Biomass Electrochemistry : from cellulose to sorbitol

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Combining voltammetry with HPLC: Application to electro-oxidation of glycerol

Abstract

The combination of cyclic voltammetry and "on-line" chromatographic techniques for product detection is limited by the typically long analysis times in chromatographic columns. Therefore, traditionally, product analysis is performed offline after long bulk electrolysis experiments. To overcome the limitation of the inherently different time scales of voltammetry and HPLC, we suggest here to adopt rapid online sample collection with a micrometer-sized sampling tip placed close to the working electrode, followed by off-line analysis of the sample fractions in an HPLC system. To demonstrate this concept, we applied online fraction collection and offline HPLC analysis to the glycerol electro-oxidation on Au and Pt electrodes in alkaline media, and show that we can successfully follow the concentration changes of glycerol and its reaction products in good correspondence with current profile obtained simultaneously with voltammetry. Moreover, the method allows for a detailed discrimination of the different mechanisms of glycerol oxidation on both electrodes. Therefore, this simple approach enables the monitoring of soluble reaction products during voltammetry with an HPLC system, and thereby allows for new insights into the mechanisms of complex multi-step electrode reactions.

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2.1 Introduction

Voltammetry, or cyclic voltammetry, is a powerful electrochemical measuring technique to study electrode reactions, to distinguish between different reaction mechanisms and to obtain information on the intermediates and products involved in the electrode reactions as well as on possible coupled chemical reactions.[1] However, the fundamental molecular-level understanding of reaction intermediates and products, requires the combination of voltammetry with microscopic, spectroscopic, and chromatographic techniques. There are two main analytical techniques to follow the formation of dissolved products during voltammetry. The first is the Rotating Ring-Disk Electrode (RRDE),[2-4] in which products formed on the disk may be analyzed electrochemically at the ring. Though fast and quantitative, the RRDE method is limited to species with a very well-defined and unique electrochemical response on the ring electrode. The second technique is online or differential electrochemical mass spectrometry (MS), which allows for the identification of volatile intermediates and products simultaneously with the voltammetry, a combination displaying considerable chemical specificity and sensitivity.[5-7] However, this technique only detects volatile species, limiting its versatility. In principle, in situ infrared spectroscopy permits the detection of intermediates and products, but the technique is difficult to quantify in an electrochemical setting, in addition to the frequent overlap of, and uncertainty in the assignment of spectroscopic bands. More recently, Zhao et al.[8] have combined voltammetry with Electrospray Ionization Mass Spectrometry to allow for the detection of non-volatile products. Combining voltammetry with chromatographic techniques such as Gas Chromatography (GC), Ion Chromatography (IC), and High Performance Liquid Chromatography (HPLC) has been limited due to the long analysis times in the column, and existing on-line analysis experiments[9] to understand reaction mechanisms or to identify reaction products have only been applied for prolonged electrolyses. Even though prolonged so-called “bulk electrolysis” experiments at fixed potentials may be helpful in studying reaction pathways and mechanisms, the link with voltammetry and its various applications is essentially lost.

We were confronted with the desire to combine voltammetry with chromatographic techniques in a project studying the electrochemical conversion of biomass and biomass-related compounds. Many industrialized societies are currently developing ways to utilize the abundant and renewable biomass resources more effectively to provide new sources of

energy, food, and value-added chemicals.[10] In order to assess the potential of electrochemistry in biomass conversion, we were in need of an analysis method that is consistent with the time scale of the electrochemist's favorite technique, i.e. voltammetry. Glycerol is an important biomass-related compound, both as a model poly-ol compound, and as an abundant byproduct of biodiesel.[11,12] The catalytic conversion of glycerol into value-added chemicals is a topic of significant current interest in biomass research. In electrochemistry, glycerol has been considered as a potential fuel for fuel cells.[13-16]

To overcome the inherent time-scale differences of voltammetry and chromatographic techniques, especially HPLC, we suggest here to employ rapid sample collection while sweeping the electrode potential, using a very small micrometer-sized tip inlet system placed close to the electrode surface, with the collected sample fractions subsequently analyzed in an HPLC system. As an example of this method, we apply it to the glycerol electro-oxidation on Au and Pt electrodes in alkaline media, visualizing the concentration changes of glycerol and its reaction products in correspondence with the current measured in voltammetry. These materials were chosen as they have been studied before in the literature,[13-16] and they serve as typical examples of catalytically active (Pt) and non-active (Au) electrodes. Alkaline media were chosen as they tend to be particularly active for the oxidation of alcohols.[17] Most importantly, however, we will show that this simple combination of voltammetry and HPLC allows for new insights into the mechanism of glycerol oxidation on platinum and gold, revealing some intriguing differences in product selectivity.

2.2 Experimental

2.2.1 Reagents

All solutions were prepared with 18.2 MΩ/cm water from Millipore MilliQ. Sodium hydroxyde (Sigma-Aldrich, 99.99%), glycerol (Merck, 85%), glyceraldehyde (Sigma, 90%), glyceric acid (Aldrich, 99%), glycolic acid (Across, 99%), formic acid (Merck, 98%), oxalic acid (Riedel-de Haën, 99.5%), tartronic acid (Alfa Aesar, 98%), and argon (purity grade 6.0) were used as received.

2.2.2 Electrochemistry

All measurements were carried out in a conventional single compartment three-electrode glass cell, which was cleaned by a standard procedure[18] to remove all traces of organic contaminations. Glycerol (0.1 M) was dissolved into a 0.1 M NaOH electrolyte solution; 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 and platinum disks of 5 mm in diameter 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 mercury-mercury oxide electrode (Hg/HgO / 0.5 M KOH) was employed as a reference electrode. All potentials reported here have been converted to the RHE scale ($E_{Hg/HgO} = E_{RHE} - 0.926$ V) in the same electrolyte. Electrochemical cell potentials were controlled with a potentiostat/galvanostat (μ-Autolab Type III).

2.2.3 Fraction collection

The reaction products were collected with a small teflon tip (0.38 mm inner diameter) positioned close (~ 10 μm) to the center of the electrode surface, which was connected to a PEEK capillary with inner/outer diameters of 0.13/1.59 mm. The tip is essentially identical to the tip that we developed previously for our online electrochemical mass spectrometry setup,[7] with the only difference that no hydrophobic membrane is present inside the capillary. The tip configurations were cleaned in a solution of 0.2 M $K_2Cr_2O_7$ and rinsed thoroughly with ultra-pure water before use. The sample volume collected in each well was 60 μL on a 96-well microtiter plate (270 μL/well, Screening Devices b.v.) using an automatic fraction collector (FRC-10A, Shimadzu). The flow rate of sample collection was adjusted to 60 μL/min with a Shimadzu pump (LC-20AT). After collecting samples, the microtiter plate was covered by a silicon mat to prevent the evaporation of collected samples.

2.2.4 Chromatographic determination of products

Collected samples during voltammetry were analyzed by high-performance liquid chromatography (Prominence HPLC, Shimadzu). The microtiter plate with the collected samples was placed in an auto-sampler (SIL-20A) holder and 1 μL of sample was injected into the column. The column used was an Aminex HPX 87-H (Bio-Rad) and diluted sulfuric acid (5 mM) was used as eluent. The temperature of column was maintained at 30°C in column oven (CTO-20A) and the separated compounds were detected with a refractive index detector (RID-10A). The expected products of glycerol oxidation[11] were analyzed as well by HPLC to produce a standard calibration curve at 30°C (i.e., glyceraldehyde, glyceric acid, glycolic acid, formic acid, oxalic acid, and tartronic acid). Since the peaks of glyceraldehyde and glyceric acid strongly overlap at 30°C, the oven temperature was increased to 80°C to effectively separate these products.

2.3 Results and discussion

In order to combine voltammetry with a determination of the product concentration during potential scanning requires optimized conditions: moderate current on the electrocatalyst, a proper flow rate of sample collection, and stability of the intermediates and products in the sampled solution. Especially, the operating conditions in terms of the voltammetric scan rate and sample collecting flow rate should be optimized. With the existing setup, the volume of one droplet from the sample disposal tip is ca. 30 μL in alkaline media, and we collected two drops in each well. Therefore, in the case of glycerol oxidation, optimal scan and flow rates were found to be 1 mV/s and 60 μL/min, respectively. As the collected sample volume per well was 60 μL, each sample represents the average concentration over a 60 mV potential range.

Figure 1 shows the voltammetry of glycerol oxidation on gold (Fig.1a) and platinum (Fig.1b) both in the absence (dashed line) and presence (solid line) of online sample collection. First of all, note that the oxidation current is significantly higher on gold, albeit at higher potentials, making gold a more active catalyst for glycerol oxidation than platinum (in alkaline media). Glycerol oxidation on gold begins at ca. 0.6 V, and the current increases significantly from 0.9 V. However, with sample collection the oxidation of

glycerol appears a little delayed compared to the current without sample collection, particularly in the range of 0.9 ~ 1.1 V. Presumably this happens because of the removal of an intermediate species in the glycerol oxidation, which can be further oxidized. The same tendency was also observed on the Pt electrode, albeit in a different potential window. On Pt, glycerol is oxidized from 0.4 V and the current without sample collection is higher than the current with sample collection in the potential range from 0.4 to 0.7 V (Figure 1(b)). Although onset potentials of each electrode are not identical due to different electrode kinetics,[13-16] we believe that the origin of these current delay phenomena at the onset of glycerol oxidation is the same on both electrodes, i.e. due to the sample collection and the removal of active intermediates. On the other hand, online sample collection caused a higher current density from 1.2 to 1.6 V on the gold electrode and from 0.7 to 1 V on the platinum electrode, respectively. We believe that this current enhancement may be due to the removal of intermediate species that have the tendency to deactivate the electrode because of their poisonous properties. On platinum, especially formic acid, one of the expected products (see below), may cause serious deactivation due to CO formation on the platinum surface.[13,19-21] On gold, CO poisoning is less likely; in this case, carboxylic acids form (see below) that may coordinate to the surface and block the active surface. Also note that on the gold electrode, a voltammetric current with periodic spikes was observed in the presence of online sample collection. Current spikes typically appear at high currents (no spikes were observed with the Pt electrode), and the frequency of the spikes appears to be related to the flow rate of sample collecting pump as shown in Figure 2. The spikes are therefore related to small irregularities in the pumping flow rate. As a general conclusion, the continuous removal of intermediates and products in the presence of online sample collection may result in substantial changes in the measured voltammetry. In the case of glycerol oxidation, both lower and higher currents may be observed, depending on what kind of intermediates and/or products are removed from the solution, and what their role is in the mechanism. Obviously, the exact sampling conditions, in relation to the voltammetric scan rate, should be chosen such that these effects are minimized.

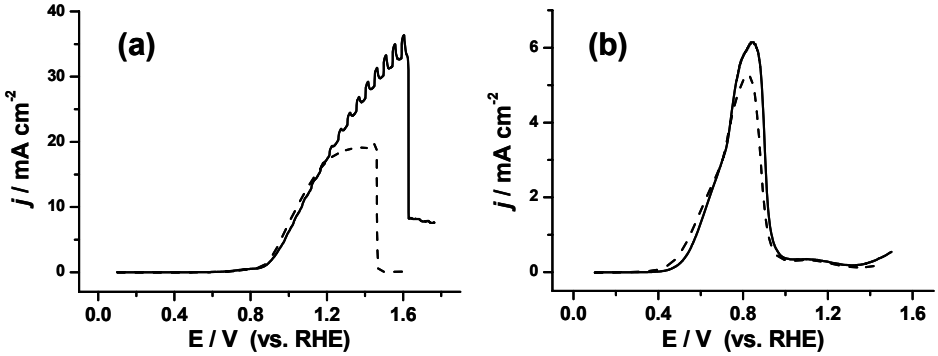

Figure 1. Effect of sample collection on the current density during linear sweep voltammetry. Glycerol oxidation (0.1 M) on (a) Au and (b) Pt electrodes with (solid line) and without (dashed line) sample collection in 0.1 M NaOH. Scan rate is 1 mV/s.

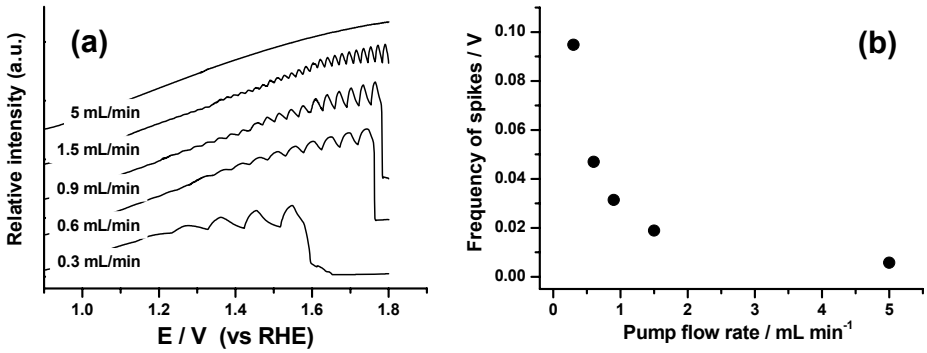

Figure 2. The relationship between pump flow rate of sample collection and frequency of spikes during glycerol oxidation on Au electrode. Scan rate is 10 mV/s.

During voltammetry, samples are continuously collected on a microtiter plate and subsequently analyzed in the HPLC system. All relevant peaks appear to be well separated at column temperature of 30°C as shown in Figure 3. However, the retention times of glyceric acid and glyceraldehyde at 30°C are almost the same (10.414 and 10.475 min, respectively), so all samples obtained for both electrodes were also analyzed at 80°C to clearly separate these species. From the analysis data at 80°C, glyceraldehyde was not detected to any significant extent during the voltammetric glycerol oxidation on Au and Pt electrodes in alkaline media, at variance with previous studies on these systems.[13,22]

However, the absence of glyceraldehyde in our samples could be due to the instability of aldehydes in alkaline media, as suggested by the literature.[23,24]

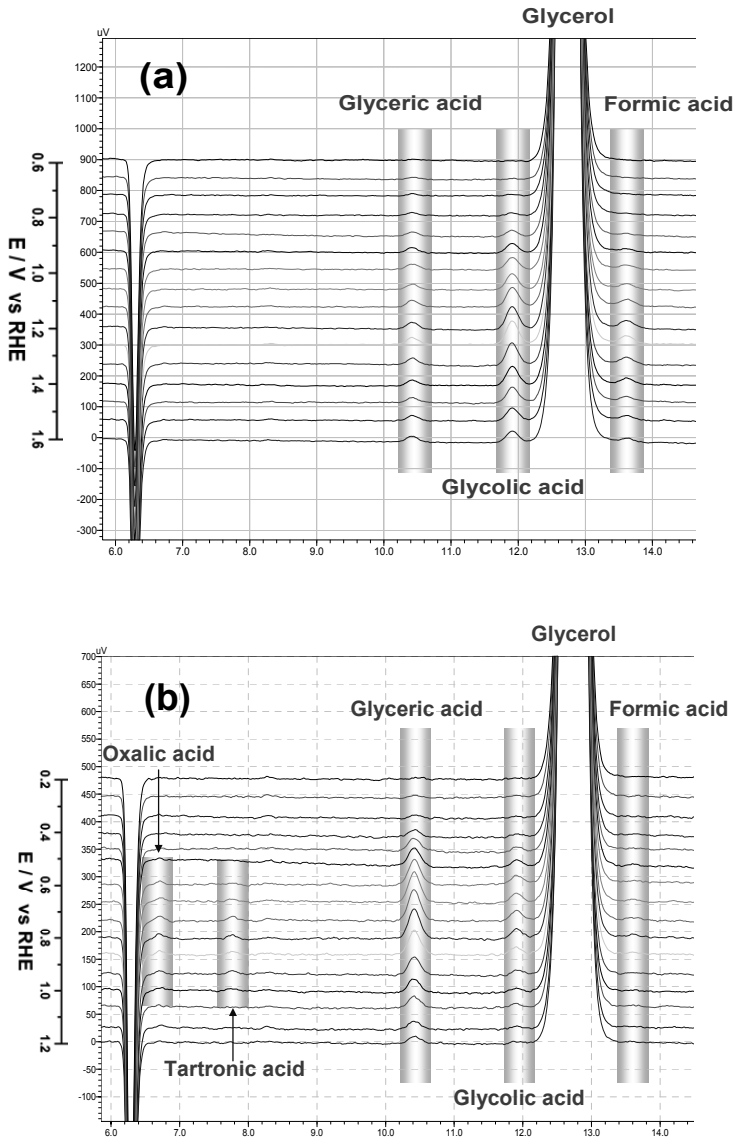

Figure 3. Chromatograms from HPLC analysis at 30ºC with collected samples during voltammetry on (a) Au and (b) Pt electrodes.

The peaks observed in the chromatograms in Figure 3 are converted to the corresponding concentrations of the various compounds, the results of which are shown in Figure 4. The initial concentration of glycerol was a little higher than 0.1 M due to solution evaporation during Ar bubbling on both electrodes. As shown in Figure 4(a), the concentration of glycerol near the Au electrode slowly decreases with the lowest value at around 1.4-1.5 V, after which it increases slightly as the potential is made more positive. The first product of glycerol oxidation on gold, glyceric acid, appears at 0.6 V and its concentration increases until 1.45 V, after which it slowly decreases. From ca. 0.8 V, the secondary products, i.e. glycolic acid and formic acid, are observed, with a concentration ca. three times higher than that of glyceric acid. Both products have an essentially identical concentration as a function of potential. Accordingly, we can conclude that glycerol is first oxidized to glyceric acid from 0.6 V, and next from 0.8 V glyceric acid is further oxidized by C-C bond breaking to equal amounts of glycolic acid and formic acid. It can be clearly seen from Figure 4(a) that these two products are the majority species formed at the electrode, and that their concentrations follow the current profile as observed in the voltammogram in Figure 1(a).

The reaction products of glycerol oxidation and their concentration profiles on the platinum electrode are illustrated in Figure 4(b). The concentration of glycerol decreases until 0.8 V, after which it slowly increases again, in agreement with the maximum in current observed at 0.8 V (Figure 1(b)). The first product of glycerol oxidation, i.e. glyceric acid, agrees with that on the Au electrode, and is detected from potentials as low as 0.35 V with its concentration steeply increasing until 0.8 V, after which it decreases again. The secondary products of glycerol oxidation from the further oxidation of glyceric acid, i.e. glycolic acid and formic acid, appear from 0.4 V. Interestingly, the concentration of formic acid is a little higher than that of glycolic acid from 0.6 to 1.0 V, which can be explained by the further oxidation of glycolic acid to oxalic acid on the Pt electrode, as evidenced by the concentration profile of oxalic acid which exactly compensates for the loss of glycolic acid (line with diamonds in Figure 4(b)). In addition, the formation of tartronic acid was observed in this potential range, which must be the product of glyceric acid oxidation on Pt electrode, as an alternative pathway for the formation of glycolic acid and formic acid. Finally, a remarkable difference with the same measurement on gold is that on platinum, the main product is glyceric acid, and the 2-electron reaction to glycolic acid and formic acid appears much less appreciable on platinum than on gold. This is consistent with the significantly higher currents observed on gold, at least at high overpotentials. A likely

explanation for this difference is the lower surface oxidation potential of platinum compared to gold. Whereas the glycerol and glyceric acid oxidation start at a lower potential on platinum, the platinum electrode becomes deactivated at ca. 0.9 V, the potential at which a surface oxide forms on the platinum electrode and consequently the electrode becomes deactivated. On a gold electrode, the surface oxide formation occurs only at much higher potential, ca. 1.3 V, and as a result there is a wider potential range available for the further oxidation of glyceric acid to glycolic acid and formic acid.

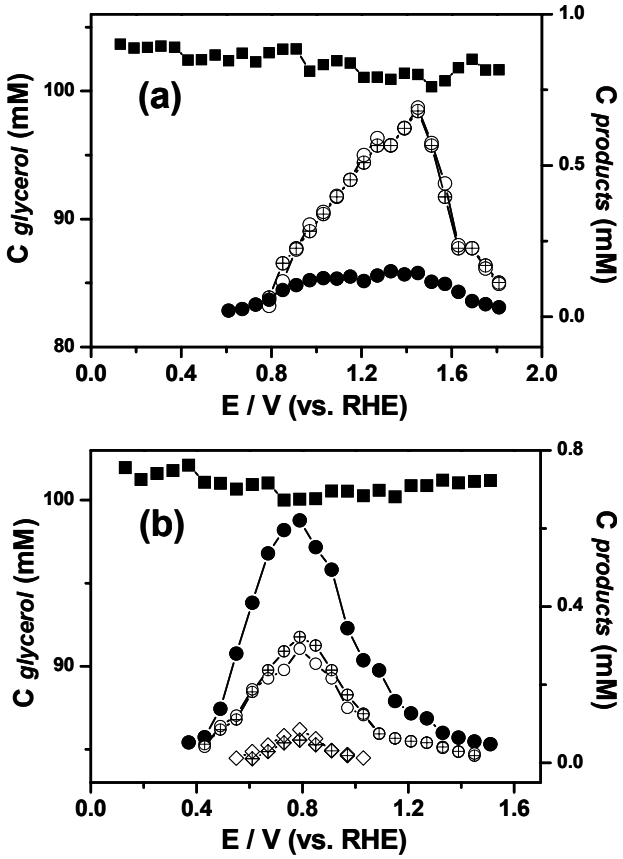

Figure 4. Plots showing the concentrations of glycerol and its electro-oxidation by-products as a function of potential on (a) Au and (b) Pt electrode: ■ glycerol, ● glyceric acid, ○ glycolic acid, ⊕ formic acid, ◇ oxalic acid, ⌖ tartronic acid.

To illustrate the current limitations of the method, we also applied a higher scan rate of 10 mV/s to the Pt electrode, with the sample collecting flow rate also increased to 600 μL/min in order to collect the same number of samples as above. The current density for 10 mV/s is almost twice that of 1 mV/s at highest current ranges in the presence of sample collection. Since the sample collecting rate is now 10 times faster, the product in each well (at 10 mV/s) is 5-10 times more diluted compared to those with 1 mV/s, so that only small peaks of glyceric acid were detected. Using a 5 times higher injection volume into the HPLC, we can obtain a plot very similar to Figure 4(b), but at the price of having a larger difference between the voltammetry with and without sample collection. Therefore, the current limiting factor to go to lower sample collecting flow rates to minimize disturbance in the voltammetry, is the final size of the collected sample drop, which in our commercial instrument is ca. 30 μL in alkaline media.

From the results illustrated in Figures 1 and 4, a reaction mechanism for the glycerol oxidation on Au and Pt electrodes may be suggested, as shown in Figure 5. In alkaline media, glycerol is first oxidized to glyceric acid in a 4-electron transfer step, both on Au and Pt electrodes, though with a lower overpotential on platinum. As a next 2-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 a platinum electrode this process becomes deactivated at potentials close to 0.9 V, where Pt forms an inhibiting surface oxide. On the Au electrode, a much higher conversion activity of glyceric acid to glycolic acid and formic acid than on Pt electrode, which we ascribe to the higher surface oxidation potential of gold. This would suggest that this bond breaking step does not require a highly catalytic material (as it takes place on a relatively inactive surface such as gold), though it does not take place on an oxidized electrode surface. In addition, glyceric acid and glycolic acid may be further oxidized on the Pt electrode to tartronic acid and oxalic acid, respectively, whereas these steps are not observed on the gold electrode.

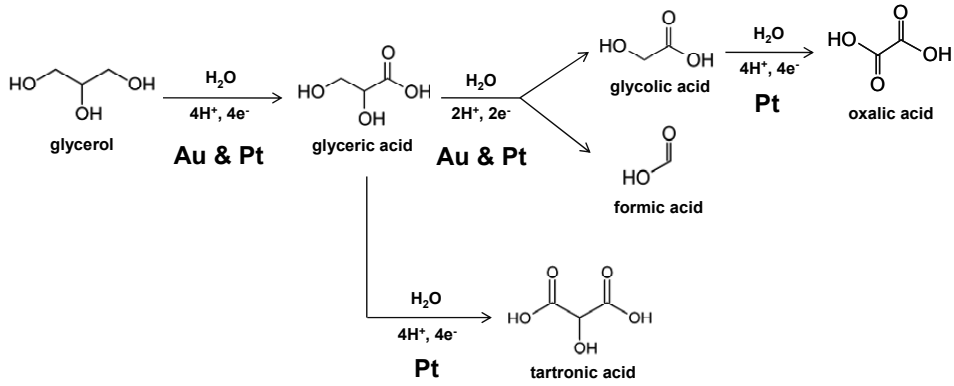

Figure 5. Schematic diagram for the reaction mechanism for the glycerol oxidation on Au and Pt electrode in alkaline media.

2.4 Conclusion

The work described here has demonstrated the possibility and potential of combining voltammetry with a chromatographic technique by online sample collecting during the potential sweep, and offline product analysis in HPLC system. We successfully visualized the relationship between the current observed in voltammetry and the concentration of the various reaction products on the example of glycerol oxidation on a platinum and gold electrode in alkaline media. Significantly, this approach provided a detailed insight into the different mechanisms of glycerol oxidation on the two electrodes. We expect that this combination may be employed for the study of many other multi-electron electrochemical reactions that produce soluble intermediates and products.

At present, this combination is limited by the volume of collected sample. Smaller volumes allow for slower sample collecting flow rates, leading to smaller disturbances on the voltammetry at high scan rates. The highest scan rate at which we have obtained reasonable data is 10 mV/s, which is already quite good, but with further improvements of the setup and a smaller volume of the collected sample (which is essentially determined by the diameter of the capillary dispensing the drop into the wells of the microtiter plate) this situation may still be further improved.

2.5 References

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