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Glycerol electro-reforming in alkaline electrolysis cells for the simultaneous production of value-added chemicals and pure hydrogen – Mini-review

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Abstract

Glycerol is a cheap, non-toxic, and renewable by-product of the rapid expansion of biodiesel and soap producers around the world. Glycerol electroforming is a method of oxidizing glycerol into valuable chemicals of interest to the pharmaceutical, cosmetics, polymer, and food industries. One of the technologies that have been studied over the past decades is to couple glycerol oxidation with the production of pure hydrogen in an electrolysis cell (so-called electrolyzer), which has shown the advantage of consuming a much lower theoretical amount of electricity than conventional water electrolysis. The efficiency of this device is influenced by the nature, structure, and composition of the electrode material. This mini-review concerns the understanding of glycerol electro-oxidation, a brief state of the art of nanomaterials currently used to prepare electrode materials, and some results concerning the performance of electrolyzers in alkaline conditions that combine the efficient production of value-added chemicals and hydrogen.

KEYWORDS

alkaline electrolyzers, electrocatalysis, glycerol electro-oxidation, hydrogen production, nano-materials

1 | INTRODUCTION

The environmental alteration caused by industrial progress in the last century is mainly due to the use of fossil fuels, whose combustion generates the accumulation of gases in the atmosphere and fine particles that have a negative impact on the environment.^[1] The use of the Earth's renewable energy sources to develop sustainable systems should significantly reduce the consumption of

fossil fuels, the efficiency of which is however limited by weather conditions.

The conversion of chemical energy into electrical, thermal, or mechanical energy without harmful impact on the environment can be an ideal route to sustainable development. Such an ideal chemical source must be able to be generated, stored, distributed, and used safely and at a competitive cost. Basically, a hydrogen atom is the most abundant element in the universe, and dihydrogen (H₂) is

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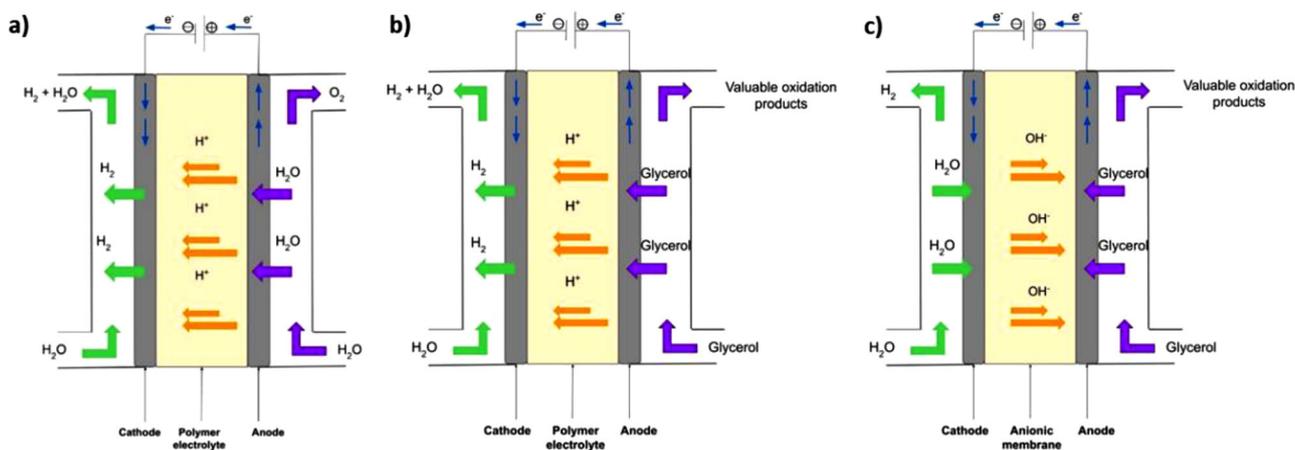


FIGURE 1 Schematic representation of the working principle of (a) water electrolysis proton exchange membrane electrolysis cell, (b) glycerol electrolysis in a proton exchange membrane electrolysis cell, and (c) glycerol electrolysis in a hydroxide exchange membrane alkaline electrolysis cell

a renewable chemical energy source.^[2] However, the buzzword of “hydrogen”, associated with the chemical form H_2 , does not naturally exist in sufficient quantity and is therefore generated mainly from fossil fuels and, to a lesser extent, from water and biomass.

Acar and Dincer presented an in-depth review of several hydrogen production methods from different perspectives such as hydrogen production efficiency, economics, and negative environmental impacts.^[3] The review covers several approaches to hydrogen synthesis, including water splitting (electrocatalytic, photocatalytic, thermal, and thermochemical), syngas production (from coal, biomass, and fossil fuel reforming), plasma-assisted methane decomposition, and other methods based on biomass fermentation. Their comparison shows that it is difficult to identify the ideal approach to obtain hydrogen at low cost, low emissions, and high yield. However, among the different approaches, hydrogen synthesis by water electrolysis has great potential to make it more affordable and environmentally friendly.^[4,5]

Water electrolysis is a process in which an electrical current (or voltage) is supplied from an external source to cause non-spontaneous oxidation and reduction half-reactions at the two electrodes (anode and cathode) of an electrochemical device. Figure 1a illustrates the general principle of operation of water electrolysis^[6] in a proton exchange membrane electrolysis cell (PEMEC). The oxidation of water produces O_2 , protons, and electrons, the latter flow from the anode (positive electrode) to the cathode (negative electrode) through the external circuit. By the exchange ability of the membrane [so-called solid polymer electrolyte technology], protons will be reduced at the cathode by the electrons to form H_2 , without any other harmful by-products ($2H_2O_{(l,g)} \rightarrow 2H_{2(g)} + O_{2(g)}$).

Although the electrolysis of water generates pure H_2 , the theoretical cell voltage of water splitting ($U = E_{anode} - E_{cathode}$) is 1.23 V under standard conditions, but it increases to 1.48 V because the reaction generates large overpotentials due to the entropy change, resulting in low energy efficiency. Such a high thermodynamic barrier necessitates using electrocatalysts deposited on the electrode surface, which are capable to enhance the kinetics of the reaction. The function of these catalysts is to reduce the activation energy of the reactions at both electrodes.^[7] Electrodes, therefore, play a crucial role in improving the effective energy efficiency of an electrolyzer, as they determine both the required energy consumption and the maximum reaction rate in the cell. Cathodes are usually made of Pt/Pd-based materials,^[8,9] while anodes are composed of RuO_2/IrO_2 catalysts.^[10] Both groups of metals make the overall cost of the electrolysis process high^[11] and are non-competitive to the current technologies based on fossils. In order to decrease the cell voltage, keeping the hydrogen production half-reaction at the cathode unchanged ($2H^+ + 2e^- \rightarrow H_2$), the target must then be to decrease the overpotential of the oxidation half-reaction at the anode. Instead of replacing the precious metal catalysts, another strategy to decrease the overpotential at the anode is to substitute the oxidation reaction of water at the anode with that of an organic molecule. Depending on the organics selected on the anode side, the performance, energy consumption, oxidation products, and consequently the emission of gases during electrolysis vary. To date, several organic molecules (coal, methanol, ethanol, glycerol, ethylene glycol, cellulose, and methane) have been proposed because of their abundance, ease of use, and lower oxidation potential than water molecules.^[12–16]

The electrolysis of alcohols is a favorable alternative to water electrolysis because they have a lower oxidation

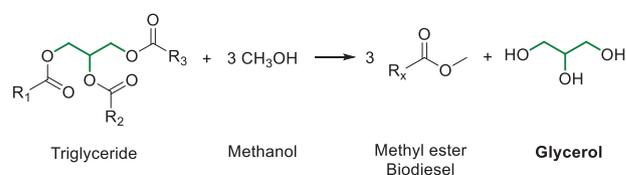
potential than water, which allows the cell potential of the electrolysis process (<1 V) and thus the energy input to be reduced, compared to conventional water splitting cells (cell potentials of 1.5–2.0 V).^[17–19] Among the alcohols, glycerol is a low-toxicity by-product of biodiesel and soap production plants. Its oxidation leads to the production of several chemical groups (acid, ketone, aldehyde, etc.) as intermediates or for the end-use of great interest. It has been studied at the anode of electrochemical devices because, on the one hand, it consumes much less electricity and, on the other hand, it can produce value-added chemicals.^[20] Several excellent studies have described promising strategies to design and construct efficient electrocatalysts for glycerol electro-oxidation with the ultimate concept of combining the production of high value-added chemicals with the production of hydrogen in electrolysis cells.^[14,21–28] They reviewed (i) the activity and selectivity of numerous electrocatalysts for the electrovalorization of glycerol, classifying them according to metal species, (ii) the specific factors that dictate the performance of the reaction mechanism, (iii) the measuring methods to quantify the value-added products, and (iv) the correlation between the composition and structure of the electrocatalysts with respect to the selectivity of the value-added products formed. However, most reported works for glycerol oxidation were developed into half-cell configurations without the corresponding extrapolation to complete cell systems (real devices).

This mini-review focuses mainly on the works carried out to design efficient electrolysis cells for the glycerol electro-oxidation in aqueous electrolytes, combining the production of high value-added chemicals with the evolution of hydrogen. A comprehensive overview of glycerol upgrading via the electro-oxidation mechanism is firstly described, followed by a brief state of the art of efficient electrocatalysts, which are the keystone of electrochemical glycerol valorization. Then, the performance and efficiency of electrolysis cells are presented by evaluating the amount of hydrogen released, the characterization of the reaction products, and the energy consumption, in comparison with water electrolysis. Under alkaline conditions, the kinetics of glycerol oxidation is much faster with the production of more usable value-added products, so only devices operating under alkaline conditions will be presented.

2 | GLYCEROL VALORIZATION

2.1 | Glycerol electrochemical conversion

Glycerol, also named as 1,2,3-propanetriol, glycerin, or glycidic alcohol, is a byproduct in biodiesel manufac-



SCHEME 1 Production of biodiesel and glycerol by triglycerides transesterification with methanol, reproduced with permission^[32].

turing resulting from the transesterification of triglycerides with methanol (Scheme 1).^[29] Each tonne of biodiesel is provided with 100 kg of pure glycerol.^[30] Bio-fuel production has significantly increased from 34 million tonnes in 2000 to 336 million tonnes in 2019,^[31] resulting in a decrease in the market cost of glycerol from €1000 (in 2000–2003) to €150 (in 2019) per tonne.^[32] It is the presence of the three hydroxyl groups in glycerol that allows it to be potentially oxidized into valuable products.

These valuable compounds are usually produced either (i) by enzymatic or microbial processes but with low conversion rates, or (ii) using strong oxidants that do not allow the selectivity of the reaction to be controlled, resulting in a large number of products and by-products.^[33] The selective oxidation of glycerol on precious metals has been developed to increase the conversion and simultaneously control the selectivity of the oxidation reactions.^[34] However, this process operates under controlled moderate conditions of temperature and O₂ pressure. Another strategy is the electrocatalytic oxidation of glycerol, which is carried out with electrocatalysts, at room temperature, without the need to remove the catalyst, and is, therefore, more economical. Furthermore, the use of electrocatalysts and the control of their structure/composition allows for improved process performance and selectivity. This parameter, together with the control of the electrode potential, governs the adsorption of glycerol and water on the surface of the catalyst and thus the selectivity of the oxidation.

The electro-oxidation of glycerol has been developed both in acidic and alkaline systems using electrolysis cells combined with water reduction. In an acidic medium with a PEMEC (Figure 1b), glycerol is oxidized at the anode and produces protons. By the exchange ability of the membrane, protons will be reduced at the cathode by the electrons to form H₂ at the cathode. In alkaline conditions with a solid alkaline membrane electrolysis cell (Figure 1c), the generation of hydrogen at the cathode co-produces hydroxyl ions that cross the anionic membrane to participate in the oxidation of glycerol at the anode. The alkaline medium in the electrolysis cell brings some advantages over the acidic conditions such as

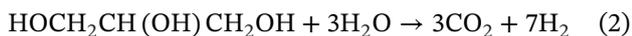
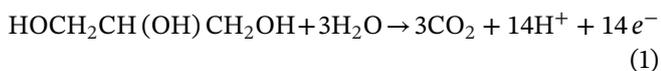
TABLE 1 Comparison of Gibbs free energy values corresponding to the oxidation of different reactants

Reactant	$\Delta G_r^0 / \frac{\text{kJ}}{\text{mol}}$
Water	237.2
Methanol	8.9
Ethanol	97.5
Ethylene glycol	5.4
Glycerol	3.9

long-term durability and the possibility to use non-noble metals.^[4]

2.2 | Thermodynamics of glycerol electro-oxidation

The complete half-oxidation reaction of glycerol tends to form CO₂ (**1**). In electrolysis cells, in the presence of water, the overall process from anode and cathode then leads to the production of CO₂ and H₂, respectively (**2**).



For the overall process under standard conditions, the reaction enthalpy ΔH^0 (**3**) and the Gibbs free energy ΔG^0 (**4**) are 324.8 and 3.9 kJmol⁻¹_{Gly}, respectively.

$$\begin{aligned} \Delta_r H^0 &= 3\Delta_f H^0(\text{CO}_2)_{\text{gas}} + 7\Delta_f H^0(\text{H}_2)_{\text{gas}} \\ &\quad - 3\Delta_f H^0(\text{H}_2\text{O})_{\text{liq}} - \Delta_f H^0(\text{Gly}) \\ &= 3 * (-393.5) + 3 * 285.8 + 665.9 = 324.8 \text{ kJmol}^{-1}_{\text{Gly}} \end{aligned} \quad (3)$$

$$\begin{aligned} \Delta_r G^0 &= 3\Delta_f G^0(\text{CO}_2)_{\text{gas}} + 7\Delta_f G^0(\text{H}_2)_{\text{gas}} - 3\Delta_f G^0(\text{H}_2\text{O})_{\text{liq}} \\ &\quad - \Delta_f G^0(\text{Gly}) = 3 * (-394.4) + 3 * 237.2 + 475.5 \\ &= 3.9 \text{ kJmol}^{-1}_{\text{Gly}} \end{aligned} \quad (4)$$

with $\Delta_f H^0(\text{H}_2)_{\text{gas}}$ and $\Delta_f G^0(\text{H}_2)_{\text{gas}}$ equal to 0 kJmol⁻¹ for any pure element.

From the Gibbs free energy value, glycerol oxidation is thus thermodynamically more favorable not only in comparison with water but also with other alcohols such as methanol, ethanol, and ethylene glycol (see Table 1). The theoretical cell voltage of the complete conversion of glycerol to CO₂ is 0.003 V, defined from the relation (5):

$$U_{\text{cell}}^0 = \Delta G^0 / nF \quad (5)$$

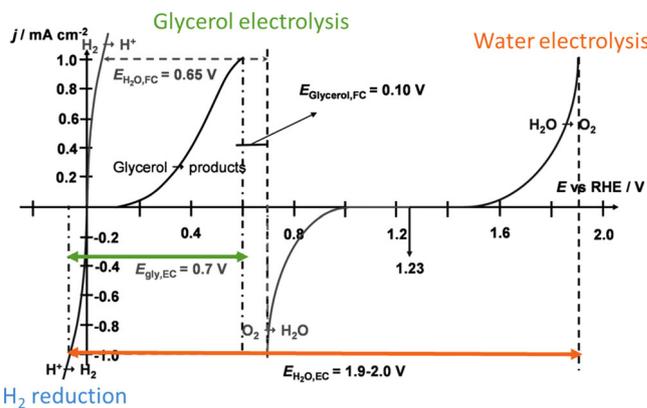


FIGURE 2 Theoretical E(V)-j (mA cm⁻²) plot representative of the Butler-Volmer kinetics law for oxidation of water, glycerol, and reduction protons. On the figure: $E_{\text{H}_2\text{O},\text{FC}}$, $E_{\text{H}_2\text{O},\text{EC}}$, $E_{\text{Gly},\text{FC}}$ and $E_{\text{Gly},\text{EC}}$ are the cell voltages for hydrogen/oxygen fuel cell, water electrolysis, glycerol/oxygen fuel cell, and glycerol electrolysis, respectively. $E_0 = 1.23$ versus reversible hydrogen electrode (RHE) is the H₂O/O₂ redox potential. Reproduced and adapted with permission.^[22]

with F, the Faraday constant is 96485 C mol⁻¹, and n the theoretical number of exchange electrons is 14, making glycerol a more thermodynamically advantageous reactant at the anode than water that leads to a cell voltage $U_{\text{cell}}^{\text{H}_2\text{O}}$ of 1.23 V. However, the complete oxidation of glycerol to CO₂ should not be encouraged because of the issues associated with the release of CO₂, although it can be reduced by a subsequent process.^[35,36] Glycerol oxidation should be thus controlled to produce valuable compounds.

The E-j relation plotted according to Butler-Volmer kinetics law (**6**) shows how the cell voltage evolves with increasing current density.

$$j = j_0 \left[\exp\left(\frac{-\alpha_c nF}{RT} \eta\right) + \exp\left(\frac{\alpha_a nF}{RT} \eta\right) \right] \quad (6)$$

where, j_0 is current exchange density; α_c and α_a ($\alpha_a + \alpha_c = 1$) are transfer coefficients at the cathode and anode, respectively; η is overpotential given by the difference between applied potential and electrode potential. The graph of Butler-Volmer kinetics in Figure 2 includes oxidation curves for water and glycerol and reduction curves for proton and oxygen. In particular, for a reference current density (j) of 1 mA cm⁻², the electrolysis of water ($E_{\text{H}_2\text{O},\text{EC}}$) requires a cell voltage of 2 V, whereas this voltage is only 0.7 V for the electrolysis of glycerol. Besides, partial oxidation of glycerol in electrolysis cells avoiding the cleavage of C-C bonds should, even more, decrease the required cell voltage.

The energy consumption (W [kW kg⁻¹]) required to produce one normal cubic meter (Nm³) of hydrogen by electrolysis depends mainly on the cell voltage (relation [7]).

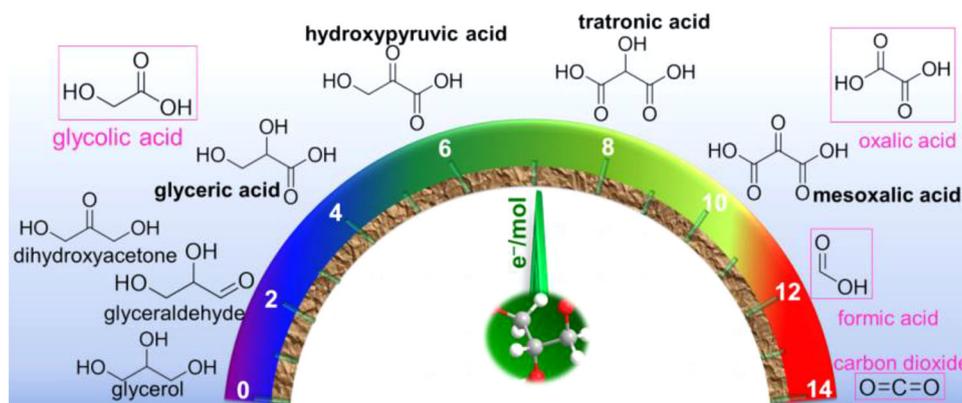


FIGURE 3 Possible valuable products of glycerol oxidation upon the different number of exchanged electrons. Pink rectangular frames depict C1 and C2 oxidation products that involved the C-C bond cleavage. Reproduced with permission.^[39]

The electrochemical splitting of water at $j = 1 \text{ A cm}^{-2}$, therefore, requires $53.6 \text{ kW kg}_{\text{H}_2}^{-1}$ of electrical energy, whereas replacing water with glycerol on the anode side only requires the application of a cell voltage of 0.7 V, which thermodynamically reduces the electrical consumption for H_2 co-production to $18.8 \text{ kW kg}_{\text{H}_2}^{-1}$. Therefore, an aqueous glycerol electrolyzer consumes 65% less energy than a water electrolyzer to produce the same amount of hydrogen. In addition, its lower market price and the possibility of obtaining valuable oxidation chemicals will lower the price of H_2 fuel.

$$W = Q \times U_{\text{EC}}(j) = \frac{1000 \times nF}{3600 \times M} \times U_{\text{EC}}(j) = 26.8 \times U_{\text{EC}}(j) \quad (7)$$

where W is given in units of kW per kg of H_2 , $M = 2 \times 10^{-3} \text{ kg mol}^{-1}$ is the molar mass H_2 and j is the current density, under standard conditions ($T = 0^\circ\text{C}$, $P = 10^5 \text{ Pa}$).

2.3 | Products of glycerol electro-oxidation

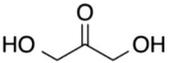
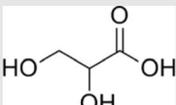
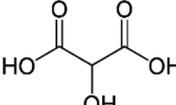
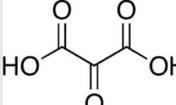
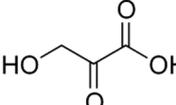
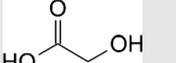
The full oxidation reaction of one mole of glycerol generates three moles of CO_2 gas (2), which makes this full decomposition reaction undesirable. However, the partial and non-selective oxidation of glycerol can lead to a mixture of many intermediates and products involving multi-electron and multi-proton transfers, which will require a purification step. Selectivity control is therefore essential in the oxidation reaction, not only to avoid the formation of greenhouse gases but also to obtain selective value-added products for industrial applications. The three hydroxyl groups attached to glycerol allow the selective oxidation of glycerol to value-added products consisting of three carbon-atoms chain (C3) such as acrylic acid,^[35]

glyceric acid, dihydroxyacetone, lactic acid,^[36–38] 1,2- and 1,3-propanediol. The formation of these products, which requires that all C-C bonds remain intact during oxidation, depends on the number of electrons exchanged,^[39] as depicted in Figure 3. For a higher number of exchanged electrons, C2 and C1 compounds such as glycolic, oxalic, acetic, and formic acids can also be formed as a result of C-C bond breaking.^[40] Electrocatalysis is therefore a powerful tool that can allow controlled selectivity to a higher or lower oxidation state, by adjusting different conditions (such as applied potential, electrocatalyst composition, and precursor concentration).

The judicious combination of electrochemical, spectroscopic, and chromatographic methods provides qualitative and quantitative information on the conversion rate of glycerol and the reaction products. The identification of the products from the electrolysis of glycerol is generally carried out using analytical tools such as in situ Fourier transform infrared (FTIR) spectroscopy, ion chromatography (IC), high-performance liquid chromatography (HPLC), electrochemical mass spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy. The mechanism of glycerol oxidation involves several steps starting with the adsorption of glycerol molecules, breaking of interatomic bonds, transfer of electrons, oxidation of the intermediates by oxygen species, and final desorption of the reaction products.^[41,42]

Desired value-added products are listed in Table 2 with their industrial applications in the field of pharmaceuticals, cosmetics, and food.^[43] Kim et al.^[33] studied the economic feasibility of the electrocatalytic and non-electrocatalytic glycerol oxidation strategies. The authors took into account the cost of the operating raw materials, taxes, and other expenses, as well as the revenues obtained from the sale of the products of selective oxidation and co-generated H_2 . For example, calculations have shown that the final minimum selling price of glyceric acid can

TABLE 2 List of value-added compounds derivable from selective oxidation of glycerol and their industrial applications. Reproduced with permission^[43]

Product structure/name	Applications
 Dihydroxyacetone	Synthon in organic chemistry, starting material in D, L-serin synthesis, tanning agent in cosmetics, monomer in polymeric biomaterials
 Glyceric acid	Application in medicine: metabolite in the glycolysis cycle and an intermediate in the synthesis of amino acids; used for the treatment of skin disorders
 Tartronic acid	Oxygen scavenger, pharmaceuticals in the treatment of osteoporosis and obesity
 Mesoxalic acid	Complexing agent, a precursor in organic synthesis, anti-HIV agents
 Hydroxypyruvic acid	Flavoring additive in the food industry plays a role of human metabolite, an intermediate for glycine and serine metabolism
 Glycolic acid	Decreasing agent, rust removal, skincare products, chemical peels performed in dermatology, textile dyeing, and leather tanning agent
 Formic acid	Used in the leather industry in Asia, agriculture in Europe, formic acid salts used for environmentally friendly runway de-icing, fuel in fuel cells

be reduced from about \$ 4.91 to \$ 2.30 per kg with an electrocatalytic process, being less sensitive to variations in key economic parameters. In addition, the prices of the dihydroxyacetone and hydroxypyruvic acid are about five and 600 times higher than that of glycerol, respectively, confirming the importance of the selective oxidation of glycerol.

Combining incomes from both the recovery of H₂ gas and the coproduced value-added C1-C3 molecules thus makes the electrocatalytic oxidation of glycerol attractive from an economic point of view. To maximize the efficiency of these transformations, the use of electrocatalysts is necessary. Therefore, the development of electrocatalysts should carefully take into account the selectivity for maxi-

mizing glycerol conversion towards a single valuable product while minimizing C–C bond cleavage.

2.4 | Electrocatalysts for glycerol oxidation

2.4.1 | Electrocatalysts

The role of a catalyst is to lower the thermodynamic barrier of the reaction to promote the adsorption of a molecule of interest. Processes that occur at the surface rather than in the bulk determine the properties of most materials. Therefore, control of the surface properties is a key to achieving high-performance materials in many important areas. Contrary to bulk materials, the reduction of particles size to the nanoscale leads to an increase in surface area, and thus in the interface area between the surface of the material and its environment (solvent, gas, and solids). Therefore, nanomaterials with an active surface can enhance different properties (e.g., catalytic, light adsorption, electrical, etc.). To achieve the same performance as bulk, significantly lesser compounds are needed in the case of nanomaterials. Nanomaterials are materials with one (or more) of the external dimensions at the nano-scale between 1 and 100 nm. They have higher activity due to their morphological, chemical, and electronic properties that influence the activity and selectivity of electrocatalytic reactions.^[44] The advantage provided by most active nanomaterials is thus the efficiency in performance as well as cost-effectiveness.

2.4.2 | Synthesis routes for electrocatalysts

Methods for the preparation of nanomaterials are generally grouped into top-down and bottom-up methods. Top-down methods are limited by several major difficulties related to the large size distribution, lack of shape control, and high energy consumption. In bottom-up methods, the formation of nanoparticles is based on the growth of single molecules and atoms into larger blocks. The most common procedures for the synthesis of electrocatalysts are impregnation-reduction (wet and dry), electrophoretic deposition, chemical vapor deposition, sol-gel, and micro-emulsion.^[27,45] During the synthesis, the control of atomic composition and microstructure is necessary to improve the electrocatalytic activity. Therefore, in order to limit the growth of metal particles while balancing their size, the most common synthetic route for the formation of metal nanoparticles is the reduction of metal ions in the presence of capping agents (e.g., surfactants and polymers).^[46,44] The reduction of metal ions is induced by electrons that

can be supplied during the oxidation of other molecules (reductants), by thermally activated redox reactions, by ionizing radiation from solvent molecules, by electric current, or by biological species. Depending on the different driving forces of the reaction, the main synthetic routes are called electrodeposition (e.g., electrical current), radiolysis (γ -radiation), chemical reduction (reducing agent), and hydrothermal (high temperature). Most bottom-up techniques carried out in solution are simple to implement and afford better control of nanoparticle shape and morphology compared to solid- and gas-phase methods.

2.4.3 | Electrocatalysts for glycerol oxidation

Tremendous works have been published on electrocatalysts synthesis to improve the performance in activity and stability for glycerol oxidation. The range of materials is relatively wide, from noble metal such as Pt, Pd, and Au, and their combination with non-noble metals (Fe, Co, Ni, Ag, and Cu) in the form of monometallic, bimetallic, or trimetallic alloys, or core-shells, which allow faster charge transfer and electronic effects.^[47–57] Insightful guidance has been successfully described for understanding the composition-property-structure correlations of electrocatalysts, the mechanism behind the catalytic ability, and the design principles needed to fabricate better electrocatalysts for the selective electro-oxidation of glycerol.^[21,42,58]

Control of the size of nano electrocatalysts during the synthesis plays an essential role. For example, Porta and Parti demonstrated that decreasing the size of gold nanoparticles from 20 to 6 nm resulted in a 10-fold increase in glycerol conversion activity, and a change in the selectivity of oxidation products favoring C2 products formation over C3 products.^[59] The higher activity of the smaller particles is related to their greater number of edges, which are responsible for promoting a more active conversion. Besides, the addition of another active metal to the catalyst composition can generate synergetic effects and more complex mechanisms that may affect the surface properties by distorting the atomic arrangement, changing the surface properties, and altering the binding of reactants and intermediates.^[60–62] Therefore, bimetallic or trimetallic electro-catalysts have become interesting in the electro-oxidation of alcohols as well. Dai et al. investigated AuPt nanoparticles deposited on carbon with different fractions for the electrocatalytic glycerol conversion in alkaline media.^[63] Their studies revealed a high selectivity for lactic acid, which was increased to 73% by optimizing the Au/Pt ratio. The highest selectivity to lactic acid and optimal conversion was achieved for the electrocatalyst comprising

15% of Pt in AuPt, at 0.45 V versus reversible hydrogen electrode (RHE) in the solution containing 1 M KOH and 0.5 M glycerol. At the same time, the monometallic Pt electrode resulted in the lowest selectivity for lactic acid (50%) and the lowest conversion of glycerol, which points to the possible synergetic effect yielded by both metals.

2.5 | Glycerol electro-oxidation and H₂ cogeneration in electrolyzers systems

In general, electrolysis processes that combine the production of organic chemicals with the production of hydrogen are often called “electrochemical reforming” or “electro-reforming”. The electro-reforming of renewable glycerol is thus a promising alternative due to its possible integration in a biorefinery process for combined clean hydrogen and raw chemical production.^[19] Through this technology, an aqueous glycerol solution is electro-oxidized at the anodic compartment of an ion exchange membrane electrolysis cell leading to the formation of organic compounds of industrial interest, electrons, and protons. By the exchange ability of the membrane, the protons are reduced to pure hydrogen in the cathodic chamber. The state of the art of glycerol electro-oxidation performance in electrolysis cells is described in this section on the basis of selected works that allow evaluating the performance of the process, compared to water electrolysis, with the quantification of the hydrogen released, the characterization of the reaction products, and the electrical energy consumption. Contrary to acid conditions, in alkaline conditions, the kinetics of glycerol is much faster, and more value-added products can be produced.^[64] For these reasons, only devices operating under alkaline conditions will be presented. The general trend observed in the presence of glycerol in the anode compartment, compared to water electrolysis, is a decrease in the voltage required for the cell, and therefore in the energy cost, associated with the production of high value-added chemicals.

The first study in 2014 reported the use of nanotechnology to combine Pd nanoparticles and nanostructured TiO₂ nanotube arrays (Pd/TNTA) for electrochemical alcohol reforming experiments including glycerol.^[12] The Pd/TNTA electrode (1.7 mg_{Pd} cm⁻²) was employed as the anode in an electrolyzer equipped with an anion exchange membrane and a Pt/C cathode (0.3 mg_{Pt} cm⁻²). From electrolysis polarization curves obtained at different temperatures in the potential range of 0 to 1.0 V, the electrolysis experiments were conducted at the current density of 1 A cm⁻² with the cell voltage 0.69 V in an aqueous electrolyte consisting of 2 M glycerol and 2 M NaOH. The result showed that the best efficiency was obtained at 80°C with energy consumption for H₂ production calculated to

20 kWh kg_{H₂}⁻¹, compared to 47 kWh kg_{H₂}⁻¹ for water electrolysis in the same conditions. The electrolysis process led to the generation of glycerate (55%), tartronate (25%), carbonate (10%), and formate (10%).

An alkaline reactor for glycerol electro-reforming was studied with commercial PtRu/C (2 mg_{PtRu} cm⁻²) and Pt/C (1 mg_{Pt} cm⁻²) at the cathode and anode electrodes, respectively, to show the influence of the solution composition.^[65] The experimental set-up consisted of a conventional polymer device formed by two graphite monopolar plates operating in aqueous KOH at 75°C. Hydrogen production was evaluated in galvanostatic mode and the oxidation products were analyzed by ion-exchange chromatographic column. The glycerol oxidation process was optimal for 2 M glycerol, as a higher concentration led to higher viscosity and excessive glycerol coverage on the catalyst surface. In this condition, glycerate (35 %) and tartronate (47 %) were mainly formed, as the oxidized products (C1 and C2) are inhibited by a high concentration of glycerol, which limits the availability of adjacent platinum sites. The efficiency of hydrogen production was shown to decrease with increased KOH concentration and the optimal concentration was for 4 M. For a current density of 80 mA cm⁻², the amount of produced hydrogen was 0.350 m³/m²/h (or 1.872 Nm_{H₂}³/m²/h from Charles' Law) with an energy consumption of 16 kWh kg_{H₂}⁻¹.

Platinum is the reference material for the electro-oxidation of glycerol. Due to its high cost and susceptibility to CO poisoning, Pt has been combined with other metals. Furthermore, the use of an additional metal significantly influences the amount and composition of chemisorbed species, the strength of their adsorption, and the rate of their electro-oxidation, compared to the use of monometallic electrocatalysts. Gonzalez-Cobos et al. studied the electrolysis of glycerol in aqueous NaOH in a direct alkaline electrolysis cell (5 cm²) fitted with a Pt/C cathode and a Pt₉Bi₁/C anode.^[66] They demonstrated the reduction of both the electro-oxidation overpotential of glycerol and the overvoltage of the electrolysis cell by adding 10 at% of bismuth, compared to pure metals. The onset potential of glycerol electro-oxidation (defined as the potential at the oxidation current 0.5 mA cm⁻²) was shifted from 0.5 V versus RHE for Pt/C to 0.3 V versus RHE for Pt₉Bi₁/C (i.e., by approximately 0.2 V). Hydrogen was produced from a cell voltage as low as 0.55 V with an electrical energy consumption of 1.3 kWh Nm_{H₂}⁻³ (i.e., 14.45 kWh kg_{H₂}⁻¹), whereas a minimum cell voltage of about 1.5 V and energy consumption of 3.55 kW Nm_{H₂}⁻³ (i.e., 39.47 kWh kg_{H₂}⁻¹) were needed to produce hydrogen from water electrolysis (2.7 times less). The effect of NaOH concentration on cell performance was studied. The hydrogen evolution rate was multiplied by three when NaOH concentration increased from 0.5 to 2 M. At 2 M NaOH, the hydrogen production

rate reached approximately 0.11 Nm_{H₂}³/m²/h with an electrical energy consumption of 1.3 kWh (Nm_{H₂})⁻³ at 0.55 V. This system has resulted in energy savings of 57%–66%, compared to traditional water electrolysis. In situ, FTIR spectroscopy and HPLC analyses showed that only the four products: glyceraldehyde (79.6%), glycerate (10.2%), hydroxypyruvate (4.1%), and tartronate (6.1%) were produced after 4 h of electrolysis with a glycerol conversion of around 6%. This result confirmed that C-C bond breakage does not occur at the Pt₉Bi₁/C. High selectivity towards glyceraldehyde production was obtained in the potential range from 0.35 to 0.55 V versus RHE, whereas carboxylate, which likely involves glyceraldehyde and dihydroxyacetone as reaction intermediates, was produced at potentials higher than 0.55 V versus RHE. It was proposed as an explanation that the presence of bismuth prevents the cleavage of C-C bonds. This resulted in a high selectivity of glyceraldehyde formation at low electrode potentials, and rather carboxylates at higher electrode potentials.

Synergistic effects of bimetallic catalyst toward glycerol electro-reforming (among other alcohols, ethanol, and ethylene glycol) were also shown by Miller et al.^[67] They designed an anionic electrolysis cell operating at 2 M KOH, based on a membrane-electrode-assembly that consisted of preformed nickel foam coated with Au-Pd core-shell nanocrystals of small size (<12 nm) dispersed on Vulcan (Au-Pd/C) (metal loading of 5 wt%). The onset potential of glycerol oxidation was 0.4 V versus RHE, determined by cyclic voltammetry. The performance was measured using potentiodynamic scans and galvanostatic experiments at 60°C. A constant electrolysis current density of 50 mA cm⁻² was applied and the electrolysis was stopped when the cell potential reached 1 V. The energy consumption was 20.4 kWh kg_{H₂}⁻¹ and 47% of glycerol was converted to a mixture of tartronate (26%), oxalate (4%), glycolate (7%), formate (6%) and carbonate (9%), resulting from a significant C-C bond scission. A change in the structure of the electrocatalyst from well-dispersed nanoparticles to cluster formation was observed during the operation without a reduction in the activity.

Electrochemical reforming of glycerol (among other ethanol, ethylene glycol, and 1,2-propanediol) was also performed on nickel foam (5 cm²) coated with Rh/C (1 mg_{Rh} cm⁻²) and using polytetrafluoroethylene as a binder at the anode, in an electrolysis cell equipped with an anion exchange membrane and a Pt/C on carbon cloth cathode (0.4 mg_{Pt} cm⁻²) (Figure 4a).^[68] Polarization curves in the potential range from 0.2 to 0.7 V at 10 mV s⁻¹ showed that the electro-reformer with glycerol reached 113 mA cm⁻² at 0.7 V. High current densities were obtained at cell potential well below 1 V, resulting in a significant energy saving when compared to traditional water electrolyzers.

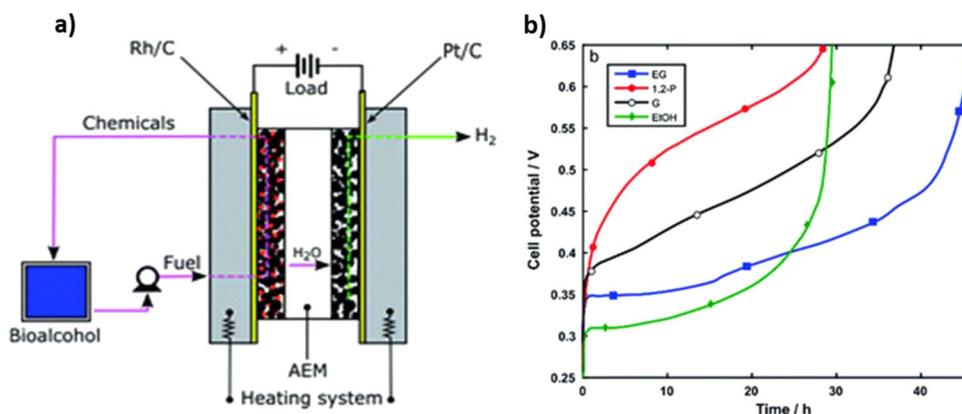


FIGURE 4 (a) Electroreformer cell equipped with an anion exchange membrane and a Pt/C on carbon cloth cathode ($0.4 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$), a nickel foam (5 cm^2) coated with Rh/C ($1 \text{ mg}_{\text{Rh}} \text{ cm}^{-2}$) as anode and a Pt/C on carbon cloth cathode ($0.4 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$), bed by aqueous solutions (30 cc) of glycerol 2 M and 2 M KOH; galvanostatic curves at 125 mA. Cell temperature 60°C , (EG: ethylene glycol, 1,2-P: 1,2-propanediol, E: ethanol, ethylene glycol, and G: glycerol); (b) galvanostatic curves at 125 mA. Reproduced with permission.^[67]

Galvanostatic experiments were performed at 60°C at a constant total current of 125 mA ($J = 25 \text{ mA cm}^{-2}$) and were stopped when the cell potential reached the value of 0.65 V (Figure 4b). H_2 production was $4.3 \text{ Nm}_{\text{H}_2}^3 \text{ m}^{-2}$ with an electrical energy consumption of $12.6 \text{ kWh kg}_{\text{H}_2}^{-1}$. Oxidation of glycerol led to a complex mixture of partial oxidation products, including glycerate (46%), tartronate (23%), and also products due to significant cleavage of the C-C bond, such as carbonate (18%), formate (8%), oxalate (2%) and glycolate (3%). Secondary alcohols such as dihydroxyacetone, hydroxypyruvate, or mesoxalate were not observed.

As glycerol is readily available on a large scale, its electrochemical oxidation using a non-noble metal electrocatalyst has shown great promise for the production of formic acid, an important industrial intermediate in fuel cell applications, and for hydrogen storage due to its relatively high hydrogen content.^[69] Li et al. reported on the catalyst nickel-molybdenum-nitride nanoplates (2.9 mg cm^{-2}) supported on Carbon Fibers Cloth (Ni-Mo-N/CFC) (Figure 5a) in a membrane-free two-electrode electrolyzer at both anode and cathode, operating at room temperature in 1 M KOH (Figure 5b). The highest activity of the electrocatalyst was achieved in 0.1 M glycerol. At the current density of 10 mA cm^{-2} , the cell potential was 1.36 V, while a higher potential of 1.62 V was required to reach the same current density for oxygen evolution reaction with the same catalysis Ni-Mo-N/CFC at both anode and cathode. Figure 5c shows clearly that the faraday efficiencies for hydrogen at varied current densities are all consistently close to 100%. The glycerol oxidation products were analyzed by ^1H , ^{13}C NMR spectroscopy, and IC analyses. Long-term electrolysis (12 h) resulted in the production of formate following successive

stepwise reactions, with methanol as one of the main intermediates. The faraday efficiencies for the production of H_2 at the cathode and formate at the anode were 99.7% and 95.0%, respectively.

A similar study was published the same year by Xu et al. on nitrogen-doped carbon-coated Ni-MO-N nanowire arrays supported on a nickel foam substrate.^[70] The bifunctional material was assembled in a two-electrode hybrid system in a 1 M KOH solution (Figure 6a). They first showed that the presence of 0.1 M glycerol reduced the cell voltage to 1.38 V at 10 mA cm^{-2} , compared to 1.57 V for oxygen evolution reaction, indicating easier oxidation of glycerol than water (Figure 6b). They showed that their system surpassed most of previously reported energy-efficient hydrogen production systems based on other earth-abundant elements. After an electrolysis measurement conducted at 1.50 V for 2 h, the amount of H_2 generated experimentally ($2.41 \text{ Nm}_{\text{H}_2}^3/\text{m}^2/\text{h}$) was close to the calculated theoretical value (Figure 6c) with a faradic efficiency as high as 99.7%. The electrocatalytic performance and the good durability for HER of the electrocatalyst (Figure 6d) were explained by the unique structural properties of the nanowires. The final product was mainly formate, suggesting a high selectivity for the oxidation of glycerol.

3 | SUMMARY AND OUTLOOK

The electro-oxidation of biomass-based organic molecules has gained tremendous interest in the last decade for the neutral-carbon processes of electricity production in various devices such as low-temperature fuel cells, CO_2 electro-conversion, and green H_2 production in low energy

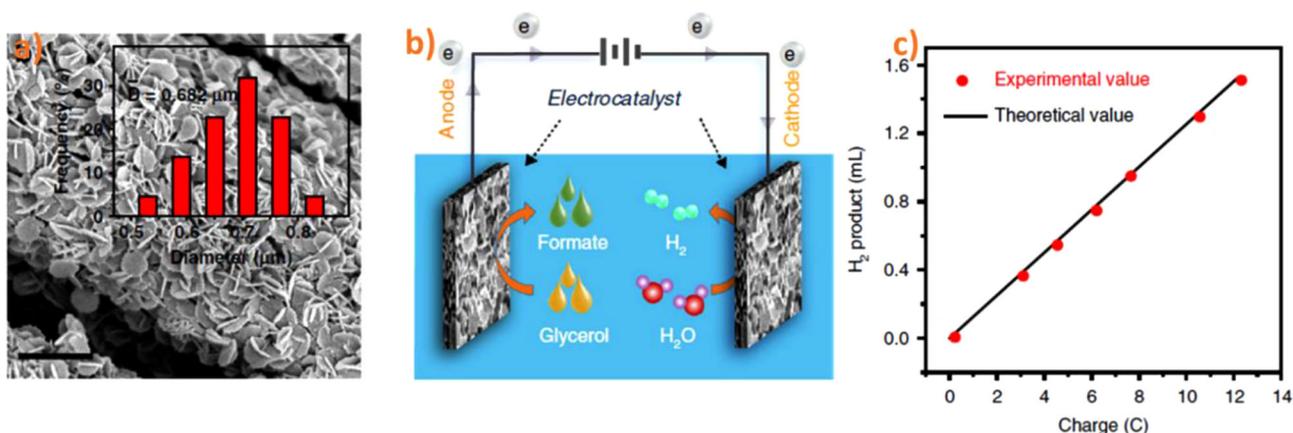


FIGURE 5 (a) Morphological characterization of Ni-Mo-N/CFC by SEM (scale bar 2 μm), (b) schematic illustration for concurrent electrolytic hydrogen and formate productions from glycerol solution, (c) Comparison between theoretical calculation and experimental measurement of H_2 evolution, indicating an up to 100% faraday efficiencies for H_2 production on Ni-Mo-N/CFC catalysts. Reproduced and adapted with permission.^[68]

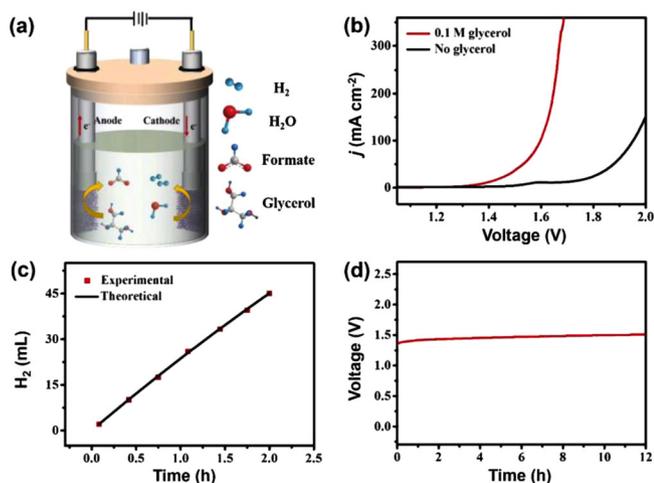


FIGURE 6 (a) Schematic illustration of two-electrode hybrid water electrolysis system by integrating GOR (glycerol oxidation reaction) with HER (hydrogen evolution reaction). (b) Linear Scanning Voltammetry (LSV) curves for the NC/Ni-Mo-N/NF || NC/Ni-Mo-N/NF cell in 1.0 M KOH solution with and without 0.1 M glycerol addition. (c) The faraday efficiencies for H_2 production in the NC/Ni-Mo-N/NF || NC/Ni-Mo-N/NF cell. (d) The V-t curve of the NC/Ni-Mo-N/NF || NC/Ni-Mo-N/NF cell with a constant current density of 10 mA cm^{-2} for 12 h. The LSV curves in (b) were iR corrected. Reproduced with permission.^[69]

input electrolyzers. In electrolyzers, the advantage of oxidizing alcohols is the reduced cost of generating pure H_2 at the cathode with the formation of valuable chemical intermediates at the anode instead of producing O_2 .

Tremendous works have been published on electrocatalysts synthesis to improve the performance in activity and stability for glycerol oxidation. Noble metals are efficient but they are expensive, scarce and their quantity should

be reduced by replacing them partially or totally with non-precious metal catalysts. However, it appears that only a few works have been carried out on the implementation of electrocatalysts in alkaline electrolysis cells for the electro-oxidation of glycerol in aqueous electrolytes (see Table 3), compared to the amount of work for water electrolysis. Evaluation of the amount of released hydrogen, characterization of the reaction products, and consumption of electrical energy is the main interesting features to evaluate the performance in electrolysis. Compared to water electrolysis, the general tendency observed in the presence of glycerol in the anode compartment of alkaline electrolysis cells is the decrease in cell voltage, combined with the production of high-value chemicals for the industry. In addition, the anode electrocatalysts have the potential to match the hydrogen production rates of water electrolysis with lower energy costs.

However, in the discussed electrolyzers, pure glycerol has been used instead of raw glycerol, which contains methanol and other impurities that require a purification step and add extra costs. Future research efforts should thus consider the use of raw glycerol as a feedstock for better commercialization of this process. Although the low oxidation potential of glycerol conversion is an obvious advantage in reducing overall energy consumption compared to water electrolysis, the challenge is the selectivity of the reaction at the anode with the formation of single or easily separable products. Promising results were shown such as the selective electro-oxidation conversion of glycerol to formate in high yield by the non-noble Ni-Mo-N based catalyst, which promotes C-C bond breaking. However, the majority of the other catalysts led to a mixture of value-added products: the $\text{Pt}_9\text{Bi}_1/\text{C}$ electrocatalyst prevents C-C bond cleavage, resulting in high

TABLE 3 Comparison electrolyser performance for glycerol electro-oxidation and H₂ cogeneration

Anodic electrocatalyst	Operating conditions	H ₂ production (Nm _{H2} ³ /m ² /h)	Energy consumption (kWh kg _{H2} ⁻¹)	Selectivity (%)	Reference
Pd/TNTA (1.7 mg cm ⁻²)	2 M NaOH 2 M glycerol 80° C J = 1 A/cm ² @ 0.76 V	–	20.37	Glycerate (55) Tartronate (25) Carbonate (10) Formate (10)	[12]
Pt/C (1 mg cm ⁻²)	4 M KOH 2 M glycerol 75° C J = 80 mA/cm ²	1.872	16	Glycerate (35) tartronate (47)	[61]
Pt ₉ Bi ₁ /C (1.6 mg cm ⁻²)	2 M NaOH 2 M glycerol 20° C @ 0.55 V	0.11	1.65	Glyceraldehyde (79.6) Glycerate (10.2) Hydroxypyruvate (4.1) Tartronate (6.1)	[62]
Au-Pd (0.75 mg cm ⁻²)	2 M KOH 2 M glycerol 60° C J = 50 mA/cm ²	–	20.4	Tartronate (26) Oxalate (4) Glycolate (7) Formate (6) Carbonate (9)	[63]
Rh/C (1 mg cm ⁻²)	60° C J = 25 mA/cm ²	4.3	12.6	Glycerate (46) Tartronate (23) Carbonate (18) Formate (8) Oxalate (2) Glycolate (3)	[64]
Ni-Mo-N/CFC	1 M KOH 0.1 M glycerol 10 mA/cm ² @1.36 V	–	–	Formate (95)	[65]
Ni-MO-N (1 mg cm ⁻²)	1 M KOH 0.2 M glycerol 10 mg cm ⁻² @1.5 V	–	–	Formate	[66]

selectivity towards C3 oxidation products (glyceraldehyde, glycerate, tartronate, and hydroxypyruvate). However, the Au-Pd and Rh/C electrocatalysts lead to a mixture of C3 oxidation products (tartronate, glycerate) and C2 and C1 oxidation products (oxalate, glycolate, formate, and carbonate), resulting in a high degree of C-C bond cleavage. For industrial application, the selectivity and conversion rates of value-added chemicals must be optimized according to the nature of the catalysts, the electrode potential, and the reactor composition.

It should be noted that the glycerol electrolysis process is still in its infancy in terms of technological development and industrial integration. Several critical challenges still need to be addressed in the development of stable electrocatalysts, efficient electrolyzers, product selectivity, chemical separation-isolation, and detailed study of the anode reaction mechanisms. The engineering of a multifunctional catalytic material capable of functioning as anode and cathode in alkaline media is particularly

important for simplifying and reducing the cost. To achieve high selectivity, empirical discoveries of new electrocatalysts must also be complemented by studies on the reaction mechanisms. Future researchers should focus on the following important aspects mentioned in this study.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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