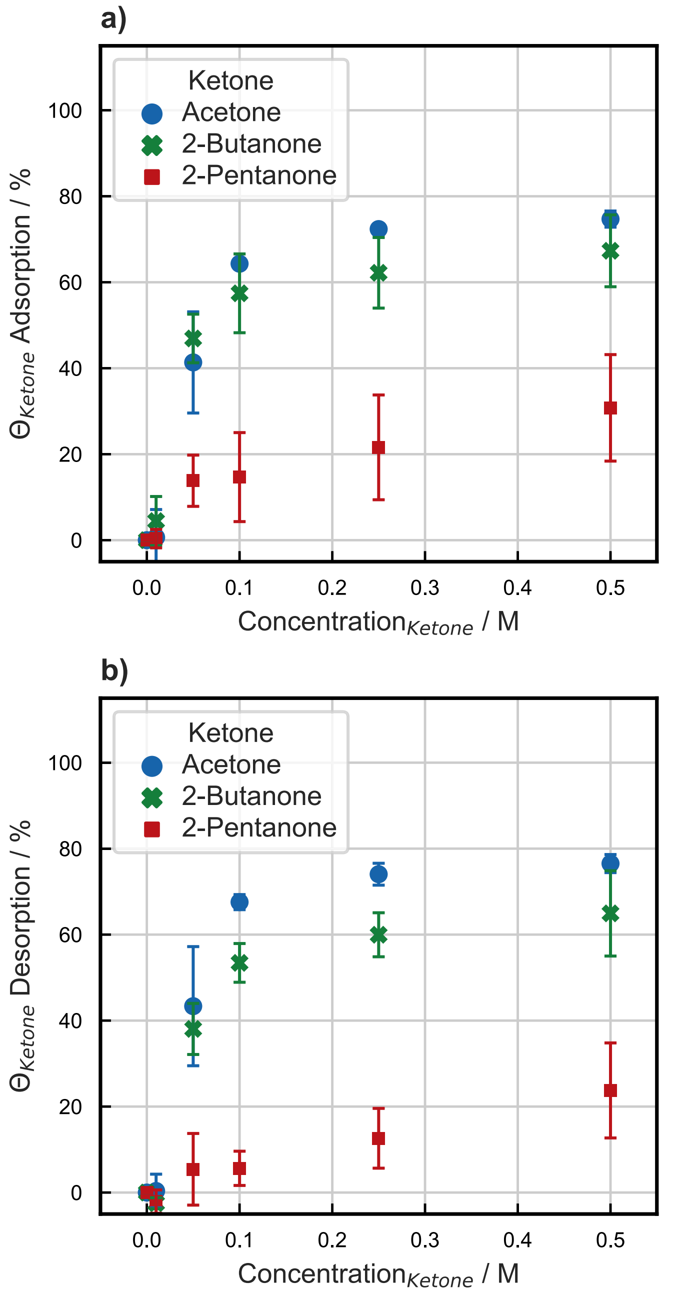

Fig. 2. Comparison of surface coverage in dependency of concentration (0, 0.01, 0.05, 0.10, 0.25, and 0.5 M) for ACE, BON, and PON. The values were obtained by CV measurements between 0.05 V and 0.65 V with a sweep rate of 10 mV s^{-1}. Both the H_{upd} adsorption (a) and desorption (b) are portrayed. Standard deviations and mean values are based on three independent measurements.

chains of the ketones, a different influence of the keto-enol equilibrium, or a different orientation of the molecules on the catalyst itself. The H_{upd} does not need a large quantity of catalyst sites to occur. Therefore, even the most minor gaps between organic molecules can lead to hydrogen adsorption and desorption. Furthermore, it is feasible that H_{upd} can also occur underneath the aliphatic side chain of ketones. This would lead to the adsorption of hydrogen underneath the side chains. Such an effect would likely be more dominant for longer side chain ketones, thus explaining the substantially higher H_{upd} charge for PON. Additional effects such as cation effects, pH influence, catalyst type, and temperature will likely play a role in the observed effect when investigating various parameters in future studies, as reported in the literature.

[19,20] A more detailed investigation both experimental and theoretical is necessary to fully understand this phenomenon.

LSVs were conducted to investigate the influence of overlapping potential of HER and ketone reduction, as well as the dependency of concentration and potential on current response. The results are depicted in Fig. 3.

For the blank electrolyte (0 M), the H_{upd} feature between 0.2 V and 0.3 V is still discernible for the LSVs. This feature is less apparent when additional ketone is added to the electrolyte. An increase in reductive current with an increase in concentration can be observed above 0 V vs. RHE, with an onset potential around 0.15 V vs. RHE. This is more discernible for ACE (a) and BON (b), while for PON (c), only a slight increase is visible (inset).

The standard potential is defined for a 1 M solution of both reduced (secondary alcohol) and oxidized (ketone) species, as only the ketone is present at first, the onset potential deviates from the standard potential of 0.118 V vs. RHE (ACE, BON) or 0.127 V vs. RHE (PON). Based on the Nernst equation, a higher reversible potential is expected if no reduced species are present in the electrolyte, which is in accordance with the observed onset potential.

When decreasing the potential below 0 V vs. RHE, a sharp increase in current can be observed. This can be correlated to the onsetting HER below 0 V vs. RHE, leading to a substantial increase in current density. For acidic ARR, competitive adsorption of hydrogen and ACE is reported, as well as for the hydrogenation of ACE in thermocatalytic setups. [13,21] Assuming that competitive adsorption takes place in alkaline media as well, this leads to the conclusion that the decreased current densities at increased concentrations of ketones are likely due to a reduced amount of catalyst available for HER, as proven by the H_{upd} evaluation. The more significant current density for the PON sample below 0 V vs. RHE correlates with the less substantial surface coverage of the ketone, thus making more catalyst sites available for the HER.

Furthermore, for every ketone, the corresponding secondary alcohol was observed in the headspace-GC measurement, thus proving the feasibility of the alkaline ketone reduction.

4.2. *Faradaic Efficiency*

A substantial difference can be identified when performing FE experiments in alkaline (pH = 14) and acidic (pH = 0). While the alkaline ARR leads to a FE of 86 ± 13 %, the acidic one leads to 31.5 ± 3.25 % (see Fig. 4). We contribute this difference to fewer side reactions (e.g., slower HER) during the reaction, leading to substantially higher FEs for the alkaline ARR. The side products in an acidic environment can be H_2 or propane, as reported in the literature. [10,13,14] The yields during the reaction were $2.56{*}10^{-5} \pm 1.32{*}10^{-5}$ mol (acidic), and a yield of $1.27{*}10^{-4} \pm 1.60\ {*}10^{-5}$ mol (alkaline). The relatively large error of the acidic measurement can be correlated to varying resistances for the setup. The FE measurements were conducted in a potentiostatic fashion. Thus, a varying resistance leads to varying currents and, thus, varying reaction rates, which is why the normalization to the absolute current (the FE) is essential for properly depicting the system. This improved FE presents the advantages of ketone hydrogenation in an alkaline environment. Furthermore, an alkaline environment enables the usage of various other catalysts, thus leading to a broader range of possible non-noble metals.

5. Conclusion

In this study, we have shown the dependency of the surface coverage of a polycrystalline Pt catalyst on the aliphatic side chain length of ketones in an alkaline environment. We have shown that the surface coverage decreased with increasing side chain length, making more sites available for H_{upd}. The aliphatic side chains lead to the repulsion of other ketones, therefore blocking the adsorption of additional ketones. This effect elevates with an increase in aliphatic side chain length and

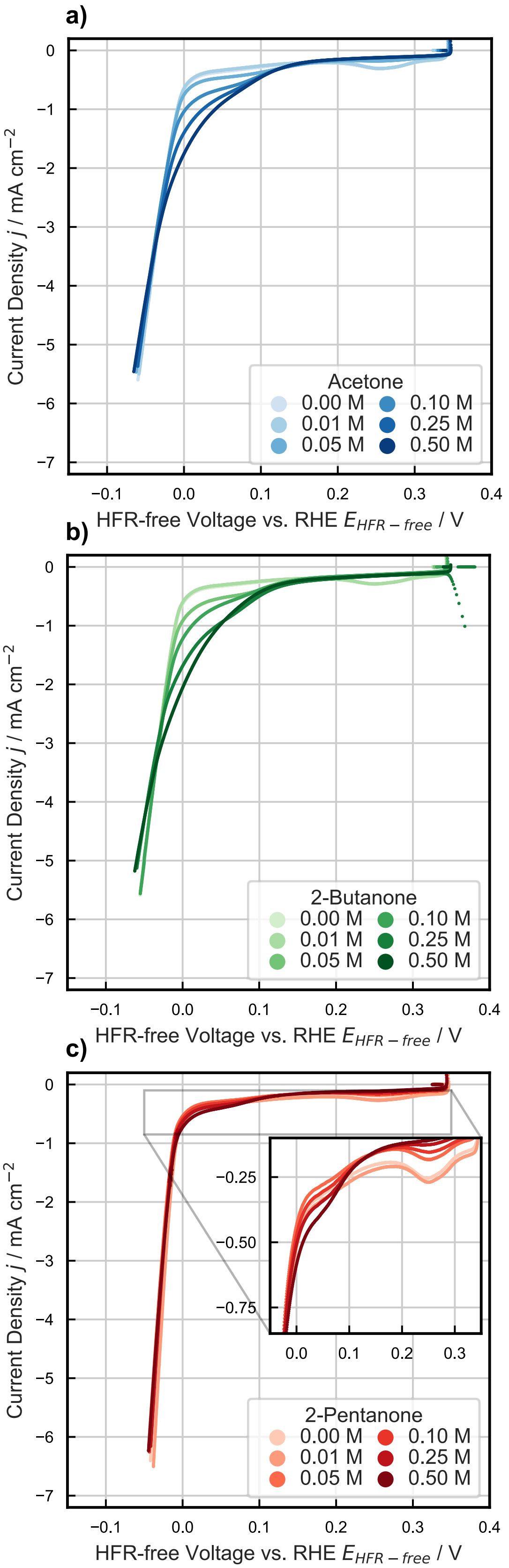

Fig. 3. LSVs of the concentration variation of ACE (a), BON (b), and PON (c) at room temperature in 1 M KOH, recorded in the voltage range 0.35 V to −0.15 V vs. RHE with a sweep rate of 1 mV s^{-1}. The inset shows the current range above −0.85 mA cm^{-2}.

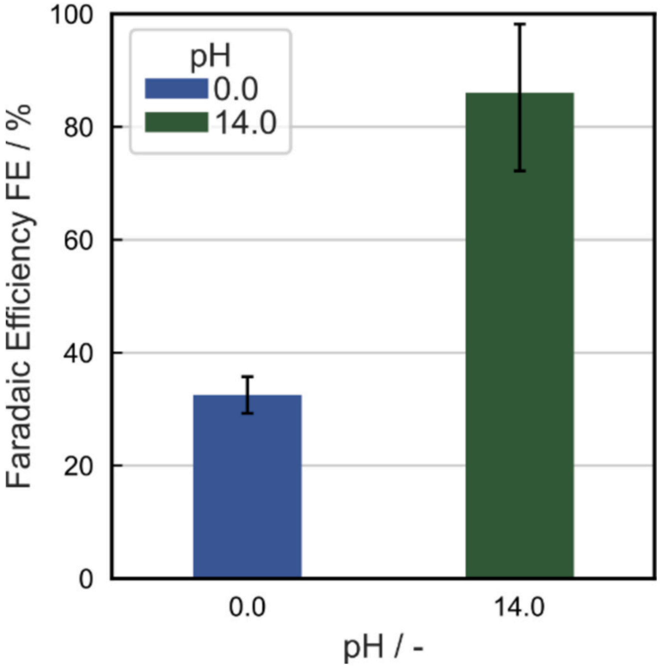

Fig. 4. Comparison of faradaic efficiency between an electrolyte with a pH of 0 and 14 at a voltage of 0.01 V vs. RHE with a Pt/C electrode in 0.5 M ACE. Error bars are min max error based on two separate measurements. For the acidic ARR, a yield of 2.56*10^{-5} ± 1.32*10^{-5} mol and a yield of 1.27*10–4 ± 1.60 *10–5 mol was achieved for the alkaline ARR.

increases the amount of catalyst sites being available for H_{upd}.

Moreover, we investigated the system's behavior upon polarization from the onset potential to potentials of −0.15 V vs. RHE. For BON and ACE, similar current densities were observed below 0 V vs. RHE. In contrast, for PON, substantially higher current densities are observed below 0 V vs. RHE. We contribute this to decreased surface coverage, leading to more sites being available for HER, thus increasing the reductive current below 0 V vs. RHE.

Furthermore, we have shown the general feasibility of electrochemically hydrogenating various ketones in an alkaline environment. In all cases, the corresponding secondary alcohol was observed by headspace-GC measurement. The FEs in the alkaline environment are substantially higher (86 % vs. 31.5 %), showcasing the relevance of alkaline ketone reduction.

In conclusion, we have shown the dependency of surface coverage on the aliphatic side chain length of simple ketones, the improved FE, and the general feasibility of electrochemically hydrogenating these ketones to their secondary alcohols in alkaline environment.

CRediT authorship contribution statement

Axel Marth: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation. **Julia Piehler:** Writing – review & editing, Data curation, Conceptualization. **Matthew Brodt:** Writing – review & editing, Writing – original draft, Supervision, Funding acquisition. **Maximilian Maier:** Writing – review & editing, Writing – original draft, Methodology. **Simon Thiele:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Methodology, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

References

[1] O. Schmidt, S. Melchior, A. Hawkes, I. Staffell, Joule 3 (2019) 81.
[2] T. Rüde, S. Dürr, P. Preuster, M. Wolf, P. Wasserscheid, Sustainable Energy Fuels 6 (2022) 1541.
[3] D. Teichmann, W. Arlt, P. Wasserscheid, R. Freymann, Energ. Environ. Sci. 4 (2011) 2767.
[4] S. Duerr, S. Zilm, M. Geisselbrecht, K. Mueller, P. Preuster, A. Boesmann, P. Wasserscheid, Int. J. Hydrogen Energy 46 (2021) 32583.
[5] M. Niermann, A. Beckendorff, M. Kaltschmitt, K. Bonhoff, Int. J. Hydrogen Energy 44 (2019) 6631.
[6] P. Preuster, C. Papp, P. Wasserscheid, Acc. Chem. Res. 50 (2017) 74.
[7] Hydrogenious LOHC Technologies, Hydrogenious LOHC Technologies, can be found under, https://hydrogenious.net/how/#technology, 2023.
[8] M. Komma, A. Marth, M. Maier, A. Hutzler, T. Böhm, S. Thiele, J. Electrochem. Soc. 171 (2024) 104502.
[9] D. Venus, A. Marth, S. Riess, A.T. Freiberg, M. Brodt, M. Wensing, P. Wasserscheid, S. Thiele, Adv. Energy Mater. (2024) 2403824.
[10] A. Marth, A.T.S. Freiberg, M. Maier, P. Wasserscheid, S. Thiele, J. Electrochem. Soc. 171 (2024) 114505.
[11] H. Kita, S. Ishikura, A. Katayama, Electrochim. Acta 19 (1974) 555.
[12] H. Kita, S. Ishikura, A. Katayama, Electrochim. Acta 20 (1975) 441.
[13] C.J. Bondue, M. Koper, J. Catal. 369 (2019) 302.
[14] C.J. Bondue, F. Calle-Vallejo, M.C. Figueiredo, M.T.M. Koper, Nat. Catal. 2 (2019) 243.
[15] C. Zinola, J. Rodriguez, M. Arevalo, E. Pastor, J. Electroanal. Chem. 454 (1998) 161.
[16] K.J.P. Schouten, M.J.T.C. van der Niet, M.T.M. Koper, Physical chemistry chemical physics : PCCP 12, 2010, p. 15217.
[17] J. Durst, A. Siebel, C. Simon, F. Hasché, J. Herranz, H.A. Gasteiger, Energ. Environ. Sci. 7 (2014) 2255.
[18] S. Nogami, K. Nagasawa, A. Fukazawa, K. Tanaka, S. Mitsushima, M. Atobe, J. Electrochem. Soc. 167 (2020) 155506.
[19] X. Yang, J. Nash, N. Oliveira, Y. Yan, B. Xu, Angew. Chem. 131 (2019) 17882.
[20] R. Gómez, J.M. Orts, B. Álvarez-Ruiz, J.M. Feliu, J. Phys. Chem. B 108 (2004) 228.
[21] B. Sen, J. Catal. 113 (1988) 52.