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Review Article

Tackling electrocatalytic oxidation of glycerol to dihydroxyacetone: A comprehensive review

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Biodiesel, developed as an alternative to natural fossils, is produced by a transesterification reaction. The main co-product of this reaction is represented by glycerol, whose production in 2020 exceeded 6 times the current demand. A consequence of the spreading of biodiesel market was a drop of glycerol price. This versatile biomass-derived compound can be used as an important raw material for the manufacture of valuable chemicals including dihydroxyacetone (DHA), which is the most high-valued glycerol-derived product. Despite all the research devoted to achieve selective oxidation of the secondary alcohol group, this issue remains a scientific challenge. Among several routes for glycerol valorization, electrochemistry is an attractive process as discussed in this review. After a short introduction, which describes non-electrochemical methods, electrochemical oxidations on precious (based on Pt, Pd, Au and Ag) and non-precious metal electrocatalysts is discussed, with a specific focus on selectivity towards DHA.

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Introduction

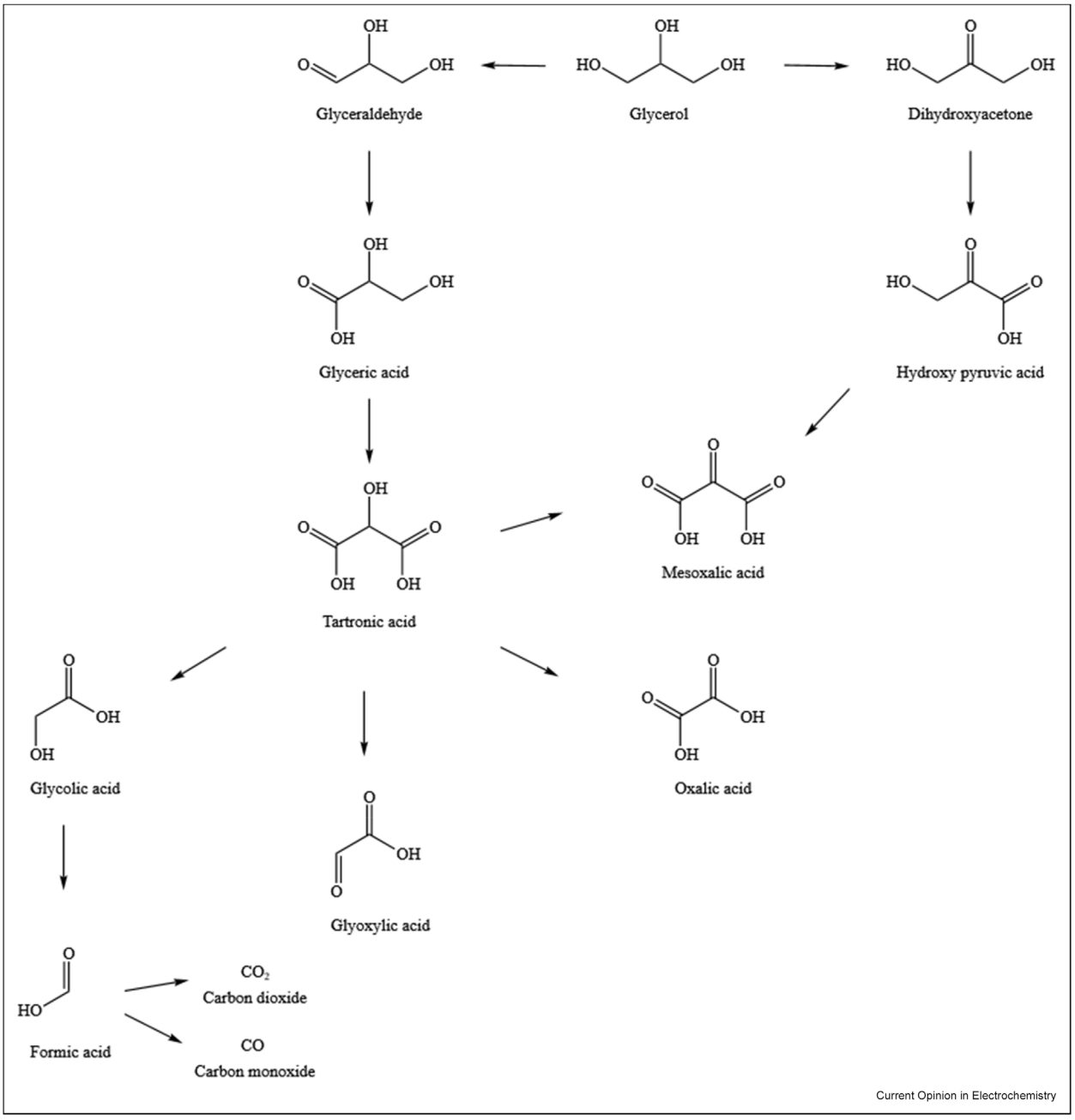
The growth of the biodiesel market has led to the availability of large amounts of glycerol, which represents one of the main coproducts of the transesterification of oils or fats. The surplus generated from the biodiesel market led to a continuous drop of its price [1]. Dihydroxyacetone (DHA) is one of the most high-valued glycerol derived product and has different applications in cosmetic and fine chemical industry [2,3]. The current production of DHA occurs through microbial fermentation, which is the only industrial-scaled route, based on the glycerol oxidation by the bacterium *Gluconobacter oxydans* [4–6]. Unfortunately, this process suffers from a number of limitations that are responsible for low productivity and high costs [7]. As a result, production has not reached the required yield to satisfy the commercial demand and there is great interest in finding alternative low-cost and selective methods for the synthesis of DHA [8–10]. A good selectivity to DHA at high glycerol conversion is difficult to achieve because of the trihydroxy structure of glycerol and rapid overoxidation of DHA (Figure 1) [11–13].

Among the alternative methods, one possibility is the glycerol oxidation in one-step process using metal catalysts in monometallic (Pt, Pd, Au), bimetallic (Pt–Bi, Pt–Au, Pt–Cu, Pd–Ag), or trimetallic form [14–24]. Oxidizing agents are H_2O_2, O_2, benzoquinone and TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl)/NaOCl [13,25–27].

Conventional oxidation procedures involve the use of homogeneous and heterogeneous catalysts [27–34]. Organometallic complexes, such as $[Pd(OAc)_2]_n$, were largely investigated as homogeneous catalysts but were often presented with decomposition problems [35].

Among heterogeneous catalysts, various studies focused on the optimization of noble metal catalysts selectivity using promoters. The best catalytic performance was observed when using bismuth (Pt–Bi/C) [17,36]. Recently, Bi_2O_3-coated carbon nanotubes (CNTs) composite (Bi_2O_3-CNTs) was synthesized and used as support to immobilize Pt catalysts using both atomic layer deposition (ALD) and impregnation methods [37]. The ALD prepared catalyst exhibited uniform Pt–Bi_2O_3 interface and positively charged Pt, resulting in improved catalytic performance in the base-free oxidation of

Figure 1



Reaction pathways to glycerol oxidation products.

glycerol to DHA with atmospheric oxygen, achieving 57 % selectivity and 43 % yield. In 2007, a new generation of catalysts, based on gold, entered the scene [38]. The synthesis of DHA by the catalytic oxidation of glycerol over carbon-supported gold nanoparticles with platinum as a promoter was reported for the first time [39]. Among factors influencing catalyst performance, it was found that the activity decreased with enlarged particle size (from 2 to 16 nm) [20,40–43]. The effect of the catalyst support and of the pH was also examined [44,45].

The selective oxidation of the secondary hydroxyl group of glycerol was also reported using a source of positive chlorine, in presence of a Lewis acid as catalyst [46]. Another procedure, via indirect oxidation of glycerol to DHA, described oxidation of the middle hydroxyl group thanks to a TEMPO/NaBr/NaClO system [25].

Although these extensive studies are interesting for increasing the selectivity towards DHA product, the use of such catalysts implies often high costs and suffers of

catalyst deactivation issues [47,48]. Recently, electrochemical glycerol oxidation, which is described in next sections, is receiving increasing attention [49–54]. It can provide high DHA selectivity, coupled with renewable energy sources, employing water as a reaction medium [55,56]. It has the intrinsic advantage of avoiding the use of oxidising agents, which apart from being problematic for transport, storage and handling can also lead to deterioration of the chemical plants' materials [57]. In addition, paired electrolysis allows to conveniently couple glycerol electro-oxidation, occurring at the anode, with hydrogen production or CO_2 electroreduction at the cathode [49,58]. Some studies reported indirect electrochemical oxidations, mainly using TEMPO-based mediators, but this review does not focus on these processes [59–61]. The following sections provide an overview of direct electrochemical oxidation methods with a focus on practical applications. Accordingly, the review delves deeper into studies using macroelectrodes or providing useful information for laboratory-scale DHA synthesis.

Electrochemical oxidation based on precious metal electrocatalysts (Pt, Pd, Au, Ag)

The catalytic activity and selectivity of glycerol oxidation can be influenced by the nature, structure, and composition of the electrode material, together with the pH and the presence of p-block promoters in solution [51,62]. Commonly used metals for direct electrochemical oxidation of glycerol include Pt, Au, and Pd [63,64]. Au is usually active at high potentials and therefore is used as a promoter of transition metal oxides. Pd has high electrocatalytic activity in alkaline solutions and has a good tolerance to poisoning during electro-oxidations [65]. Simões et al. showed that Pd outperformed Pt and Au in electro-oxidation reaction of glycerol (GEOR) in alkaline media [66]. Moreover, investigations performed with Pd-based catalysts modified with Bi [67] and Sn [68] have shown to favour glycerol electro-oxidation to DHA [69].

Studies with *in-situ* Fourier transform infrared spectroscopy (FTIR) on polycrystalline Au revealed that GEOR in alkaline medium produced DHA, tartronic acid, mesoxalic acid, glyoxylic acid and CO_2, while in acidic medium only tartronic acid, formic acid and CO_2 were detected at higher potentials than those in an alkaline medium, with a very low activity [70,71]. Other studies on gold electrocatalysts demonstrated high GEOR activity under alkaline conditions, producing mainly glyceric acid, whereas Au was almost inactive at neutral and acidic pH, although selective for DHA [72]. The activity and selectivity seem to be controlled by surface-bound hydroxyl groups. Under alkaline conditions, modest OH coverage is preferred, indicating that both $Au(OH)_{ads}$ and Au can be active sites, facilitating the formation of glyceric acid. On the contrary, under acidic conditions the hydroxyl coverage is very low and DHA becomes the favourite product but very low activity has been reported [72].

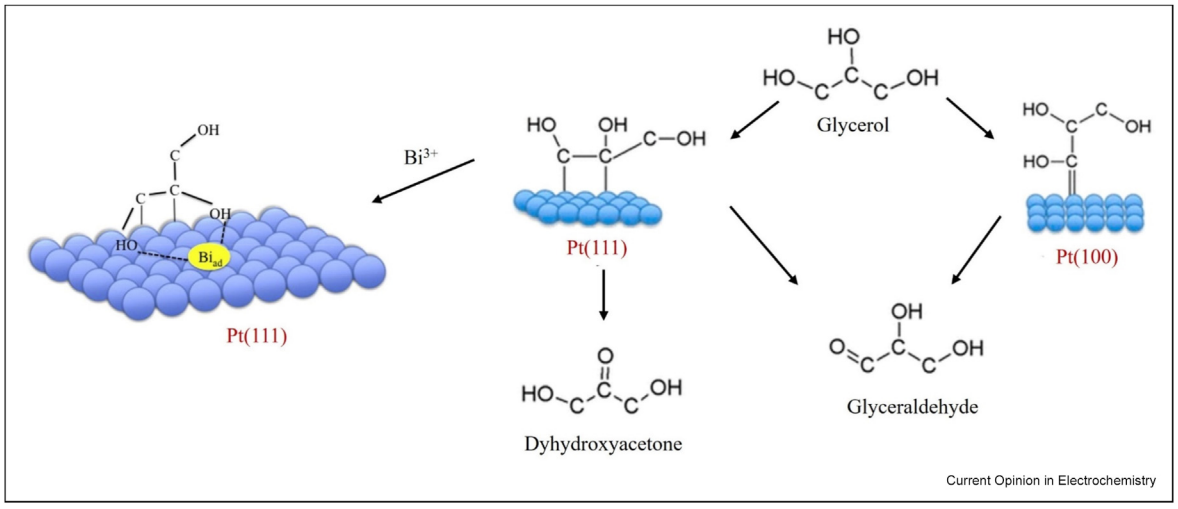
Instead, DHA production on Pt is more favoured in acidic media [70]. However, pure Pt is easily poisoned by intermediates (such as CO) and for this reason a series of metal elements, such as Bi, Ru, Ag, Au, Cu and Sb have been introduced to improve activity and selectivity [73–78] The best performing elements so far have been Bi and Sb, increasing the selectivity towards DHA over glyceraldehyde (GALD) to almost 100 % [79]. An up-to-date study delved into the use of p-block elements (like Bi, Pb, Sb, Sn, In and S) adsorbed on platinum electrodes, showing that some adatoms (Pb, Bi, Tl) are able to increase the activity of Pt electrodes towards glycerol oxidation in alkaline media [80]. They act increasing the OH coverage on Pt surface and stabilizing adsorbed hydroxyl species. Density functional theory (DFT) and electrochemical results suggested that adatoms provide the active sites for the generation of reactive OH species, which then react with the adsorbed glycerol derivative intermediates on Pt surface.

In a combined experimental and computational study, the electrochemical glycerol oxidation was examined in acidic media on Pt(111) and Pt(100) electrodes [81]. While Pt(100) resulted selective for primary alcohol oxidation, with GALD as the main reaction product, Pt(111) led to both primary and secondary alcohol oxidation, obtaining GALD, glyceric acid and DHA as products. Thanks to DFT calculations, the difference in selectivity was explained by the different binding modes of dehydrogenated glycerol to the Pt surface (Figure 2). On Pt(100), the dehydrogenated glycerol intermediate is bound to the surface through one double Pt=C bond, with GALD as the main product, while on Pt(111) the glycerol intermediate is bound through two single Pt–C bonds to the surface, yielding an enediol-like intermediate which is the precursor of both GALD and DHA.

According to cyclic voltammetry (CV) and high-performance liquid chromatography (HPLC) data, on Pt(111) GALD was detected at the lowest potentials at increasing concentration from 0.48 V vs. RHE until 0.85 V. DHA was the second product detected, in lower amount, which appeared, together with glyceric acid, from 0.6 V.

A study using a Pt electrode and bismuth as promoter of selective glycerol oxidation to DHA was reported in 0.5 M H_2SO_4 electrolyte [73]. Two types of bismuth adsorption were evaluated: an irreversible adsorption on the Pt/C surface (producing a Bi-modified Pt/C electrode) and a reversible adsorption/desorption, in which Bi_2O_3 was introduced directly into the electrochemical cell to obtain a bismuth-saturated solution (producing a Pt/C in a saturated Bi solution). Concerning the Bi-

Figure 2



Dehydrogenated glycerol binding modes to the Pt surface. Adapted with permission from Refs. [79,81]. Copyright 2016 American Chemical Society.

modified Pt/C electrode, lower overall currents were observed compared with the Pt/C electrode, suggesting that Bi was able to block the active sites for primary oxidation on Pt surface. This hypothesis was confirmed by Fourier transform infrared spectroscopy studies. At low potential (0.5−0.6 V vs. RHE), DHA was formed preferentially with 75 % selectivity. At higher potentials, the DHA selectivity dropped considerably, probably because of the oxidative desorption of the adsorbed Bi, which takes place around 0.6−0.7 V. A different behaviour was displayed by the Pt/C in saturated Bi solution. In this case, selectivity to DHA was close to 90 % even at maximum current, while GALD and glyceric acid formation was suppressed for all the considered potential range. The reason of the increased activity and selectivity was attributed not only to the interaction of Bi with Pt, but also of Bi with the carbon-supported Pt nanoparticles. The preferred potential of 0.5 V allowed to obtain almost 100 % selectivity for DHA. The improved catalytic performance of Bi-modified Pt catalysts was attributed to the geometrical effect of Bi on Pt surface, inhibiting the formation and adsorption of poisoning intermediates [82]. An important evidence from these studies is that, to have optimal activity and selectivity, it seems necessary to have a constant and full coverage of Bi on Pt/C surface that could explain why the Bi-modified Pt/C electrode performed worse than Pt/C in saturated Bi solution [73].

The role of Bi was analysed also in another study, describing the role of Bi adatom irreversibly adsorbed (Bi_{ir}) on platinum single-crystal electrodes [79]. The results showed that, in the case of Pt(111) surface, the presence of Bi improved the selectivity towards DHA and activity of the reaction by preventing the adsorption of carbon monoxide and other poisoning intermediates. The selectivity to DHA on the Pt(111)/Bi_{ir} electrode was attributed to the interaction between Bi^{3+} and the enediol intermediate (Figure 2), which catalysed the isomerization reaction from GALD to DHA. The rate of isomerization is enhanced, by Bi, towards the thermodynamically most stable isomer, DHA. This adsorbed intermediate exists only on Pt(111), while it is much less stable on Pt(100). The main conclusion was that the presence of Bi^{3+} does not introduce a new pathway to the secondary alcohol oxidation, but it interacts with an existing pathway on Pt(111), favouring the formation of DHA [79]. These results were in agreement with previous studies of glycerol oxidation on Pt(111) and Pt(100) electrodes [81]. Concerning the role of pH, in acidic media, Bi prevented the oxidation of primary alcohol and promoted the formation of DHA, whereas, in alkaline media, glycerate was the main product with no DHA production [79]. This observation was confirmed by de Souza et al., who found that adding some Bi ions into an alkaline glycerol solution increased the catalytic activity and production of glycerate over polycrystalline Pt [83,84].

In contrast, in a recent study for the electro-oxidation of glycerol, Bi_2O_3 particles were added in 1 M KOH anolyte solution acting as Bi atom suppliers, while Pt particulate electrodes (Pt/C-PE) were used as anode [85]. The electrolysis, in a flow cell reactor (1 M glycerol), demonstrated a DHA production of 283 μmol m^{-2} s^{-1}.

Another promoter that seems to increase the glycerol oxidation selectivity towards DHA is antimony (Sb). A study reported the oxidation of glycerol in the presence of antimony irreversibly adsorbed on a carbon-supported Pt electrode [78]. Two deposition methods were used,

generating reversibly and irreversibly ($Sb_{irrev.}$) deposited Sb on Pt/C, studied in a 0.5 M H_2SO_4 electrolyte solution. The results showed that the best performances were achieved with Sb_{irrev} on Pt/C electrode, that was able to oxidize the secondary alcohol to DHA with 80 % selectivity, working in the range between 0.35 and 0.55 V vs. RHE. In contrast with Bi [73], the irreversible/reversible adsorption of the Sb adatom was not able to achieve the 100 % surface coverage on Pt/C electrode. However, also in the case of Sb, it has been shown that higher surface coverage by adatoms led to higher activity.

Another study on carbon-supported PtSb (PtSb/C) catalyst highlighted that the product selectivity is strongly dependent on the applied electrode potential and catalyst surface composition [86]. In this study, it was possible to obtain a high DHA yield (61.4 % at 90.3 % glycerol conversion) at 0.797 V vs. SHE under acidic conditions. As the glycerol conversion increased, DHA selectivity decreased, most likely because of further oxidation. The same behaviour was observed increasing the applied potential to 1.197 V, which may facilitate the C—C, C—H and O—H bond cleavage.

Regarding other catalysts active for the selective electro-oxidation of glycerol, three-dimensional nanoporous PtAg skeleton has been reported [75]. The electrochemical activity of this catalyst was studied by CV, linear sweep voltammetry and chronoamperometry. A maximum DHA selectivity of 82.6 % was detected at 0.7 V vs. RHE, which was attributed to the large surface area and abundant Pt(111) facets. The presence of Ag seemed to change the structure of Pt, improving the catalytic activity and selectivity. Moreover, the presence of interconnected pores was able to increase the surface area facilitating the diffusion of reactants and intermediates. The pH influenced the product distribution as, when KOH was higher than 0.5 M, the production of DHA decreased in favour of formic acid.

Tetrametallic PtAuPdAg catalyst exhibited also high activity towards glycerol oxidation compared with Pt/C catalyst [87]. Electrochemical activity was investigated by CV and HPLC results showed that this catalyst yielded a remarkable DHA selectivity of 79.6 % at 1.3 V vs. RHE in alkaline solution.

A significant increase in GEOR activity and selectivity towards DHA was achieved by Ahmad et al. that investigated NP-doped Pd carbon nanotubes nanoparticles (NP-doped/PdCNTs) in alkaline media [88]. Doping of supported Pd catalysts by incorporating nitrogen (N) and phosphorous (P) can create defects facilitating glycerol adsorption and conversion into the targeted products. DHA yield was indeed higher than Pd/CNTs, N-doped/PdCNTs and P-doped/PdCNTs. Electrochemical and physicochemical characterisation attributed the higher yield and selectivity, 76.71 %, towards DHA to the synchronized effect and uniform distribution of nitrogen and phosphorus doping [89,90]. N and P were effectively integrated into the pore channels of Pd/CNTs, enhancing the reduction of Pd. N and P interaction with Pd and CNT helped also to inhibit the formation of CO and CO_2 intermediates, increasing the overall efficiency for GEOR and current density (76.67 mA cm^{-2}), working at 0.09 V vs. Ag/AgCl in a solution of 0.5 M glycerol in 0.5 M KOH. The alkaline media (pH 13) favoured the desired oxidation by promoting the deprotonation of H ions [91].

Ceria-supported Pd catalysts encompassing oxides of Cu, Co and Fe were synthesized and characterised by Ngwenya et al. for GEOR in alkaline media [92]. The aim was to develop cost-effective transition metal-based catalysts as an alternative to traditional platinum group metal catalysts. Ceria was chosen as support for its oxygen vacancies that facilitate mass transfer and stabilize Pd. The production of oxygenated species by ceria during alcohol oxidation facilitated the process [93]. The electro-oxidation of glycerol was evaluated by CV (solution of 1 M glycerol in 1 M KOH), showing that glycerol oxidation occurred between 0.15 and 0.25 V vs. Ag/AgCl. The products were identified and quantified by GC—MS, finding that DHA product was dominant over Pd—Fe_2O_3/CeO_2, achieving 18 % yield.

Palma et al. prepared ruthenium-based Pd and Pt nanoparticles, studying their activities during electro-oxidation of glycerol in alkaline media [94]. HPLC evidenced that, on PdRu/C anode, the adsorption of glycerol occurred through one of the primary alcohol groups (at the extremity of the molecule), resulting in the glycerate product. On the other hand, on PtRu/C anode, glycerol was adsorbed through the secondary alcohol, producing DHA. 4-hour chronoamperometry experiments were carried out at 0.7 V vs. RHE in a solution of 0.5 M glycerol in 1 M NaOH. Electro-oxidation of glycerol was investigated also on a series of Ru-modified Pt/C catalysts in acidic media, achieving 31.5 % glycerol conversion and 35 % DHA selectivity over a Pt_5Ru_5/C catalyst after 7-h electrolysis at 1.1 V vs. SHE [95].

Electrochemical oxidation with non-precious metal electrocatalysts

Many studies of electrochemical glycerol oxidation imply catalysts based on noble metals, but their high cost hinders practical application. Moreover, Pt and its alloys often suffer from slow kinetics, CO poisoning and the blocking of active sites by the formation of adsorbed species [96,97]. This could explain why very low current densities (about 0.1 mA cm^{-2}) were obtained on Pt electrodes, also in presence of promoters, which limits DHA yield [73].

In an attempt to solve these issues, non-noble metal-containing electrocatalysts have been explored and the

Ni-based ones are the most employed. For most of these, the active catalyst layer is NiOOH. A study demonstrated that NiOOH was able to oxidize alcohols via two electrochemical dehydrogenation mechanisms: an indirect mechanism via hydrogen atom transfer (HAT) and a potential-dependent mechanism via hydride transfer (PD), displayed in Figure 3 (box A) [98].

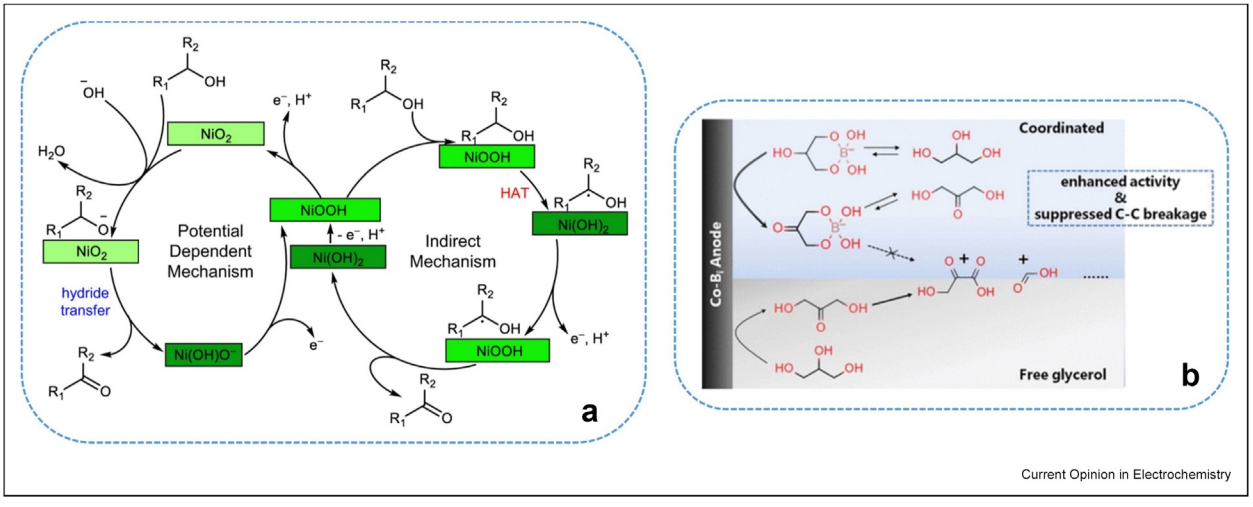
Previous studies showed that aliphatic primary alcohols were oxidized mainly through the PD mechanism. A hypothesis is that the homolytic cleavage of the strong C_α—H bond of a primary alcohol required for HAT (indirect mechanism) is difficult and the resulting C_α radical is unstable. In contrast, secondary alcohols should be easier to oxidize via the indirect mechanism since the C_α—H bond is weaker and the resultant radical is more stable. This means that a strategy to promote secondary alcohol over primary alcohol oxidation could imply the suppression of the PD mechanism in favour of the HAT mechanism. In this context, an important role is played by pH, which influenced the selectivity of glycerol oxidation, showing that DHA was mainly formed at mild alkaline conditions (pH 9—10). Indeed, at lower pH, the direct, potential-dependent mechanism was largely suppressed in favour of the indirect oxidation. This promoted secondary alcohol oxidation, increasing DHA selectivity and avoiding C—C cleavage reactions. In the study mentioned above, the best selectivity to DHA (71 %) was achieved at 1.52 V vs. RHE (pH 9—10) [98].

Another non-precious electrocatalyst, CuO, showed ability to oxidize the secondary hydroxyl group of glycerol under higher current density (3 mA cm^{-2}) than Pt/C with Bi and Sb promoters (10^{-1} mA cm^{-2}) [100]. The activity of the CuO catalyst was evaluated both in 0.1 M NaOH (pH 13) or 0.1 M $Na_2B_4O_7$ (pH 9) electrolyte. DHA production was favoured at pH 9 while at pH 13 DHA was converted to GLAD spontaneously (without applying potential). After 3-h oxidation process at 2.06 V vs. RHE, formate and DHA were detected, and 60 % DHA selectivity was achieved.

Manganese oxide (MnO_2) also showed high DHA selectivity at relatively high current density (6 mA cm^{-2}) in 0.1 M $Na_2B_4O_7$ solution [101]. Interestingly, it was found that, at low potential, there was a high selectivity to formic acid product that was attributed to the predominant coverage of α-MnO_2 on catalyst surface. Meanwhile, at high applied potential, the selectivity towards DHA increased because of partial transformation of α-MnO_2 to δ-MnO_2, which caused a decrease of C—C bond cleavage. As the potential increased from 1.45 V to 2.05 V vs. RHE, DHA turned out to be the main product with a maximum selectivity of 46 % at 2.05 V. Recently, a copper manganese self-supported electrode, MnO_2—CuO/copper foam (MnO_2—CuO/CF), was developed, attaining 10.7 mA cm^{-2} current density during potentiostatic electrolysis at 1.3 V vs. RHE [102]. The synergistic effect between CuO and MnO_2 enhanced glycerol adsorption, while the overlap configuration of CuO and MnO_2 resulted in lower electron density on MnO_2, promoting DHA desorption and preventing its further oxidation. As a result, DHA selectivity increased to 60 %.

An alternative way to improve selectivity towards secondary alcohol oxidation was reported, achieving 67 % DHA selectivity after electrolysis at 1.56 V vs. RHE [99]. In this study, a borax ($Na_2B_4O_7 \cdot 10H_2O$) electrolyte was selected. Borax hydrolyses in water to produce $B(OH)_3$ and $B(OH)_4$ anions, the latter could then react

Figure 3



Two alcohol dehydrogenation mechanisms on NiOOH (box A) and mechanism of formation of anionic borate–glycerol complexes (box B). Adapted with permission from Refs. [98,99]. Copyright 2021([99]) and 2022 ([98]) American Chemical Society.

with polyols to form anionic borate–glycerol complexes, which are able to protect the primary hydroxyl groups from oxidation (Figure 3, box B). Cobalt borate on carbon fibre cloth (Co–B_i/CF) was selected as the electro-oxidation catalyst. The selectivity to DHA during chronoamperometry experiments decreased dramatically to 28 % when the potential was increased from 1.56 V to 1.86 V as over-oxidation was favoured at the anode. Likewise, the selectivity toward DHA was increased by the high pH, which promoted the formation of glycerol–borate complexes. A systematic study on the electrochemical oxidation of C_3 saturated alcohols on a Co_3O_4 electrode in alkaline solution proposed an indirect mechanism of alcohol oxidation on cobalt-based materials [103]. The abundant and diverse *d*-orbitals of cobalt oxides seem to increase the reactivity of the more dynamic and highly active electrons [104,105]. Amorphous cobalt oxide (CoO_X) has been demonstrated as an efficient electrocatalyst for DHA production in another work, achieving 60 % DHA selectivity during potentiostatic electrolysis of a solution of 0.1 M glycerol in 0.1 M $Na_2B_4O_7$, applying a potential of 1.5 V vs. RHE (3 mA cm^{-2} current density) [106]. In this study, amorphous oxides were chosen because they offer a higher number of surface-exposed defects and randomly oriented bonds than their crystalline counterpart, facilitating the adsorption of the reactants on the catalyst surface [107,108].

In a recent work by Fernández-Caso et al., Ni–Co foam anodes were employed in a membrane-electrode assembly reactor for glycerol oxidation, achieving Faradaic efficiency up to 19 % and production rates for DHA of 0.437 mmol m^{-2} s^{-1} in alkaline conditions [109].

A summary of the main parameters of mentioned studies is reported in Table 1.

Conclusions

In this review, we summarized the current state of the art for glycerol oxidation to dihydroxyacetone, with a focus on electrochemical oxidation, which could offer considerable advantages compared with conventional methods. Indeed, electrochemical oxidation is an attractive process able to provide the desired product at the anode, while it can be coupled, through paired electrolysis, with convenient reductions at the cathode. The result is an energy-efficient approach, especially if a renewable energy source is used to power the system. Moreover, in most of the electrochemical oxidations described in this review, water is used as solvent, which has the intrinsic advantage of being greener and easy to handle. Electrosynthesis nowadays has become an important and promising tool to achieve new compounds, avoiding many disadvantages of conventional methods [113–115]. Within this framework, electrochemistry can significantly help to reduce carbon footprint in view of industry decarbonisation. Important improvements in the electrochemical reactor design and electrode characteristics have been crucial in enabling the emergence and competitiveness of this technology. In the short-term future, research should focus on the upscaling of the most promising electrochemical oxidations of glycerol to DHA, to increase the technology readiness level.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as

Table 1

Glycerol electro-oxidation by various catalysts.

Electrode	Electrolyte	Potential	DHA selectivity	Ref.
Pt/C in Bi-saturated solution	0.5 M H_2SO_4	0.50 V_{RHE}	100 %	[73]
Sb_{irrev} on Pt/C	0.5 M H_2SO_4	0.35–0.55 V_{RHE}	80 %	[78]
PtSb/C	0.5 M H_2SO_4	0.80 V_{SHE}	61 %	[86]
PtAg skeleton	0.5 M KOH	0.70 V_{RHE}	83 %	[75]
PtAuPdAg NPs	0.1 M KOH	1.30 V_{RHE}	80 %	[87]
Pt_4Au_6@Ag	0.5 M KOH	1.10 V_{RHE}	77 %	[76]
P-doped Pd/CNT	0.5 M KOH	–0.13 $V_{Ag/AgCl}$	91 %	[110]
NP-doped/PdCNTs	0.5 M KOH	0.09 $V_{Ag/AgCl}$	77 %	[88]
Pt_5Ru_5/C	0.5 M H_2SO_4	1.10 V_{SHE}	35 %	[95]
NiOOH	Borate buffer pH 9–10	1.52 V_{RHE}	71 %	[98]
CuO	0.1 M $Na_2B_4O_7$	2.06 V_{RHE}	60 %	[100]
MnO_2	0.1 M $Na_2B_4O_7$	2.05 V_{RHE}	46 %	[101]
γ-MnO_2	0.1 M $Na_2B_4O_7$	1.85 V_{RHE}	50 %	[111]
MnO_2–CuO/CF	1 M KOH	1.30 V_{RHE}	60 %	[102]
Co–B_i/CF	0.2 M $Na_2B_4O_7$	1.56 V_{RHE}	67 %	[99]
CoO_X	0.1 M $Na_2B_4O_7$	1.50 V_{RHE}	60 %	[106]
Co_3O_4	0.1 M $Na_2B_4O_7$	1.70 V_{RHE}	60 %	[112]

DHA, dihydroxyacetone.

potential competing interests:Fiammetta Vitulano reports financial support was provided by Bracco SpA. Alessandro Minguzzi reports a relationship with Bracco SpA that includes funding grants. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

No data was used for the research described in the article.

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* of special interest
** of outstanding interest

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