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Thermodynamic and Economic Potential of Glycerol Oxidation to Replace Oxygen Evolution in Water Electrolysis

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Abstract

In electrochemical hydrogen production, a major contribution to the energy demand is the anodic oxygen evolution reaction, although the byproduct oxygen is often not utilized. That motivates the search for alternative anodic oxidation reactions. Glycerol has been proposed as a promising reagent for the anode since it is widely available, cheap, and green. However, it is still unclear if this would have energetic and economic benefits. To this end, we evaluated the anodic oxidation of glycerol to the 14 alternative products that are mentioned in the literature. We screened these possible oxidation products based on two criteria: (*i*) a surrogate for the energy demand (reversible and thermoneutral voltage) and (*ii*) economic value. To address the challenge of data availability, we took thermodynamic properties estimated by group contribution methods and machine learning. For the economic data, we use both laboratory price data from Sigma Aldrich and industry price data from ChemAnalyst and Kahlstorf et al. We also compare the current and projected production rates of hydrogen and find that the current glycerol supply will not suffice to cover the hydrogen demand, yet still coupled glycerol oxidation and hydrogen evolution can serve as an alternative to convert glycerol waste streams from biodiesel plants to higher value while additionally producing hydrogen. All glycerol oxidation reactions considered have the potential to significantly reduce the energy demand of green hydrogen production. Some of them potentially add value through byproducts although product prices are highly uncertain.

Introduction

Hydrogen is crucial for the transition to a climate-neutral society with energy from renewable sources.[1] As means of renewable-based hydrogen production, electrolysis is regarded as the most advantageous.[2] However, it still suffers from high production costs due to high voltage requirement, especially at the high current densities necessary to minimize capital expenditures, resulting in high electricity consumption.[3] Hence, current research in water electrolysis aims to reduce the total energy consumption of the electrolyzer.

While the desired product of a water electrolyzer is the hydrogen produced at the cathode, the coupled oxygen evolution reaction at the anode is only required to provide the electrons. Under acidic conditions, we additionally require the anode-side reaction to provide protons, whereas under alkaline conditions, the hydroxide ions will be provided by the cathode-side. However, oxygen has a rather low economic value. Furthermore, both the thermodynamic limit and the kinetic limitations of the oxygen evolution reaction substantially increase the (over)potential and therefore the energy requirements to produce hydrogen.[4] As a consequence, to reduce the energy demand, it is hence advisable to either try to reduce the overpotential of the oxygen evolution reaction, e.g., by developing better catalysts, or to replace it with a different half-cell reaction. The latter could also produce a valuable chemical byproduct. Such coupling of cathodic hydrogen formation with anodic chemical manufacturing, also known as "paired electrolysis"[5] or "hybrid electrolysis", is reported to have advantages over conventional chemical manufacturing in terms of net greenhouse gas emission reduction even with the current energy mix if high enough selectivities are obtained.[6]

For such different half-cell reactions, corresponding reagents must be favorable regarding the total energy consumption, yet also cheap, abundant, and green. Glycerol is claimed to be a promising candidate in that sense.[7] The majority (63%) of the current glycerol supply (approximately $4 \cdot 10^9$ kg/a) stems from biodiesel production, which has increased greatly in the past decades.[8] Biodiesel production is expected to rise even further, which would result in a growing mismatch between glycerol supply and demand.[9,10] This mismatch motivates extensive research in converting glycerol into value-added products.[11–13] As a paired reaction for hydrogen production, stoichiometry dictates for the overall electrolyzer reaction that approximately 10 to 100 g of glycerol are required per g of hydrogen produced, depending on the oxidation product. Currently, the available glycerol would thus cover only about 0,4% of the global hydrogen demand, which is about $94 \cdot 10^9$ kg/a.[14] Additionally, the growth rate of hydrogen production (up to 20%)[14] is expected to outrun that of biodiesel (4-15%).[15] Sometimes, coupled glycerol oxidation and hydrogen production is thus somewhat misleadingly hinted to be promising for the global challenge of reducing the green hydrogen production costs.[16–19] Unfortunately, this will not be the case due to the insufficient availability of glycerol. However, coupled glycerol oxidation and hydrogen production can serve as one of multiple pathways to fulfill the growing hydrogen demand. Additionally, coupled glycerol oxidation and hydrogen production could still serve as an alternative to convert glycerol streams from biodiesel plants to higher values. In that sense, it would also be beneficial for the environment since it provides a large sink for glycerol-waste from biodiesel plants.[20] Obviously, the generated products would also need to have a sufficiently high demand.

There are many publications concerning catalyst research for different glycerol oxidation reactions, including overviews with a comparison of different electrocatalysts,[21] research on specific catalyst reaction pathways,[22–24] and studies that aim to increase the selectivity to one individual glycerol oxidation product.[25–27] According to Demirel-Gülen et al.[28] and Katryniok et al.[29], the C_3, C_2 and C_1 molecules shown in Figure 1 are the main possible products that occur in electrochemical glycerol oxidation. For all of these products, there are studies that focus either on one of the possible products, e.g., lactic acid,[30] formic acid,[31] glycolic acid,[25] dihydroxyacetone,[27] tartronic acid,[32] or even mixtures of C_3 products.[26,29,33] Many of the products can be formed with sufficiently high selectivity and conversion under either alkaline[34] or acidic conditions,[35] with different catalysts, with distinct electrolyzer setups, etc. For the application areas of the different oxidation products, we refer to Alaba et al.[36] and Rahim et al.[37]. In general, most of them are used in healthcare, as food, or specialty chemicals. Some of the products are also under research as reagents in novel process concepts, e.g. for polymeric biomaterials.[7,38]

However, these studies rely on the current state of catalyst research, while the potential of coupled glycerol oxidation and hydrogen production in the long run and at process level is not evaluated. Finding good or even optimal pathways and conditions of production is very resource-consuming because predicting the performance of catalysts often requires empirical data and experimental testing. The catalyst's effectiveness can depend on factors such as reaction conditions, substrate properties, and the mechanism of the reaction, making it complex and context-dependent. Especially understanding the detailed mechanisms by which

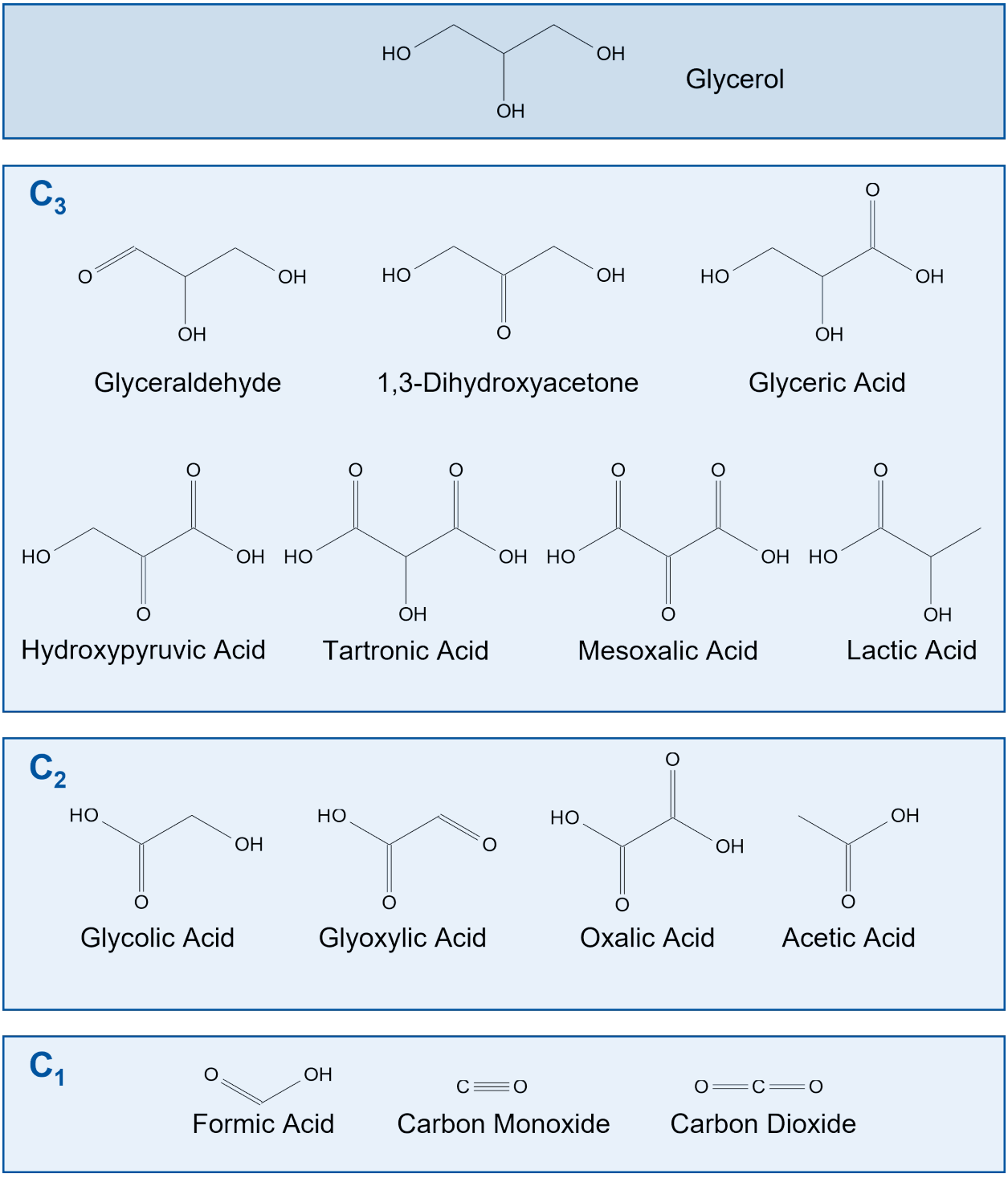


Figure 1: Overview of the considered glycerol oxidation products, data taken from Demirel-Gülen et al.[28]

catalysts operate, often requires extensive experimental investigation, although the reputation of quantum chemical calculations is growing.[39] Hence, it is desirable to quickly decide on the most promising products to be focused on.

To address this gap, we provide an early-stage techno-economic screening of alternative glycerol oxidation products. We base our calculations on thermodynamics in order to quantify the potential of the alternative routes, as the electrocatalysts for glycerol oxidation are still under development and thus far from ultimate performance. Our contribution aims to reduce the number of possible glycerol oxidation products, as a first step towards identifying optimal products. We compare the products by evaluating their thermodynamic voltage contribution at isothermal & reversible ("reversible voltage") and additionally at isothermal & adiabatic ("thermoneutral voltage") operation. We use standard references conditions, i.e., standard temperature (T = 298.15 K), pressure (p= 1 bar) and unit activity (1 mol/l for dissolved products, 1 bar for gaseous products and x_i=1 for water). Similar analyses have been successfully applied to pre-screen fuel cells for portable micropower generation processes, cf. Mitsos et al.[40]. Additionally, we compare the added economic value due to byproduct formation in conducting these glycerol oxidation reactions instead of oxygen evolution in water electrolysis. For this purpose, we introduce the theoretical background of the thermodynamic and economic properties in Section Methods. We discuss the meaning and correct use of reversible voltage and thermoneutral voltage. Additionally, we explain how we addressed the challenge of limited availability and comparability of data. In Section Results and Discussion, the derived voltages and prices are presented. Comparing the obtained results, we can narrow the amount of different glycerol oxidation products. The main conclusion from our work and its meaning for further evaluation of electrochemical glycerol oxidation are summarized in Section Conclusion and Outlook. In the Supporting Information, we provide the thermodynamic data (Gibbs free energies and enthalpies of formation and reaction) taken from the rmg database[41] and NIST,[42] and pKa values taken from Lange's handbook of chemistry.[43] Additionally, we provide a derivation of both voltages from first and second law of thermodynamics there.

Methods

The overall aim of our screening approach is to quickly estimate which glycerol oxidation products are favorable and thus guide research for coupling with green hydrogen production. We evaluate two criteria for screening for favorable products: (*i*) a surrogate for the energy demand of the electrolyzer based on thermodynamic properties, see Section Thermodynamic Properties, and (*ii*) potentially added revenue due to the sale of side products, see Section Economic Value. To enable screening at such a general level, we only consider the overall (idealized and desired) reaction for the sake of simplicity and thereby neglect the influence of pH values and detailed reactor designs. That implies the interpretation of the thermodynamic properties as surrogates to the minimum energy demand of the overall process rather than the real electrolyzer as explained below.

Thermodynamic Properties

The energy demand of an electrolyzer can be split in electricity demand and heat (resp. cooling) demand. To lower the energy costs, trying to reduce the operating voltage E is

advisable, as the current I is proportional to the production rate, assuming constant Faraday efficiency. However, the objective to minimize energy costs might differ from that to maximize energy efficiency.[44]

The operating voltage E of an electrolyzer can be separated into three main parts: (*i*) the reversible voltage E_{rev}, corresponding to the thermodynamic limit of the overall electrochemical reaction(s); (*ii*) the (summed up) ohmic overpotential η_{ohm}, due to electrical resistances; (*iii*) the (summed up) kinetic overpotentials η_{k} primarily due to reaction kinetic resistances,[45,46]

$$E = E_{\text{rev}} + \eta_{\text{ohm}} + \eta_{\text{k}}.$$

The overpotentials depend on the design of the electrolyzer, the catalyst, and the operating conditions (i.e., temperature T, pressure p, species concentrations c_i, current density j). In contrast, the reversible voltage is less dependent of design, catalyst, and current density. It is a lower bound on the potential needed for a given operating point, and as such can act as the foundation for any electrolyzer model. As the reversible voltage makes up about two-thirds of the operating voltage for a typical PEM water electrolyzer,[47] it serves as a suitable screening criterion for alternative reactions. For instance, in Mitsos et al.[40], we used it to screen alternative fuels for manportable electricity production by fuel cells.
We evaluate two important (lower) limits to the energy demand: (*i*) the isothermal and reversible case at standard conditions, evaluating only the electricity demand to drive the reaction ("reversible voltage", see Section Standard Reversible Voltages) and assuming any heat needed is provided/removed without thermodynamic or economic penalty; (*ii*) the isothermal and adiabatic case at standard conditions in which all energy to drive the reaction is provided as electricity ("thermoneutral voltage", see Section Standard Thermoneutral Voltages). In this second case, for all considered cases, the process is irreversible with the minimal dissipation required to maintain a constant temperature. A (standard) derivation of both the reversible and thermoneutral voltage from first and second law of thermodynamics is given in the Supporting Information.

Standard Reversible Voltages

The "reversible voltage" E_{rev} (also known as "equilibrium" or "theoretical" open circuit voltage[48]) is the minimal amount of electricity to reversibly drive the reaction, i.e., without any losses, at a given temperature (isothermal conditions) (see derivation in the Supporting Information). For calculating it at system temperature T, pressure p and activity a_i, the Nernst equation is commonly used:

$$E_{\text{rev}}\left(T, p, a_i\right) = E^{\theta}_{\text{rev}}\left(T, p\right) - \frac{RT}{zF}\sum_{i=1}^{n}\nu_i \ln(a_i). \tag{1}$$

It describes the difference between the standard reversible voltage with unit activities as a reference state E^{θ}_{rev}, with θ denoting an arbitrary reference condition, and the activities of the system species a_i at operating concentrations.[49] As the activities are concentration-dependent, defining them would mean to already design the electrolyzer including mass

transport, inlet concentration of glycerol, etc. Therefore, we focused on the standard reversible voltage as a fixed constant, thus assuming reference concentrations. The specific reference states used in this study as well as what that means in terms of an actual electrolyzer, are explained in Section Regarding Reference States. Moreover, the reversible voltage is reaction-dependent and proportional to the molar-based Gibbs free energy of reaction $\Delta_R G$ divided by the number of electrons transferred z:[48]

$$E^{\theta}_{\text{rev}}(T,p) = \frac{\Delta_R G^{\theta}(T,p)}{zF}.$$

Depending on the available data, the Gibbs free energy of reaction, for any state thus dropping the superscript θ here, can either be calculated by summing over the individual species Gibbs free energies of formation $\Delta_f G_i$ (multiplied by the stoichiometric coefficients ν_i) or alternatively directly by the enthalpy of reaction $\Delta_R H$, the entropy of reaction $\Delta_R S$ and the reaction temperature T:

$$\Delta_R G(T,p) = \sum_{i=1}^{N} \nu_i \Delta_f G_i(T,p) = \Delta_R H(T,p) - T\Delta_R S(T,p),$$

where

$$\Delta_f G_i(T,p) = \Delta_f H_i(T,p) - T\Delta S_i(T,p).$$

Thus, it is possible to calculate the standard reversible voltage at an arbitrary standard state θ, depending on the state for which formation data is available:

$$E^{\theta}_{\text{rev}}(T,p) = \frac{\sum_{i=1}^{N} \nu_i (\Delta_f H^{\theta}_i - T\Delta S^{\theta}_i)}{zF}.$$

If T is equal to the ambient temperature, the Gibbs free energy of reaction can be interpreted as the minimum exergy required if we consider the overall process as a black box that conducts the desired overall reaction (and thus irrespective of the actual reactions, pH values and changes occurring in the electrolyzer). This minimum exergy corresponds to the electricity consumption if (i) the process operates reversibly, (ii) all work input is in the form of electricity, and (iii) the correct amount of heat (determined by the entropy of reaction) is transferred to the process in addition to the work input. In case of 100% Faraday efficiency, the required voltage of such a process would then be the standard reversible voltage.

Standard Thermoneutral Voltages

In addition, we also calculate the voltage for isothermal & adiabatic operation at standard state, which is commonly referred to as standard "thermoneutral" voltage. It is obtained by an energy balance around the adiabatic electrolyzer, thus requiring all energy to be provided electrically, with just enough (irreversible) dissipation losses to maintain a constant temperature (see derivation in the Supporting Information). The thermoneutral voltage is typically higher than the reversible voltage as for most cases $\Delta_R H(T,p) > \Delta_R G(T,p)$. Most often, the thermoneutral voltage is still a lower bound on the actual operating voltage, as generally, low-temperature electrolyzers operate at high current densities that correspond to

high overpotentials, i.e., dissipation losses. In fact, typically the overpotentials more than cover the difference between the reversible and thermoneutral voltage, and electrolyzers require cooling.[50] The standard thermoneutral voltage can be calculated analogously to the standard reversible voltage:[48]

$$E^{\theta}_{\mathrm{th}}(T,p) = \frac{\Delta_{\mathrm{R}} H^{\theta}(T,p)}{zF}.$$

where the enthalpy of reaction is either directly available or calculated from the individual enthalpies of formation:

$$\Delta_{\mathrm{R}} H^{\theta}(T,p) = \sum_{i=1}^{N} \nu_i \Delta_{\mathrm{f}} H^{\theta}_i(T,p).$$

Note that the standard thermoneutral voltage $E^{\theta}_{\mathrm{th}}(T^0,p^0)$ is only applicable, i.e., only has physical meaning as representing isothermal & adiabatic operation, if the entropy of reaction $\Delta_{\mathrm{R}} S^{\theta}(T^0,p^0)$ is positive. Else, isothermal & adiabatic operation would imply entropy destruction by entropy balance, which is impossible by the second law of thermodynamics.

In contrast to the reversible voltage, the thermoneutral voltage (determined by the difference in enthalpy) can be interpreted as the net energy required for an overall process as a black box that conducts the desired overall reaction. This net energy corresponds to the electricity consumption if (i) the process operates adiabatically, i.e., without external heat transfer, and (ii) all work input is in the form of electricity. In case of 100% Faraday efficiency, the required voltage of such a process would then be the standard thermoneutral voltage. Note that such a process will in general have entropy production and thus does not operate reversibly. Accordingly, the thermoneutral voltage will be higher than the reversible voltage. If this is not the case for a specific reaction, there would be entropy destruction, which implies that an adiabatic process at equal inlet and outlet temperatures would not be possible for this reaction.

Databases

Values for the enthalpies of formation $\Delta_{\mathrm{f}} H_i$ and entropy S_i of pure species at standard conditions (T^{θ}=298.15 K, p^{θ}=1 bar) can be found tabulated in databases. The NIST database[42] provides a large collection of validated experimental property data and thus is checked as a first resource. However, it lacks data for several of the species considered in this study, which is why we used the reaction mechanism generator (rmg) database[51] to obtain property values for all species. Wherever possible, we compared the values from the different databases to each other.

The rmg database includes methods to estimate thermodynamic properties, both for the ideal gas state and the transition from gaseous to dissolved state. For the calculation of the ideal gas state thermodynamic properties, we use the *Group additivity* method, as this is the only available method providing values for all relevant species. For solvation properties, both group additivity (*SoluteGC*) and machine learning (*SoluteML* and *DirectML*) methods are available. For more details regarding the specific methods, we refer to Chung et al.[52]. According to Johnson et al.[53], the methods are in general sufficiently accurate for H, C and

O molecules though without general error bars being available, due to the high variability between different sorts of molecules.

In the results shown in Section Results and Discussion, we also indicate an estimated error bar for the data obtained from the rmg database to show the influence of data uncertainty on the voltages: As the relative difference between the individual methods for the solvation properties is in general less than 3 %, and for the ideal gas properties less than 2 %, we set the error to 5 % for the species properties in aqueous solution. Note that the actual error is likely less for most species, apart from glyceric acid and lactic acid, which exist in enatiomeric forms not covered by the rmg database. For the calculation of the error in the reaction data ($\Delta_\mathrm{R}G$, $\Delta_\mathrm{R}H$), we took this estimated 5 % error for all the rmg thermodynamic formation data. In cases where we had (presumably accurate) NIST data, we took instead the actual difference between NIST and rmg as error for the specific thermodynamic formation data.

Regarding Reference States

Before using thermodynamic data, its reference state must be evident to convert correctly to the reference state implied by a calculation. As we are limited by available data, we assume unit activity coefficient and thus chose the reference state of pure species (denoted in the following by 0) for the solvent water (ideal liquid) as well as product gases (ideal gas). For the non-gaseous glycerol oxidation products, as well as for glycerol itself, we chose the reference state of an ideal dilution in water (denoted by ∞).

For the Nernst equation (1), the reference state has by definition unit activities and system pressure and temperature. As we neglect the activity coefficients, a concentration scale, for example, molality b_i, molarity c_i, mole fraction x_i, or partial pressure p_i, is obtained instead of the activity.[45] Often enough, the difference between the reference concentration scale (i.e. $b_i = 1$ mol/kg ; $c_i = 1$ mol/l ; $x_i = 1$; $p_i = 1$ bar) and the reference state of either pure species (i.e. $\lim_{x_i \to 1}$) or ideal diluted species (i.e. $\lim_{x_i \to 0}$) is included in the reference state, resulting in different values for different concentration scales. In this case, it is obviously necessary to stick with the same concentration scale for both the reference state and the logarithmic term accounting for the concentration difference or to add a term accounting for the concentration scale difference in the Nernst equation.[54] The latter can be derived from the term $R\ln(x_i)$ stemming from ideal species entropies of formation, and thus is only required for the Gibbs free energy and not the enthalpy.

From the available data in the rmg database, the Gibbs free energy of the species in the reference state of a hypothetical ideal solute in aqueous solution ($\Delta G^\infty_\mathrm{aq}$) at 1 mol/l concentration, is calculated as follows:[53]

$$\Delta_f G^\infty_\mathrm{aq} = \Delta_\mathrm{f} G^0_\mathrm{g} + \Delta G^{0\to\infty}_\mathrm{g} + \Delta G^\infty_\mathrm{solv},$$

where $\Delta_f G^0_g$ denotes the Gibbs free energy of formation of the species as pure ideal gas; $\Delta G^{0\to\infty}$ the change in the reference concentration from pure gas at pure gas molar density to that of the ideal solute at 1 mol/l; $\Delta G^\infty_\mathrm{solv}$ the Gibbs free energy of solvation in aqueous

solution from pure gas at 1 mol/l to ideal solute at 1 mol/l. The middle term is calculated from the difference in molar based volume between the ideal gas ($Vn^{-1} = RTp^{-1}$) and that in the solution $(Vn^{-1})^{\infty}$ which is 10^{-3} $\mathrm{m}^3/\mathrm{mol}$:

$$\Delta G_{\mathrm{g}}^{0\to\infty} = -RT \ln\left(\frac{(Vn^{-1})^{\infty}}{RTp^{-1}}\right),$$

which is equal to 7.958 kJ/mol at standard conditions.[53] While the rmg database provides values for $\Delta_{\mathrm{f}}G_g^0$ and $\Delta G_{\mathrm{solv}}^{\infty}$, the NIST database uses the ideal pure substance as a reference, i.e., $\Delta_{\mathrm{f}}G_{\mathrm{g}}^0$ and $\Delta_{\mathrm{f}}G_{\mathrm{l}}^0$. To compare the values, the following constant must thus be added to eliminate the difference between the ideal liquid and hypothetical ideal solution reference state of every species i :

$$\Delta G_{\mathrm{l,i}}^{0\to\infty} = -RT \ln\left(\frac{(Vn^{-1})^{\infty}}{M_i \rho_i^{-1}}\right).$$

With that, the Gibbs free energy of the species in the reference state of a hypothetical ideal solute in aqueous solution can analogously be calculated from a pure ideal liquid reference state:

$$\Delta_f G_{\mathrm{aq}}^{\infty} = \Delta_{\mathrm{f}}G_{\mathrm{l}}^0 + \Delta G_{\mathrm{l}}^{0\to\infty}.$$

According to this available data, we set the system conditions to the standard of p=1 bar and T=298.15 K. As the practical application of our screening problem aims at aqueous solutions of glycerol and its non-gaseous oxidation products, we set only the reference state of the gaseous molecules hydrogen, oxygen, carbon dioxide, and carbon monoxide to that of pure ideal gas and the reference state of water to that of the pure liquid species. The reference state of the remaining molecules, i.e., the solutes, is set to that of hypothetically 1 mol/l ideally dissolved species in pure water. However, for our reactions considered, the difference in voltage for choosing the ideal solution (at 1 mol/l) or pure species reference state (at $x_i = 1$) is only about 0.03 V and thus negligible for most cases.

Economic Value

Getting reliable and comparable prices is even more challenging as getting the thermodynamic properties. Ideally, we would like to compare current market prices of industrial scale for glycerol and all its oxidation products in a similar range of purity. However, we could not find a source that provides such prices for all products. An alternative would be to gather data from different sources and/or different years, which however has the downside of limited comparability. Most sources do not mention the purity and order of magnitude of product sales to obtain the price mentioned, limiting the reliability of the price data. For these reasons, we decided to include two types of prices: (i) laboratory-scale prices taken from the Sigma-Aldrich website,[55] as it provides economic data for the majority of the considered species in comparable amounts and purities. (ii) industry-scale prices taken from ChemAnalyst[56] and Kahlstorf et al.[57] for the products for which prices are available. The industry-scale prices (of ChemAnalyst) might be the most realisitc, yet only available for about half of the products considered. The prices of Kahlstorf et al. have the aforementioned

downside of being gathered from different years and different sources with the downside of limited comparability and therefore reliability. In particular only products with a sufficiently high market demand have a chance. We argue that nevertheless using the laboratory-scale prices from Sigma-Aldrich, having no better alternative for most of the C_3 molecules, which are expected to be particularly promising[29] and some also under research for novel processess,[7,38] is useful as a shortcut and has at least an informative value in the qualitative comparison of products.

As the absolute prices are highly dependent on both purity and amount, a price range is obtained. Its lower value is that of lowest purity and highest amount, and its upper value that of highest purity and lowest amount. The average of highest of lowest price is also obtained. For both the gases and mesoxalic acid, no prices were found via Sigma-Aldrich, thus we did not consider them here.

We then calculate the economic potential of all products on the basis of unit glycerol mass:

$$p_{\mathrm{rel,Gly},i} = \frac{M_i}{M_{\mathrm{Gly}}} \frac{\nu_i}{|\nu_{\mathrm{Gly}}|} p_{\mathrm{abs},i} - p_{\mathrm{abs,Gly}}, \tag{2}$$

with M_i denoting the species molar mass, ν_i its stoichiometric coefficient and $p_{\mathrm{abs},i}$ its absolute price. The index Gly denotes the species glycerol. This economic potential describes the net revenue per unit mass of glycerol converted for the idealized case of 100 mol% selectivity of glycerol to the respective product. Both the conservative case of calculating the relative price with the highest price for glycerol and the lowest price for the oxidation product i as well as the best case with lowest price for glycerol and the highest price for the oxidation product i were taken to estimate and compare the maximum economic potential.

Results and Discussion

Table 1 shows the reaction equations that lead to the formation of the products introduced in Figure 1. In addition to the overall reaction stoichiometry, the number of transferred electrons z is given. It shall be noted that for the sake of simplicity, we consider the overall reaction only, which implies a system border drawn not only around the electrolyzer but also around the separation system, potential recycle streams etc. Under the assumption that the complete system is designed to conduct this overall reaction, the thermoneutral voltage can then be interpreted as a surrogate for the energy demand of a process built around the electrochemical reactor for which the targeted overall reaction is valid, as discussed in Section Standard Thermoneutral Voltages. Analogously, the reversible voltage can be interpreted as surrogate for the exergy that needs to be supplied to the system, as discussed in Section Standard Reversible Voltages. Thus, both reversible and thermoneutral voltage give us a lower bound to the actual energy demand without closer consideration of pH values.

With that, we avoid a more concrete design of the electrolyzer, which we argue is unwanted and, due to the lack of data, infeasible for a high-level screening at the current technology readiness level. If more details for the design of a real process are known and the actual

electricity demand of the process is to be evaluated, it is important to account for the real concentrations and state of the species consumed and produced as well as the pH value of the solution.[58] In that case, please note that the assumption to take the overall reaction is only valid if the acids are not dissociating, which, according to the Henderson-Hasselbalch equation and the respective pKa value of the acids (see Table S4 in Supporting Information), holds only for pH values less equal than 4 for most.[43] Additionally, we need to make sure that the anode half-cell reaction provides protons in addition to electrons under acidic conditions.

Table 1: Net reaction equations of the considered glycerol oxidation reactions with z denoting the number of transferred electrons.

Product	Total Reaction	z
Oxygen	$H_2O \longrightarrow H_2 + 0.5\,O_2$	2
Glyceraldehyde	$C_3H_8O_3 \longrightarrow H_2 + C_3H_6O_3$	2
Glyceric Acid	$C_3H_8O_3 + 2\,H_2O \longrightarrow 4\,H_2 + C_3H_4O_5$	4
Tartronic Acid	$C_3H_8O_3 + 2\,H_2O \longrightarrow 4\,H_2 + C_3H_4O_5$	8
Dihydroxyacetone	$C_3H_8O_3 \longrightarrow H_2 + C_3H_6O_3$	2
Hydroxypyruvic Acid	$C_3H_8O_3 + H_2O \longrightarrow C_3H_4O_4 + 3\,H_2$	6
Mesoxalic Acid	$C_3H_8O_3 + 2\,H_2O \longrightarrow C_3H_2O_5 + 5\,H_2$	10
Lactic Acid	$C_3H_8O_3 \longrightarrow H_2 + C_3H_6O_3$	2
Glycolic Acid	$2\,C_3H_8O_3 + 3\,H_2O \longrightarrow 3\,C_2H_4O_3 + 5\,H_2$	10
Glyoxylic Acid	$2\,C_3H_8O_3 + 3\,H_2O \longrightarrow 3\,C_2H_2O_3 + 8\,H_2$	16
Oxalic Acid	$2\,C_3H_8O_3 + 6\,H_2O \longrightarrow 3\,C_2H_2O_4 + 11\,H_2$	22
Acetic Acid	$2\,C_3H_8O_3 \longrightarrow 3\,C_2H_4O_2 + 2\,H_2$	4
Formic Acid	$C_3H_8O_3 + 3\,H_2O \longrightarrow 3\,CH_2O_2 + 4\,H_2$	8
Carbon Monoxide	$C_3H_8O_3 \longrightarrow 3\,CO + 4\,H_2$	8
Carbon Dioxide	$C_3H_8O_3 + 3\,H_2O \longrightarrow 3\,CO_2 + 7\,H_2$	14

Thermodynamics

From the species thermodynamic properties shown in Table S1 and S2 in the Supporting Information, the properties for these reactions were calculated, which are listed in Table S3 in the Supporting Information. This includes the standard enthalpy of reaction $\Delta_R H^\theta$, the corresponding standard thermoneutral voltage E^θ_{th} as well as the standard Gibbs free energy of the reaction $\Delta_R G^\theta$ and the corresponding standard reversible voltage E^θ_{rev}. All values are at standard conditions, i.e. T^θ=298.15 K and p^θ=1 bar. The values for the voltages are also written to the bars in Figure 2 and Figure 3.

As seen in Figure 2, all standard reversible voltages of glycerol oxidation reactions coupled with hydrogen evolution reaction are less than half as high as that of the combined oxygen and hydrogen formation. Thus, glycerol oxidation demonstrates a potential to substantially lower the energy consumption of hydrogen production compared to normal water electrolysis.

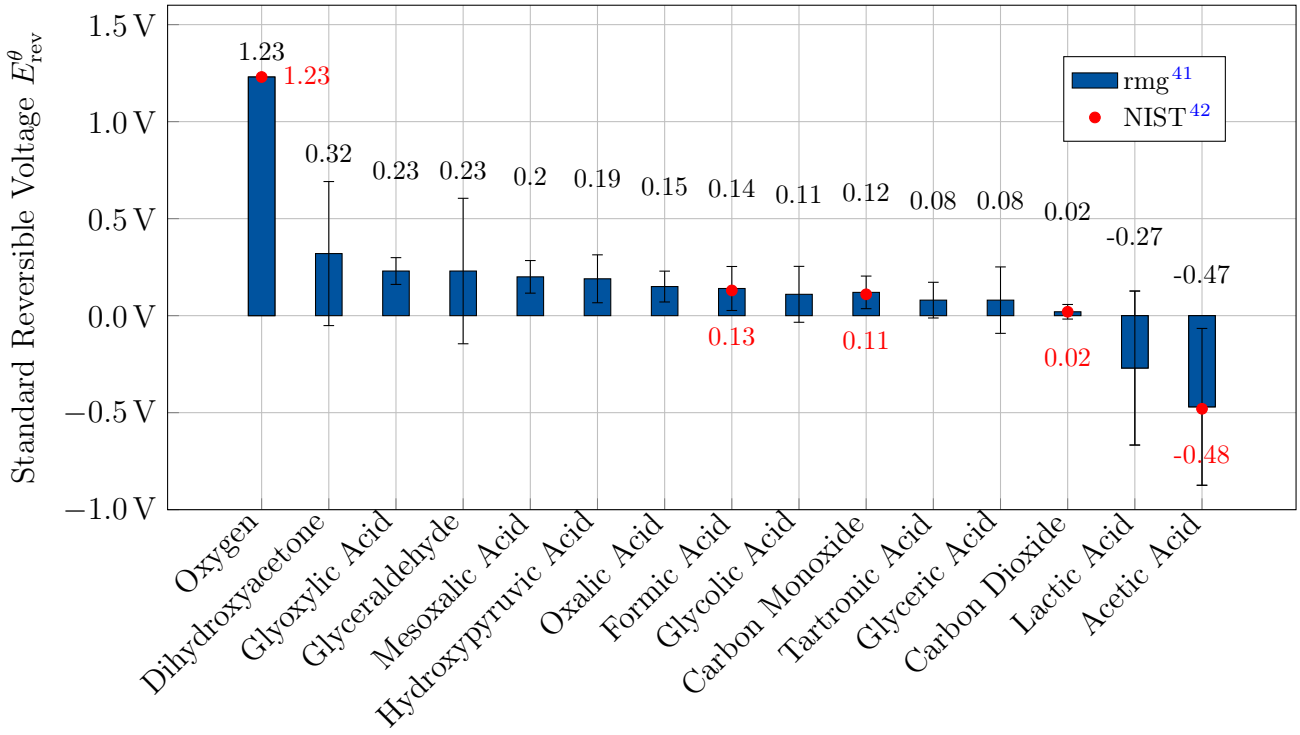


Figure 2: Standard Reversible Voltages for Different Oxidation Products
With standard Gibbs energies of formation taken from either rmg[41] or NIST[42] database. The error bars show the summed up error of the individual species data, taking the difference between rmg and NIST Gibbs free energy values if NIST data is available or else assuming a 5% error in each of the rmg Gibbs free energies of formation

Overall, the values obtained from NIST meet those from rmg with good agreement. This indicates less uncertainty than that shown with the error bars derived as described in Section Databases. Potentially, however, this good agreement is due to the potential use of the NIST data in training the rmg database. There are two reactions with negative values, namely the formation of lactic acid and acetic acid. Negative values mean that these reactions would run in galvanic mode (i.e. spontaneous reaction converting chemical energy into electricity) unless the overpotential losses lead to positive operating voltages in total (which is observed in experiments). We may also call this mode "fuel cell mode" according to the definition of a fuel cell (e.g. Lipman et al.[48] "Electrochemical device converting the chemical energy (Gibbs free energy) stored in a [...] fuel [...] into work of electrical energy (direct current electricity) at constant temperature").

The results of the standard thermoneutral voltages (i.e., isothermal, adiabatic and irreversible operation), shown in Figure 3, show a similar trend to those for standard reversible voltage (i.e., isothermal, reversible and non-adiabatic operation). As the entropy of reaction at standard conditions is positive for all considered reaction, the thermoneutral voltage is more positive than the reversible voltage. The additional voltage due to the entropic term

can be interpreted as minimal dissipation losses to maintain a constant temperature. Thus, if the overpotentials added to the reversible voltage are higher than the thermoneutral voltage, cooling is required (vice versa heating). As, typically, the overpotentials more than cover the difference between reversible and thermoneutral voltage, the thermoneutral voltage can be seen as well as a closer lower bound to the operating voltage.

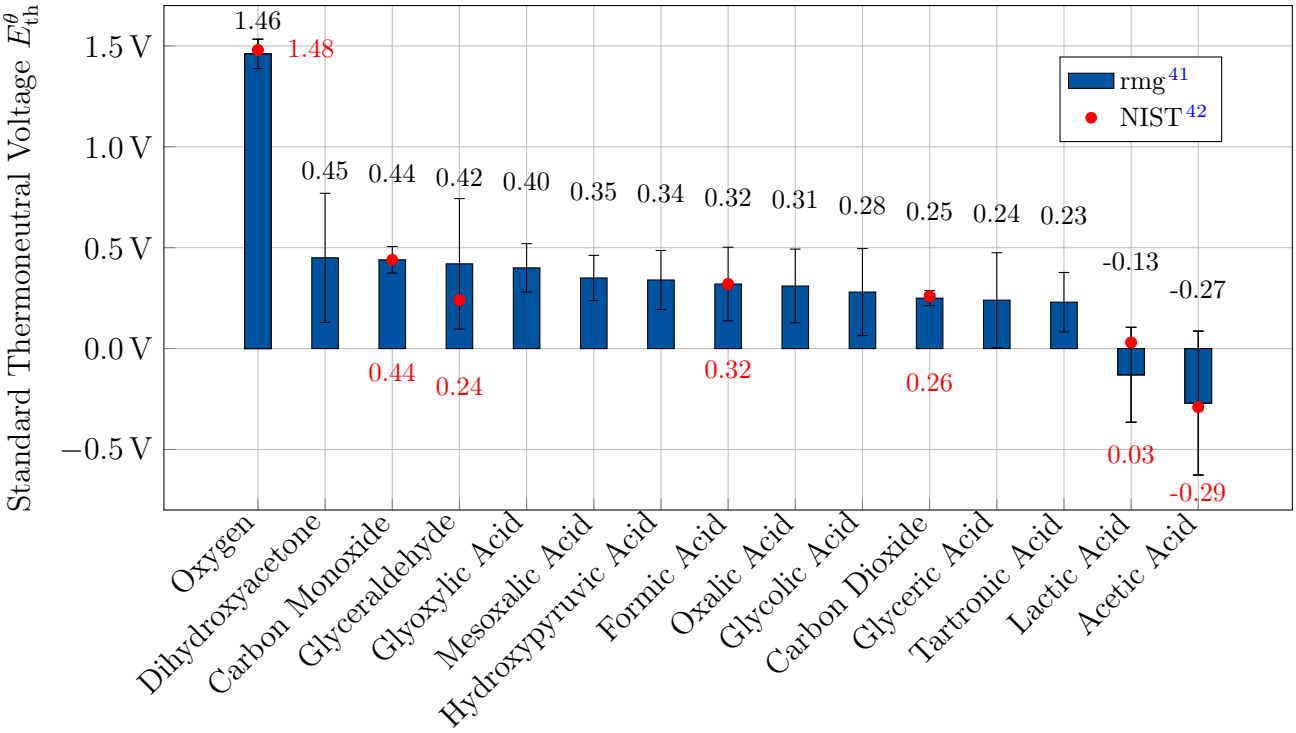


Figure 3: Standard Thermoneutral Voltages for Different Oxidation Products
With standard enthalpies of formation taken from either rmg[41] or NIST[42] database. The error bars show the summed up error of the individual species data, taking the difference between rmg and NIST enthalpy values if NIST data is available or else assuming a 5% error in each of the rmg Gibbs free energies of formation

While again, almost all rmg values show good agreement to the NIST values, there are two molecules with greater divergence: Glyceraldehyde and Lactic Acid. Both molecules are the only ones considered that exist in different enatiomeric structures, which are not accounted for by the rmg database, thus resulting in a systematic error. The NIST database provides different values for both enatiomeric forms as well as for the racematic mixture, which was chosen here for the species properties. Whether this error due to enatiomery is of relevance, depends on the feasibility of producing the individual enatiomeric structures experimentally.

In total, the differences between the standard reversible voltages of the different glycerol oxidation products are each in the same range as the assumed error bars. The same holds

for the standard thermoneutral voltages. With the unknown kinetic impact and economics, no final conclusion on which product shall be aimed, can be drawn at this stage. However, our results show that all glycerol oxidation reactions coupled with hydrogen formation are energetically very promising.

Economics

In contrast to the voltages, the prices of the oxidation products per mass of product differ significantly, as shown in Figure 4. At first, it is apparent that the laboratory prices are mostly higher than the industry prices. That is as expected since industrial prices generally account for higher scales of product sales, which usually leads to lower prices. Interestingly, however, the aspect that laboratory prices are higher than industry prices does not hold for species with relatively low prices, namely glycerol, formic acid, glyoxylic acid, and lactic acid. The latter three, as well as oxalic acid and acetic acid, have a lower price than glycerol in at least one of the three price sources, suggesting that they are unlikely to add value.

In contrast, the C_3 molecules are higher priced (with the exception of lactic acid) than glycerol and the C_1 and C_2 molecules, indicating that they are likely to be favored. Please remark, however, that industry prices (from Sigma-Aldrich) should generally be more appropriate and reliable than laboratory prices, which makes this conclusion subject to uncertainty as no industry prices could be found for the majority of C_3 molecules. While the Kahlstorf et al.[57] prices offer some prices for C_3 molecules, as shown in Figure 4, they also need to be treated with care. We argue this since they collected the prices from different sources of different years, with partially unknown origins, making these prices of only limited use for comparison. Nevertheless, they confirm the order of magnitude of some of the industry prices. Please note that, for the sake of readability, we do not show the price ranges for industry prices in Figure 4. In any case, the range is very narrow, yet still, we respect it for analyzing the economic potential in Figure 5 and 6.

Of the high-priced products, Glyceric acid and dihydroxyacetone even cross the mark of 1000 € per gram for their highest (laboratory) prices. However, their highest prices found were with purities of pharmaceutical reference standard and very low quantities in the range of mg. It is also noticeable that the difference between highest and lowest price found for the two most expensive molecules is about two (for glyceric acid) to four (for dihydroxyacetone) orders of magnitude, indicating high uncertainties for the evaluation, as it is unclear if the very expensive high purities can be generated. Glyceric acid, just as formic acid, exists in two enatiomeric structures. However, only laboratory prices for the L-isomer chemically bound with sodium salt and as hemicalcium salt monohydrate were found. For the industrial price of formic acid, it is not known whether it is refering to one of the isomers or a mean of both. As for all of the molecules, downstream processing is required to reach certain purities anyway, we argue that these prices should be at least considered for further process design. For the remaining molecules, the laboratory prices are taken with amounts in the scale of g, or even kg for some of the C_2-molecules lowest prices, with purities ranging from 89-99.8 wt%. The only exception is glyoxylic acid, for which only the price of a 50 wt% aqueous solution could be obtained. Missing are the prices of mesoxalic acid and

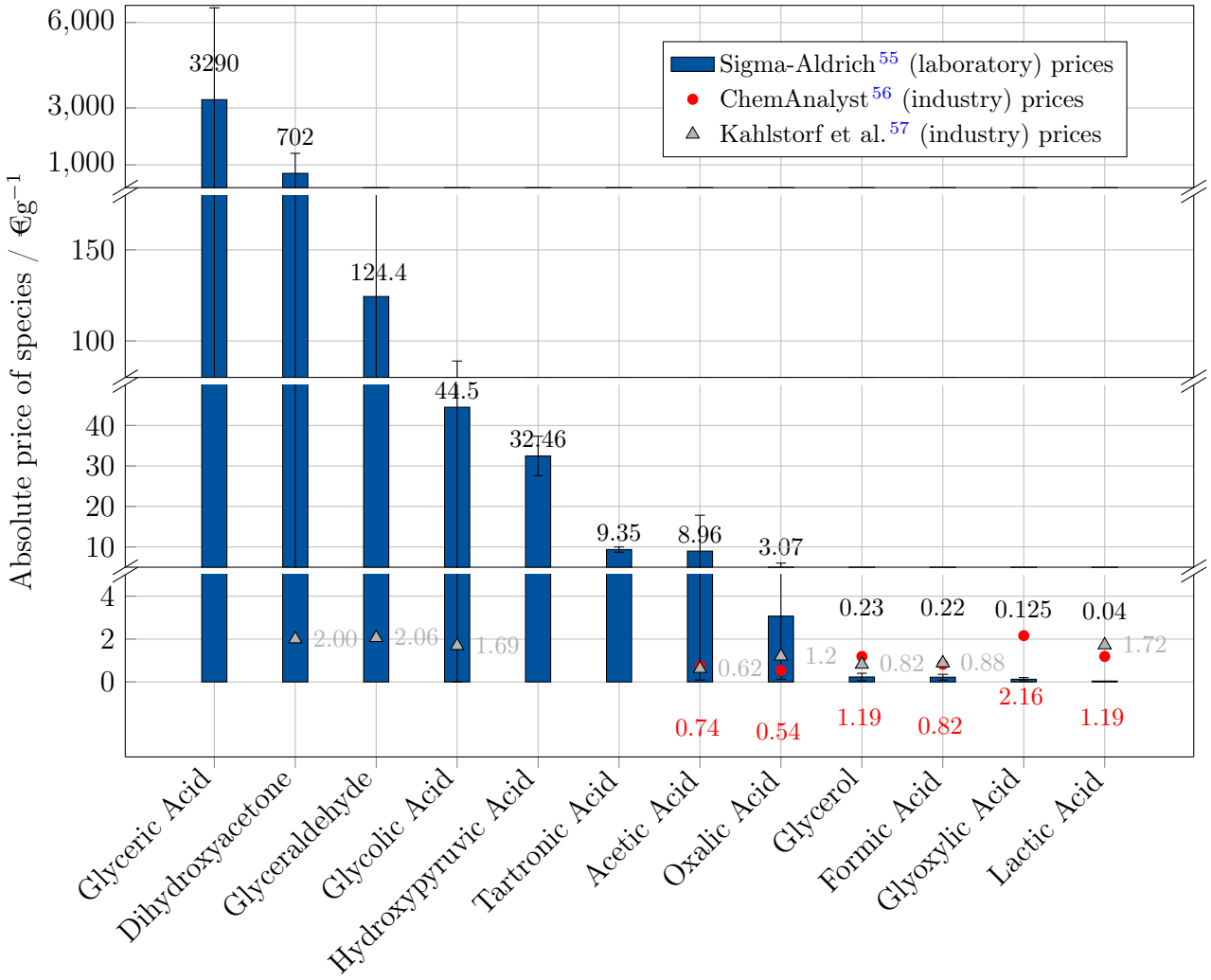


Figure 4: Absolute prices of glycerol and its oxidation products per gram of each species, averaged between highest and lowest price taken from Merck[55] for data of laboratory prices and from ChemAnalyst[56] and Kahlstorf et al.[57] for data of industry prices. *Remark: Laboratory prices cannot be taken as market prices for industry-scale processes, and are only given as an indication, since industry prices are not available for all species.*

the gases (oxygen, carbon monoxide, carbon dioxide) which are not offered by Sigma-Aldrich.

The economic potential, calculated by Equation (2), given in €/g related to one gram of glycerol, is evaluated for two cases: (i) for the conservative case, i.e., with the highest price for glycerol and the lowest for its oxidation products, shown in Figure 5; and (ii) for the best case, i.e., with the lowest price for glycerol and the highest price for the products, shown in Figure 6. For both cases, glyceric acid is the most profitable glycerol oxidation product to produce. The high price range of dihydroxacetone and glycolic acid indicated by the error bars in Figure 4 results in both species being favourable in the best case, yet unfavourable in the conservative case. This means that it must be certain that the corresponding purities

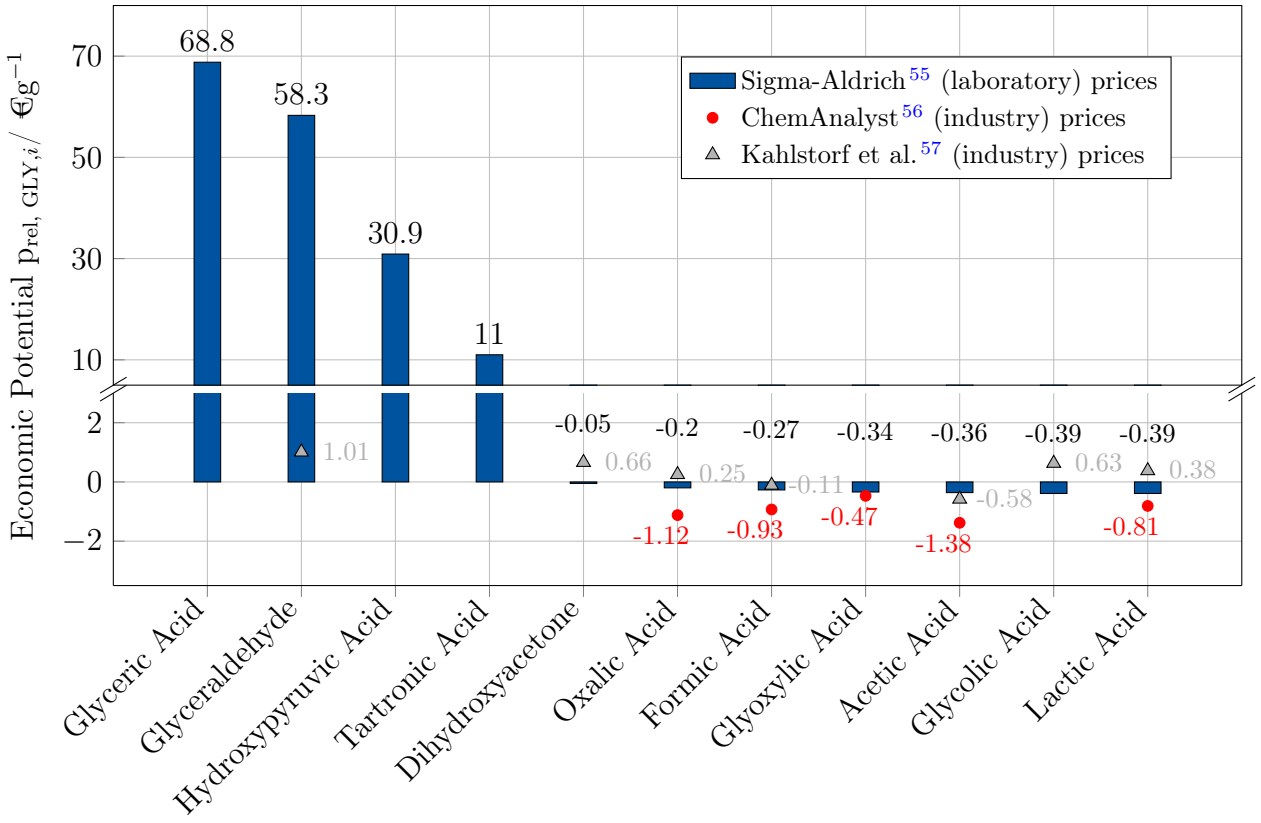


Figure 5: Economic potential of the different glycerol oxidation products per gram of initial glycerol according to Equation (2) for the conservative case (i), i.e., with the highest price for glycerol and the lowest for its products taken from Sigma-Aldrich[55] for data of laboratory prices and ChemAnalyst[56] and Kahlstorf et al.[57] for data of industry prices. *Remark: Laboratory prices cannot be taken as market prices for industry-scale processes, and are only given as an indication, since industry prices are not available for all species.*

are obtainable if these products are to be aimed at. While for the best case, the economic potential of all products is greater than zero, with lactic acid having the lowest value of less than 1 ct/g, a negative potential is obtained for the conservative case for almost all but the four C_3 products glyceric acid, glyceraldehyde, hydroxyperuvic acid, and tartronic acid for both the Sigma-Aldrich and ChemAnalyst prices. It is insufficient, however, to exclude products with a low or even negative economic potential from further analysis, as they may still be beneficial in the context of the overall process. For instance, they may allow the electrolyzer to operate at lower voltages or they might be easier to separate from aqueous product mixtures. Plus, market prices, as well as demands, may change significantly over time, especially if the respective species are part of novel processes under research. However, low or even negative economic potentials indicate that such products likely do not add value.

Please note that we can only say that the four C_3 products glyceric acid, glyceraldehyde, hydroxyperuvic acid, and tartronic acid offer a highly positive economic potential based on their laboratory prices since comparable industry prices were not available for them. The

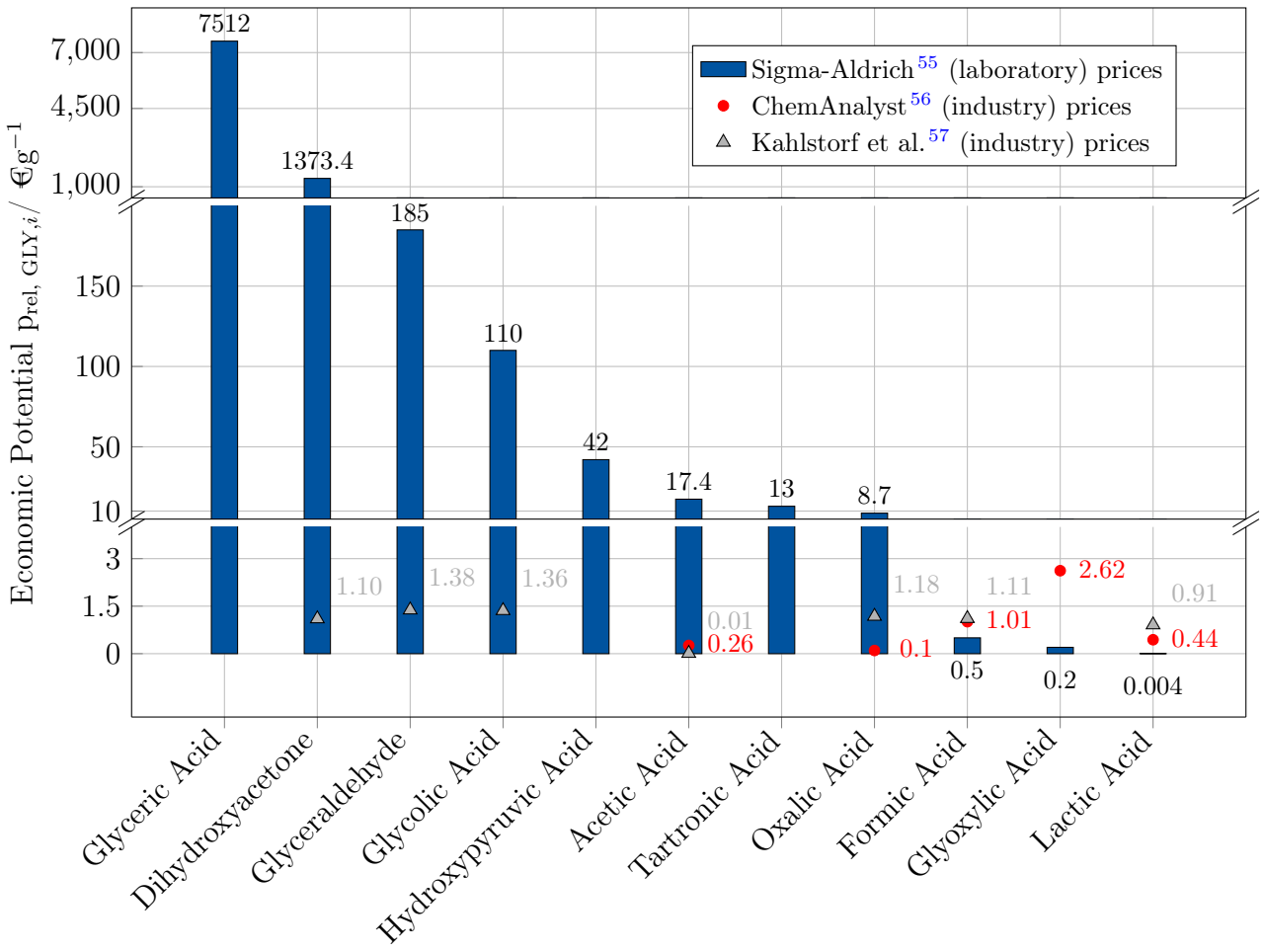


Figure 6: Economic potential of the different glycerol oxidation products per gram of initial glycerol according to Equation (2) for the best case (ii), i.e., with the lowest price for glycerol and the highest for its products taken from Sigma-Aldrich[55] for data of laboratory prices and ChemAnalyst[56] and Kahlstorf et al.[57] for data of industry prices. *Remark: Laboratory prices cannot be taken as market prices for industry-scale processes, and are only given as an indication, since industry prices are not available for all species.*

only exception is the glyceraldehyde price from Kahlstorf et al., which, however, needs to be treated carefully as the source from which the price originates has calculated this price for a proposed process, which means that it is not directly a market price. However, since the economic potential of the laboratory prices is else roughly in the same order of magnitude as for the industry prices for the products where we have both of them, it may still be reasonable to conclude, nevertheless, that likely, the four species glyceric acid, glyceraldehyde, hydroxypyruvic acid and tartronic acid have a positive economic potential. We argue that if the laboratory price of one species is significantly higher than the laboratory price of another species, even though the quantitative value of the economic potential should be treated with care, the qualitative conclusion that to the current market state the first species is more valuable, will still be valid. Please also note that the demands of most of the

products are currently not very big.[57] However, since many of them are under research for novel process concepts,[7,38] product demands and prices may change significantly in future. Since supply, demand, and price are closely linked, it is hard to foresee in which directions these trends may evolve, i.e., if the demand remains unchanged, an improved production via electrochemical glycerol oxidation could lead the market prices to approach zero, while on the other hand, novel process concepts that lead to an increase in demand may even lead to a significant rise in the market prices.

Conclusion and Outlook

We evaluated the prospects of the most relevant glycerol oxidation products by calculating both their standard thermoneutral and reversible voltages as well as comparing their market prices. Moreover, the present contribution highlights that data availability is an issue for screening of alternative anode side reactions, both in terms of thermodynamic properties and comparable prices, since often, important details for a reliable comparison are missing or values are not even available. With the voltage results, we showed that all products are thermodynamically favored over the co-production of oxygen, as they contribute less to the operating voltage. This implies for green hydrogen production that electricity reductions of more than 50% might be possible. By calculating the economic potential from the absolute market prices, we were able to point out that at least four products may provide (considering the uncertainty in the price data) an economic gain in addition to hydrogen production.

For further evaluation, the adjustment in the reversible voltage to the operating conditions suitable for certain catalysts and the corresponding product formations, as well as lower bounds to the overpotentials of the glycerol oxidation reactions, have to be evaluated to calculate the expected real operating voltage. Especially, one should compare the reversible and thermoneutral voltage with the operating voltage observed in experiments to evaluate where significant improvements are still possible. For such an analysis, a method needs to be developed that enables a meaningful comparison of experiments with different conditions (temperature, setup, current density, dynamic vs. steady-state, product mixtures, etc.). Furthermore, the economic properties of the whole electrolyzer, including options for downstream processing, are to be evaluated, with a special focus on the downstream processing of the aqueous mixture since that is expected to be crucial for the overall economics of the process.[59] Also, the electrochemical glycerol valorization coupled with hydrogen production is to be compared with other uses and valorization ways of glycerol, to evaluate if it makes sense to use it for this application. This should also include an analysis of (potential) market usages of both pure products and product mixtures. In addition, it should be clarified what impurities are admissible in the input glycerol, if not pure glycerol but crude or partly purified glycerol from a biodiesel production plant is to be used. The very promising results obtained so far, with energetically promising reactions of which several products even additionally provide revenue, show that such further screening is indeed of great interest.

Author Contribution

Katharina M. Ebeling: Conceptualization, Methodology, Validation, Formal analysis, Inves-

tigation, Writing - Original Draft, Writing -Review & Editing, Visualization
Dominik Bongartz: Supervision, Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – Review & Editing, Funding acquisition.
Sonja Mürtz: Writing -Review & Editing
Regina Palkovits: Conceptualization, Writing -Review & Editing,
Alexander Mitsos: Supervision, Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – Review & Editing, Funding acquisition.

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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.

Supporting Information
We listed the thermodynamic values obtained from the rmg and NIST databases, as well as the pKa values we found for the considered acids in our Supporting Information. Additionally, we provide a derivation of both the reversible and thermoneutral voltage from first and second law of thermodynamics there. This information is available free of charge via the Internet at http://pubs.acs.org/.

References

(1) Zhang, F.; Zhao, P.; Niu, M.; Maddy, J. The survey of key technologies in hydrogen energy storage. *International Journal of Hydrogen Energy* **2016**, *41*, 14535–14552.

(2) Acar, C.; Dincer, I. Review and evaluation of hydrogen production options for better environment. *Journal of Cleaner Production* **2019**, *218*, 835–849.

(3) Brauns, J.; Turek, T. Alkaline Water Electrolysis Powered by Renewable Energy: A Review. *Processes* **2020**, *8*, 248.

(4) Verma, S.; Lu, S.; Kenis, P. J. A. Co-electrolysis of CO2 and glycerol as a pathway to carbon chemicals with improved technoeconomics due to low electricity consumption. *Nature Energy* **2019**, *4*, 466–474.

(5) Sbei, N.; Hardwick, T.; Ahmed, N. Green Chemistry: Electrochemical Organic Transformations via Paired Electrolysis. *ACS Sustainable Chemistry & Engineering* **2021**, *9*, 6148–6169.

(6) Leow, W. R.; Völker, S.; Meys, R.; Huang, J. E.; Jaffer, S. A.; Bardow, A.; Sargent, E. H. Electrified hydrocarbon-to-oxygenates coupled to hydrogen evolution for efficient greenhouse gas mitigation. *Nature Communications* **2023**, *14*, 1954.

(7) Behr, A.; Eilting, J.; Irawadi, K.; Leschinski, J.; Lindner, F. Improved utilisation of renewable resources: New important derivatives of glycerol. *Green Chemistry* **2008**, *10*, 13–30.

(8) Attarbachi, T.; Kingsley, M. D.; Spallina, V. New trends on crude glycerol purification: A review. *Fuel* **2023**, *340*, 127485.

(9) International Energy Agency (IEA), Global biofuel production in 2019 and forecast to 2025. https://www.iea.org/data-and-statistics/charts/global-biofuel-production-in-2019-and-forecast-to-2025, 2022; Online; accessed 21 March 2023.

(10) Adhikari, S.; Fernando, S. D.; Haryanto, A. Hydrogen production from glycerin by steam reforming over nickel catalysts. *Renewable Energy* **2008**, *33*, 1097–1100.

(11) Aroua, M. K.; Cognet, P. Editorial: From Glycerol to Value-Added Products. *Frontiers in Chemistry* **2020**, *8*, 69.

(12) Pagliaro, M.; Ciriminna, R.; Kimura, H.; Rossi, M.; Della Pina, C. Von Glycerin zu höherwertigen Produkten. *Angewandte Chemie* **2007**, *119*, 4516–4522.

(13) Checa, M.; Nogales-Delgado, S.; Montes, V.; Encinar, J. M. Recent Advances in Glycerol Catalytic Valorization: A Review. *Catalysts* **2020**, *10*, 1279.

(14) International Energy Agency (IEA), Hydrogen: Energy system overview. https://www.iea.org/reports/hydrogen, 2022; Online; accessed 21 March 2023.

(15) International Energy Agency (IEA), Renewables 2021: Forecast summary. https://www.iea.org/reports/renewables-2021/biofuels?mode=transport&region=World&publication=2021&flow=Consumption&product=Biodiesel, 2021; Online; accessed 21 March 2023.

(16) Xu, Y.; Zhang, B. Recent Advances in Electrochemical Hydrogen Production from Water Assisted by Alternative Oxidation Reactions. *ChemElectroChem* **2019**, *6*, 3214–3226.

(17) Garlyyev, B.; Xue, S.; Fichtner, J.; Bandarenka, A. S.; Andronescu, C. Prospects of Value-Added Chemicals and Hydrogen via Electrolysis. *ChemSusChem* **2020**, *13*, 2513–2521.

(18) Tuleushova, N.; Holade, Y.; Cornu, D.; Tingry, S. Glycerol electro–reforming in alkaline electrolysis cells for the simultaneous production of value–added chemicals and pure hydrogen – Mini–review. *Electrochemical Science Advances* **2022**,

(19) Chen, Y. X.; Lavacchi, A.; Miller, H. A.; Bevilacqua, M.; Filippi, J.; Innocenti, M.; Marchionni, A.; Oberhauser, W.; Wang, L.; Vizza, F. Nanotechnology makes biomass electrolysis more energy efficient than water electrolysis. *Nature communications* **2014**, *5*, 4036.

(20) Chilakamarry, C. R.; Sakinah, A. M. M.; Zularisam, A. W.; Pandey, A. Glycerol waste to value added products and its potential applications. *Systems Microbiology and Biomanufacturing* **2021**, *1*, 378–396.

(21) Costa Santos, J. B.; Vieira, C.; Crisafulli, R.; Linares, J. J. Promotional effect of auxiliary metals Bi on Pt, Pd, and Ag on Au, for glycerol electrolysis. *International Journal of Hydrogen Energy* **2020**, *45*, 25658–25671.

(22) Kwon, Y.; Schouten, K. J. P.; Koper, M. T. M. Mechanism of the Catalytic Oxidation of Glycerol on Polycrystalline Gold and Platinum Electrodes. *ChemCatChem* **2011**, *3*, 1176–1185.

(23) Ahmad, M. S.; Ab Rahim, M. H.; Alqahtani, T. M.; Witoon, T.; Lim, J.-W.; Cheng, C. K. A review on advances in green treatment of glycerol waste with a focus on electro-oxidation pathway. *Chemosphere* **2021**, *276*, 130128.

(24) Valter, M.; Busch, M.; Wickman, B.; Grönbeck, H.; Baltrusaitis, J.; Hellman, A. Electrooxidation of Glycerol on Gold in Acidic Medium: A Combined Experimental and DFT Study. *The Journal of Physical Chemistry C* **2018**, *122*, 10489–10494.

(25) Lee, C. S.; Aroua, M. K.; Wan Daud, W. A.; Cognet, P.; Pérès, Y.; Ajeel, M. A. Selective Electrochemical Conversion of Glycerol to Glycolic Acid and Lactic Acid on a Mixed Carbon-Black Activated Carbon Electrode in a Single Compartment Electrochemical Cell. *Frontiers in chemistry* **2019**, *7*, 110.

(26) Simões, M.; Baranton, S.; Coutanceau, C. Electrochemical valorisation of glycerol. *ChemSusChem* **2012**, *5*, 2106–2124.

(27) Ciriminna, R.; Palmisano, G.; Della Pina, C.; Rossi, M.; Pagliaro, M. One-pot electrocatalytic oxidation of glycerol to DHA. *Tetrahedron Letters* **2006**, *47*, 6993–6995.

(28) Demirel-Gülen, S.; Lucas, M.; Claus, P. Liquid phase oxidation of glycerol over carbon supported gold catalysts. *Catalysis Today* **2005**, *102-103*, 166–172.

(29) Katryniok, B.; Kimura, H.; Skrzyńska, E.; Girardon, J.-S.; Fongarland, P.; Capron, M.; Ducoulombier, R.; Mimura, N.; Paul, S.; Dumeignil, F. Selective catalytic oxidation of glycerol: perspectives for high value chemicals. *Green Chemistry* **2011**, *13*, 1960.

(30) Dai, C.; Sun, L.; Liao, H.; Khezri, B.; Webster, R. D.; Fisher, A. C.; Xu, Z. J. Electrochemical production of lactic acid from glycerol oxidation catalyzed by AuPt nanoparticles. *Journal of Catalysis* **2017**, *356*, 14–21.

(31) Han, X.; Sheng, H.; Yu, C.; Walker, T. W.; Huber, G. W.; Qiu, J.; Jin, S. Electrocatalytic Oxidation of Glycerol to Formic Acid by CuCo 2 O 4 Spinel Oxide Nanostructure Catalysts. *ACS Catalysis* **2020**, *10*, 6741–6752.

(32) Li, J.; Jiang, K.; Bai, S.; Guan, C.; Wei, H.; Chu, H. High productivity of tartronate from electrocatalytic oxidation of high concentration glycerol through facilitating the intermediate conversion. *Applied Catalysis B: Environmental* **2022**, *317*, 121784.

(33) Prati, L.; Spontoni, P.; Gaiassi, A. From Renewable to Fine Chemicals Through Selective Oxidation: The Case of Glycerol. *ChemSusChem* **2009**, *5*, 2106–2124.

(34) Kwon, Y.; Koper, M. T. M. Combining voltammetry with HPLC: application to electrooxidation of glycerol. *Analytical Chemistry* **2010**, *82*, 5420–5424.

(35) Kim, H. J.; Kim, Y.; Lee, D.; Kim, J.-R.; Chae, H.-J.; Jeong, S.-Y.; Kim, B.-S.; Lee, J.; Huber, G. W.; Byun, J.; Kim, S.; Han, J. Coproducing Value-Added Chemicals and Hydrogen with Electrocatalytic Glycerol Oxidation Technology: Experimental and Techno-Economic Investigations. *ACS Sustainable Chemistry & Engineering* **2017**, *5*, 6626–6634.

(36) Alaba, P. A.; Lee, C. S.; Abnisa, F.; Aroua, M. K.; Cognet, P.; Pérès, Y.; Wan Daud, W. M. A. A review of recent progress on electrocatalysts toward efficient glycerol electrooxidation. *Reviews in Chemical Engineering* **2021**, *37*, 779–811.

(37) Rahim, S. A. N. M.; Lee, C. S.; Abnisa, F.; Aroua, M. K.; Daud, W. A. W.; Cognet, P.; Pérès, Y. A review of recent developments on kinetics parameters for glycerol electrochemical conversion - A by-product of biodiesel. *The Science of the Total Environment* **2020**, *705*, 135137.

(38) Bricotte, L.; Chougrani, K.; Alard, V.; Ladmiral, V.; Caillol, S. Dihydroxyacetone: A User Guide for a Challenging Bio-Based Synthon. *Molecules (Basel, Switzerland)* **2023**, *28*.

(39) Ahn, S.; Hong, M.; Sundararajan, M.; Ess, D. H.; Baik, M.-H. Design and Optimization of Catalysts Based on Mechanistic Insights Derived from Quantum Chemical Reaction Modeling. *Chemical reviews* **2019**, *119*, 6509–6560.

(40) Mitsos, A.; Palou-Rivera, I.; Barton, P. I. Alternatives for Micropower Generation Processes. *Industrial & Engineering Chemistry Research* **2004**, *43*, 74–84.

(41) Green, W. H.; West, R. H. RMG Database. https://rmg.mit.edu/database/, 2023; Online; accessed 23 June 2023.

(42) National Institute of Standards and Technology, NIST Standard Reference Data. https://webbook.nist.gov/chemistry/name-ser/, 2022; Online; accessed December 2022.

(43) Lange, N. A. *Lange's handbook of chemistry*, 15th ed.; McGraw-Hill handbooks; McGraw-Hill: New York, NY, 1999; pp 864–912.

(44) Mitsos, A. Man-Portable Power Generation Devices: Product Design and Supporting Algorithms. Ph.D. thesis, Massachusetts Institute of Technology, 2006; Online; accessed 10 September 2023.

(45) Newman, J.; Thomas-Alyea, K. E. *Electrochemical Systems*, 3rd ed.; Electrochemical Society Series; John Wiley & Sons, Inc.: Hoboken, New Jersey, 2004; pp 21–25, 31–43.

(46) Barbaro, P.; Bianchini, C. *Catalysis for Sustainable Energy Production*, 1st ed.; Wiley-VCH: Weinheim, 2009; pp 239–247.

(47) Smolinka, T.; Ojong, E. T.; Garche, J. In *Electrochemical Energy Storage for Renewable Sources and Grid Balancing*; Moseley, P. T., Garche, J., Eds.; Elsevier: Amsterdam, 2015; Vol. 8; pp 103–128.

(48) Lipman, T.; Weber, A. Z. *Fuel cells and hydrogen production: A volume in the Encyclopedia of sustainability science and technology*, 2nd ed.; Springer reference; Springer: New York, NY, 2019; pp 86–88.

(49) Bard, A. J.; Inzelt, G.; Scholz, F. *Electrochemical dictionary*, 1st ed.; Springer: Berlin and Heidelberg, 2008; pp 444–445.

(50) Mori, M.; Mržljak, T.; Drobnič, B.; Sekavčnik, M. Integral Characteristics of Hydrogen Production in Alkaline Electrolysers. *Strojniški vestnik – Journal of Mechanical Engineering* **2013**, *10*, 585–594.

(51) Gao, C. W.; Allen, J. W.; Green, W. H.; West, R. H. Reaction Mechanism Generator: Automatic construction of chemical kinetic mechanisms. *Computer Physics Communications* **2016**, *203*, 212–225.

(52) Chung, Y.; Vermeire, F. H.; Wu, H.; Walker, P. J.; Abraham, M. H.; Green, W. H. Group Contribution and Machine Learning Approaches to Predict Abraham Solute Parameters, Solvation Free Energy, and Solvation Enthalpy. *Journal of Chemical Information and Modeling* **2022**, *62*, 433–446.

(53) Johnson, M. S. et al. RMG Database for Chemical Property Prediction. *Journal of chemical information and modeling* **2022**, *62*, 4906–4915.

(54) Haase, R., Ed. *Thermodynamik*, 2nd ed.; Grundzüge der Physikalischen Chemie; Steinkopff: Heidelberg, 1985; Vol. 1; pp 238–241.

(55) Merck, Merck website. https://www.sigmaaldrich.com/, Online; accessed 11 July 2023.

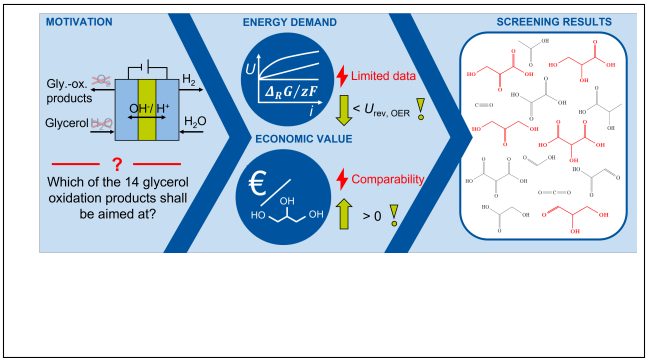
(56) ChemAnalyst, Price Trend and Forecast. https://www.chemanalyst.com/Pricing/Pricingoverview, Online; accessed 10 January 2024.

(57) Kahlstorf, T.; Hausmann, J. N.; Sontheimer, T.; Menezes, P. W. Challenges for Hybrid Water Electrolysis to Replace the Oxygen Evolution Reaction on an Industrial Scale. *Global challenges (Hoboken, NJ)* **2023**, *7*, 2200242.

(58) Hausmann, J. N.; Traynor, B.; Myers, R. J.; Driess, M.; Menezes, P. W. The pH of Aqueous NaOH/KOH Solutions: A Critical and Non-trivial Parameter for Electrocatalysis. *ACS Energy Letters* **2021**, *6*, 3567–3571.

(59) Nabil, S. K.; Muzibur Raghuman, M. A.; Kannimuthu, K.; Rashid, M.; Shiran, H. S.; Kibria, M. G.; Khan, M. A. Acid–base chemistry and the economic implication of electrocatalytic carboxylate production in alkaline electrolytes. *Nature Catalysis* **2024**,

TOC Graphic


MOTIVATION
ENERGY DEMAND
SCREENING RESULTS
Gly.-ox. products
Glycerol
OH⁻ / H⁺
H2
H2O
Which of the 14 glycerol oxidation products shall be aimed at?
Limited data
< U rev, OER
ECONOMIC VALUE
Comparability
> 0