Biomass Electrochemistry : from cellulose to sorbitol

Kwon, Y.

3

Mechanism of the catalytic oxidation of glycerol on polycrystalline gold and platinum electrodes

Abstract

This chapter addresses the electro-oxidation mechanisms of glycerol on Au and Pt electrodes under different pH conditions. Intermediates and/or reaction products were detected by an online high-performance liquid chromatography technique (for soluble products) and by online electrochemical mass spectrometry (for CO_2). In alkaline media, the main product of glycerol oxidation on the Pt electrode is glyceric acid produced via glyceraldehyde. Glyceric acid is the primary oxidation product on the Au electrode, and is further oxidized to glycolic acid and formic acid at high potentials ($\geq$ 0.8 V) yielding high current densities. Lowering the pH of the solution, the glycerol oxidation becomes significantly more sluggish on both Au and Pt electrodes, resulting in glyceraldehyde being the main oxidation product in neutral condition, especially on gold. In acidic solution, only the Pt electrode shows catalytic activity with a relatively low conversion rate mainly to glyceraldehyde. At positive potentials corresponding to the formation of a Pt surface oxide, the PtO_x surface catalyzes the conversion from glyceraldehyde finally to formic acid and CO_2, but only in acidic condition. Gold only catalyzes glycerol oxidation under alkaline conditions, in contrast to a "real catalyst", i.e. platinum, which catalyzes glycerol oxidation over the entire pH range.

The contents of this chapter have been published: Y. Kwon, K. J. P. Schouten, M. T. M. Koper, *ChemCatChem*, **2011**, *3*, 1176-1185.

3.1 Introduction

Glycerol is an important biomass-related compound, both as a model poly-ol compound and as an abundant byproduct of biodiesel.[1-3] New applications of glycerol are being sought and have been found as a low-cost feedstock for functional derivatives either for mass consumption, such as additives for concrete, or as a precursor of fine chemicals of added value.[1] For the cogeneration of energy and chemicals, selective electrocatalytic oxidation for converting glycerol into commercially valuable products such as dihydroxyacetone (DHA), glyceraldehyde, glyceric acid etc. is regarded with particular interest.[4,5] Even though most glycerol oxygenated derivatives are of practical value, the fundamental molecular-level understanding of catalytic reaction intermediates and products is still incomplete.[6-8] Since most of the relevant reactions of glycerol in aqueous media are redox reactions, electrochemistry and electrochemical methods are particularly useful in scrutinizing such mechanistic details.

Voltammetric studies of glycerol oxidation have been reported for both alkaline and acidic media.[6-10] However, the disadvantage of purely electrochemical methods is that no specific information on the adsorbates or the (intermediate) oxidation products is obtained. Therefore, a spectroscopic technique, such as Fourier Transform Infrared Spectroscopy (FTIRS)[7,8] has to be applied to probe reaction intermediates/products and mechanisms. Since for the oxidation of glycerol, incomplete oxidation products such as aldehydes, ketones and carboxylic acids tend to dominate the product spectrum, High Performance Liquid Chromatography (HPLC) is the method of choice to study glycerol oxidation products both at a qualitative and quantitative level.

Recently, we introduced a new combination of voltammetry and HPLC by adopting rapid online sample collection with a micrometer-sized sample collecting tip, and we successfully demonstrated the application of the method to the glycerol electro-oxidation on Au and Pt electrodes in alkaline media.[11] The absence of primary oxidation products, i.e. glyceraldehyde and dihydroxyacetone, in the reaction mechanism suggested in that work, was primarily due to the instability of these aldehydes in alkaline media. Therefore, a modification of the sample collection system is necessary to provide clear product detection and separation and their relative selectivity of formation in dependence on the applied electrode potential. Additionally, the very high activity of the Au electrode compared to the

Pt electrode is partially due to the participation of OH^- in the glycerol oxidation mechanism,[8,9,12] and therefore it is worth studying the effect of different pH conditions for both electrocatalysts. Moreover, the online electrochemical mass spectrometry (OLEMS) technique is useful for the identification of volatile intermediates and products and to follow the formation of the complete oxidation product CO_2 during the voltammetry.

In this chapter, we aim at formulating complete reaction mechanisms for the glycerol oxidation on Au and Pt electrodes in alkaline, neutral, and acidic conditions, both with respect to the quantitative and qualitative product distributions, as determined by the combination of voltammetry with online HPLC and OLEMS. We believe these results and mechanisms are very relevant to the aqueous-phase reforming of glycerol on gold and platinum catalysts as depolarized by oxygen.[13-17] The essential electrocatalytic nature of the alcohol oxidation under liquid-phase heterogeneous catalytic conditions was recently confirmed by the groups of Neurock and Davis.[18]

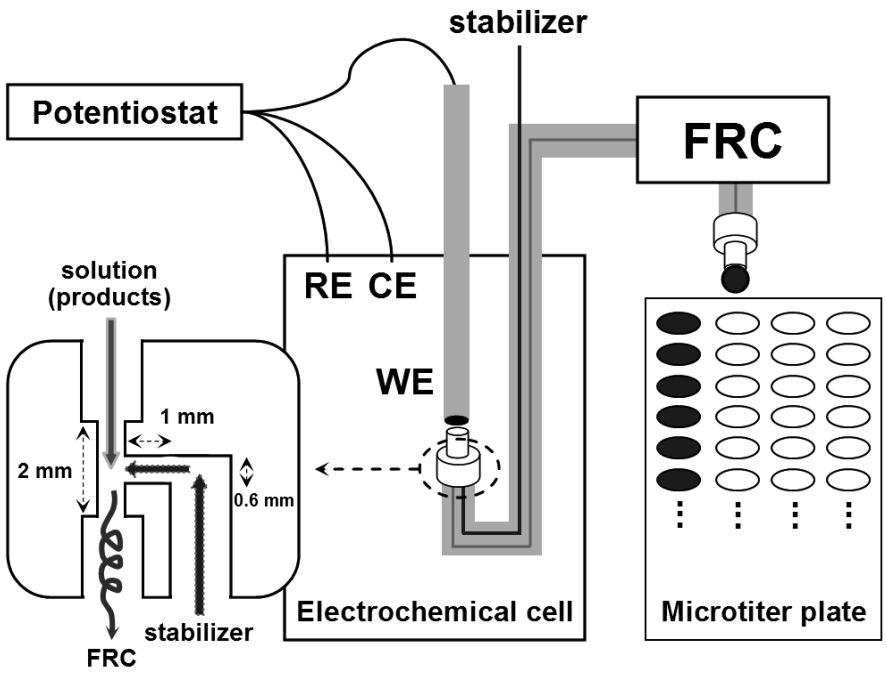
3.2 Experimental Section

3.2.1 Electrochemistry

All measurements were carried out in a conventional single compartment three-electrode glass cell, which was cleaned by a standard procedure[19] to remove all traces of organic contaminations. Glycerol (0.1 M) was dissolved into solutions of different pH (0.1 M NaOH, 0.1 M Na_2SO_4, and 0.5 M H_2SO_4). Prior to the experiments oxygen was removed by bubbling argon through the solution for at least 30 minutes. Working electrodes in the experiment were polycrystalline gold (dia. 5 mm) and platinum disks (dia. 6.1 mm) embedded in PTFE shrouds, which were mechanically polished with alumina (up to 0.05 μm), and cleaned ultrasonically in ultrapure water before use. In all experiments, a platinum plate was used as a counter electrode, while a reversible hydrogen electrode (RHE) was employed as a reference electrode. Electrochemical cell potentials were controlled with a Potentiostat/galvanostat (μ-Autolab Type III). All chemicals used for this work were at least analytical grade.

3.2.2 Fraction Collection

The reaction products in neutral and acidic conditions were collected with the same sample collecting tip as already described in our previous work.[11] Considering the stability of collected products in alkaline solution, in particular glyceraldehyde and dihydroxyacetone, the tip for sample collection was modified as illustrated in Scheme 1. While collecting products from electrode surface, a small amount of stabilizer (i.e. buffer or acidic solution) is injected into the tip-block and immediately mixed with the collected sample. Well mixed and stabilized samples are collected onto the microtiter plate for further analysis in the HPLC system.



Scheme 1. Schematic diagram of the on-line sample collection by fraction collector (FRC) with a special sample collecting tip for the stabilization of collected samples.
WE - Working Electrode, RE - Reference Electrode, CE - Counter Electrode.

3.2.3 Chromatographic Determination of Products

The samples collected during voltammetry were analyzed in an HPLC system. The microtiter plate with the collected samples was placed in an auto-sampler holder and diverse volumes (2~20 μL) of sample were injected into the column. The columns used were a single Aminex HPX 87-H (Bio-Rad) column or the Aminex with Sugar SH1011 (Shodex) column in series, especially for the detection of dihydroxyacetone. Diluted sulfuric acid (0.5~5 mM) was used as eluent. The selected temperature of column oven was changed from 30 to 85°C in order to confirm reaction products. Details of system configuration are described elsewhere.[11]

3.2.4 On-line Electrochemical Mass Spectrometry (OLEMS)

OLEMS measurements were performed on an EvoLution mass spectrometer system (European Spectrometry Systems Ltd.).[20] The system consists of a Prisma QMS200 (Pfeiffer), brought to vacuum with a TMH-071P turbo molecular pump (60 l/s, Pfeiffer) and a Duo 2.5 rotary vane pump (2.5 m^3/h, Pfeiffer). During measurements, the pressure inside the MS was 1-5 × 10^{-9} bar. Pretreatment procedures and details were explained in a previous paper.[21] For the OLEMS experiments, bead type Au and Pt electrodes were used.

3.3 Results and discussion

3.3.1 Glycerol oxidation in alkaline condition

Considering the glycerol oxidation pathway, glyceraldehyde and/or dihydroxyacetone (DHA) should be produced as intermediate species and/or product. However, in our previous Chapter 2,[11] we assumed that they were not produced during the voltammetric glycerol oxidation on Au and Pt electrodes in alkaline media due to their absence in chromatograms. Generally, however, aldehydes are not stable in alkaline condition, but undergo base-catalyzed dimerization or aldol condensation reactions.[22,23] Therefore, in order to probe the importance of such a non-Faradaic reaction during glycerol oxidation, we investigated the time-dependent degradation of glyceraldehyde (1 mM), an isomer of

dihydroxyacetone, under oxygen-present and -free solutions (0.1 M NaOH). Samples were collected at different reaction times and collected samples were immediately neutralized with the same volume of 50 mM H_2SO_4, and then analyzed in an HPLC system. Figure 1 shows the concentration changes of glyceraldehyde and its chemical reaction products in alkaline condition, both in the absence (Figure 1a) and presence (Figure 1b) of oxygen in solution. Regardless of the presence of oxygen, glyceraldehyde evolves into its isomer (DHA), dimer (incl. fructose) and lactic acid. In a non-deaerated solution, glyceraldehyde decays much faster than in oxygen-free solution, and note that we detected many products that have been claimed as the products of catalytic glycerol oxidation such as glyceric acid, glycolic acid, and formic acid.[6,7,11,24] We note in particular that the concentration of glyceric acid reached 0.35 mM in 15 min, which means glyceraldehyde is predominantly oxidized to glyceric acid, even in the absence of a catalyst. In addition, the concentrations of glycolic acid and formic acid increased gradually, with a constant ratio, but slowly compared to glyceric acid due to the lower rate of C-C bond breaking (glycolic acid and formic acid are formed by decomposition of glyceric acid[6,11]). Even after glyceraldehyde is no longer detected, both the concentrations of glycolic acid and formic acid still increase, which can be explained by the decomposition of fructose after 15 min, since fructose also generally undergoes chemical degradation and oxidation under alkaline conditions.[25,26]

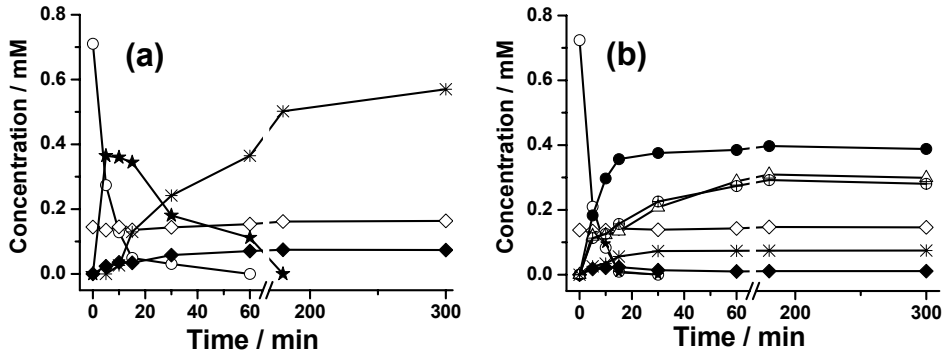


Figure 1. Glyceraldehyde degradation in 0.1 M NaOH as a function of reaction time under (a) argon-saturated and (b) non-deaerated condition. ○ glyceraldehyde, ★ dihydroxyacetone (DHA), ● glyceric acid, △ glycolic acid, ⊕ formic acid, ◇ dimer, ◆ fructose, and ✳ lactic acid.

In our previous work, the samples collected during voltammetry were open to air even in alkaline media, which accelerated the base-catalyzed degradation of unstable glycerol

oxidation intermediates. For an unequivocal understanding of the Faradaic reaction pathways (i.e. those requiring interfacial electron transfer) during glycerol oxidation, the stabilization of collected samples by lowering pH of the collected samples is essential, since the degradation of glyceraldehyde or dihydroxyacetone occurs only under alkaline conditions at room temperature[22,23] or under acidic conditions at high temperature.[27] To improve the existing system, we considered the modified sample collecting-tip illustrated in the Experimental Section (Scheme 1) as an optimal solution, because the collected sample may continue to degrade inside the tubing during the long traveling time (ca. 10 min) from sample collecting-tip to microtiter plate. Therefore, whilst collecting glycerol oxidation products during voltammetry in alkaline solution, a small amount of 0.5 M H_2SO_4 solution was continuously injected into the tip-block and immediately mixed with collected samples. The pH of samples in microtiter plate was ca. 3 ~ 5.

Figure 2 shows the voltammograms recorded in the presence of online sample collection with the modified sample collecting tip, alongside the reaction products of glycerol oxidation on platinum (Figure 2A) and gold (Figure 2B) in alkaline condition as detected by the HPLC system. Note that the voltammograms of glycerol oxidation on both electrodes are similar to the results in our previous paper,[11] which implies that the modified sample collecting tip does not seriously affect the glycerol oxidation reaction. The gold electrode shows an almost 10 times higher current density than the Pt electrode, but only at higher potentials. Both catalysts also have very different onset potentials: ca. 0.4 and 0.8 V for Pt and Au electrodes, respectively. We have ascribed the higher activity of gold to the delayed surface oxidation of Au compared to Pt, which allows for the application of higher effective overpotentials on gold. In the potential region where both Pt and Au are not covered by an oxide layer, platinum is always more active than gold. Both on the Pt and the Au electrode, the onset of glycerol oxidation exhibits a Tafel slope of ca. 120 mV/dec, suggesting that the first electron transfer is rate determining.

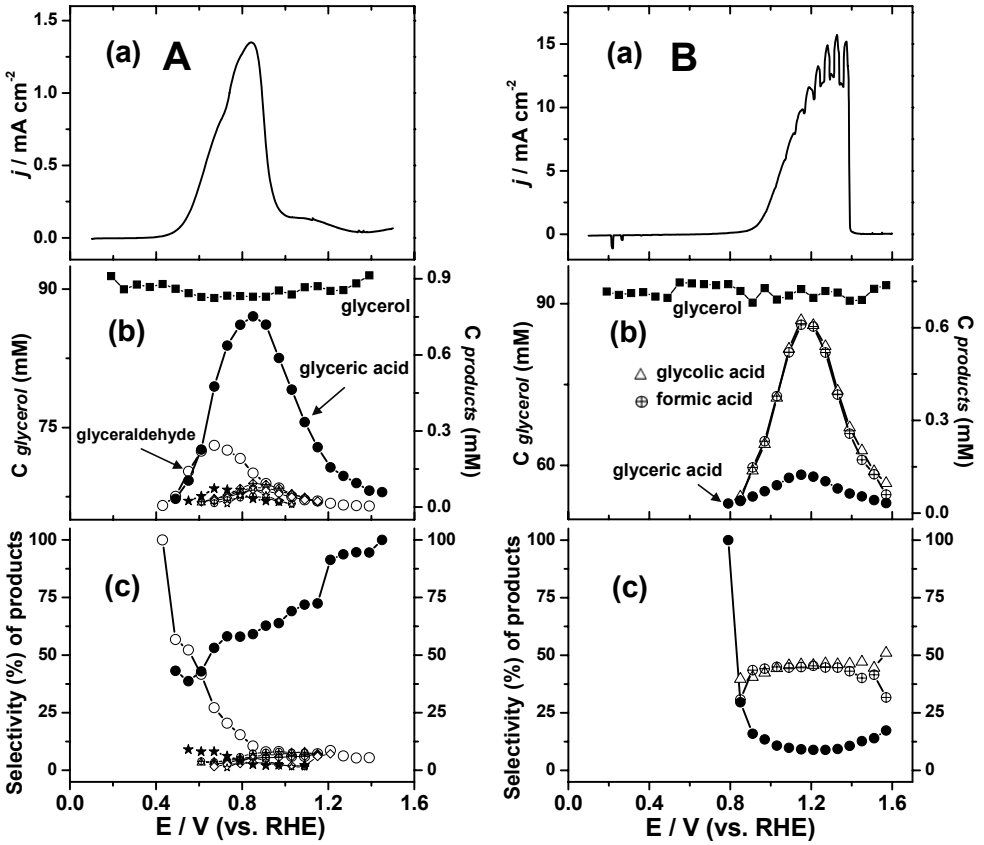


Figure 2. Glycerol oxidation (0.1 M) on (A) Pt and (B) Au electrodes in 0.1 M NaOH: (a) current density during linear sweep voltammetry with scan rate of 1 mV/s, (b) concentration changes of glycerol and its reaction products collected with the modified sample collecting tip and analyzed in an HPLC system, and (c) selectivity (%) of products as a function of potential. ■ glycerol, ○ glyceraldehyde, ★ dihydroxyacetone (DHA), ● glyceric acid, △ glycolic acid, ⊕ formic acid, ◇ oxalic acid, ⌖ tartronic acid, and ☆ hydroxypyruvic acid.

The key result here is that in the product distribution on Pt (Figure 2A-b), glyceraldehyde, dihydroxyacetone, and hydroxypyruvic acid were detected by stabilization of collected samples with the modified sample collecting tip and by an extended product analysis window using two columns in series in the HPLC. These three products are not observed on Au, and were also not observed on Pt in our previous paper using the "old" sample collecting tip.[11] The peaks observed in the chromatograms are converted to the

corresponding concentrations of the various compounds, the results of which are shown in Figure 2A-b and Figure 2B-b. The measured concentration of glycerol was lower than 0.1 M due to the dilution by the continuous injection of stabilizer into the sample collecting tip-block. The concentration of glycerol near the Pt electrode slowly decreases as a function of potential with the lowest value between 0.6 and 1 V, after which it increases slightly as the potential increases positively, although this trend is less clear on the Au electrode. Glyceraldehyde was detected as the first glycerol oxidation product from 0.4 V and observed in whole potential range with its maximum concentration at 0.65 V. As the potential increases, the concentration of glyceric acid steeply increases showing its highest concentration at ca. 0.85 V, which corresponds well with the potential of highest current density in the voltammogram. Based on the sequence of the detected products, we may conclude that glyceric acid is formed from the further oxidation of glyceraldehyde. In addition to glyceraldehyde as the product of primary alcohol oxidation, a relatively low concentration of dihydroxyacetone was also observed and its concentration profile follows that of glyceraldehyde. Especially hydroxypyruvic acid, a compound derived from further oxidation of dihydroxyacetone, was also observed at the highest current values. Interestingly, the concentrations of glycolic acid and formic acid shown in Figure 2A-b are relatively small compared to our previous results,[11] primarily because the stabilized samples containing glyceraldehyde and dihydroxyacetone do not decompose to glycolic acid and formic acid even if samples are open to oxygen. As already mentioned, glyceraldehyde is the first product of glycerol oxidation with close to 100% selectivity at 0.4 V; however, it drops to 10% at 0.8 V in Figure 2A-c because of its conversion to glyceric acid. Therefore, the selectivity toward glyceric acid increases gradually from 40% at 0.6 V to 100 % at the highest potential, though the efficiency at these high potentials is low.

On a gold electrode, we observe only three products as previously reported,[11] and glyceric acid was detected first instead of glyceraldehyde, which means glycerol was oxidized to glyceric acid through glyceraldehyde rapidly, primarily due to the higher overpotentials applicable to gold. The main difference with platinum is that on gold glyceric acid is actively oxidized to glycolic acid and formic acid each with ca. 45 % selectivity after 0.85 V, since there is a wider potential range available for the further oxidation given the higher onset potential of surface oxide formation on gold (~ 1.3 V) compared to platinum (~ 0.85 V).

Based on the results in Figure 2, a reaction mechanism for the glycerol oxidation on Au and Pt electrodes in alkaline media is suggested in Figure 3. In the pathway of primary alcohol oxidation, glycerol is first oxidized to glyceraldehyde in a two-electron transfer step and glyceraldehyde is further oxidized to glyceric acid in a subsequent two-electron transfer step. In the case of the gold electrode, glyceric acid is apparently directly produced from glycerol through glyceraldehyde, because of the high effective overpotential on gold, making glyceraldehyde an unstable intermediate. As a next two-electron transfer step, glyceric acid is further oxidized by cleavage of a C-C bond into glycolic acid and formic acid on both electrodes. However, on the platinum electrode this process becomes deactivated at potentials close to 0.9 V, where Pt forms an inhibiting surface oxide. The Au electrode has a much higher conversion activity of glyceric acid to glycolic acid and formic acid than the Pt electrode, which we ascribe to the higher surface oxidation potential of gold compared to platinum. In addition, glyceric acid and glycolic acid are further oxidized on the platinum electrode to tartronic acid and oxalic acid, respectively. In the pathway of secondary alcohol oxidation, dihydroxyacetone is produced in a two-electron transfer step, but only on the Pt electrode. As a next two-electron transfer step, dihydroxyacetone is oxidized to hydroxypyruvic acid, which can be further oxidized to ketomalonic acid even though it was not detected due to the detection limit of our current system. Recently, the formation of CO_2 as the final oxidation product of glycerol on a gold electrode in alkaline media was observed during FTIR experiments,[7] although CO_2 should appear as carbonate (CO_3^{2-}) in alkaline media by its combination with OH^-. However the assumption of total oxidation of glycerol to CO_2 suggested in that article is unrealistic, because only a limited amount of CO_2 can be produced through formic acid oxidation, considering the similar concentrations of glycolic acid and formic acid in Figure 2B-b. It is also important to point out an important artifact that often appears with the detection of oxidation products using FTIR in the thin-layer configuration. As the oxidation of these organic molecules produces protons which become subsequently trapped in the thin layer, the pH in the thin layer is effectively (much) higher than in the bulk of the solution. Formic acid (or formate) has a very low oxidation activity on gold in alkaline media,[28] but a much better oxidation activity in acidic media.[29] This pH change is probably the main reason why the formic acid intermediate is oxidized on gold and why CO_2 is observed and not carbonate. Normally, in alkaline media, we would expect that only Pt is capable of oxidizing formic acid to carbonate. Therefore, we believe that any complete oxidation of glycerol to carbon dioxide on gold is highly questionable.

As a brief intermediate conclusion concerning alkaline conditions, we can observe both primary and secondary alcohol oxidation pathways on a Pt electrode in alkaline condition with the modified sample collecting-tip. Glyceraldehyde is the main product at low potentials, but is essentially unstable in alkaline media, and is easily oxidized to glyceric acid as the dominant product at higher potentials ($\geq$ 0.6 V). The observation of glyceric acid as the first product on Au electrode shows that glyceraldehyde and dihydroxyacetone are intermediate oxidation products. On gold, glyceraldehyde is oxidized to glyceric acid due to the higher oxidation potentials accessible on Au compared to Pt.

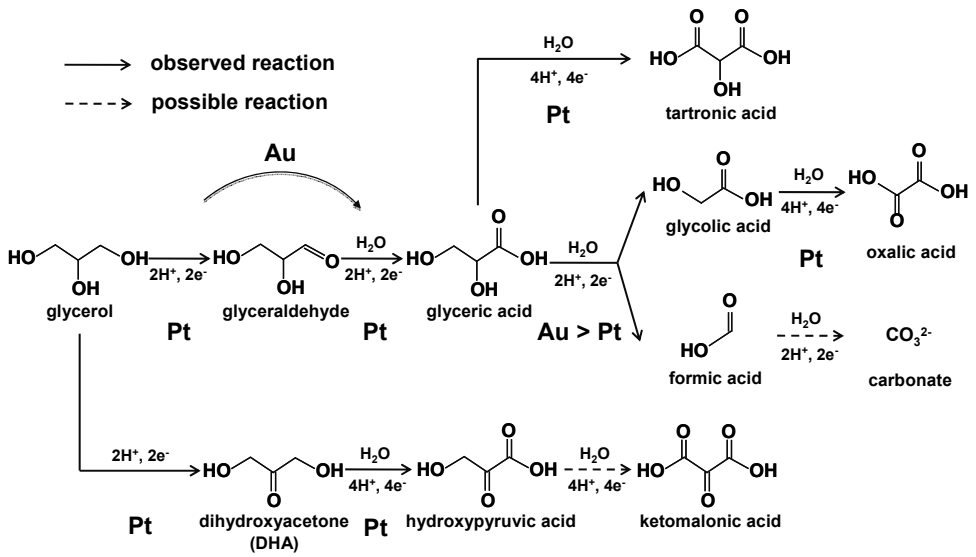


Figure 3. Schematic diagram for the glycerol oxidation mechanism on Au and Pt electrodes in alkaline media.

3.3.2 Glycerol oxidation in neutral condition

The investigation of the electro-oxidation of glycerol in neutral media has been limited to research related to microorganisms, i.e. bio-catalysis in a microbial fuel cell (MFC), to provide optimum pH conditions for bacteria.[30] However, studying neutral conditions as an intermediate between alkaline and acid conditions, is important for the understanding of the catalytic activity changes on gold and platinum electrodes in various media. Below, we report on the oxidation of glycerol in 0.1 M Na_2SO_4. Because of the low sweep rate applied, which should limit the effect of pH changes by the reaction occurring, and because we did

not want to introduce new anion (compared to acidic media), we did not work with buffered solutions. Similar reactivities were found, however, in phosphate buffered solutions, and therefore we believe that the general qualitative conclusions given below are valid.

Figure 4 shows the voltammetry of glycerol oxidation in 0.1 M Na_2SO_4 alongside the concentration profiles of glycerol and its oxidation products on platinum (Figure 4A) and on gold (Figure 4B) electrodes, both in the absence (dotted line) and presence (solid line) of online sample collection. The effect of online sample collection on the voltammogram was described in our previous work.[11] First of all, note that the oxidation current is significantly higher on platinum than on gold, in contrast with the situation in alkaline media. Glycerol oxidation on platinum begins from 0.45 V, and the current increases significantly from 0.6 V. In spite of the presence of sample collection, the oxidation current of glycerol was not delayed compared to the current without sample collection, particularly in the range up to 0.7 V. Presumably this happens because the intermediate species is oxidized further only very slowly. In other words, the first oxidation product (glyceraldehyde) is the final product in that potential range. The same tendency was also observed on the gold electrode, albeit in a different potential window. On Au, glycerol is oxidized from 0.8 V and sample collection did not cause any current changes until 1.1 V. Although the onset potentials of two electrodes are not identical, the kinetics of glycerol oxidation in neutral conditions are significantly slower than in alkaline conditions, and the removal of intermediate species has no effect on current at low potentials. On the other hand, online sample collection caused a small current increase from 0.7 to 1.5 V on the platinum electrode and from 1.1 to 1.5 V on gold electrode, respectively. This current enhancement is probably due to the removal of poisonous intermediate species such as CO on platinum or carboxylic acids on the gold electrode.[11,31-33]

Collected samples during voltammetry were analyzed in an HPLC system, and the peaks observed in the chromatograms were converted to the corresponding concentrations of the various compounds, the results of which are shown in Figure 4A-b and Figure 4B-b. The first product of glycerol oxidation on platinum, glyceraldehyde, appears at 0.43 V and its concentration increases until 0.8 V, after which it decreases due to the formation of surface oxide until 1.1 V. For higher potentials, the concentration of glyceraldehyde increases again slightly until 1.2 V, and then decreases steeply. There is a small disagreement between the potentials of the peak in current density and the maximum glyceraldehyde concentration

near 0.8-0.9 V, due to the further oxidation of glyceraldehyde to glyceric acid. Glyceric acid appears as a product from 0.6 V. The concentration of glyceric acid increases slowly until 0.8 V as the maximum current is observed, after which it shows a plateau, and then steeply increases from 1 V to 1.3 V, implying that the oxidation of glyceraldehyde at these high potentials is accelerated. Interestingly, one of the oxidation products of glyceric acid, glycolic acid, is observed without the observation of formic acid from 0.65 V with a peak in concentration at 0.8 V. Glycolic acid and formic acid appear as a pair from 1.1 V and higher potentials with almost the same concentration profiles. The absence of formic acid until 1.1 V strongly suggests that it is further oxidized to CO_2, probably through the formation of chemisorbed CO which is a poisoning intermediate. To obtain additional evidence for the formation of CO_2, an online electrochemical mass spectrometry (OLEMS) experiment was carried out. Figure 4A-c shows the MS ion current for m/z = 44, which implies CO_2 formation, clearly demonstrating that formic acid is further oxidized to CO_2 at around 0.8 V. Moreover, the steep increase of the CO_2 intensity from 1.4 V should also be ascribed to formic acid oxidation, but it is then hard to explain why there is a slightly higher concentration of formic acid than that of glycolic acid in Figure 4A-b. The reason for this will be further discussed in the next section on the glycerol oxidation in acidic conditions, and it is mainly due to the glycolic acid oxidation to formic acid. As a product of secondary alcohol oxidation, dihydroxyacetone was also observed, but its concentration is negligible in the entire potential range except for the region corresponding to a PtO_x surface. Even though dihydroxyacetone is not produced in great amounts, it was further oxidized to hydroxypyruvic acid, a trace of which was observed in the chromatograms.

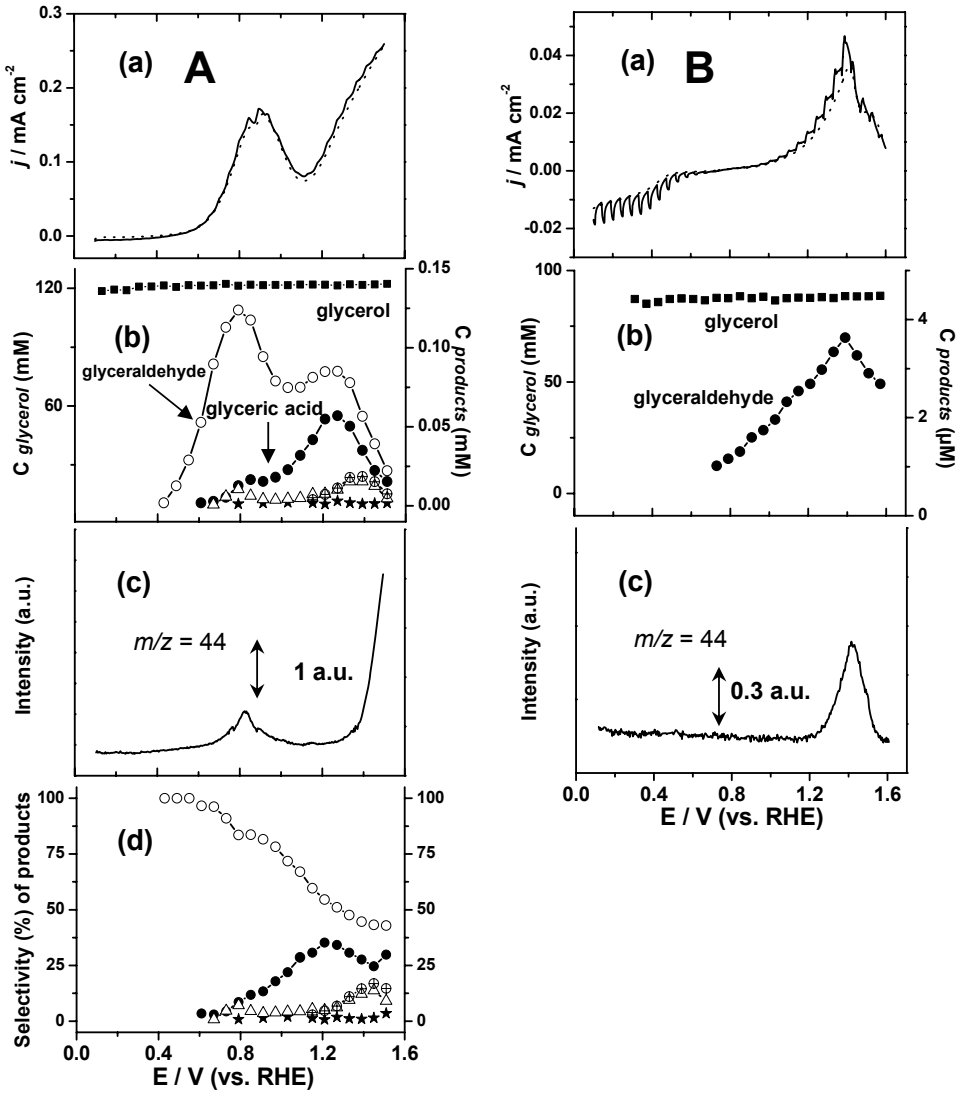


Figure 4. Glycerol oxidation (0.1 M) on Pt (A) and Au (B) electrodes in 0.1 M Na_2SO_4: (a) current density profile with (solid line) and without (dotted line) sample collection during linear sweep voltammetry with scan rate of 1 mV/s, (b) concentration changes of glycerol and its reaction products collected with modified sample collecting tip, (c) ion current profiles for m/z = 44 (CO_2) in OLEMS measured during voltammetry, and (d) selectivity (%) of products as a function of potential. ■ glycerol, ○ glyceraldehyde, ★ dihydroxyacetone (DHA), ● glyceric acid, △ glycolic acid, ⊕ formic acid.

On a gold electrode, only glyceraldehyde was detected as a glycerol oxidation product in the HPLC system. Glyceraldehyde appears from 0.8 V and its concentration slowly increases until 1.4 V, after which it decreases in good correspondence with its current profile. To estimate the detection limit of our current HPLC system, an OLEMS experiment was carried out and disclosed that a relatively small amount of CO_2 is also produced during glycerol oxidation on Au electrode, but only at very high potentials. Considering the high sensitivity of OLEMS for product detection, we can conclude that a small amount of glyceraldehyde must be further oxidized to glyceric acid, glycolic acid and formic acid in this potential range.

The main product of glycerol oxidation on Pt in neutral conditions is glyceraldehyde as shown in Figure 4A-d. The selectivity to glyceraldehyde is over than 80% until 0.8 V, and it is slowly oxidized further to glyceric acid as the potential increases. Interestingly, the amount of glyceric acid decreases from 1.2 V, which matches well with the increase of the selectivity toward glycolic acid and formic acid.

From the results shown in Figure 4, a reaction mechanism for the glycerol oxidation in neutral condition on Au and Pt electrodes is suggested in Figure 5. The general glycerol oxidation pathways in neutral condition are essentially identical to alkaline media, although some products, i.e. oxalic acid and tartronic acid, are absent in the product spectrum. The dominant product of glycerol oxidation is glyceraldehyde formed in a two-electron transfer step on both electrodes. Especially gold shows a very high selectivity to glyceraldehyde in neutral media. Interestingly, the PtO_x surface, though normally considered inactive, shows activity for glycerol oxidation, but its selectivity to glyceraldehyde is less than on a clean Pt surface since glyceraldehyde is further oxidized to glyceric acid, glycolic acid, formic acid and CO_2 on PtO_x. This would suggest that the Pt surface at these high potentials is not fully oxidized to PtO_x in the presence of glycerol, or the high anodic potential makes PtO_x catalytically active. Dihydroxyacetone, the product of secondary alcohol oxidation is produced in small amounts in a two-electron transfer step on the Pt electrode and further oxidized to hydroxypyruvic acid at high potentials.

Although only glyceraldehyde was observed as the glycerol oxidation product on gold electrode in an HPLC analysis, the formation of (small amounts of) CO_2 as the full oxidation product is observed during OLEMS measurements on both electrodes. The

consistency of the appearance of CO_2 with the concentration patterns observed for formic acid (see Figure 4AB-c) prove that CO_2 is formed from formic acid oxidation.

As a general conclusion concerning neutral conditions, we can observe glyceraldehyde as the main oxidation product, although both primary and secondary alcohol oxidation pathways are available on the Pt electrode. The current density of glycerol oxidation on platinum and gold electrodes in neutral conditions is 10 and 50 times lower than in alkaline conditions, respectively, which is well reflected in the product distributions. Furthermore, the onset potential of glycerol oxidation on both electrodes shifted slightly positive. Both observations imply that OH^- strongly encourages the glycerol oxidation reaction and plays an important role as proton acceptor or reaction mediator, especially on an Au electrode.

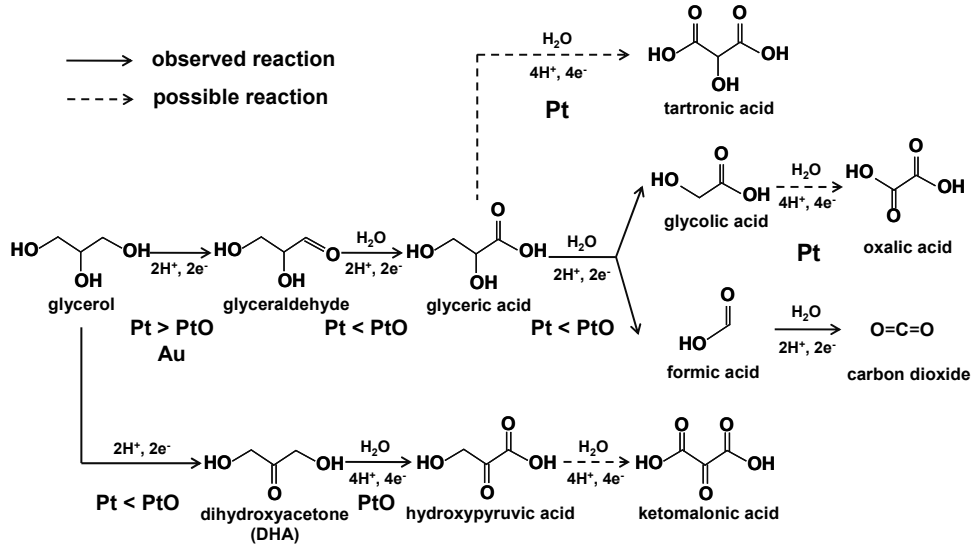


Figure 5. Schematic diagram for glycerol oxidation mechanism on Au and Pt electrodes in neutral media.

3.3.3 Glycerol oxidation in acidic condition

In acid medium, only the platinum electrode shows electrocatalytic activity for the oxidation of glycerol. Figure 6 shows the voltammetry of glycerol oxidation both in the absence (dotted line) and presence (solid line) of online sample collection alongside the concentrations of glycerol and its oxidation products on a platinum electrode in 0.5 M

H_2SO_4 acidic solution. First of all, the general tendency of glycerol oxidation in acidic solution is similar to neutral solution with small deviations of onset potential and maximum current density as shown in Figure 6a. Glycerol oxidation on platinum begins from 0.4 V, and the current increases steeply from 0.55 V, both at ca. 50 mV lower potential than in neutral condition. However, with sample collection the oxidation of glycerol appears a little delayed compared to the current without sample collection, particularly in the range of 0.6-0.9 V. The origin of the current delay during glycerol oxidation is the removal of active intermediates by the sample tip, as supported by the appearance of further oxidation products, i.e. glyceric acid, in that potential range. The current density of the first oxidation feature in the potential range between 0.55 and 1 V, which consists of two peaks, is almost half of that in neutral condition, and it increases to the same values as in neutral solution at high potentials (>1.3 V).

The concentrations of glycerol oxidation products in acidic condition are shown in Figure 6b, as converted from the chromatograms. The first product, glyceraldehyde, appears at 0.37 V and its concentration increases until 0.65 V in good correspondence with the current profile, after which it decreases due to the further oxidation of glyceraldehyde to glyceric acid. The appearance of glyceric acid is observed from 0.6 V and shows a slight first maximum concentration at 0.8 V, coinciding with the current density maximum in that potential range. We point out that the oxidation of glyceric acid to glycolic acid and formic acid in acidic condition is not favored compared to alkaline and neutral solution since no glycolic acid and formic acid were observed until 1.1 V in Figure 6b. This suggests that glyceric acid conversion to glycolic acid and formic acid is strongly base catalyzed. Nevertheless, the formation of CO_2 (presumably from formic acid oxidation) at around 0.65 V is observed in the OLEMS experiment, as shown in Figure 6c. The complete absence of glycolic acid until 1.1 V testifies for the low activity of the Pt electrode for the conversion of glyceric acid. The most interesting observation concerning glycerol oxidation in acidic condition is the potential range above 1.1 V, where a relatively high selectivity to formic acid is observed. The oxidation of glyceric acid to glycolic acid and formic acid on PtO_x was also observed in neutral solution, and the slightly higher concentration of formic acid compared to glycolic acid together with the formation of CO_2 in that potential range was explained by the further oxidation of glycolic acid to formic acid. In acidic solution, the maximum concentration of formic acid is ca. 5 times higher than that of glycolic acid. To prove the importance of the glycolic acid oxidation reaction, the oxidation of glycolic acid

(10 mM) on a Pt electrode was studied separately and it clearly showed the production of formic acid from glycolic acid in the same potential ranges from 1.1 V. Finally, as a product of secondary alcohol oxidation, dihydroxyacetone was observed from 0.5 V to 1.5 V, and its concentration is a little higher on PtO_x than on a clean Pt surface.

The main product of glycerol oxidation on Pt in acidic condition is glyceraldehyde as shown by selectivity patterns in Figure 6d. The selectivity to glyceraldehyde is 100% at 0.4 V and decreases slowly to ca. 80% until 1.1 V, after which its decay is accelerated to ca. 40% at the highest potential, where it matches the selectivity to formic acid.

Based on the results described in Figure 6, a reaction mechanism for the glycerol oxidation on Pt in an acidic medium is suggested in Figure 7. The general glycerol oxidation pathways in acidic condition are essentially identical to in neutral and alkaline media, which means the pH of the solution does not change the existence of the reaction pathways but pH plays an important role in their relative importance. The dominant product of glycerol oxidation is glyceraldehyde and also the PtO_x surface shows activity for glycerol oxidation as in neutral solution (whereas in alkaline it does not). Interestingly, PtO_x encourages the further oxidation of glyceraldehyde and produces mainly formic acid and CO_2 through glyceric acid and glycolic acid intermediates at high potential. Dihydroxyacetone, the product of secondary alcohol oxidation is produced in a two-electron transfer step and its measured concentration is higher than at the other pH's, which suggests that the DHA production is favored in acidic media.[4,34-37]

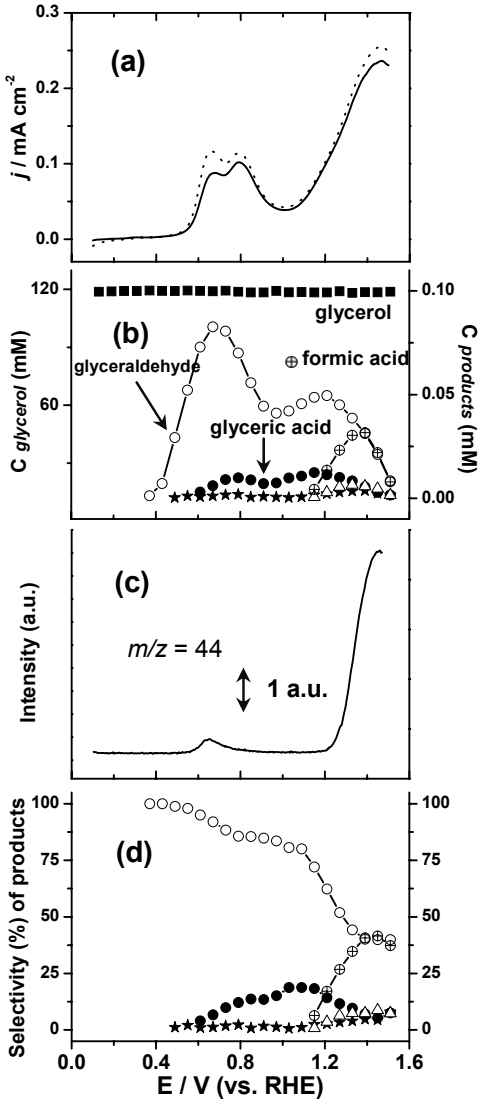


Figure 6. Glycerol oxidation (0.1 M) on a Pt electrode in 0.5 M H_2SO_4: (a) current density profile with (solid line) and without (dotted line) sample collection during linear sweep voltammetry with scan rate of 1 mV/s, (b) concentration changes of glycerol and its reaction products collected with modified sample collecting tip, (c) ion current profiles for m/z = 44 (CO_2) in OLEMS measured during voltammetry, and (d) selectivity (%) of products as a function of potential. ■ glycerol, ○ glyceraldehyde, ★ dihydroxyacetone (DHA), ● glyceric acid, △ glycolic acid, ⊕ formic acid.

As a brief intermediate conclusion concerning acidic media, we observe both primary and secondary alcohol oxidation pathways on Pt electrode. Gold has no activity. The current density of glycerol oxidation on a clean Pt surface in acidic condition is about 2 and 20 times lower than in neutral and in alkaline conditions, respectively. The onset potential of glycerol oxidation on Pt electrode is not seriously affected by the pH of the solution. Acidic media seem to promote the oxidation of the secondary alcohol as compared to alkaline media, and thereby provide more favorable conditions for selective alcohol oxidation.

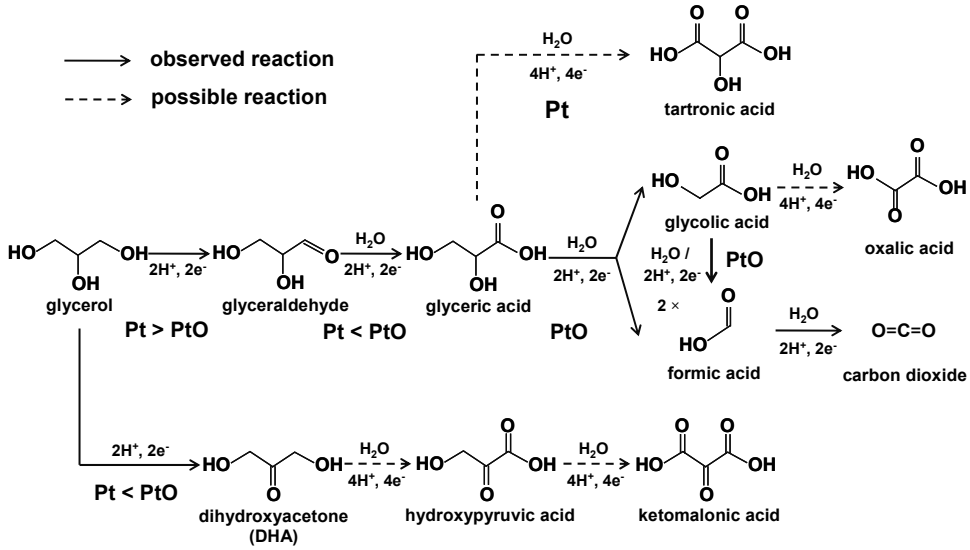


Figure 7. Schematic diagram for glycerol oxidation mechanism on Pt electrode in acidic media.

3.4 Conclusion

This work has elucidated the electro-oxidation mechanisms of glycerol on Au and Pt electrodes under different pH conditions by applying a new HPLC method to study the dissolved reaction products and by online mass spectrometry for CO_2 detection. Our main result is that both the activity and product distributions of glycerol oxidation are strongly dependent on pH and catalyst, however the general reaction pathways do not change. In alkaline media, a modified sample collecting tip for the stabilization of collected samples was applied and successfully allowed for the detection of unstable reaction intermediates,

i.e. glyceraldehyde and dihydroxyacetone, on a Pt electrode. Glyceric acid is the main product on a Pt electrode (with glyceraldehyde as reactive intermediate). Glyceric acid appears as the primary oxidation product on Au electrode in alkaline, but it is rapidly further oxidized to glycolic acid and formic acid due to high oxidation potentials necessary on gold. Interestingly, at these high potentials, gold appears as the most active catalyst for glycerol oxidation, but this is primarily due to the fact that gold stays "clean" even at these high potentials so that turnover can still take place. Lowering the pH significantly deactivates the glycerol oxidation on both Au and Pt electrodes, with Au having lost its activity completely in acidic condition. This effect is very similar to what has been observed for the oxidation of ethanol on Pt and Au,[38] and is believed to be related to the acidity of alcohol groups in glycerol, leading to a deprotonated glycerol species as the main reactant in alkaline media. Interestingly, neutral media appear particularly well suited for a high selectively toward glyceraldehyde, the first oxidation product of glycerol, especially on gold (although the activity is low). The activity and selectivity patterns for Pt are similar in neutral and acidic media (though neutral conditions lead to a slightly higher activity), and remarkably enough the PtO_x surface is active for glycerol oxidation at high potentials, and encourages the conversion of glyceraldehyde through glyceric acid and glycolic acid to formic acid and CO_2 at low pH.

3.5 References

[1] M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi, C. D. Pina, *Angew. Chem. Int. Ed.* **2007**, *46*, 4434-4440.

[2] C. Zhou, J. N. Beltramini, Y. -X. Fan, G. Q. Lu, *Chem. Soc. Rev.* **2008**, *37*, 527-549.

[3] O. M. Daniel, A. DeLaRiva, E. L. Kunkes, A. K. Datye, J. A. Dumesic, R. J. Davis, *ChemCatChem* **2010**, *2*, 1107-1114.

[4] N. Wörz, A. Brandner, P. Claus, *J. Phys. Chem. C* **2010**, *114*, 1164-1172.

[5] A. Behr, J. Eilting, K. Irawadi, J. Leschinski, F. Lindner, *Green Chem.* **2008**, *10*, 13-30.

[6] L. Roquet, E. Belgsir. J. M. Léger, C. Lamy, *Electrochim. Acta* **1994**, *39*, 2387-2394.

[7] D. Z. Jeffery, G. A. Camara, *Electrochem. Comm.* **2010**, *12*, 1129-1132.

[8] M. Simões, S. Baranton, C. Coutanceau, *Appl. Catal. B: Env.* **2010**, *93*, 354-362.

[9] M. Avramov-Ivić, J. -M. Léger, C. Lamy, V. D. Jović, S. D. Petrović, *J. Electroanal. Chem.* **1991**, *308*, 309-317.

[10] M. Avramov-Ivić, J. -M. Léger, B. Beden, F. Hahn, C. Lamy, *J. Electroanal. Chem.* **1993**, *351*, 285-297.

[11] Y. Kwon, M. T. M. Koper, *Anal. Chem.* **2010**, *82*, 5420-5424.

[12] Z. -Y. Zhou, N. Tian, Y. -J. Chen, S. -P. Chen, S. -G. Sun, *J. Electroanal. Chem.* **2004**, *573*, 111-119.

[13] W. C. Ketchie, Y. -L. Fang, M. S. Wong, M. Murayama, R. J. Davis, *J. Catal.* **2007**, *250*, 94-101.

[14] W. C. Ketchie, M. Murayama, R. J. Davis, *J. Catal.* **2007**, *250*, 264-273.

[15] S. Carrettin, P. Mcmorn, P. Johnston, K. Griffin, G. J. Hutchings, *Chem. Commun.* **2002**, 696-697.

[16] S. Carrettin, P. Mcmorn, P. Johnston, K. Griffin, C. J. Kiely, G. J. Hutchings, *Phys. Chem. Chem. Phys.* **2003**, *5*, 1329-1336.

[17] R. R. Soares, D. A. Simonetti, J. A. Dumesic, *Angew. Chem. Int. Ed.* **2006**, *45*, 3982-3985.

[18] B. N. Zope, D. D. Hibbitts, M. Neurock, R. J. Davis, *Science*, **2010**, *330*, 74-78.

[19] S. C. S. Lai, M. T. M. Koper, *Faraday Discuss.* **2008**, *140*, 399-416.

[20] A. H. Wonders, T. H. M. Housmans, V. Rosca, M. T. M. Koper, *J. Appl. Electrochem.* **2006**, *36*, 1215-1221.

[21] M. Duca, V. Kavvadia, P. Rodriguez, S. C. S. Lai, T. Hoogenboom, M. T. M. Koper, *J. Electroanal. Chem.* **2010**, *649*, 59-68.

[22] W. L. Evans, W. R. Cornthwaite, *J. Am. Chem. Soc.* **1928**, *50*, 486-492.

[23] V. A. Yaylayan, S. Harty-Majors, A. A. Ismail, *Carbohydr. Res.* **1999**, *318*, 20-25.

[24] A. N. Grace, K. Pandian, *Electrochem. Comm.* **2006**, *8*, 1340-1348.

[25] S. P. Moulik, D. Basu, P. K. Bhattacharya, *Carbohydr. Res.* **1978**, *63*, 165-172.

[26] B. Y. Yang, R. Montgomery, *Carbohydr. Res.* **1996**, *280*, 27-45.

[27] G. L. Lookhart, M. S. Feather, *Carbohydr. Res.* **1978**, *60*, 259-265.

[28] J. Hernández, J. Solla-Gullón, E. Herrero, A. Aldaz, J. M. Feliu, *Electrochim. Acta* **2006**, *52*, 1662-1669.

[29] G. L. Beltramo, T. E. Shubina, M. T. M. Koper, *ChemPhysChem* **2005**, *6*, 2597-2606.

[30] R. L. Arechederra, B. L. Treu, S. D. Minteer, *J. Power Sources* **2007**, *173*, 156-161.

[31] A. Capon, R. Parsons, *J. Electroanal. Chem.* **1973**, *44*, 1-7.

[32] A. Capon, R. Parsons, *J. Electroanal. Chem.* **1973**, *45*, 205-231.

[33] R. Parsons, T. VanderNoot, *J. Electroanal. Chem.* **1988**, *257*, 9-45.

[34] H. Kimura, K. Tsuto, T. Wakisaka, Y. Kazumi, Y. Inaya, *Appl. Catal. A* **1993**, *96*, 217-228.

[35] H. Kimura, *Appl. Catal. A* **1993**, *105*, 147-158.

[36] P. Gallezot, *Catal. Tod.* **1997**, *37*, 405-418.

[37] W. Hu, D. Knight, B. Lowry, A. Varma, *Ind. Eng. Chem. Res.* **2010**, *49*, 10876-10882.

[38] S. C. S. Lai, S. E. F. Kleijn, F. T. Z. Öztürk, V. C. Van Rees Vellinga, J. Koning, P. Rodriguez, M. T. M. Koper, *Catal. Tod.* **2010**, *154*, 92-104.