

[Review]

DOI: 10.13208/j.electrochem.201252

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Recent Advances in Glycerol Electrooxidation on Pt and Pd: from Reaction Mechanisms to Catalytic Materials

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Abstract: The conversion of glycerol to value-added products has received considerable attention recently because the booming biodiesel industry produces a large amount of glycerol as a byproduct. Among various means, electrocatalytic oxidation of glycerol is appealing owing to its environmental friendliness and high efficiency. However, electrooxidation of glycerol is very complex, involving multiple electron and proton transfer processes with many reaction pathways. How to rationally design catalysts with high selectivity toward targeted products is an overarching challenge, and of both fundamental and practical significance. In this minireview we aim to provide an overview of recent advancements in electrooxidation of glycerol focusing mainly on Pt- and Pd-based catalysts. We start with summarizing fundamental understandings of factors dictating catalytic activity and selectivity garnered from *in-situ* and online spectrometric experimental studies as well as from theoretical works. We then use selective examples to demonstrate how these factors are manifested in the development of highly efficient glycerol electrooxidation catalysts. Finally, we summarize the key issues to be addressed in future studies.

Key words: glycerol electrooxidation; electrosynthesis; electrocatalysis mechanism; rational design of electrocatalysts

1 Introduction

Electrosynthesis has attracted intense interests recently because the activation energy of reactions can be reduced by applying a potential without the need of harsh conditions of high temperature and high pressure, and the selectivity of the reaction can be directly controlled by changing the applied potential. A variety of valuable chemicals can be obtained by the electrooxidation of different bio-derived alcohols^[1]. It has been proposed and demonstrated that in an electrolysis cell, value-added chemicals can be obtained at

the anode and hydrogen gas at the cathode^[2-4]. Similarly, in fuel cells using carbon-based fuels, it is possible to control the anode reaction selectivity towards valuable chemicals instead of forming CO₂^[5]. Glycerol provides a perfect example for this concept (Figure 1).

Glycerol is a byproduct of the biodiesel industry through the transesterification of oils and fats with large quantity and low price. The complete oxidation of glycerol to CO₂ involves 14 electrons and 14 protons, therefore, is unlikely to occur efficiently.



Citation: Zhang W Y, Ma X Y, Zou S Z, Cai W B. Recent advances in glycerol electrooxidation on Pt and Pd: from reaction mechanisms to catalytic materials. *J. Electrochem.*, 2021, 27(3): 233-256.

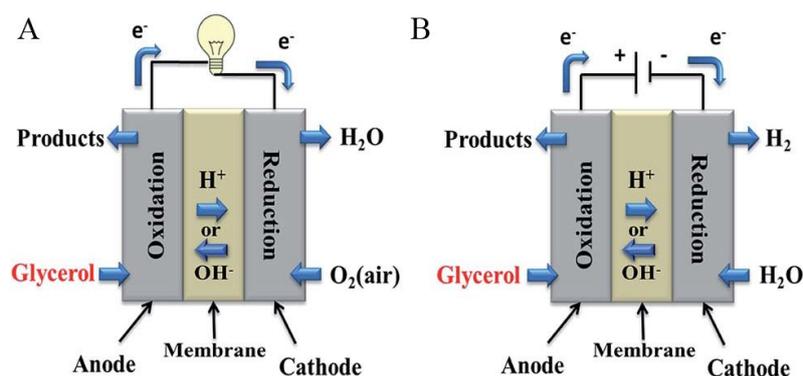


Figure 1 Electro-oxidative valorization of glycerol by means of (A) fuel cell and (B) electrolysis cell. Reproduced with permission^[6]. (color on line) Copyright © 2019, The Royal Society of Chemistry.

Instead, selective oxidation of glycerol enables conversion to value-added chemicals^[7, 8], which can be achieved through a wide range of reactions including etherification, esterification, dehydration, pyrolysis and oligomerization^[9-12]. However, poor yields and harsh conditions have impeded their commercial applications. Electrocatalysis, which is expected to circumvent these problems, has received increasing attention. The electrooxidation of glycerol can produce a series of value-added products, such as glyceraldehyde, glyceric acid and hydroxypyruvic acid^[13-15]. These reactions can take place in both a fuel cell and an electrolysis cell as shown in Figure 1. In fuel cells, the electricity is generated through the glycerol oxidation at the anode where value-added chemicals are produced, and oxygen reduction at the cathode. In electrolysis, valuable chemicals are produced at the anode and hydrogen is produced at the cathode.

Numerous studies have been devoted to the glycerol electrooxidation reaction (GEOR) with the use of Fourier transform infrared spectroscopy (FTIR), differential electrochemical mass spectrometry (DEMS), high-performance liquid chromatography (HPLC) and density functional theory (DFT) calculations. Several recent reviews have summarized studies on GEOR. Baranova et al.^[6] and Coutanceau et al.^[16] showed general trends concerning the activity and selectivity of glycerol oxidation reaction where the catalyst selection and reaction conditions play an important role. Rahim et al.^[17] discussed how different experimental

parameters such as electrode materials, pH of electrolyte, applied potential, current density, temperature and catalyst surface additives affect the reaction pathways. Antolini^[18] put emphasis on GEOR in alkaline media and its use in fuel cells. Alaba et al.^[19] provided an overview of different catalyst materials. It has been recognized that a great challenge in glycerol electrooxidation research is to selectively oxidize glycerol to important industry products without promoting C-C bond breaking therefore formation of carbon oxides. A detailed understanding of the mechanism is crucial for rational design of competent catalysts with desired selectivity and activity.

In this review, we start with the discussion of selected publications on mechanistic studies of GEOR which provides an overview of rational design of electrocatalysts. We then use selective examples to demonstrate how the rational design rules are at play in the development of highly efficient GEOR catalysts. Finally, we summarize the remaining key issues in the mechanism research of GEOR, and provide perspectives for the future development of GEOR catalysts. Because the electrooxidation of glycerol has been studied extensively and it is impossible to cover all aspects of the new developments, we will focus our discussion on Pt- and Pd-based catalysts.

2 Mechanistic Aspects of Glycerol Electrooxidation

Glycerol electrooxidation is an intricate process. The possible reaction pathways of GEOR are shown

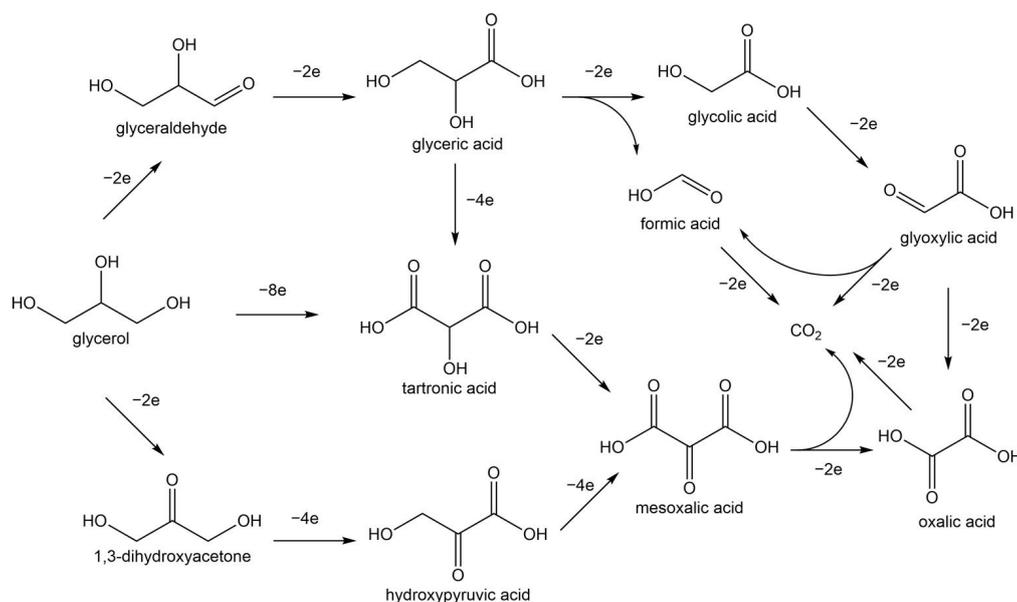


Figure 2 Plausible reaction pathways with intermediates and products of glycerol oxidation.

in Figure 2. There are mainly three pathways. First is the oxidation of primary hydroxyl to form glyceraldehyde and the oxidation of glyceraldehyde to glyceric acid, followed by C-C bond cleavage and further oxidation to CO₂. The second is the oxidation of secondary hydroxyl to form 1,3-dihydroxyacetone and then the terminal hydroxyl is oxidized to generate hydroxypyruvic acid. The third is that both terminal hydroxyl groups are oxidized to produce tartronic acid. Tartronic acid and hydroxypyruvic acid may be oxidized to mesoxalic acid and oxalic acid, and further oxidized to CO₂. Many of the above products have wider applications and much higher values than glycerol. For example, 1,3-dihydroxyacetone has been used increasingly in self-tanning industry^[20] and is more than 200 times more expensive than glycerol. Glycolic acid is extensively used in skin care for both therapeutic and cosmetic purposes^[21], and mesoxalic acid is a precursor for an anti-HIV agent^[22].

2.1 Experimental Studies

Considering the complexity of GEOR products, it is critical to detect and identify various reaction products and adsorbed intermediates for mechanistic studies. By combining electrochemical methods with various spectroscopic methods such as infrared spectroscopy^[23-44], mass spectroscopy^[24, 33, 45], chromatogra-

phy^[24-27, 38, 45-48], nuclear magnetic resonance spectroscopy (NMR)^[34, 49], sum frequency generation spectroscopy (SFG)^[50], researchers have been able to perform qualitative or quantitative analysis of reaction products and intermediates on the molecular level. In the following, we will use selective examples to illustrate the determination of key reaction intermediates and products. We then summarize experimental findings on the effects of catalyst structure and composition on GEOR.

Carbon monoxide and carbon dioxide are probably the first products detected from GEOR on Pt. Leung and Weaver^[44] reported the *in-situ* FTIR spectroscopic studies of GEOR on Pt in acidic solutions. A band at 2056 cm⁻¹ was assigned to adsorbed CO (CO_{ad}) on Pt atop sites and an absorption band at 2343 cm⁻¹ was assigned to CO₂ dissolved in the solution. The CO_{ad} was attributed to the dissociative adsorption of glycerol at low potentials. More recently, Schnaidt et al.^[33] investigated GEOR on Pt film electrodes in acidic media with a combined spectro-electrochemical DEMS/attenuated total reflection(ATR)-FTIR set-up under flow conditions. The absorption bands at about 2050 and 1880 cm⁻¹ were assigned to linearly and multiply bonded CO_{ad}, respectively. CO_{ad} was generated at potentials between 0.1 and 0.7 V from dissocia-

tive adsorption of glycerol and oxidation products. CO_2 was detected at potentials higher than 0.5 V vs. RHE in a small amount, indicating the prevalence of the incomplete oxidation of glycerol which was attributed to a high barrier of C-C bond breaking on Pt. Adsorbed glyceroyl and glycerate were identified through the observations of absorption bands at 1640 cm^{-1} and 1380 and 1315 cm^{-1} in the ATR-FTIR spectra, respectively. They suggested that glyceric acid was a dead end in GEOR due to its inertness for further the oxidation and that glyceraldehyde was an intermediate to the formation of CO_{ad} and glyceric acid.

Fernández et al.^[29] studied GEOR on Pt nanoparticles supported on multi-walled carbon nanotubes and further elucidated the formation pathways of CO_2 . Their results suggest that CO_2 is produced through two ways. At low potentials, CO_2 was formed through the oxidation of adsorbed CO arising from the dissociative adsorption of glycerol through one of its terminal carbons. At high potentials, CO_2 was formed by glycerol reacting with Pt-O. This assertion was confirmed using glycerol with isotopically labeled terminal carbons in their *in-situ* FTIR studies, which showed that as the potential increased, the Pt-O coverage also increased which brought about different degree of oxidation. At low potentials, in addition to CO_{ad} , glycerol produced glyceraldehyde by dehydrogenation and glyceric acid by reacting with a single Pt-O. At intermediate potentials, the increase in Pt-O coverage was beneficial to the formation of further oxidized species, and glycerol reacted with two Pt-O through its terminal carbons to generate tartronic acid. Above 1.1 V (vs. RHE), CO_2 was formed through the interaction of carbons with O-species. The same group performed further isotope-labeled investigations^[30, 31]. Their results showed that the terminal ($^{-13}\text{CH}_2\text{OH}$) and central ($^{-12}\text{CHOH}$) groups of glycerol formed adsorbed CO at low potentials, indicating that glycerol could be completely dissociated on the Pt nanoparticles. The electrooxidation of isotope-labeled glycerol produced $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$ at the same time, but the oxidation of the terminal $^{-13}\text{CH}_2\text{OH}$ group was easier than that of the central

group, due to the steric effect of $^{-13}\text{CH}_2\text{OH}$ on the $^{-12}\text{CHOH}$ group. Therefore, in all potential ranges, $^{13}\text{CO}_2$ was the main source of CO_2 . In addition, glyceraldehyde appeared to be an intermediate in the production of glyceric acid.

High-performance liquid chromatography (HPLC) is instrumental for determining soluble reaction products of GEOR. Roquet et al. used HPLC to monitor reaction products of GEOR on Pt in both acidic and alkaline solutions at selected potentials for hours^[48]. They found that the product distribution depended strongly on the applied potential and solution pH. In an acidic medium, at potentials where Pt surface oxidation occurs, formic acid, oxalic acid and glycolic acid were the main products. At lower potentials where Pt is not oxidized, glyceraldehyde was dominant. In an alkaline medium, selectivity toward glyceraldehyde was the highest. Kwon et al.^[45, 46] did more thorough mechanistic studies by combining HPLC with linear scan voltammetry to detect soluble reaction products of GEOR on polycrystalline Au and Pt electrodes and applied online electrochemical mass spectrometry for CO_2 detection in acidic, neutral and alkaline media. They found that the activity and product distributions were strongly dependent on the solution pH and the catalyst material, while the general reaction pathways remained the same. For the two electrode materials, the activity in an alkaline medium was higher than that in an acid medium, and Au was more active than Pt at high potentials in an alkaline medium. In alkaline media, glyceric acid was the main product on Pt electrodes through oxidation of glyceraldehyde, while on Au electrodes, glyceric acid was readily oxidized to glycolic acid and formic acid, and no glyceraldehyde was detected. These differences were attributed to the higher onset potential of GEOR on Au (0.85 V vs. RHE) than on Pt (0.43 V vs. RHE). At potentials where significant GEOR current was observed on Au, glyceraldehyde is oxidized to glyceric acid, and then to glycolic and formic acid. At these potentials Pt surface is significantly oxidized and GEOR activity is lower. It should be emphasized that in this work to minimize glycer

aldehyde degradation in alkaline solutions, the samples were stabilized by neutralizing the solution at the sampling tip. Given the rapid degradation of glyceraldehyde, cares should be taken in quantifying this product. In the neutral solution, the current density of GEOR significantly decreased on both electrodes. On Pt, glyceraldehyde became the dominant product, followed by glyceric acid, formic acid and glycolic acid. Glyceraldehyde was the only product detected on Au. In acidic media, glyceraldehyde was the main product on Pt electrodes with a low conversion under potentials lower than 1.1 V, while Au did not show catalytic activity. Formic acid and CO₂ were final products in acidic media at potentials where PtO_x surface oxide formed on Pt electrodes and facilitated the further oxidation of glyceraldehyde. Dihydroxyacetone was more favored in acidic media than in alkaline media.

Gomes et al.^[28] investigated GEOR on polycrystalline Au and Pt with *in-situ* FTIR in both acid and alkaline media, and draw the similar conclusions as those reported by Kwon et al.^[45,46] In an alkaline medium, dihydroxyacetone, tartronic acid, mesoxalic acid, glyoxylic acid and CO₂ were formed on Au; in an acidic medium, tartronic acid, formic acid and CO₂ were detected at higher potentials than those in an alkaline medium, and the activity was very low as indicated by the nearly identical cyclic voltammograms obtained with and without glycerol. The GEOR on Pt generated tartronic acid, glycolic acid, glyoxylic acid, formic acid and CO₂, regardless of the solution pH. CO₂ was detected on both electrodes, indicating that the C-C-C bond can be broken.

GEOR is a structure-sensitive reaction. Sandrini et al.^[35,36] found that Pt(100) in an alkaline medium was resistant to poisoning during multiple potential cycles, while Pt(110) and Pt(111) were severely poisoned during the first forward scan. FTIR results revealed glycerol dehydrogenated (C-H bond cleavage) into alkoxy groups and subsequent aldehyde intermediates, which adsorbed as $\eta^1(\text{O})$ -aldehyde and $\eta^1(\text{C})$ -acyl, respectively. The acyl intermediate characterized by the $\nu(\text{C}=\text{O})$ acyl vibration mode remained ad-

sorbed even at high potentials, which was believed to be the cause of the severe deactivation of the electrode throughout the potential cycles. Among the three basal plane surfaces, only Pt(110) surface was able to break C-C bond at low potentials.

Gomes et al.^[37] studied GEOR on the three basal planes of Pt in an acidic medium. CO was one of the residues of glycerol adsorption and dissociation, and linearly bonded CO was a common adsorption intermediate for GEOR on Pt(111), Pt(100) and Pt(110) in acidic media. The formation of CO at low potentials on Pt(100) and Pt(110) suggests that these surfaces are beneficial to break the C-C-C bond. The formed CO remained adsorbed on Pt(100) and Pt(110), and poisoned these surfaces even at high potentials because its oxidation requires a higher potential on Pt(100) and Pt(110) than on Pt(111). The surface structure of Pt(111) is not favorable for the breaking of C-C-C bonds at low potentials. However, the glycerol dissociation residue has less poisoning effect on Pt(111). Therefore, Pt(111) had a higher oxidation activity for glycerol than Pt(100) and Pt(110) at low potentials.

The effect of surface defects on GEOR was also studied on a series of Pt crystal planes. Fernández et al.^[23,32,51] conducted GEOR on well-ordered and disordered Pt(100). The CV profiles combined with FTIR spectra indicated that the highly ordered surface can oxidize glycerol at lower potentials than the disordered surface. DFT calculations showed that CO and glycerol bonded more strongly on the disordered surfaces, indicating the Pt-CO bond cleavage was the rate-determining step in GEOR. Defects on Pt(111) only slightly changed the initial potential of glycerol electrooxidation, but significantly changed the ratio of CO₂ and carbonyl-containing compound C=O. FTIR also confirmed that the lower activity of the defective electrode at a lower potential was related to a higher degree of CO poisoning. Therefore, it is difficult to oxidize glycerol at a potential lower than 0.6 V due to the CO poisoning. The density of defects had different effects on the selectivities of Pt(111) and Pt(100) surfaces. Defects increased the relative

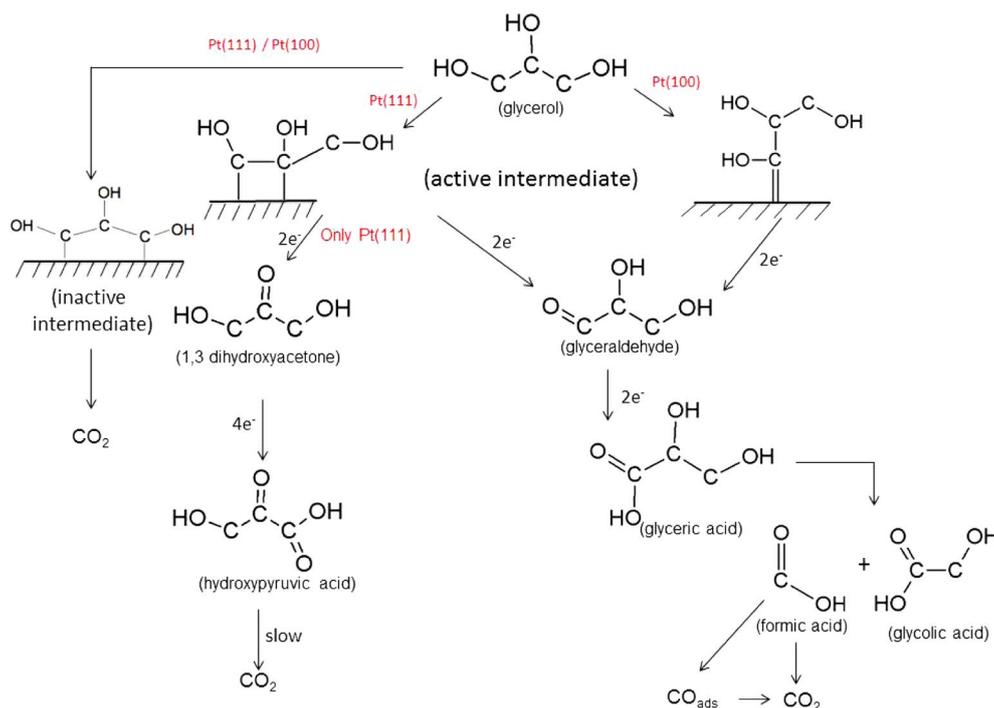


Figure 3 Glycerol oxidation mechanism on Pt(111) and Pt(100) electrodes in an acidic solution. Reproduced with permission^[24]. Copyright © 2016, American Chemical Society.

production of glyceric acid on Pt(100), while decreased the production of dihydroxyacetone on Pt(111).

Garcia et al.^[24] also studied GEOR on Pt(111) and Pt(100) electrodes. Online HPLC and online electrochemical mass spectroscopy showed glycer-aldehyde, glyceric acid, and dihydroxyacetone were products on Pt(111), while glycer-aldehyde was the only product on Pt(100). Combining DFT calculations with spectroscopic results, they proposed a mechanism (Figure 3) to elucidate the selectivity difference. On Pt(111), an enediol-type intermediate with two Pt-C bonds on adjacent carbons was formed by dehydrogenation and prone to be oxidized to dihydroxyacetone and glycer-aldehyde. On Pt(100), the intermediate with a double Pt=C bond on the edge could only be oxidized to glycer-aldehyde. Besides these two active intermediates, a third inactive intermediate with two Pt-C bonds at two ends was proposed. Although not yet clear, the intermediate was resistant to oxidation and could only be removed from the Pt surface after multiple potential scans.

The electrocatalytic performance of GEOR on Pt can be enhanced by adding other metals to form

binary or ternary catalysts. Bismuth is the most studied ad-atom for GEOR. Kwon et al.^[25] demonstrated high selectivity for dihydroxyacetone on Pt-Bi in an acidic solution, which was attributed to Bi blocking the active sites for primary alcohol oxidation and providing active sites for secondary alcohol oxidation. Garcia et al.^[41] studied the effect of Bi atoms on improving the electrooxidation activity and selectivity of glycerol on Pt single crystal electrodes in HClO₃ solutions. The presence of Bi on Pt(111) improved the reaction activity and the selectivity to dihydroxyacetone, while it decreased the activity on Pt(100) and like unmodified Pt(100) only glycer-aldehyde was produced. The improved activity on Pt(111) was attributed to that Bi prevented the adsorption of poisonous intermediates (such as CO), and the increase in selectivity was explained by invoking the interaction of adsorbed Bi atoms with enediol-type intermediates, which existed on Pt(111) but not on Pt(100). Enediol is a key intermediate in the isomerization reaction between glycer-aldehyde and dihydroxyacetone. The enediol-type intermediates were believed to be stabilized by the interaction with Bi atoms which promoted

the isomerization reaction to the most thermodynamically stable isomer dihydroxyacetone. Antimony (Sb) has also been reported to promote secondary alcohol oxidation. However, the addition of Pb, In, and Sn did not change the pathway towards primary alcohol oxidation^[47].

Huang et al.^[34] conducted a detailed mechanistic study of GEOR on Pt/C, PtRu/C and PtRh/C in acidic media by *in-situ* FTIR and ¹³C-NMR. At high potentials (0.45 V), oxygen insertion reactions were more favored on PtRh than PtRu, so tartronic acid was preferred on PtRh/C. Otherwise, C-C cleavage of glyceric acid was more favored. NMR results confirmed that glyceric acid could not be oxidized to tartronic acid and tartronic acid was produced from direct oxygen insertion reaction on the two terminal carbons of glycerol. A mechanism of GEOR on Pt/C, PtRu/C and PtRh/C was proposed by these authors as shown in Figure 4. Bifunctional mechanism may account for the enhancement of GEOR activity after alloying Pt with Ru or Rh. Glycolic acid was formed either by C-C bond breaking of the vicinal diol group in glyceric acid or by oxidation of the C2 fragment generated from dissociative adsorption of glycerol. Tartronic acid was generated by reaction of glycerol with two Pt-O via its two terminal carbons at high potentials,

as Fernández et al. also proposed^[29].

By combining electrochemical *in-situ* FTIR and online HPLC, de Souza et al.^[26, 27] studied Bi- and Pb-modified polycrystalline Pt(Pt_p) electrodes in alkaline solutions. In the presence of Bi or Pb, the activity of polycrystalline Pt increased. Contrary to the behavior in acidic media, FTIR indicated that the adatoms suppressed C-C bond cleavage and CO formation, and promoted the selectivity toward glycerate, formate, and glycolate in alkaline media. As discussed above, in acidic media Bi prevented the oxidation of primary alcohol and promoted the formation of dihydroxyacetone. In contrast, glycerate was the main product in alkaline media while dihydroxyacetone was rarely produced. Also, tartronate was observed in the presence of adatoms, which was absent on unmodified polycrystalline Pt. The behaviors of Bi- and Pb-modified Pt(110) were similar to those of Pt_p-Bi and Pt_p-Pb, respectively. Therefore, it was proposed that adsorbed atoms mainly activated the low-coordinated Pt atoms. Low-coordinated Pt atoms usually bind to the adsorbate more tightly, thus more likely to suffer from poisoning. The presence of adsorbed atoms reduces the number of adjacent Pt atoms and prevents the formation of multiple bond intermediates. This is likely due to a combination of

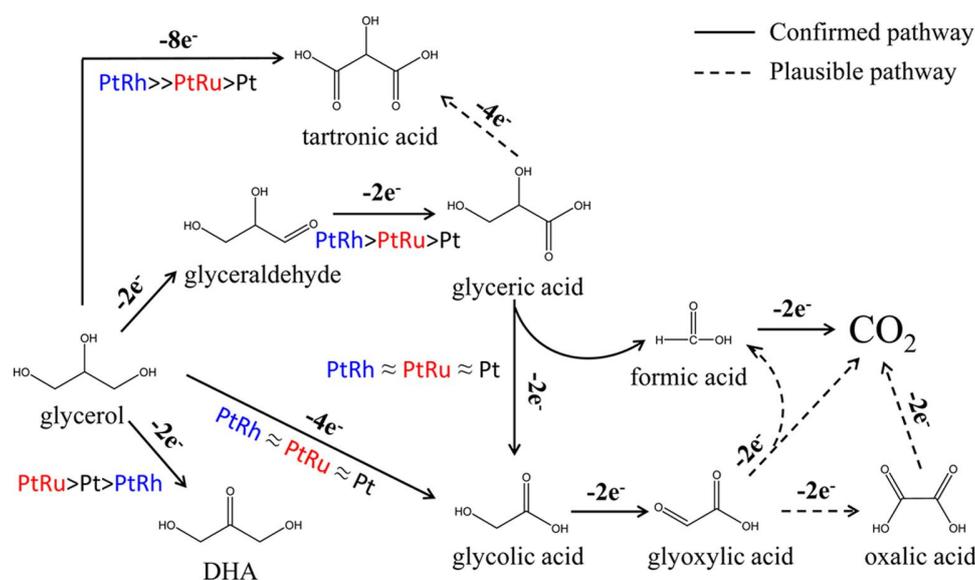


Figure 4 Schematic of glycerol electrooxidation mechanism on Pt, PtRu and PtRh in acidic media. Reproduced with permission^[34]. (color on line) Copyright © 2016, American Chemical Society.

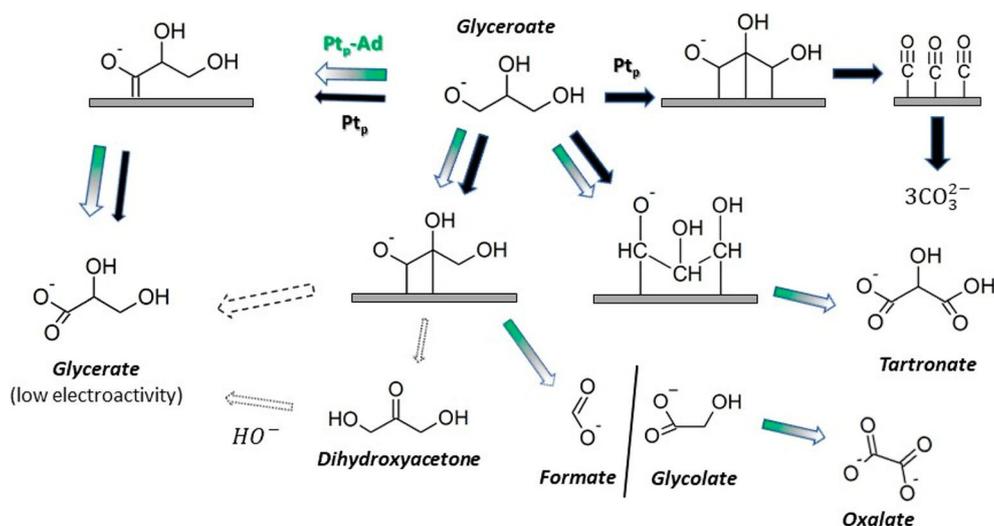


Figure 5 Reaction pathways proposed for the electrooxidation of glycerol on the bare polycrystalline Pt (Pt_p) electrode and after modification by Bi and Pb in alkaline media. Black arrows represent the pathway for the clean Pt_p , whereas the green and gray arrows indicate the pathways for the modified electrode. Reproduced with permission^[27]. Copyright © 2020, American Chemical Society.

the third-body effect and electronic configuration changes on the catalyst surface. The better promotion effect of the adsorbed atoms in the alkaline medium was ascribed to the stabilization of the negatively charged intermediate by the Coulomb interaction with the positively charged adsorbed atoms. Reaction pathways proposed by de Souza et al. is shown in Figure 5. Briefly, on polycrystalline Pt, CO_{ad} was formed via an intermediate with three Pt-C bonds and was oxidized to CO_3^{2-} . Glycerate ion adsorbed on Pt surface through Pt=C on the edge to form glycerate ion. Since glycerate was confirmed unreactive, tartronate was formed from glycerate directly via an intermediate with two terminal carbons bonded to the electrode surface; formate and glycolate were formed from the C-C cleavage of an intermediate with two adjacent carbons bonded to the surface.

2.2 Theoretical Studies

Theoretical studies play an important role in unravelling the mechanisms of catalytic glycerol conversions to value-added chemicals^[52]. Liu and Greeley^[53-55] showed that the transition state energies of C-C bond cleavage decreased on Pt(111) as more hydrogen atoms were abstracted, finally being comparable to those of C-H and O-H bond. Therefore, C-C bond could not be broken without significant dehydrogena-

tion. C-O bond scission was slow in the early stages of dehydrogenation and thermodynamically unfavored in the late stages of dehydrogenation. By conducting periodic DFT calculations on Pt(111), Pd(111), Rh(111), Cu(111) and Ni(111), they determined the trends in the decomposition of glycerol on these metals. Pt(111) and Pd(111) were predicted to have high selectivity for C-C bond breaking and the former had a slightly higher activity than the latter. Rh(111) was of average selectivity and activity. Ni(111) did not show good selectivity towards C-C bond cleavage versus C-O bond cleavage. Cu(111) showed a low activity of glycerol decomposition.

Fernández et al.^[52] showed by DFT calculations that CO bonded directly to the defects on Pt(111), while most of the water and glycerol molecules formed a network by hydrogen bonds farther from the surface. CO had a stronger adsorption energy on Pt than water or glycerol, suggesting that Pt-CO bond breaking was the rate-determining step.

Gold has been considered to be active for GEOR only in alkaline media. However, Valter et al.^[56] detected a low activity of GEOR on Au in an acidic solution and speculated a higher activity in $HClO_4$ than in H_2SO_4 . They ascribed the difference to the Competitive adsorption since sulfate ions adsorb stronger

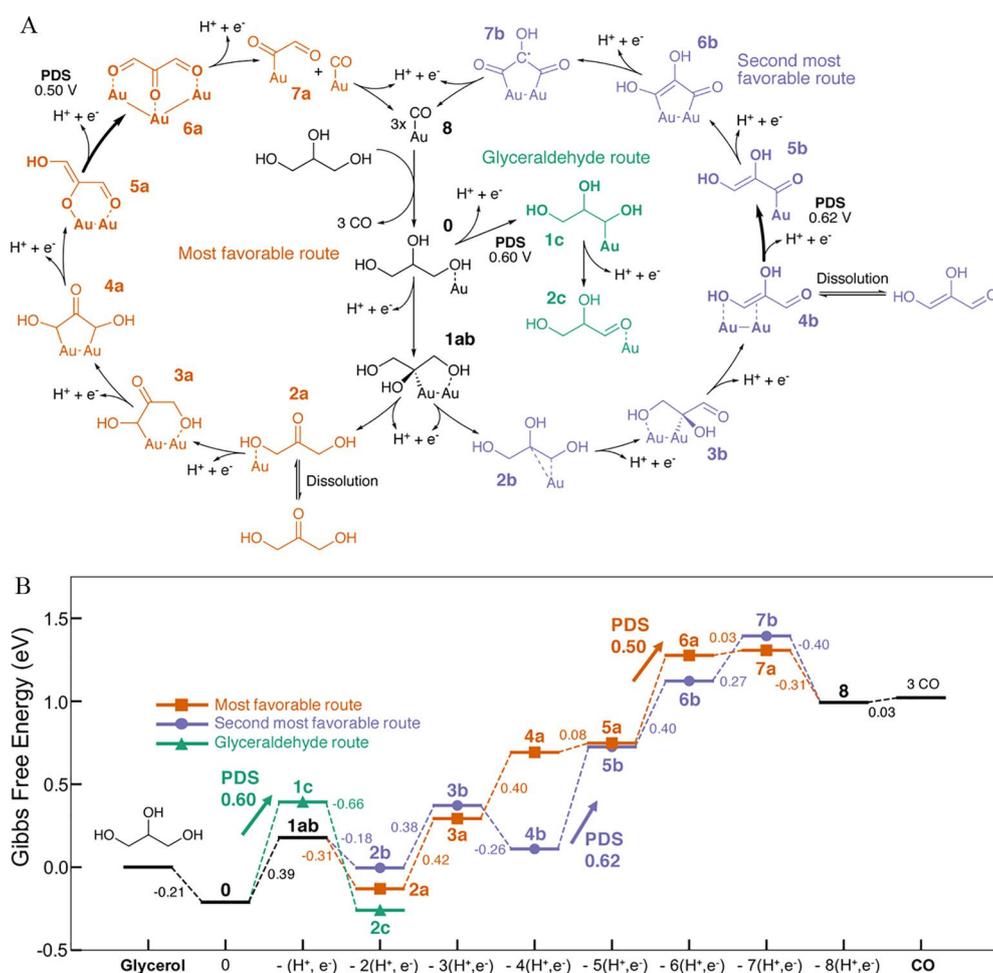


Figure 6 Catalytic routes of glycerol dehydrogenation on Au(111), presented as (A) catalytic cycles and (B) energy landscape. Reproduced with permission^[56]. (color on line) Copyright © 2018, American Chemical Society.

than perchlorate ions. Catalytic pathways and the Gibbs free energies of the intermediates on Au(111) were calculated as shown in Figure 6. The most favorable route started by the dehydrogenation of the secondary carbon of glycerol and dihydroxyacetone was formed at 0.39 V vs. RHE, which is consistent with their experimental onset potential.

Valter et al. further calculated the preferred pathways for the first and second deprotonation steps for glycerol on Pt(111), Ag(111), Pd(111), Ru(0001), Ir(111), Rh(111), Cu(111), Ni(111), Co(0001), and Au(111), as shown in Figure 7^[57]. In the first deprotonation, Rh, Ir, Pd, Pt and Au preferred carbon deprotonation, while Ru, Ni, Co, Cu and Ag preferred oxygen deprotonation. In the second deprotonation step, on Co, Ni and Cu glycerol underwent another oxygen

deprotonation to form a six-membered ring intermediate with two M-O bonds and produced hydroxypyruvic acid. Pd(111) and Pt(111) were prone to form a four-membered ring with two M-C bonds through a second carbon deprotonation and were selective towards either glyceraldehyde or dihydroxyacetone. On the other five metals glycerol underwent one carbon deprotonation and one oxygen deprotonation, and favored dihydroxyacetone production. These results were explained in terms of the relative bonding strength of carbon and oxygen on these metals.

3 Catalyst Materials

3.1 Catalysts Design Concepts

From the discussion of mechanistic studies presented in the last section, several design concepts of high performance GEOR catalysts can be obtained.

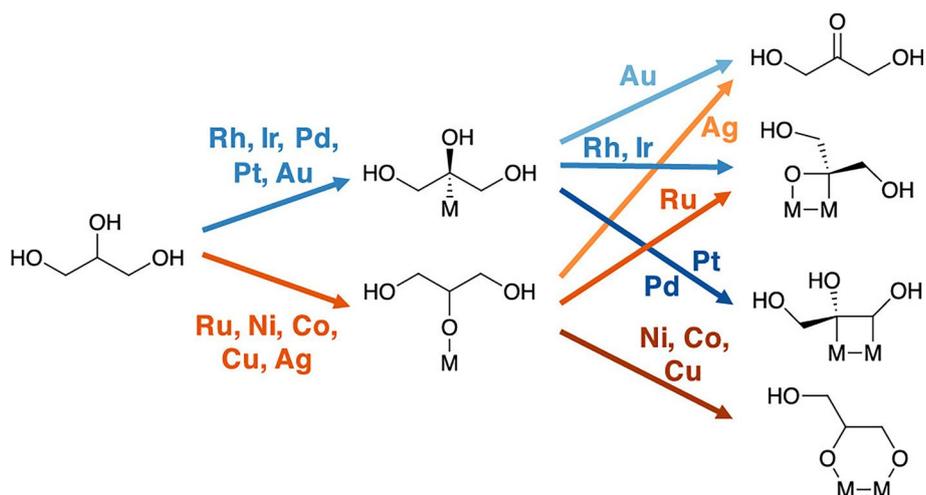


Figure 7 Calculated thermodynamically favorable routes. (color on line) Reproduced with permission^[57]. Copyright © 2020, American Chemical Society.

First, the chemical nature of the catalyst material plays a central role in GEOR activity and selectivity. Pt is by far the most active metal for GEOR, followed by Pd. The product distribution is a strong function of the catalytic material as well.

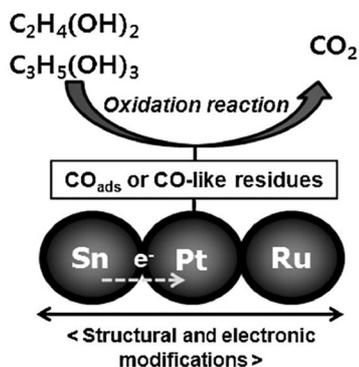
Second, GEOR is a surface-sensitive reaction, and therefore, the catalytic activity largely depends on the crystal plane orientation of the catalysts. The surface structure of Pt(110) is beneficial for breaking the C-C bond at a low potential, but it is easily poisoned by CO. Pt(111) has a higher oxidation activity for glycerol than Pt(100) and Pt(110) at low potentials. The

introduction of surface defects can also significantly alter the activity and selectivity of the catalysts.

Third, modifying Pt with other metals through alloying or irreversible adsorption can improve its GEOR activity. The improvement can be explained in part in the framework of the d-band center theory (ϵ_d) which was populated by Nørskov and coworkers^[58-61]. At the heart of the theory is that the adsorption energy is strongly dependent on the metal d-band center position, the higher the d-band center, the stronger the adsorption. The d-band center can be manipulated by alloying or modifying with a second metal, which is

(i) Structural & electronic effect

- Consecutive dehydrogenation & C-C cleavage



(ii) Synergistic effect of Ru & Sn

- CO (CO-like residues) oxidation to CO₂

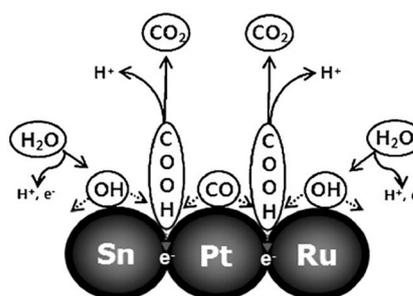


Figure 8 Schematic illustration of catalytic surface reactions over the ternary PtRuSn/C catalyst for the electrooxidations of glycerol. Reproduced with permission^[62]. Copyright © 2011, Elsevier B.V.

attributed to the ligand effect and strain effect. Another rationale for the improving activity through modifying catalyst surfaces with another metal is the bifunctional mechanism, where the second metal facilitates water dissociation to form surface hydroxides at lower potentials than unmodified catalyst surfaces, which can then more easily oxidize the CO intermediate, and therefore, reduce the onset potential and exhibit relatively high activity. The underlying mechanism is a surface reaction between CO (or other carbonaceous species) and OH (or oxygen-containing substances) on the surface of the catalyst, i.e., $\text{CO}_{\text{ad}} + \text{OH}_{\text{ad}} \rightarrow \text{CO}_2 + \text{H}^+ + \text{e}^-$, as shown in Figure 8.

In addition to the catalyst composition and structure, the experimental conditions also play important role in the observed activity and product distribution. For example, it has been generally accepted that GEOR is more facile in alkaline media than in acidic media, and glycerol concentration can also affect the reaction path^[63]. Therefore, when results from different groups are compared, it is important to recognize the differences in experimental conditions. In the following, we use selective examples to illustrate how the different structural factors discussed above have been manifested in catalyst designs in the literature.

Because of the extensive work in GEOR, we will focus mainly on Pt- and Pd-based catalysts.

3.2 Pt-Based Catalysts

Platinum is the most studied glycerol electrooxidation catalyst due to its high activity and wide applicable pH range. Whether in acidic or alkaline media, Pt-based catalysts are often used as benchmarks for new GEOR catalysts. However, pure Pt is easily poisoned by intermediates (such as CO). A series of metal elements, such as Bi^[25-27, 64-67], Ru^[62, 68-76], Sn^[42, 62, 68, 76], Ni^[71, 76-79], Ag^[80-83], Pd^[77, 84-86], Cu^[84, 87-89], Sb^[90-92], Co^[93], Pb^[79, 94], Rh^[71, 95], Au^[83, 96-98] and Fe^[86, 99], have been adopted to enhance activity and selectivity. In addition, the enhancement effects of metal oxides, such as MnO_x^[82], IrO_x^[95], CeO₂^[100], Ni(OH)₂^[101], and nonmetal element P^[102] and supports^[103-105] have also been investigated. Selective examples of Pt-based electrocatalysts with reported quantitative selectivity toward representative products are shown in Table 1.

González-Cobos et al.^[64] synthesized Bi-modified carbon-supported Pt-based nano-catalysts and tested their GEOR performance in alkaline media. Pt₉Bi₁/C with modification of about 10a.t.% of Bi is the most active catalyst, and the oxidation onset potential is as low as 0.3 V (vs. RHE). The *in-situ* FTIR spectroscop-

Table 1 Quantitative selectivity of Pt-based electrocatalysts

Catalyst	Electrolyte	Condition	Selectivity	Ref.
Pt ₉ Bi ₁ /C	2 mol·L ⁻¹ glycerol + 0.5 mol·L ⁻¹ NaOH	0.55 V vs. RHE, 4 h, 20 °C	glyceraldehyde 79.6%	[64]
Pt/C	0.1 mol·L ⁻¹ glycerol + 0.5 mol·L ⁻¹ H ₂ SO ₄	1.1 V vs. SHE, 7 h, 60 °C	glyceric acid 57.8%	[69]
Pt ₅ Ru ₅ /C			dihydroxyacetone 35.0%	
Pt/GNS	0.5 mol·L ⁻¹ glycerol + 0.5 mol·L ⁻¹ KOH	0.2 V vs. SCE, 2 h	glycolate 65.4%	
PtNi/GNS		0.1 V vs. SCE, 2 h	glycerate 47.7%	[71]
PtRuNi/GNS		0.2 V vs. SCE, 2 h	glyceraldehyde 39.2%	
PtRhNi/GNS		-0.4 V vs. SCE, 2 h	oxalate 37.6%	
PtAg skeleton	0.5 mol·L ⁻¹ glycerol + 0.5 mol·L ⁻¹ KOH	0.7 V vs. RHE, 2 h	dihydroxyacetone 82.6%	[81]
Pt ₄ Au ₆ @Ag	0.5 mol·L ⁻¹ glycerol + 0.5 mol·L ⁻¹ KOH	1.1 V vs. RHE, 2 h	dihydroxyacetone 77.1%	[83]
PtSb/C	0.1 mol·L ⁻¹ glycerol + 0.5 mol·L ⁻¹ H ₂ SO ₄	0.797 V vs. SHE, 10 h, 60 °C	dihydroxyacetone 61.4%	[92]
Pt ₂ Rh ₁ /C	0.1 mol·L ⁻¹ glycerol + 0.1 mol·L ⁻¹ HClO ₄	0.45 V vs. SCE, 8 h, 60 °C	tartronic acid ~40%	[34]
P-doped Pt/MCNTs	0.5 mol·L ⁻¹ glycerol + 0.5 mol·L ⁻¹ KOH	0.28 V vs. Ag/AgCl, 1 h	tartronate ~52%	[102]

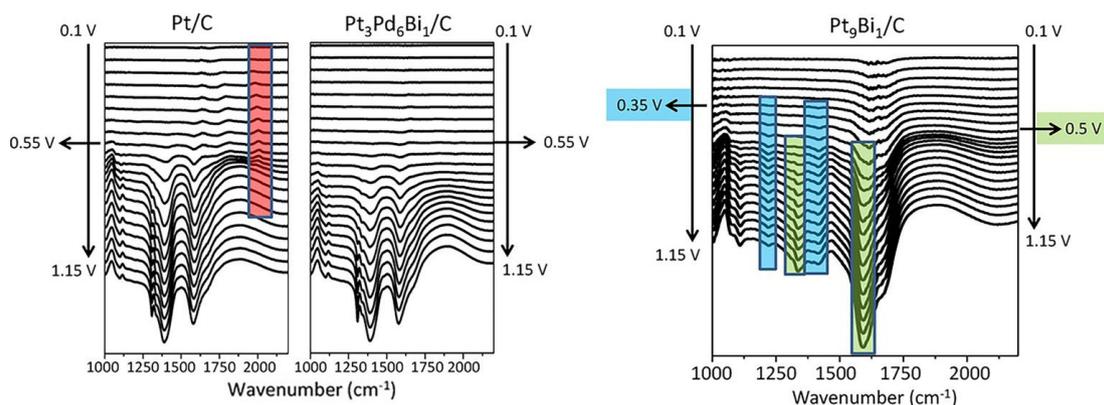


Figure 9 Infrared spectra recorded for glycerol oxidation on Pt/C, Pt₃Pd₆Bi₁/C, and Pt₉Bi₁/C catalysts in 0.1 mol·L⁻¹ glycerol + 1.0 mol·L⁻¹ NaOH electrolyte (scan rate = 1 mV·s⁻¹, resolution 4 cm⁻¹, *T* = 293 K). Reproduced with permission^[64]. (color on line) Copyright © 2016, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

ic analysis (Figure 9) also showed that the modification of Pt with Bi avoided the cleavage of the C-C bond as suggested by the absence of CO_{ad} absorption band in the red box region at around 2050 cm⁻¹, thereby, improving the selectivity for high-value C3 compounds. The emergence of bands at 1220, 1390, and 1415 cm⁻¹ (blue boxes) at low potentials (0.35 V) was attributed to the formation of glyceraldehyde. At high potentials (above 0.5 V), glyceraldehyde and dihydroxyacetone could be further oxidized to form carboxylate, characterized by peaks at 1355 and 1590 cm⁻¹ (green boxes).

PtRu and PtSn are two bimetallic catalysts that are often studied. Falase et al.^[68] studied GEOR on Pt₈₄Ru₁₆, Pt₉₆Sn₄, Pt₈₈Ru₆Sn₆ and Pt nanostructured catalysts prepared by spray pyrolysis. Their results showed that the binary catalyst Pt₈₄Ru₁₆ had the higher oxidation current and better stability than other catalysts. The higher ratio of the forward peak current to the reverse peak current (I_f/I_r) in the cyclic voltammograms of GEOR on the binary and ternary catalysts indicated that the accumulation of oxidation products on these catalysts was much less than that on Pt. The addition of Ru and Sn together to Pt is not conducive to maximize the current generation as suggested by the lower current density observed on this catalyst compared to two binary catalysts, but the coverage of reaction intermediates that will block the electrode and reduce the performance on the ternary catalyst was lower than that of the binary PtRu, PtSn

and Pt nanocatalysts as deduced from the higher I_f/I_r .

Interestingly, others found that ternary nano-alloys show higher electrocatalytic performance^[62,71,77,95]. Kim et al.^[62] synthesized PtRu/C and PtRuSn/C ternary catalysts, and found that the catalyst with the atomic ratio of Pt:Ru:Sn being 5:4:1 had a lower onset potential (0.44 V) and higher peak current density (41.6 mA·cm⁻² @ 0.871 V) for GEOR than Pt₅Ru₄/C and Pt/C. The I_f/I_r ratio on Pt₅Ru₄Sn₁ was significantly greater than those on Pt and PtRu, indicating that there was less accumulation of intermediate residues on this catalyst during GEOR. This observation was explained by that the addition of Sn changed the electronic structure of Pt₅Ru₄Sn₁ catalyst through affecting the electron affinity of the surface Pt atoms, and generating surface oxygen-containing species effectively oxidizing surface poisoning substances at a lower potential and improving stability.

The activity and product selectivity of GEOR can be improved by carefully designing the structure and morphology of the electrocatalysts^[65, 80, 81, 85, 88, 93, 94, 106]. Kim et al.^[80] synthesized PtAg nanotubes (PtAgNTs) through a partial galvanic exchange on Ag nanowires by Pt. In alkaline media, the activity of PtAgNTs was increased by 50% compared with those of Pt nanotubes (PtNTs) and Pt/C, and 3 times compared with that of Pt black. The enhanced performance was largely attributed to the structural effect of nanotube morphology and the electronic effect of doping Ag into Pt. Zhou et al.^[81] studied GEOR on three-dimen-

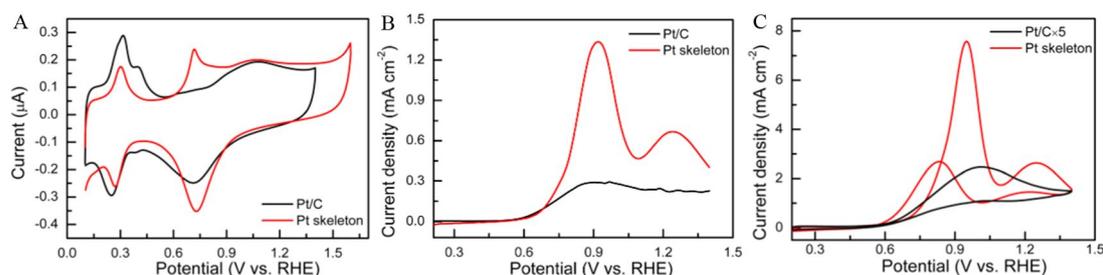


Figure 10 Voltammograms of PtAg skeletons and Pt/C. (A) Cyclic voltammograms (CVs) recorded in $1 \text{ mol} \cdot \text{L}^{-1}$ KOH with a scan rate of $50 \text{ mV} \cdot \text{s}^{-1}$, (B) linear sweep voltammograms (LSVs) recorded in $0.1 \text{ mol} \cdot \text{L}^{-1}$ KOH and $1 \text{ mol} \cdot \text{L}^{-1}$ glycerol with a scan rate of $1 \text{ mV} \cdot \text{s}^{-1}$ and (C) CVs recorded in $0.1 \text{ mol} \cdot \text{L}^{-1}$ KOH + $1 \text{ mol} \cdot \text{L}^{-1}$ glycerol with a scan rate of $50 \text{ mV} \cdot \text{s}^{-1}$. Both catalysts show a higher current peak in the forward potential scan. Note that the current density of Pt/C was enlarged 5 times. (color on line) Reproduced with permission^[81]. Copyright © 2019, American Chemical Society.

sional nanoporous PtAg skeletons. The observed peak current density was $7.57 \text{ mA} \cdot \text{cm}^{-2}$, which was about 15.4 times of that on Pt/C, as shown in Figure 10(C). In addition, the selectivity of dihydroxyacetone on PtAg skeletons measured by HPLC was as high as 82.6% at 0.7 V (vs. RHE), which was attributed to the abundant Pt(111) facets on the PtAg skeletons that greatly promoted GEOR through the secondary alcohol oxidation pathway. They further studied the dependence of product distribution on the reaction conditions. The low concentration of glycerol was beneficial to the formation of glyceraldehyde and its selectivity reached 92.6% when the glycerol concentration was $0.05 \text{ mol} \cdot \text{L}^{-1}$. When the KOH concentration was higher than $0.5 \text{ mol} \cdot \text{L}^{-1}$, the production of dihydroxyacetone decreased, but the formation of formic acid increased. Morphology can also be tuned by electrochemical methods. Hersbach et al.^[106] performed cathodic corrosion of Pt(111) in $10 \text{ mol} \cdot \text{L}^{-1}$ NaOH at -3.0 V vs. RHE. After the pretreatment, Pt(100) terraces were formed on the electrode and became dominating. As a result, the etched Pt electrode behaved like Pt(100) and the selectivity towards glyceraldehyde correspondingly increased as that of dihydroxyacetone decreased.

3.3 Pd-Based Catalysts

Due to its excellent performance under alkaline conditions, Pd-based catalysts are receiving more and more attention. By adding metals such as Bi^[39, 40, 107-109], Au^[98, 110-117], Ni^[38, 49, 75, 110, 117, 118], Ag^[38, 115, 118, 119], Pb^[120],

Cu^[121-123], Pt^[122-125], Sn^[126, 127], Co^[128-130], Fe^[129-131], Mn^[131], Ir^[132], Ru^[74], Rh^[133], or metal oxides (CeO₂, NiO, Co₃O₄, Mn₃O₄^[134], MnO₂^[135]), and nonmetal element P^[136, 137], or adopting different supports^[138-144], modifying the morphology of Pd^[145, 146], a series of novel catalysts have been synthesized for enhanced GEOR performance. The quantitative selectivity of selective Pd-based electrocatalysts toward representative products is summarized in Table 2.

Bambagioni et al.^[138] adopted multi-walled carbon nanotubes (MWCNT) as the support for Pd nanoparticles and obtained a GEOR peak current density of $2800 \text{ A} \cdot \text{g}_{\text{Pd}}^{-1}$ in a half cell containing $2 \text{ mol} \cdot \text{L}^{-1}$ KOH and 5wt.% glycerol. Wang et al.^[139] synthesized a mixed support composed of carbon nitride and graphene (CN_x/G), which had a larger surface area than CN_x, resulting in smaller Pd nanoparticles loaded on its surface. Due to the smaller particle size and the interaction with nitrogen, Pd-CN_x/G showed better activity and higher selectivity for C3 products. HPLC analysis showed that when Pd nanoparticles supported on carbon black (Pd-CB) was used as a catalyst, part of glycolic acid was oxidized to formic acid. However, when Pd-CN_x/G was used as a catalyst, this pathway was demoted, leading to a reduction in the formation of formic acid. Compared with Pd-CB, the selectivity of Pd-CN_x/G to glyceric acid was increased by about 10% ~ 15%, and the selectivity to formic acid was reduced by about 15%. Although the concentration of oxalic acid also increased, the ratio of

Table 2 Quantitative selectivity of Pd-based electro catalysts

Catalyst	Electrolyte	Condition	Selectivity	Ref.
Pd/CNT	1.0 mol · L ⁻¹ glycerol + 6.0 mol · L ⁻¹ KOH	0.2 V vs. SHE, 2 h, 60 °C	tartronate ~ 60%	[113]
PdAg ₃ /CNT			oxalate 32%	
Pd/CNT	1.0 mol · L ⁻¹ glycerol + 4.0 mol · L ⁻¹ KOH	0.1 V vs. SHE, 2 h, 60 °C	tartronate 39.5%	[119]
PdAg ₃ /CNT			oxalate 39.2%	
Pd NCs	0.5 mol · L ⁻¹ glycerol + 0.5 mol · L ⁻¹ KOH	-0.4 V vs. SCE, 2 h, ambient temperature.	glyceraldehyde 61.2%	[125]
Pt@Pd NCs			glycolate ~ 40%	
PdMn/C	0.1 mol · L ⁻¹ glycerol + 0.1 mol · L ⁻¹ NaOH	0.8 V vs. RHE, 4 h	glycerate ~ 56%	[131]
P-doped Pd/CNT	0.5 mol · L ⁻¹ glycerol + 0.5 mol · L ⁻¹ KOH	-0.13 V vs. Ag/AgCl, 0.5 h	dihydroxyacetone 90.8%	[136]
Pd-CN _x /G	0.5 mol · L ⁻¹ glycerol + 0.5 mol · L ⁻¹ NaOH	0 V vs. Hg/HgO, 2 h	glycerate ~ 32%	[139]
Pd nanocubes	0.2 mol · L ⁻¹ glycerol + 0.1 mol · L ⁻¹ KOH	0.87 V vs. RHE, 9 h	tartronate 99%	[146]

C3 products to other products in Pd-CN_x/G was much higher than that in Pd-CB.

Zalineeva et al.^[107] synthesized self-supporting Pd_xBi catalysts by a sacrificial support method with high surface areas (75 ~ 100 m² · g⁻¹) and porous nanostructure morphology as illustrated in Figure 11. Pd₄Bi showed the highest activity for GEOR. *In-situ* FTIR revealed that the high selectivity was dependent on the electrode potential: aldehydes and ketones were primary products at low potentials, hydroxypyruvate at moderate potentials, and CO₂ at high potentials. The high selectivity to form hydroxypyruvate under moderate potentials (0.6 to 0.8 V vs. RHE) was not observed in other Pd-based catalysts. When the potential was scanned in the negative direction, the catalyst was selective for the generation of carboxylate. This unique catalytic behavior was explained by the confinement of reactants and intermediates in the catalyst pores as nanoreactors.

Simões et al. showed that Pt-free Pd_{0.9}Bi_{0.1}/C had the same catalytic GEOR activity as Pt/C and Pt_{0.9}Bi_{0.1}/C displayed a GEOR onset potential that was 0.2 V

more negative than Pt/C. Interestingly, the ternary catalyst Pd_{0.45}Pt_{0.45}Bi_{0.1}/C with Pd atoms replacing half of the Pt atoms achieved the same catalytic activity as Pt_{0.9}Bi_{0.1}/C^[108]. Results from the electrochemical experiments and *in-situ* FTIR revealed that the modification of Pd and Pt surfaces by Bi did not change the mechanism of GEOR, and only the applied potential affected the distribution of the final products. Chronoamperometric experiments combined with HPLC measurements showed that the main reaction products at low potentials were glycerate, dihydroxyacetone and tartronate. The increase of electrode potential resulted in the formation of mesoxalate. When the potential was higher than 0.8 V, oxalate and formate resulted from C-C bond breaking were detected.

Au and Ni are also promising atoms to improve the activity of GEOR. simões et al.^[110] synthesized Pd_{0.3}Au_{0.7}/C, Pd_{0.5}Au_{0.5}/C and Pd_{0.5}Ni_{0.5}/C catalysts, and showed that the onset potentials of Pd_xM_{1-x}/C were lower than those of Au/C and Pd/C, but higher than that of Pt/C, which was about 0.15 V lower than those of Pd/C and Au/C. For bimetallic catalysts, the

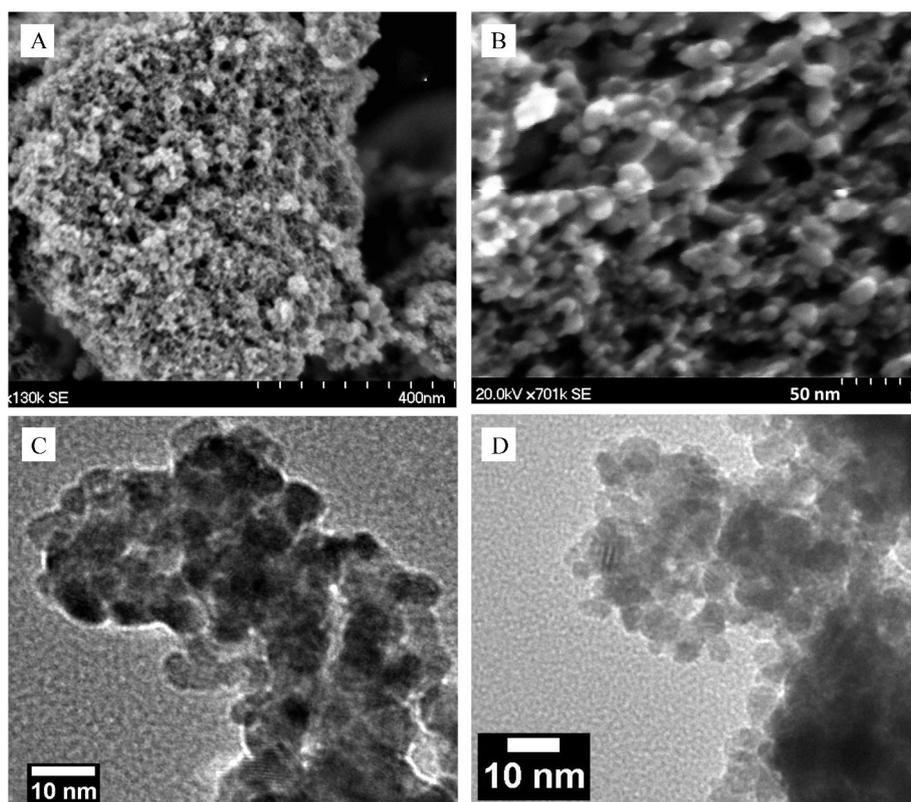


Figure 11 (A,B) SEM and (C,D) TEM micrographs for a self-supported Pd₄Bi sample. Reproduced with permission^[107]. Copyright © 2014, American Chemical Society.

order of activity at a low potential was: Pd_{0.3}Au_{0.7}/C > Pd_{0.5}Au_{0.5}/C > Pd_{0.5}Ni_{0.5}/C. *In-situ* FTIR (Figure 12) at an interval of 0.1 V exhibited two bands of glycerol consumption at 1000 ~ 1100 cm⁻¹ and six characteristic absorption bands of the products denoted as bands A-F between 1100 ~ 1600 cm⁻¹. The gray areas marked the water absorption band from the OH bending mode. Adsorbed CO at 1900 cm⁻¹ was detected on Pd_{0.5}Au_{0.5}/C and Pd_{0.5}Ni_{0.5}/C, but not on Pd_{0.3}Au_{0.7}/C, indicating the absence of dissociative adsorption on gold-rich catalysts. The formation of hydroxypyruvate ions was exclusive on the pure gold catalysts characterized by an absorption band at 1350 cm⁻¹, which was not observed on the Pd-based bimetallic catalysts.

Pd nanoparticles supported on Ni-Zn phase (Pd-(Ni-Zn)/C) have been shown to be active catalysts for the electrooxidation of many small alcohol molecules. A peak current density of 2150 A · g_{Pd}⁻¹ for GEOR on Pd-(Ni-Zn)/C was obtained in a half-cell^[49]. The prod-

uct distribution was dominated by the oxidation products of primary alcohols, including glycolic acid, glyceric acid, tartronate, oxalate, formate and carbonate. No secondary alcohol oxidation products were observed. The excellent electrocatalytic activity of Pd-(Ni-Zn)/C was attributed to the high dispersibility of metal particles and the inherent characteristics of the Ni-Zn phase. The latter may increase the number of OH_{ad} groups on the catalyst surface, which is required for the formation of carboxylates.

Holade et al.^[38, 118] synthesized PdNi/C and PdAg/C catalysts with different atomic ratios by a bromide ion exchange method. The CVs showed that the reaction kinetics at low potentials was enhanced. By combining HPLC and *in-situ* FTIR measurements, the authors confirmed that GEOR on the catalysts involved glyceraldehyde as a reaction intermediate, and the main products were glycolate and glycerate ions. In addition, CO₂ (2343 cm⁻¹) and carboxylic acid (3000 cm⁻¹) produced during GEOR in an alkaline

medium (pH = 13) confirmed the important change of pH near the electrode surface.

Doping metal oxides in Pd is another way to improve the efficiency of GEOR. Xu et al.^[134] showed that the addition of oxides such as CeO₂, NiO, Co₃O₄ and Mn₃O₄ to Pd/C significantly promoted the catalytic activity and stability of the electrooxidation of alcohols. Among them, Pd-Co₃O₄ (2:1, w:w)/C had the highest GEOR activity, while Pd-Mn₃O₄/C showed better performance stability than other oxides. Non-metallic components also play a role in the rational design of catalysts. Kang et al.^[137] developed a composite catalyst (Pd-NiO_x-P/C) in which phosphorus and nickel oxide coexisted for improving GEOR activity.

4 Conclusions and Perspectives

As shown by the literature discussed above, extensive efforts have been devoted to the fundamental understanding of GEOR mechanisms and the development of high performance GEOR catalysts in recent decades. Armed with *in-situ* or online analysis techniques such as HPLC, MS, NMR, and FTIR for qualitative identification and quantitative determination of reaction intermediates and products, together with

DFT theoretical calculations, researchers have made significant progress in understanding the mechanism of GEOR. In general, it has been shown that the GEOR product distribution is dependent on the applied potential, and the structure and composition of the catalysts. Typically, at low potentials, the C-C-C bond is not broken and C3 products are often dominant. At higher potentials, more complete glycerol oxidation occurs, and C2 and C1 products become dominant. On Pt and Pd, although the overall GEOR activity is high, glycerol dissociates even at low potentials and forms strongly adsorbed intermediates, such as CO that poisons the catalysts. To mitigate the surface poisoning, a second, or sometimes, a third metal or metal oxides is introduced in the form of adatoms or alloys. The removal of surface poisoning species is through either a bifunctional mechanism or electronic effects or both. In addition to reduce surface poisoning, the adatoms or alloys may also promote a desired reaction pathway thereby increase the catalyst selectivity for products of high value through modification of the adsorption energy of intermediates or third body effect. Like many other surface reactions, GEOR is structure sensitive, which has mostly demonstrated on low-index Pt single crystal electrodes, with

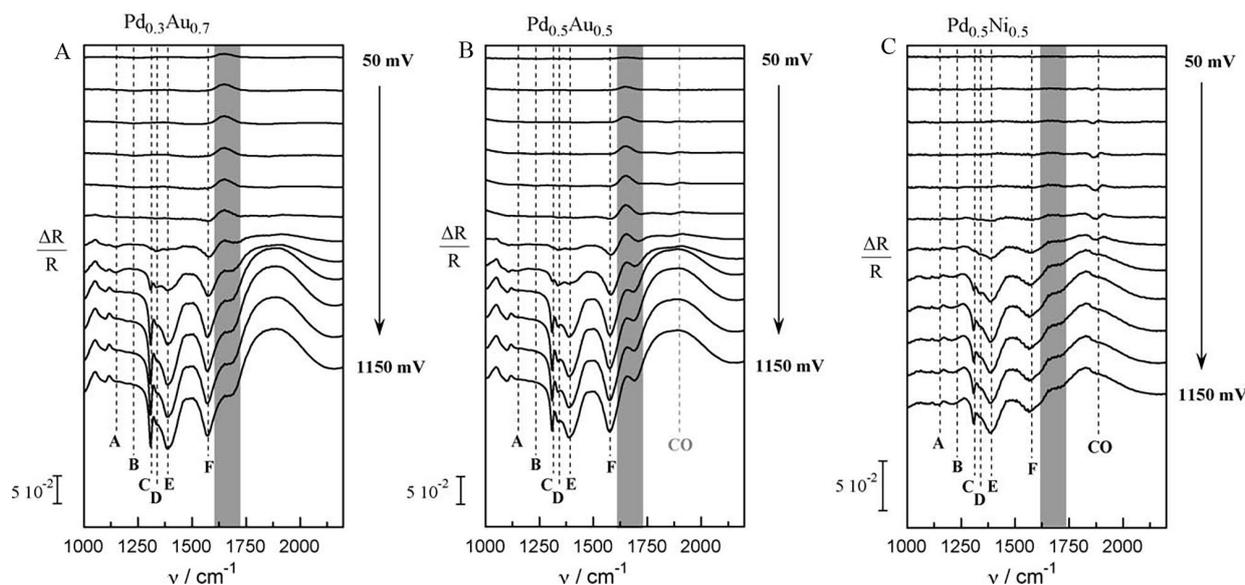


Figure 12 Infrared spectra recorded during glycerol oxidation on (A) Pd_{0.3}Au_{0.7}/C, (B) Pd_{0.5}Au_{0.5}/C and (C) Pd_{0.5}Ni_{0.5}/C catalysts in 0.1 mol·L⁻¹ glycerol + 1.0 mol·L⁻¹ NaOH electrolyte at 293 K. Scan rate: 1 mV·s⁻¹, resolution 4 cm⁻¹. Reproduced with permission^[110]. Copyright © 2009, Elsevier B.V.

the highest activity observed on Pt(111).

These fundamental understandings lay the foundations for future work in GEOR. The complex nature of GEOR presents many challenges, but also opportunities for further advancing the field. In the following we attempt to provide some brief perspectives of the areas that are of importance for developing GEOR catalysts with high activity and selectivity. Given that in general the lower potentials have higher product selectivity, efforts in increasing the activity at lower potential region are much needed. It has been shown that defect sites on Pt surfaces are more active for GEOR. However, these sites are also very active for C-C bond cleavage and therefore prone to be poisoned. How to strike a balance between high activity and keeping the C-C bond intact remains a challenge. It is conceivable that high index surfaces, such as multi-facet nanocrystals^[147-149], with high density of unsaturated surface atoms are active for GEOR. Modifying these surfaces with adatoms may be a plausible approach to fine tune the adsorption energy and thereby the selectivity of the catalysts. Moving beyond Pt and Pd-based nanoparticle catalysts, atomically dispersed Pt or Pd catalysts^[150-152] may be an alternative to promote C3 products because of the absence of neighboring Pt or Pd necessary for the C-C bond cleavage.

From practical point of view, in addition to developing high performance catalysts through rational design, studies of GEOR under operating conditions of fuel cells^[49, 75, 113, 116, 119, 122, 130, 138, 153] or electrolysis cells for hydrogen production^[64, 154] or CO₂ coelectrolysis^[155] are critical for realization of valorization of glycerol through electrocatalysis. Finally, finding efficient catalysts for the conversion of crude glycerol from biodiesel industry, which contains impurities such as CH₃OH, residual heterogeneous or homogeneous catalysts and other salts, into value-added products will pave the way for practical applications of these catalysts^[114, 153, 156].

Acknowledgements:

This work was supported by the Natural Science Foundation of China (NSFC) (21733004, 21327901), the National Basic Research Program of China (973

Program, 2015CB932303), and the International Cooperation Program of Shanghai Science and Technology Committee (STCSM)(17520711200). This work was partially supported by American University.

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铂和钯上丙三醇电氧化研究进展： 从反应机理到催化材料

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摘要: 生物柴油工业的蓬勃发展带来大量副产品丙三醇(甘油), 因此如何将甘油转化为高附加值产品具有重要的研究价值。在各种方法中, 电催化氧化由于其条件温和、环境友好和高效率而备受关注。然而, 甘油的电氧化非常复杂, 涉及许多反应途径和多个电子和质子转移过程, 如何合理设计对目标产物具有高选择性的催化剂是很大的挑战。在本文中, 我们主要概述了铂和钯基催化剂上甘油电氧化研究的最新进展。我们首先总结了基于原位和在线谱学研究以及理论计算获得的影响其电催化活性和选择性的因素。然后, 选择代表性文献来说明这些因素如何应用于研制高效甘油电氧化催化剂。最后, 提出了未来研究中要解决的关键问题。

关键词: 丙三醇电氧化; 甘油电氧化; 电合成; 电催化机理; 电催化剂理性设计