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Influence of the local pH on the electrooxidation of glycerol on Palladium–Rhodium electrodeposits



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ABSTRACT

Here we investigate the electrooxidation of glycerol on Palladium–Rhodium electrodeposits (atomic composition 78:22) in alkaline media. We follow the voltammetric response of the electrodeposit in the presence of Glycerol by using FTIR in situ. Results show that CO_3^{2-} is the main product of glycerol electrooxidation. When low concentrations of alkaline electrolyte are used, the spectroscopic results do not emulate regular electrochemical experiments, because the consumption of OH^- inside the thin layer forces the reaction to proceed through a pathway that involves the production of CO_2 , instead of CO_3^{2-} . When 1.0 mol dm^{-3} KOH is used as electrolyte, large amounts of carbonate are produced in regions of potential which coincide with the rising of high-level currents during glycerol electrooxidation. The results attest that Palladium–Rhodium surfaces present a suitable catalytic activity towards glycerol electrooxidation and suggest that the presence of Rhodium helps to increase the low ability of Palladium to cleave C–C bonds in the strongly alkaline media.

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1. Introduction

The search for materials able to electrooxidize those alcohols used as fuels in power sources has experienced an impressive increasing in the last decades. Such interest is motivated by the high energy densities and easier storage, transport and handling associated with these compounds. Among the myriad of systems investigated, it is possible to point out the growing interest in alkaline fuel cells due to the recent development of alkaline polymer membranes [1–3]. Additionally, the advent of alkaline systems makes the use of platinum-free catalysts practicable, because metals as Palladium [4–6] and Gold [7–10] present suitable catalytic activity in alkaline media. Particularly, Palladium-based electrodes have been proposed as catalysts for the electrooxidation of alcohols as ethanol [4] and glycerol [5].

Concerning the electrooxidation of alcohols, glycerol has motivated a renewed interest for application in direct alcohol fuel cells [5,8–13] due to its relative high charge density (14 F mol^{-1}), its abundance and its structure partially oxidized. In this context, the efforts of several research groups worldwide have provided important information about the mechanism of glycerol electrooxidation in alkaline media on different surfaces [5,8–10,14], and now is consensual that it suffers partial oxidation [5,8,9,14], generating glyceraldehyde, glycerate, mesoxalate, dihydroxyacetone and

hydroxypyruvate, among other substances, which causes loss of energetic efficiency.

Specifically concerning platinum-free surfaces, some works have recently investigated the use of Pd as a possible catalyst for the electrooxidation of glycerol [5,6,15–19], but just a few of them bring some mechanistic information [5,16,17]. By using $^{13}\text{C}\{1\text{H}\}$ NMR spectroscopy to analyze the anode exhausts of alkaline fuel cells fed by glycerol, Bambagioni et al. found a wide distribution of products, including glycolate, glycerate, tartronate, oxalate, formate and carbonate, during the oxidation of glycerol on Pd/MWCNT catalysts [16]. In another study, Simões et al. investigated the electrooxidation of glycerol in alkaline media on Pd, PdAu and PdNi nanocatalysts by in situ FTIR spectroscopy [5]. The authors identified glyceraldehyde, glycerate, tartronate and mesoxalate as oxidation products [5], being the distribution among them dependent on the nature of the catalyst [5]. In a more recent paper, the same authors have used high performance liquid chromatography to investigate the oxidation products of glycerol on Pd catalysts modified by Bi [17]. The authors concluded that Bi promotes a sensible increase in the catalytic activity of Pd toward glycerol electrooxidation [17]. Also according to the authors, PdBi catalysts do not change the oxidation mechanism of glycerol compared to pure Pd electrodes. The only apparent effect is an anticipation of oxidation steps, induced by a bifunctional mechanism in which Bi promotes the formation of hydroxyl species that facilitate the oxidation of glycerol [17].

Based on these findings, the design of appropriate catalysts envisaging practical systems has to be associated to the knowledge

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about the electrooxidation mechanism of this alcohol, particularly in platinum-free catalysts. In this context, in the present paper we investigate the electrocatalysis of glycerol on PdRh electrodeposits (real atomic ratio of 78:22) in alkaline media, though cyclic voltammetry performed simultaneously to in situ FTIR spectroscopy. Since Pd presents limited ability to cleave C–C bonds in alkaline media [6], Rh was chosen as a co-catalyst because it has been considered as a suitable candidate to promote the scission of C–C bonds during the electrooxidation of molecules like ethanol [20] and 2-propanol [21].

Results show that when associated to Pd, Rh produces surfaces able to dissociate glycerol into fragments containing a single carbon even in strong alkaline media, which is evidenced by the production of carbonate. Additionally, experiments performed at two OH^- concentrations make clear that this species plays a central role during the electrooxidation of the alcohol.

2. Experimental

2.1. Chemicals, solutions and electrochemical experiments

Solutions were prepared with Milli-Q® (18.2 M Ω cm) water, glycerol (Labsynth p.a.) and KOH (Suprapur, Merck). Nitrogen (99.999%) was used to purge the electrolyte solution before and during the experiments.

The working electrode was an electrodeposit of PdRh prepared by electrochemical reduction of Pd^{+2} and Rh^{+3} obtained from PdCl_2 and RhCl_3 aqueous solutions in 0.1 mol dm $^{-3}$ HClO_4 and 0.165 V vs. RHE, during 10 min. PdRh was electrodeposited on a polished gold disk of 0.78 cm 2 of geometric area. The potential of deposition was chosen as follows: First a gold disk was immersed into a 0.1 mol dm $^{-3}$ HClO_4 solution containing the appropriate moieties of PdCl_2 and RhCl_3 to obtain a nominal atomic composition of PdRh 70:30 (the global concentration was 5 mmol dm $^{-3}$). Next, a potential scan was carried out from 1.0 to 0.0 V in the negative direction at 20 mV s $^{-1}$ (Fig. 1). Fig. 1 shows that after de reduction of AuO a huge cathodic wave starts to develop around 0.9 V. Based on previous works of Kibler et al., we attribute this first reduction wave to the deposition of Pd [22 and references therein]. Next, nearly at 0.18 V, a cathodic current attributed to the reduction of both

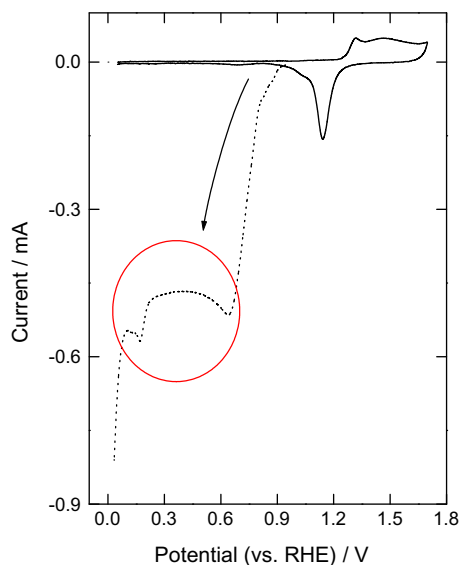


Fig. 1. Cyclic voltammogram of gold in presence of 0.1 mol dm $^{-3}$ HClO_4 (solid line). Linear voltammogram of the same substrate in $(\text{PdCl}_2 + \text{RhCl}_3)$ aqueous solution in 0.1 mol dm $^{-3}$ HClO_4 (dashed line). $v = 20$ mV s $^{-1}$.

metals on the gold surface was observed. Based on this signal, the potential of electrodeposition was elected (0.165 V). Pure N_2 was used to purge the solutions before and during the experiments.

The counter electrode was a platinum sheet. All the potentials were measured against a silver/silver chloride electrode but are presented with respect to the reversible hydrogen electrode scale (RHE). Before each experiment, the working electrode was immersed in concentrated sulfuric acid for 2 min, thoroughly washed with Milli-Q water and transferred to an electrochemical cell containing 0.1 mol dm $^{-3}$ KOH. The electrode surface was checked by cyclic voltammetry in the potential range comprised between 0.05 and 1.30 V. Then, the potential was kept at 0.05 V and 0.1 mol dm $^{-3}$ glycerol was admitted to the cell. Next, cyclic voltammograms were obtained at 20 mV s $^{-1}$ (electrochemical experiments) or at 1 mV s $^{-1}$ (FTIR in situ). All the experiments were made at room temperature (25.0 ± 1.0 °C).

The PdRh atomic composition of the catalyst represent the average of five different measurements on the same sample and was determined by energy dispersive X-ray spectroscopy (EDS), using a Thermo Noran spectrometer with a SiLi detector and an electron beam of 20 keV. Atomic compositions presented a deviation of $\sim 2.7\%$. It is wise noting that because of the penetration depth of the electrons in EDS analysis, this technique provides bulk compositions, that not necessarily correspond to the surface composition. The values determined by EDS (PdRh 78:22) were close to the nominal composition initially desired (70:30). This particular composition was chosen based in a previous work of our group in which Pt-based catalysts with Rh atomic compositions of $\sim 33\%$ showed the maximum yield for the production of CO_2 during the electrooxidation of acetaldehyde [23]. However, we are aware that the composition which presents the best electroactivity for a particular reaction cannot be simply extrapolated for other molecules, particularly for those containing a different number of reactive carbons. Hence, the study with other PdRh compositions is being currently carried out and will be published in due course.

2.2. FTIR in situ experiments

FTIR in situ experiments were carried out by using a MB-100 spectrometer (Bomem). The experiments were made at 25.0 ± 1.0 °C in the presence of 0.1 mol dm $^{-3}$ glycerol + 0.1 mol dm $^{-3}$ KOH p.a. solutions. Details of the spectroelectrochemical cell can be consulted in [24]. The electrochemical IR cell was fitted with a CaF_2 planar window for the collection of bands in the range of 3000–1000 cm^{-1} .

Reflectance spectra were collected as the ratio (R/R_0) where R represents a spectrum at a given potential and R_0 is the spectrum collected at 0.05 V. In this configuration negative bands correspond to species formed or whose concentration has increased at the sampling potential whereas positive bands are associated with a diminution of the concentration of the species. Spectra were computed from 32 interferograms averaged. The spectral resolution was set to 8 cm^{-1} . Spectra were obtained during a slow cyclic voltammogram ($v = 1$ mV s $^{-1}$). Such conditions were chosen to allow that spectra were collected at intervals of c.a. 0.04 V between 0.05 and 1.30 V.

3. Results and discussion

3.1. Electrooxidation of glycerol on PdRh

Cyclic voltammograms were recorded at 20 mV s $^{-1}$ in the presence of 0.1 mol dm $^{-3}$ glycerol (Fig. 2, solid line) and 0.1 mol dm $^{-3}$ KOH (Fig. 2, dashed line). In the presence of glycerol the hydrogen

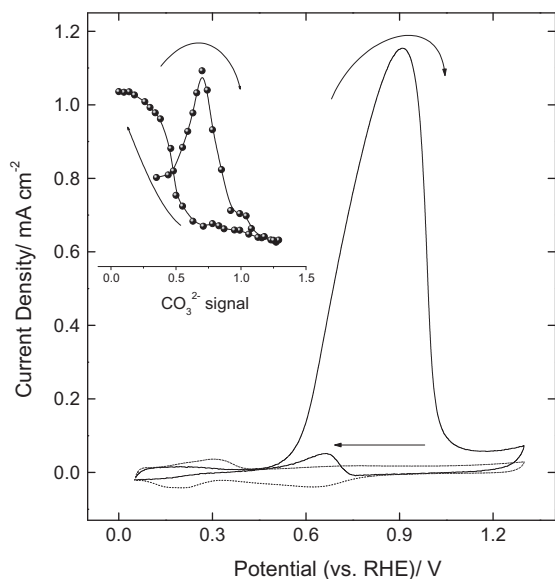


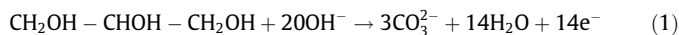
Fig. 2. Cyclic Voltammograms of PdRh in 0.1 mol dm⁻³ KOH (dashed line) and in 0.1 mol dm⁻³ KOH + 0.1 mol dm⁻³ glycerol (solid line). $\nu = 20$ mV s⁻¹. Insert: CO₃²⁻ intensity band as a function of the potential, obtained by in situ FTIR.

oxidation is partially inhibited in the potential region of 0.05–0.40 V, a typical behavior in the presence of alcohols, which indicates that the adsorption of glycerol (or its fragments) takes place at low potentials [11,25]. The first electrooxidation currents appear at ~0.45 V. This potential is 0.3 V lower than that reported for gold [8] and 0.15 V lower than that observed for pure Pd [5], indicating that PdRh present some catalytic activity towards glycerol oxidation in alkaline media. Based on these findings, Rh seems to act as a co-catalyst, probably promoting the scission of C–C bonds, as previously observed for ethanol [20] and 2-propanol [21].

Results show that when associated to Pd, Rh produces surfaces able to dissociate glycerol into fragments containing a single carbon even in strong alkaline media, which is evidenced by the production of carbonate. Afterwards, the current increases and reaches a wide single peak around 0.9 V and then diminishes continuously until the vertex potential. This behavior is similar to that reported by Simões et al. for glycerol electrooxidation on Pd surfaces [5]. During the reversing sweep, the electrooxidation currents experience a little increase around 0.75 V, peaking at 0.66 V. As an attempt to assign this peak to the corresponding electrode process in the insert of Fig. 2 we show the signal corresponding to the production of CO₃²⁻ obtained by in situ FTIR. The CO₃²⁻ band intensity shows that both peaks (during direct and reverse sweeps) are at least partially provoked by the production of carbonate. Further details about a possible interpretation to the currents of Fig. 2 in terms of the reaction pathways will be given in the next section.

3.2. The production of carbonate observed by FTIR

Representative FTIR spectra recorded during the electrooxidation of glycerol (0.05 V < E < 1.30 V) are depicted in Fig. 3. The first band appears around 0.48 V and is centered at 1398 cm⁻¹, indicating the presence of carbonate [26], according to reaction:



Another feature of the spectra is the development of a wide band at ~1650 cm⁻¹. This band corresponds to the bending of HOH from interfacial water present inside the thin layer [5,14]. The growing of such band at potentials higher than 0.48 V probably

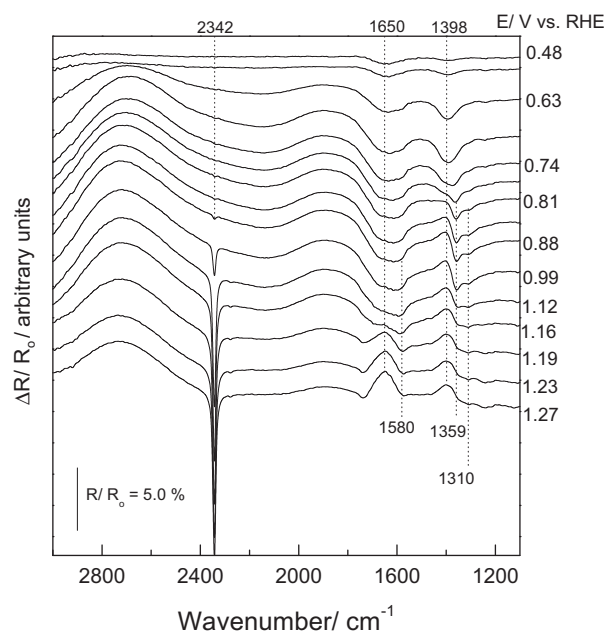
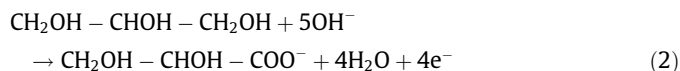
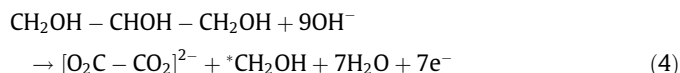
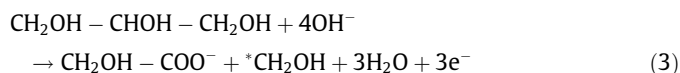


Fig. 3. In situ FTIR spectra in 0.1 mol dm⁻³ KOH + 0.1 mol dm⁻³ glycerol on PdRh. Potentials indicated. Background collected at 0.05 V (RHE scale). $\nu = 1$ mV s⁻¹.

corresponds to the production of water during the oxidation of glycerol, according to Eq. (1). When this band starts to diminish (at potentials higher than 1.0 V), it becomes clear that there is another band, located at around 1580 cm⁻¹, which probably was hidden by the presence of the water band. This band has been recently observed by Simões et al. and is attributed to the stretching of COO⁻, associated to the formation of glycerate ions [5], according to reaction:



Turning back our attention to the early potentials in Fig. 3, the appearance of bands corresponding to the formation of water and carbonate is fairly coincident with the raising of glycerol oxidation currents in Fig. 2. Although the band centered at 1398 cm⁻¹ presents a further development, qualitatively the spectra remain almost unchanged in the range of potential of 0.48–0.70 V. However, at 0.77 V the carbonate band suffers an abrupt diminution, whilst two small, asymmetric bands can be discriminated at 1359 and 1310 cm⁻¹. It is not possible to know if the band at 1359 cm⁻¹ was already present at lower potentials – being superimposed by the carbonate band – or if its raising coincides with the disappearing of the band at 1398 cm⁻¹. These absorption bands were previously assigned to the production of glycolate and oxalate, as products of ethylene glycol oxidation in alkaline medium [27]. Interestingly, both substances can also be formed from glycerol (at least on Pt surfaces), as recently demonstrated by Koper et al. by using high-performance liquid chromatography [9]. The respective oxidation reactions are given below:

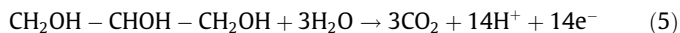


where *CH₂OH stands for a radical which can react with hydroxyl groups (or even water, as will be discussed later) to produce carbonate, or CO₂, respectively.

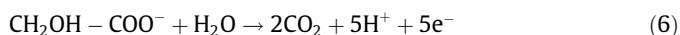
Turning our attention to higher potentials, at ~ 0.9 V CO_2 starts to be produced. The corresponding band (2342 cm^{-1}) experiences a fast increase and becomes the main feature of the spectra above 1.0 V. The production of CO_2 in alkaline media has been first discussed by Christensen and Hamnett and takes place due to a lack of hydroxyl groups provoked by the electrooxidation of small organic molecules [27]. Indeed, if we assume that reactions (1)–(4) are taking place at potentials above 0.5 V, great amounts of hydroxyl are being consumed inside the thin layer. Correspondingly, in this potential range we observed the development of a broad band between 2500 and 3000 cm^{-1} ascribed to the consumption of OH^- [27,28].

Moreover, the presence of CO_2 coincides with the disappearing of the band at 1359 cm^{-1} , which suggests that glycolate may be an intermediate of the production of CO_2 .

A remarkable feature of the spectra in Fig. 3 is the inversion of the band corresponding to interfacial water (1650 cm^{-1}) at potentials above 1.16 V. The inversion means that water is produced in the first stages of the electrooxidation of glycerol and starts to be consumed afterwards. These results can be rationalized as follows: Once the present results were obtained in a thin-layer configuration, the depletion of hydroxyl groups caused by the occurrence of reactions (1)–(4) provokes a noticeable lowering of pH at high potentials, inducing the reaction to follow pathways which involve H_2O instead of OH^- . Hence, the production of CO_2 may proceed through reaction:



Or through reaction (6), if we assume that glycolate generates CO_2 :



Note that in both reactions, an important release of protons takes place and provokes a further decrease of pH.

Furthermore, the carbonate band seems to point upwards at potentials greater than 0.81 V. Since carbonate is not expected to be present at the starting potential, and considering that the alkaline solution will have a greater capacity to convert dissolved carbon dioxide to carbonate, we decided to perform a control experiment in presence of a monolayer of carbon monoxide (CO) previously adsorbed.

Fig. 4 shows that the carbonate band (1398 cm^{-1}) begins to develop around 0.32 V. Afterwards, this band shows a fast increase, peaking at 0.55 V. For higher potentials, the band shows a slow decrease, characteristic from the diffusion of carbonate to outside the thin layer. The other feature of the spectra is a small band at 1650 cm^{-1} , which shows the changes in the concentration of interfacial water as a consequence of the production of carbonate. Note from Fig. 4 that there is no inversion of the band located at 1398 cm^{-1} , as will be expected if carbonate is already present in the early potentials. Based on this observation, it seems probable that the apparent inversion visualized in Fig. 3 is caused by a band from glycerol consumption. Indeed, if the spectrum obtained at 1.19 V is plotted against pure glycerol (Fig. 5). Glycerol standard spectrum provided by the software Essential FTIR, version v1.50.282© some vibrational modes present a fair similarity with the standard, particularly that one centered at 1398 cm^{-1} . Here is wise noting that the bands point towards opposite directions because glycerol is being consumed at 1.19 V. These observations lead us to suggest that there are two superimposed bands at 1398 cm^{-1} , one of those provoked by the production of carbonate and the other due to the consumption of glycerol. At low potentials carbonate is being formed and glycerol is not yet being consumed at full rates, so the negative band prevails. At high potentials, carbonate diffuses while glycerol consumption increases, so the positive character of the band appears.

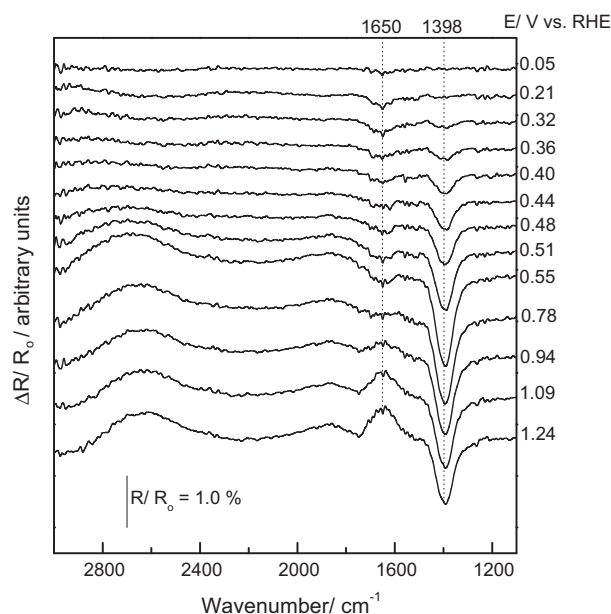


Fig. 4. In situ FTIR spectra collected during the stripping of a CO monolayer on PdRh electrodeposits. Potentials indicated. Background collected at 0.05 V (RHE scale), $\nu = 1\text{ mV s}^{-1}$.

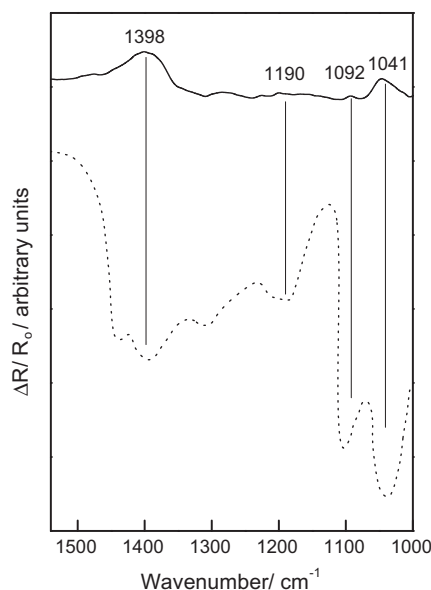


Fig. 5. Spectrum collected at 1.19 V during glycerol electrooxidation in $0.1\text{ mol dm}^{-3}\text{ KOH} + 0.1\text{ mol dm}^{-3}\text{ glycerol}$ (solid line) on PdRh compared to the spectrum obtained for pure glycerol (dashed line).

Concerning the presence of adsorbed CO, according to Jiang et al. for Pd two bands located at 1960 and 2050 cm^{-1} (due to the presence of linearly and bridge-bonded CO, respectively) are expected [29]. Noticeably, in the present case, no bands associated to CO can be observed even if spectra of Fig. 3 are analyzed in further details (not shown). The apparent lack of CO is surprising at a first glance, since it is well-known that CO adsorbs on Pd [29]. However, as showed by Simões et al., the signal of adsorbed CO on Pd is very low compared to that on Pt [5]. Furthermore, as stated by de Lima et al., the use of electrodeposited surfaces reduces considerably the band intensities for adsorbed species [30]. According to the authors, the reason for this effect probably originates from the rough structure of such surfaces [30]. Hence,

we believe that the apparent absence of CO is only an optical artifact caused by the electrodeposited surface used in the present work associated to a very low signal of adsorbed CO on Pd.

3.3. The persistence of carbonate at higher OH⁻ concentrations

Fig. 6 shows FTIR spectra obtained during the electrooxidation of 0.1 mol dm⁻³ glycerol in 1.0 mol dm⁻³ KOH. Conversely to Fig. 3, as the potential increases there is no fast decrease of carbonate band nor CO₂ formation. This result reinforces that the production of CO₂ is a consequence of the lack of OH⁻ species inside the thin layer. The carbonate band grows until 0.9 V and then experiences a slow decrease, which is probably associated with the low diffusion of this substance outside the thin layer. In contrast with Fig. 3, in this case we cannot observe the emergence of a positive-going band at 1398 cm⁻¹, probably because the massive production of carbonate precludes the visualization of the less intense band due to the consumption of glycerol. The maximum absorbance of the carbonate band is several times higher than that observed in Fig. 3 (compare the scales used in Figs. 3 and 6), reinforcing that the amount of OH⁻ available is a key factor for the production of carbonate from glycerol. The high amounts of carbonate can be explained by the presence of Rh, which has been considered as a suitable co-catalyst to enhance the break of C–C bonds during the electrooxidation of molecules as ethanol [20], 2-propanol [21] and acetaldehyde [23]. Accordingly, the band at 1650 cm⁻¹ suggests that water remains being produced at long of the whole potential range, which is justified by the fact that at this concentration of KOH the consumption of hydroxyl groups is not enough to provoke their exhaustion. Consequently, water is produced (but never consumed) during glycerol electrooxidation.

Another remarkable feature of the spectra is the appearing of small bands at ~1308 and 1574 cm⁻¹ at $E > 0.7$ V. These bands have been associated to the stretching modes of C–O and COO⁻, due to the formation of glyceraldehyde and glycerate, respectively [5]. However they are clearly a minor feature in a spectrum dominated by the carbonate band.

These observations have important mechanistic implications and show that the growing development of specific membranes for alkaline fuel cells allows the design of a whole new series of Pt-free catalysts.

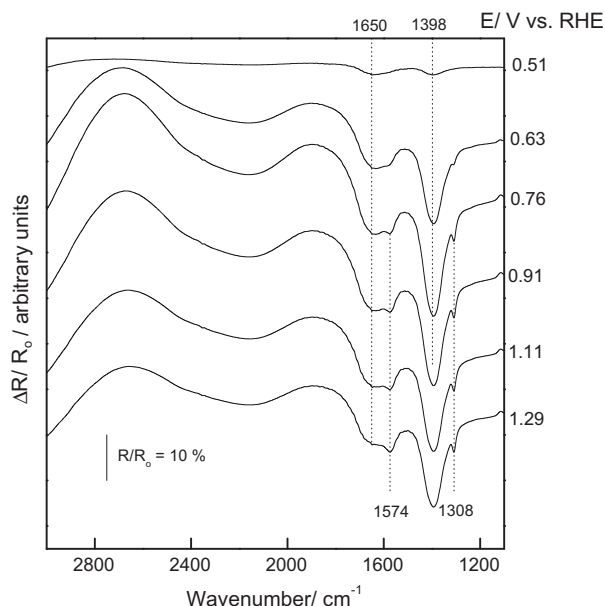


Fig. 6. In situ FTIR spectra in 1.0 mol dm⁻³ KOH + 0.1 mol dm⁻³ glycerol. Experimental conditions as in Fig. 3.

4. Conclusions

- One of the products of glycerol electrooxidation on PdRh is carbonate, which indicates that this catalyst is able to provoke the cleavage of glycerol to some extent.
- Besides carbonate, bands associated to several other oxidation products, as glyceraldehyde, glycerate, glycolate and oxalate are also detected. The multiplicity of oxidation products illustrates a complex electrooxidation kinetics.
- When low OH⁻ concentrations are used, the production of carbonate is abruptly replaced by a pathway that generates CO₂ at high potentials. Signals associated to glycolate and oxalate are also detected under these conditions.
- CO₂ is not observed in 1.0 mol dm⁻³ KOH solutions, which indicates that the occurrence of this pathway is due to the consumption of OH⁻ in the thin layer during glycerol electrooxidation. Also, the amounts of carbonate depend on the concentration of OH⁻ species.

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