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## **Biomass Electrochemistry : from cellulose to sorbitol**

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# 4

## **Highly selective electro-oxidation of glycerol to dihydroxyacetone on platinum in the presence of bismuth**

### **Abstract**

A carbon supported platinum electrode in a bismuth saturated solution at a carefully chosen potential is capable of oxidizing glycerol to dihydroxyacetone with 100% selectivity. In the absence of bismuth, the primary alcohol oxidation is dominant. Using a combination of online HPLC and in situ FTIR, it is shown that Bi blocks the pathway for primary oxidation but also provides a specific Pt-Bi surface site poised for secondary alcohol oxidation.

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## 4.1 Introduction

In recent years, there has been a growing interest in converting glycerol to valuable chemicals. Glycerol, a surplus byproduct of biodiesel, can be selectively transformed to functionalized feedstocks such as dihydroxyacetone and glyceric acid.<sup>[1,2]</sup> Especially dihydroxyacetone (DHA), the product of secondary alcohol oxidation, is widely used in the cosmetic industry as a self-tanning agent. It is currently produced by biological fermentation.<sup>[3]</sup> In spite of its high conversion and selectivity, microbial oxidation suffers from a low glycerol concentration and a long operating time. In heterogeneous catalysis, several monometallic (Pt, Pd, Au)<sup>[4,5]</sup> and bimetallic catalysts (Pt-Bi, Au-Pt)<sup>[4,6-9]</sup> have been investigated and revealed that the Pt-Bi bimetallic system shows a promising conversion and selectivity toward DHA at low pH and mild operating conditions.<sup>[8]</sup> Also homogeneous catalysts have been reported for the selective glycerol oxidation to DHA.<sup>[10]</sup>

In this chapter, we show that the selective conversion of glycerol to DHA may be achieved by electro-catalytic oxidation on a carbon-supported platinum (Pt/C) electrode in a bismuth-saturated acidic solution. Such a half cell could eventually be incorporated in an electrolysis cell co-producing hydrogen and DHA (incidentally, PtBi is also an active electrocatalyst for hydrogen evolution<sup>[11]</sup>), or in a fuel cell co-producing electricity and DHA. A previous electro-chemical method employing a glassy carbon electrode for glycerol oxidation mediated by TEMPO showed 30% selectivity to DHA and 35% selectivity to hydroxypyruvic acid after 200 h,<sup>[12]</sup> which is still inferior to metal-based heterogeneous catalysis. Our results show that by careful selection of the electrode potential, very high selectivity for glycerol conversion to DHA may be achieved. This high selectivity is related to a selective blocking of the Pt electrode by Bi adatoms.

## 4.2 Experimental

Electrochemical characterization was carried out in a standard three-electrode cell controlled by a potentiostat/galvanostat ( $\mu$ -Autolab Type III). A thin-film electrode with 3 nm Pt/C nanoparticles (50wt%, Tanaka) was fabricated by loading defined amounts of nanoparticle suspension in water (1 mg mL<sup>-1</sup>) onto a polished glassy carbon substrate, subsequently dried at room temperature. In order to confirm the electrochemically active

surface area of the loaded catalyst, a blank voltammogram was recorded before each experiment. A large Pt plate was employed as a counter electrode and a reversible hydrogen electrode (RHE) as a reference. Oxidation of glycerol was performed in a mixture of glycerol (0.1 M, analytical grade) and 0.5 M H<sub>2</sub>SO<sub>4</sub> under deaerated conditions by purging Ar.

For the Pt/C surface modification, irreversible adsorption of bismuth was performed by placing the freshly prepared Pt/C electrode in contact with a Bi<sub>2</sub>O<sub>3</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, and full coverage is determined by a complete suppression of the hydrogen region,<sup>[15]</sup> and then rinsed with water and transferred to the electrochemical cell. For reversible bismuth adsorption/desorption, a sufficiently large amount of Bi<sub>2</sub>O<sub>3</sub> was introduced directly into the electrochemical cell to obtain a bismuth saturated solution, which corresponds to a concentration of ca. 10<sup>-5</sup>-10<sup>-4</sup> M.<sup>[13]</sup>

The reaction products during voltammetry were collected and analyzed with an online HPLC system as described in our previous work.<sup>[14,15]</sup> Sample volumes of 20 μL were injected into the columns in series of Aminex HPX 87-H (Bio-Rad) and Sugar SH1011 (Shodex) with diluted sulfuric acid (0.5 mM) as eluent. The selected temperature of column oven was 85°C. Details of system configuration are described elsewhere.<sup>[14]</sup>

The FTIRRAS experiments were carried out with a Bruker Vertex80V IR spectrophotometer; a CaF<sub>2</sub> prism bevelled at 60° was used. Fifty interferograms were averaged for each spectrum, with a resolution of 8 cm<sup>-1</sup>, resulting in a spectrum every 100 mV. All spectra were recorded using an angle of incidence of 60°, using p- polarised light. The reference spectrum was acquired at the CV starting potential where no Faradaic process takes place and the current is almost zero. Then, spectra at different potentials were collected, and the difference with respect to the reference spectrum was evaluated as the normalised change in reflectivity, ΔR/R. In these difference spectra, negative bands (pointing down) correspond to the generation of species at the electrode-electrolyte interface and positive bands (pointing up) to the consumption of species.

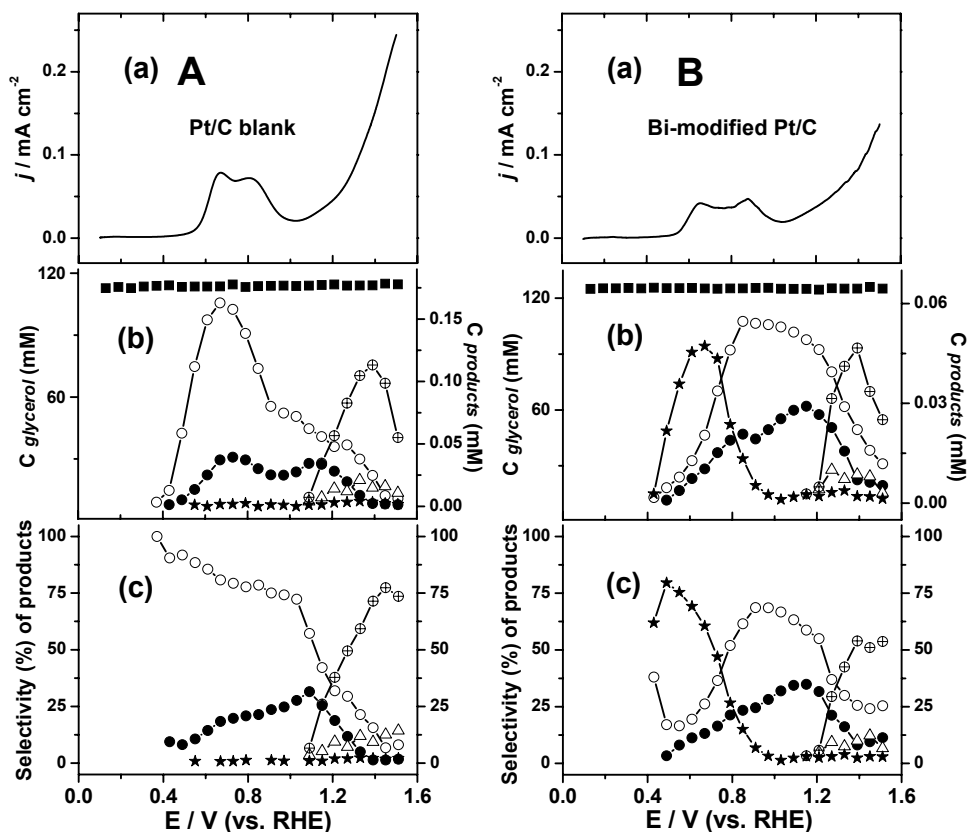
## 4.3 Results and discussion

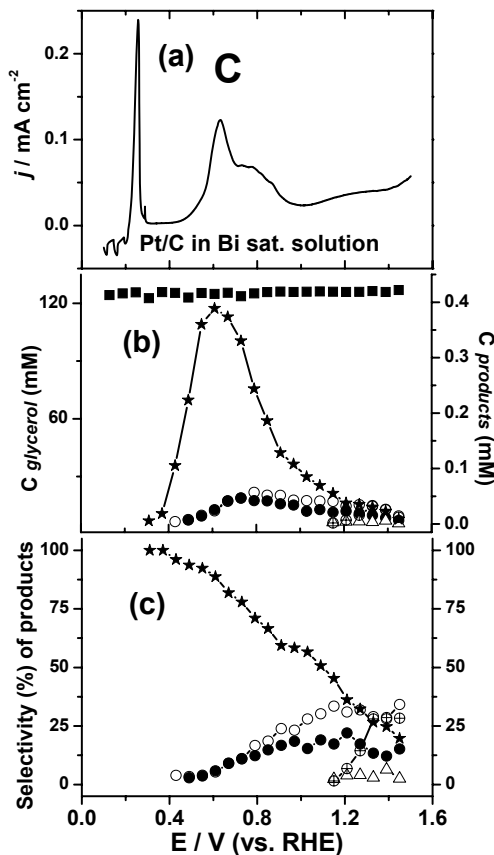
On pure Pt electrodes in acidic media, primary alcohol oxidation (to glyceraldehyde and glyceric acid) is favored over secondary alcohol oxidation at all potentials, the selectivity to DHA never exceeding 5% in Chapter 3.<sup>[14]</sup> The effect of bismuth on the selective oxidation of glycerol is illustrated in Figure 1, which compares the positive-going potential sweeps and the associated product spectrum as detected by online HPLC<sup>[15]</sup> at 1 mV/s for 0.1 M glycerol oxidation in 0.5 M H<sub>2</sub>SO<sub>4</sub> on a Pt/C electrode (A), a bismuth-modified Pt/C electrode as obtained by irreversible Bi adsorption (corresponding to “full” Bi coverage, see experimental section)<sup>[13]</sup> (B), and for a Pt/C electrode in a solution saturated with Bi (C). The presence of bismuth in solution enhances the glycerol oxidation as shown by a peak at 0.65 V with a ca. 50 mV lower onset potential than that of the Pt/C electrode. The Pt-Bi electrode without Bi in solution exhibits a somewhat lower current density in the potential region of glycerol oxidation. At high overpotential, in the oxygen evolution region, a lower activity is observed in the presence of Bi, both for Bi on the surface and with Bi in solution. We note that the sharp peak at 0.25 V for the Pt/C electrode in Bi-containing solution in Figure 1 is due to oxidative desorption of multilayer bismuth,<sup>[16]</sup> the peak charge being proportional to the time at which the potential is kept at 0.1 V.

Panels (b) and (c) in Figure 1 compare the concentrations and the corresponding selectivity of the various products of glycerol oxidation as measured by online HPLC<sup>[15]</sup> for the three different electrodes (A), (B) and (C). The HPLC results confirm that in the absence of Bi, the Pt/C electrode is selective to oxidizing the primary alcohol, and the main products observed are glyceraldehyde and glyceric acid at low potential, and formic acid at high potential.<sup>[14]</sup> On the other hand, a Bi-modified Pt/C electrode shows a very different selectivity pattern, as one would expect from the results obtained in the heterogeneous catalysis literature.<sup>[6-9]</sup> At low potential, DHA is formed preferentially, leading to a peak in production and selectivity of ca. 75% at around 0.5-0.6 V. At higher potentials, similar selectivities as on Pt/C are obtained, and the selectivity to DHA drops to zero. It is logical to ascribe this effect to the oxidative desorption of the adsorbed Bi, which according to the literature takes place around 0.6-0.7 V.<sup>[13,16,17]</sup> As lower overall currents and activities are observed for the Bi-modified Pt/C electrode, the role of Bi seems to be to block the pathway for primary glycerol oxidation, in agreement with the original explanation offered by Kimura<sup>[6,7]</sup> and supported by Wörz et al..<sup>[9]</sup> However, in the presence of Bi in solution,

*Highly selective electro-oxidation of glycerol to dihydroxyacetone on platinum in the presence of bismuth*

both activity and selectivity are significantly enhanced compared to the Bi-modified Pt/C electrode. Interestingly, the higher current observed at lower potential can be associated with an almost completely selective oxidation to DHA (see Figure 1(c) in column (C)). Even at maximum current, selectivity to DHA is close to 90%. Glyceraldehyde and glyceric acid formation are suppressed over the entire potential range, DHA always being the preferred product, and also much less formic acid is obtained at high potential. We note that, importantly, the enhanced activity and selectivity not only originates from the interaction of Bi with Pt, but also from the interaction of Bi with the carbon-supported Pt nanoparticles.

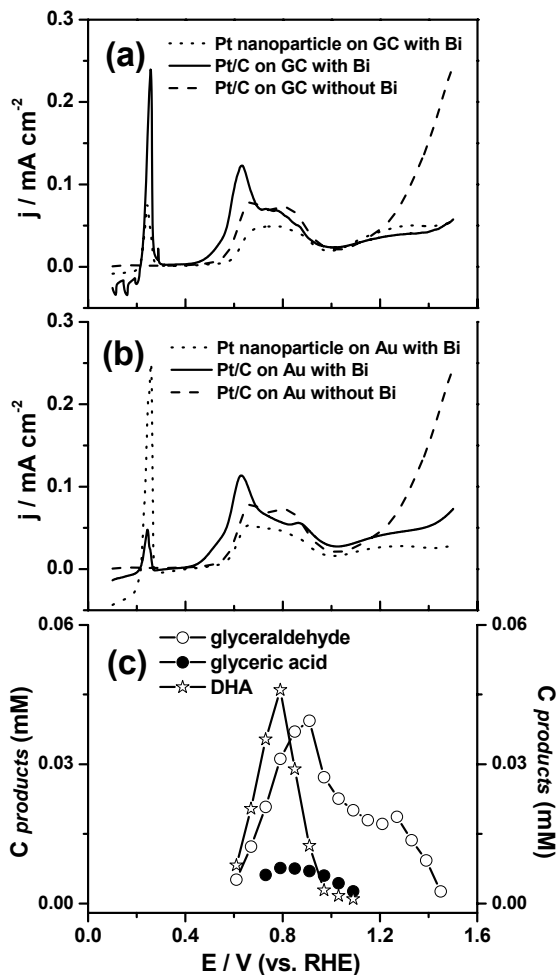




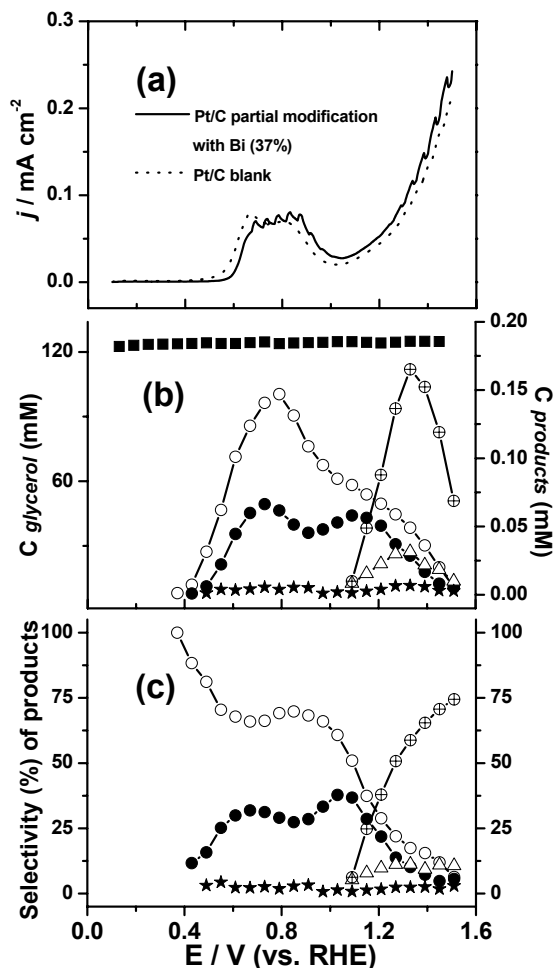
**Figure 1.** Glycerol oxidation (0.1 M) in 0.5 M  $\text{H}_2\text{SO}_4$  for (A) a Pt/C electrode, (B) a Bi-modified Pt/C, and (C) a Pt/C electrode in Bi-saturated solution: (a) current density profile at scan rate of 1 mV/s, (b) concentration changes of glycerol and its reaction products, and (c) selectivity (%) of products as a function of potential. ■ glycerol, ○ glyceraldehyde, ★ dihydroxyacetone (DHA), ● glyceric acid, △ glycolic acid, ⊕ formic acid.

Figure 2 shows that in the presence of other supports, such as gold, Bi blocks the active sites of Pt nanoparticles, causing a lower activity and higher overpotential than for glycerol oxidation compared to Bi free solution, even though there is still an enhanced selectivity to DHA at low potentials. Therefore we conclude that Bi-modified Pt surface determines the reaction pathway toward secondary alcohol oxidation and the interaction of carbon

supported Pt with glycerol and Bi lowers the onset potential and thereby enhances the turnover frequency. Returning to Figure 1, note that, although the voltammetric profiles for glycerol oxidation on the three electrodes look rather similar, they actually correspond to significantly different oxidation products. The decrease in overall current for potentials higher than 0.65 V is observed for the oxidation of many organic molecules, and should be ascribed to the initial stages of Pt surface oxidation,<sup>[18]</sup> in the present case in conjunction with Bi on the surface. We have verified that the selectivity pattern shown in Figure 1 for the Pt/C electrode in Bi-containing solution is not dependent on the number of voltammetric scans. Second voltammetric scan showed essentially identical results (note that at a scan rate of 1 mV/s, as is required for a meaningful online HPLC analysis,<sup>[15]</sup> a single sweep takes about 20 minutes). Moreover, we have checked the effect of sample collection during voltammetry with the online HPLC system, as the sample collection removes active intermediate species. Various flow rates were applied and verified that the onset potential and the current density are not affected by sample collection. Finally, a lower coverage of Bi (ca. 37% of full coverage) for the Bi-modified Pt/C electrode leads to a severe increase in the primary oxidation products (see Figure 3), showing the importance of a high Bi surface coverage for selective secondary alcohol oxidation.



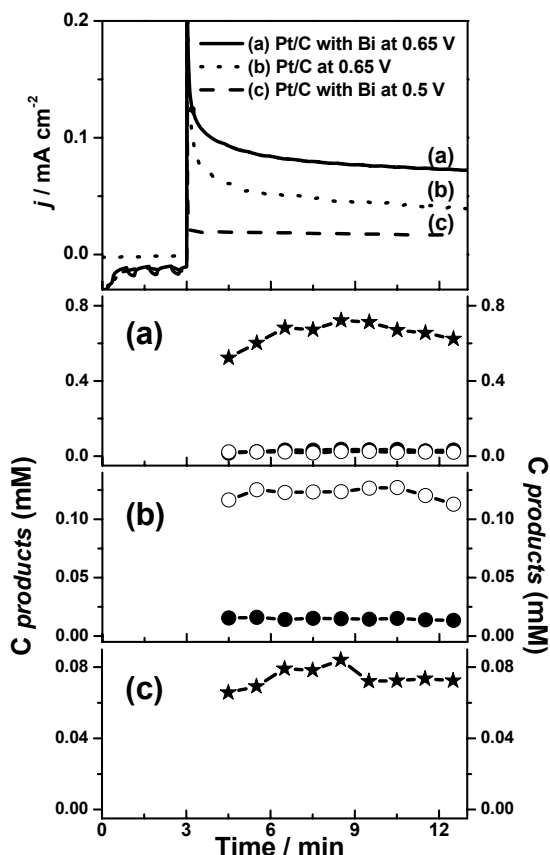
**Figure 2.** Pt nanoparticles with the effect of carbon support in glycerol oxidation (0.1 M) in Bi-saturated 0.5 M  $\text{H}_2\text{SO}_4$  on of (a) glassy carbon (GC), (b) gold substrates, and (c) shows the reaction products of Pt nanoparticles in Bi-saturated solution on GC substrate: current density profiles of Pt nanoparticle (---), Pt/C electrode (—) in Bi-saturated solution, and Pt/C blank (···) without Bi. Thin-film electrodes with Pt nanoparticles (Alfa Aesar) and Pt/C nanoparticles (50wt%, Tanaka) were fabricated by loading defined amounts of nanoparticle suspension in water onto polished glassy carbon and gold substrates, subsequently dried at room temperature. Scan rate is 1 mV/s. ★ dihydroxyacetone (DHA), ○ glyceraldehyde, ● glyceric acid.



**Figure 3.** Glycerol oxidation (0.1 M) on a partially Bi modified Pt/C electrode (37% coverage) in 0.5 M  $\text{H}_2\text{SO}_4$ : (a) current density profile with (—) and without (····) Bi modification with scan rate of 1 mV/s, (b) concentration changes of glycerol and its reaction products, and (c) selectivity (%) of products as a function of potential. ■ glycerol, ○ glyceraldehyde, ★ dihydroxyacetone (DHA), ● glyceric acid, △ glycolic acid, ⊕ formic acid.

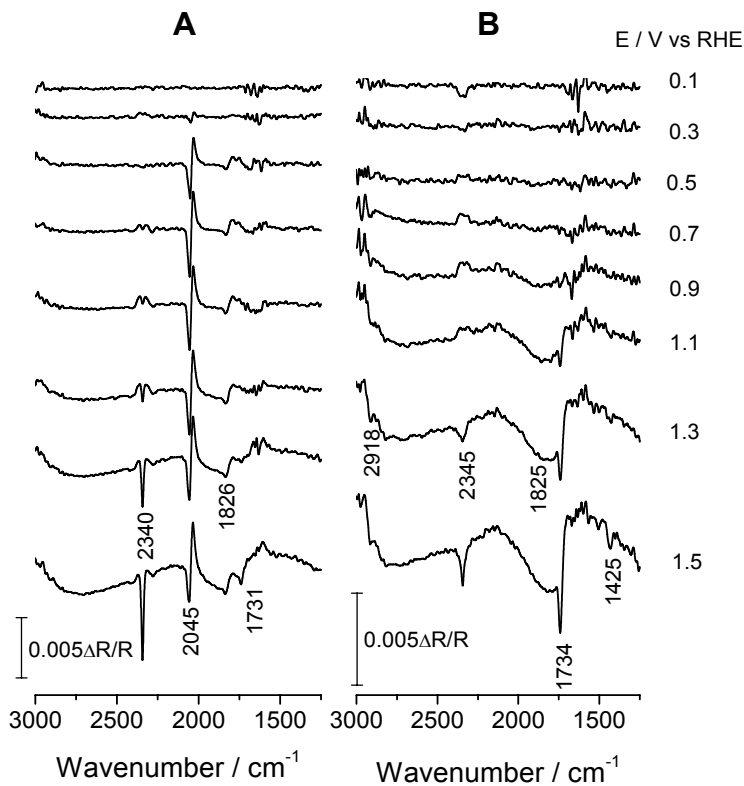
The continuous oxidation of glycerol at constant potentials was also studied and the corresponding current transients and reaction products are shown in Figure 4. Referring to the peak current density in Figure 1 A(a) and C(a), the potential of 0.65 V was selected to

study product generation for a Pt/C electrode in Bi-free solution (Figure 4b) and a Pt/C electrode in Bi-saturated solution (Figure 4a). A potential of 0.5 V (Figure 4c) was chosen for the Pt/C electrode in Bi-saturated solution for highly selective DHA formation. A comparison of currents and the product formation between (a) and (b) confirms that Bi in the solution enhances the catalytic activity at 0.65 V and predominantly produces DHA (over than 90% selectivity) but still shows some current decay presumably because of the formation of a catalyst poisoning species such as CO at this potential.<sup>[14]</sup> However, a constant, albeit lower, current was obtained at 0.5 V with an essentially 100% selectivity of DHA (see Figure 4c). This shows that by precise control of the potential, glycerol can be converted to DHA with very high selectivity.



**Figure 4.** Potentiostatic glycerol oxidation (0.1 M) in 0.5 M  $\text{H}_2\text{SO}_4$  for (a) Pt/C electrode in Bi-sat. solution at 0.65 V, (b) Pt/C electrode blank at 0.65 V, and (c) Pt/C electrode in Bi-sat. solution at 0.5 V.  $\star$  dihydroxyacetone (DHA),  $\circ$  glycerinaldehyde,  $\bullet$  glyceric acid.

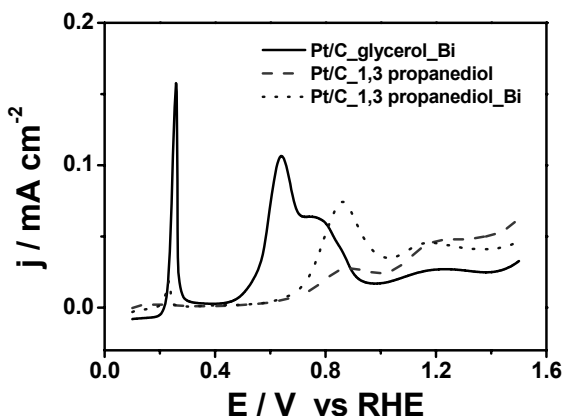
The results shown in Figure 1 and 4 show that there is a steering role for bismuth in the selectivity of glycerol oxidation. As already referred to, the presence of bismuth on the Pt surface is supposed to block the active sites for primary oxidation.<sup>[6,7]</sup> To proof such a blocking effect under electrochemical conditions, we have performed in situ Fourier-Transform Infrared (FTIR) spectroscopy. Figure 5 shows the reflection-adsorption spectra obtained at various potentials during glycerol oxidation on a clean Pt electrode and a Pt electrode modified with Bi.<sup>[13]</sup> We emphasize that these experiments were carried out in the thin-layer configuration in which the electrode is pushed against the CaF<sub>2</sub> window, meaning that the method is less suitable for the quantitative detection of solution species, as these species get trapped in the thin layer. The main interest in Figure 5 lies therefore in assessing any possible differences in the adsorbed species accumulating on the Pt surface during glycerol oxidation in the absence (Figure 5A) and presence (Figure 5B) of Bi on the surface. In the absence of Bi on the Pt electrode, the most conspicuous spectral features are the appearance of (bimodal) bands at ca. 2045 cm<sup>-1</sup> and 1826 cm<sup>-1</sup> with increasingly positive potential, ascribable to the build-up of linearly and bridge-bonded adsorbed carbon monoxide resp., and the appearance of carbon dioxide at 2340 cm<sup>-1</sup> in the thin layer electrolyte. The weak band at 1731 cm<sup>-1</sup> may be ascribed to the C=O stretching vibration of an aldehyde or ketone species in solution.<sup>[19]</sup> The results displayed in Figure 5A are in good agreement with earlier FTIR results obtained by Martins et al.,<sup>[20]</sup> in particular in evidencing the formation of a poisoning surface-adsorbed CO species (though others did not observe adsorbed CO in a similar experiment<sup>[19]</sup>). In the presence of Bi on the Pt surface (Figure 5B), the IR spectra obtained with increasingly positive potential show that the formation of surface-adsorbed CO is completely suppressed. Carbon dioxide is still observed, but only at higher potentials. The 1734 cm<sup>-1</sup> feature corresponding to an aldehyde or ketone species in solution is now more pronounced than in the absence of Bi on Pt.



**Figure 5.** Potential dependent FTIR spectra for (A) clean Pt electrode and (B) Bi modified Pt electrode in 0.01 M HClO<sub>4</sub> + 0.1 M glycerol recorded with p-polarized light.  $E_{ref}$  = 0.1 V vs. RHE.

The role of Bi in favoring secondary alcohol oxidation can be rationalized by combining the general reaction mechanism for glycerol oxidation on Pt as suggested previously (see Figure 6)<sup>[14]</sup> with the known effects of Bi adatoms on the oxidation of alcohols and formic acid.<sup>[21-23]</sup> As Figure 6 illustrates, primary alcohol oxidation leads to the formation of glyceraldehyde and glyceric acid, the latter species being subsequently oxidized to glycolic acid and formic acid. Formic acid has been shown to be the species leading to the formation of CO<sub>2</sub>.<sup>[14]</sup> However, formic acid may also easily dehydrate on Pt to give rise to adsorbed carbon monoxide, and this is the most plausible pathway for the formation of carbon monoxide during glycerol oxidation. In the presence of Bi on the surface, glyceraldehyde and glyceric acid formation is much reduced, and adsorbed carbon monoxide is not observed, which indicates that the pathway for primary alcohol oxidation is blocked at

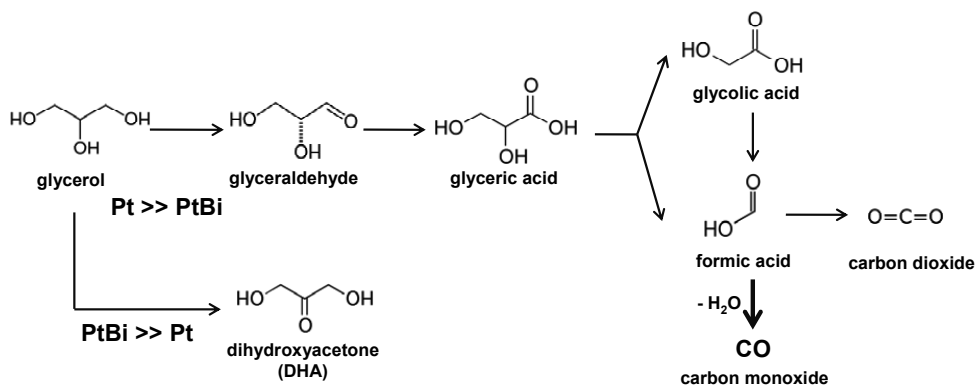
several stages. However, there is a clearly enhanced formation of DHA, not only relatively, but also in an absolute sense. Various authors have discussed the role of promoters, such as Bi, in the (selective) catalytic oxidation on metal catalysts.<sup>[22,23]</sup> It is well known that Bi blocks the formation of poisonous CO from small organic molecules, such as formic acid, through a third-body effect.<sup>[21,22,24]</sup> However, to explain the significantly enhanced activity for secondary alcohol oxidation, one needs to invoke a specific interaction of the glycerol with the adsorbed Bi. Such a specific coordination of glycerol and other poly-ols to Bi<sup>[25,26]</sup> or PtBi has been suggested by various authors to explain the selective liquid phase oxidation of alcohols promoted by Bi.<sup>[27-30]</sup> Note that glycerol has been found to coordinate to a zinc cation in a bidentate fashion via its two primary hydroxyl groups.<sup>[31]</sup> The formation of complexes has also been used to explain the leaching of Bi from the Pt surface.<sup>[9]</sup> We have studied a possible complexation of Bi by glycerol in the liquid phase by transmission FTIR and NMR, but were unable to obtain direct evidence for the formation of Bi-glycerol complexes in solution under the conditions of our experiment. Further evidence in favour of a surface complexation is provided by the oxidation of 1,3 propanediol in Figure 6. A Pt/C electrode in Bi-saturated solution shows an almost 3 times higher current density compared to Pt/C, but the onset potential of 1,3 propanediol oxidation is identical with that on Bi-free Pt/C, suggesting that the interaction of Bi with the primary alcoholic groups might play an important role in selectively enhancing the activity for secondary alcohol oxidation.



**Figure 6.** Voltammograms of 1,3 propanediol oxidation (0.1 M) on Pt/C electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> in comparison with glycerol oxidation at scan rate of 1 mV/s.

## 4.4 Conclusion

On the basis of the results presented in this chapter, we propose the tentative reaction mechanism for the selective glycerol oxidation to dihydroxyacetone promoted by bismuth shown in Figure 7. Bismuth on the Pt surface blocks the active surface for the primary alcohol oxidation as well as for the formation of adsorbed CO from formic acid. The Pt/C-Bi ensemble on the surface coordinates the glycerol in such a way that oxidation of the secondary alcohol is favored. For optimal activity and selectivity, it is necessary to have a constant and full coverage of Bi on the Pt/C surface, this being a possible explanation why having Bi in solution is important. At higher potentials, Bi desorbs from the surface, and primary oxidation predominates.



**Figure 7.** Schematic diagram of the selective oxidation of glycerol.

In conclusion, we have shown that in presence of bismuth in an acidic solution, glycerol may be oxidized to dihydroxyacetone on a Pt/C electrode with very high selectivity. Bismuth blocks the active sites for primary alcohol oxidation on Pt/C electrode, lowers the onset potential, and enhances the turnover frequency by forming a Bi-related active site on the surface poised for secondary oxidation. The mechanistic details and the structure sensitivity of this highly selective catalytic interface remain to be understood in detail. Under the model conditions employed in this experiment, the yield of DHA is still rather low but not unfavourable compared to the only other electrochemical example of selective glycerol oxidation: Ciriminna et al.<sup>[12]</sup> obtained a maximum current density of ca. 0.24 mA cm<sup>-2</sup> for a solution of 0.05 M glycerol with 25-30 % selectivity to DHA (but no Faradaic

efficiency was reported) at ca. 1.3 V (vs. NHE), versus our experiment which gives ca. 0.05-0.1 mA cm<sup>-2</sup> for a solution of 0.1 M glycerol, but with a close to 100% DHA and Faraday efficiency, and a much lower potential (0.5-0.6 V vs. NHE). It remains to be seen whether this same selectivity can be reached at high glycerol concentrations in a batch or continuous reactor process. However, the main purpose of this chapter was to show that bismuth in combination with electrochemical potential control may be used as a highly potent and remarkable steering method for selective oxidation.

## 4.5 References

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