



Effect of mass transport on the glycerol electro-oxidation

G.B. Melle, E.G. Machado, L.H. Mascaro, E. Sitta*

Department of Chemistry (DQ), Federal University of Sao Carlos (UFSCar), Rodovia Washington Luis s/n, km 235, CP 676, 13565-905, Sao Carlos, SP, Brazil



ARTICLE INFO

Article history:

Received 30 May 2018

Received in revised form

25 September 2018

Accepted 12 November 2018

Available online 19 November 2018

Keywords:

Glycerol
Electro-oxidation
Platinum
RDE
Mass transport

ABSTRACT

The search for greener energy sources has led to the development of biodiesel. One of its by-product, glycerol, is usually converted into more valuable products by organic synthesis or homogeneous catalysis. There is still room for the research on converting this molecule by means of an electrolytic or fuel cell - for that goal, a deeper understanding of the process and its variables is desirable. This work aims at describing the role of mass transport at the glycerol electro-oxidation on polycrystalline platinum in acidic media. We found that at a proper condition, a new faradaic process is observable in the cyclic voltammetry at ~ 0.55 V, regarding the oxidation of glycerol at lower potentials. By means of a numerical experiment it is proposed that a soluble intermediate, namely glyceraldehyde, is the main actor in the inhibition of the process and that its removal, by the electrode rotation, yields a less poisoned surface. The results presented suggest that the aim for electrolytic or fuel cells should be the development of catalysts less active for glyceraldehyde and that the mass transport is a key factor in designing those devices.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

The ever-increasing efforts towards more sustainable sources of energy have led to the development of biodiesel as an alternative to fossil fuels [1]. During its synthesis, glycerol is generated as by-product and much has been discussed on how to convert this molecule into more economically interesting products [2]. Among many proposals, the most common are organic-chemistry reactions performed by heterogeneous or homogeneous catalysts [3–6]. However, according to Coutanceau and co-workers [7] the use of glycerol in a fuel or electrolysis cell still presents as a scarce option. Also, in opposition to these classical heterogeneous, electrocatalytic oxidation processes are more easily tunable by means of electrocatalyst composition, as well as other parameters, such as the electrode potential. This fine control could lead to a higher selectivity in conversion, which in turn leads to an overall cheaper process. Moreover, as proposed by Li and co-workers [8], one interesting possibility is the electrocatalytic oxidation of glycerol in anion-exchange membrane fuel cell, to cogenerate electricity (124.5 mW cm^{-2} at 80°C) and valuable chemicals (91% conversion to C_3 acids), according to the authors. On a different approach, Li and co-workers [9] assembled a direct glycerol fuel cell with a

polytetrafluoroethylene thin film as separator. In this setup, the authors achieved 214.7 mW cm^{-2} at 80°C . The optimization of the parameters for the operation of such devices has the potential to increase the economic interest in glycerol. To this end, understanding the process by which the electro-oxidation of this molecule takes place and with which variables it changes, is of utmost importance.

One important variable that should be accounted for in electrocatalytic process is the mass transport of species from/to the interface. Currently, the oxygen reduction reaction (ORR), for its application in hydrogen fuel cells, is a hot topic where the diffusion of species is studied at length [10–12]. It is also noteworthy more prototypical models, such as the one studied by Arvía et al. [13], on the diffusion of ferro- and ferricyanide ions in aqueous solutions, and Man et al. [14], on the electrodeposition of copper at a rotating disc electrode. By using a simple model of multistep electrochemical reactions, Danilov and co-workers [15–17] were able to describe the transport of intermediates between the interface and the bulk of the cell. The model employed by the authors accounted for the dependence of the individual rates of the consecutive reactions with the diffusion of the species. These numerical experiments support the results presented by Hardacre and co-workers [18], which describes the effect of mass transport on the electro-oxidation of four different alcohols, namely methanol, ethanol, n-butanol and 2-butanol. The main conclusion from their work is that increasing mass transport impacted negatively on the oxidation of

* Corresponding author.

E-mail address: esitta@ufscar.br (E. Sitta).

the molecules, caused by a combination of factors, mainly the removal of intermediates preventing further oxidation and a shift on the reaction pathway forming more strongly adsorbed intermediates. Hardacre and co-workers show that there are important aspects on the electrocatalytic reactions regarding the mass transport that are not well understood. In this work we are going to show that for electro-oxidation of glycerol a new feature appears when the proper mass transport condition is achieved, and its interpretation leads to a new understanding of the process. In order to completely discuss the relevance of this feature, it is mandatory to understand the mechanism by which glycerol is electro-oxidized.

The electro-oxidation of glycerol is a complicated reaction with many soluble intermediates, which can re-adsorb or diffuse, and there is still debate regarding the nature of these species. One of the first propositions on the mechanism of glycerol electro-oxidation on platinum was made by Gonçalves et al. [19] where the authors employed cyclic voltammetry experiments and proposed two different pathways by which glycerol would be oxidized: one with CO as intermediate and another with COH. From that point on, many studies were devoted to measure the influence of the process with different variables, such as pH, catalyst composition, among others [20–26]. In 2011, Gomes and co-workers [27] described that gold is the most active catalyst for glycerol oxidation in alkaline media, but for acidic media platinum is more active. Additionally, the authors discussed that the following research on glycerol oxidation should focus on the identification of the adsorbed intermediates and final products of this reaction, which was performed by Koper et al. and Behm et al. coupling HPLC analysis with electrochemical experiments [25,28] and *in situ* FTIR and online differential electrochemical mass spectrometry [29], respectively. More recently, Koper and co-workers [30], by means of electrochemical experiments, spectroscopy and density functional theory calculations, proposed that depending on the surface arrangement of platinum atoms, the reaction pathway differs on acidic media. Also, that there are two different active intermediates produced by the dehydrogenation of glycerol on the platinum surface: one bound by two adjacent carbon atoms on the surface of Pt (111) and another bound by only one carbon, on the surface Pt(100). From these intermediates, the reaction can proceed to yield dihydroxyacetone or glyceraldehyde. In alkaline media and on Pt(111) surfaces, Angelucci and co-workers [31] reported that carboxylates and acyl to be the main intermediates formed during the glycerol oxidation reaction. The authors also stated that the acyl intermediate remains on the surface of the electrode even at potentials where platinum oxide is formed. All these new data being provided on the amount and nature of glycerol oxidation intermediates reveal a somewhat open field regarding the dependence of these species on reaction conditions, such as mass transport.

The present paper aims at demonstrating that when a certain mass transport condition is achieved, a new voltammetric feature is present in the glycerol electro-oxidation, at lower potentials than the usual peak. By testing different voltammetric scan rates, it will be shown at which set of parameters it can be found. Also, by varying the mass transport conditions by means of a rotatory disc electrode, it is shown that this process is related to a consecutive reaction with soluble intermediates. All these data, alongside with the discussion presented, suggest a new look into the *operando* conditions for electrolytic or fuel cells operated by glycerol directly.

2. Experimental

All experiments were done in a conventional three-electrodes glass cell at room temperature (25 °C). Before and during all measurements, the atmosphere in the cell was kept inert by a positive

pressure of nitrogen. The working electrode consisted of a rotating disk electrode (RDE) in which a 5 mm diameter Pt disc is embedded in Teflon and polished with diamond paste up to 0.25 μm. The counter electrode was a platinum flag with high superficial area and the reference electrode was a reversible hydrogen electrode (RHE) prepared in the electrolyte solution. The electrolyte used was 0.5 mol L⁻¹ sulfuric acid (Sigma-Aldrich, Puris P.A.). All solutions were prepared using ultrapure water (18.2 MΩ cm, Millipore). Glycerol (Sigma-Aldrich, >99% GC) and Glycolaldehyde (Sigma-Aldrich, >99% GC) were directly inserted into the cell in sufficient amount to yield a concentration of 0.1 mol L⁻¹ and 0.01 mol L⁻¹, respectively. The measurements were done in a Metrohm-Autolab Potentiostat/Galvanostat PGSTAT-128N equipped with a Scan250 modulus. The RDE was controlled by a Princeton Applied Research rotatory module and the results showed in term of rotations per minutes (rpm). Before all measurements, an electrochemical annealing procedure was employed to ensure a clean electrode surface, as described in more details elsewhere [32].

2.1. Calculations

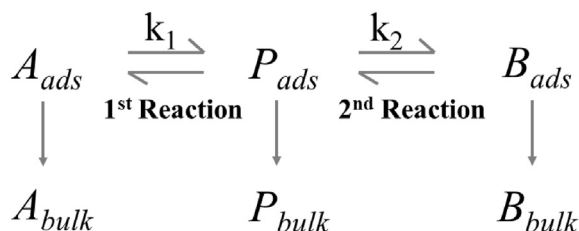
The numerical experiment in this work has the purpose to point if the direction of our proposed hypothesis is acceptable or if it should be rejected. That could be achieved if there is a, at least, qualitative correspondence between the solution for the set of kinetic equations and the experimental data obtained. Danilov et al. [17] described a set of kinetic equations for a sequential, multi-step electrochemical process, with a soluble intermediate. Among their results, one described the variation of the current of each step with the diffusion of the species, namely Fig. 4 in their work (reproduced in the [Supplementary Information Files – Section 1](#)). In their work, this diffusion is represented by a variable called k_D , representing the rate constant of the diffusion mass transfer of the species and determined by Equation (1):

$$k_{D,x} = \frac{D_x}{\delta} \quad (1)$$

where D_x is the diffusion coefficient of a given species x and δ is the thickness of the diffusion layer. In this work, we draw a qualitative correlation between k_D and the electrode rotation. Since an increase in the latter produces a decrease in δ , an increase in D_x , and thus an increase in k_D , we can qualitatively substitute k_D for electrode rotation, in the following discussion.

The numerical experiment was accomplished by firstly reproducing the results presented by Danilov et al. [17] and later adjusting the value of one parameter, namely k_1^0 (The equations employed for used as well as the numerical value of the parameters are described in [Supplementary Information Files – Section 1](#)). By successfully fitting an experimental data by a set of kinetic equations, it is possible to infer on the behavior of experimentally inaccessible variables. In their work, the authors describe among other variables, how the current of consecutive electrochemical steps would vary with the electrode rotation. [Scheme 1](#) brings the summary of the two steps considered.

We adapted this scheme by assigning A to glycerol, Ps to glyceraldehyde (the main intermediate, we did not consider the 1,3 dihydroxyacetone for reasons further discussed in Section 3) and B to glyceric acid. Afterwards, by decreasing the parameter k_1^0 by five times, which regards the reaction rate for the formation of glyceraldehyde, there was a successful fitting of the experimental data ([Fig. 6](#)). Further discussion on the impact of this consideration will be provided in Section 3.



Scheme 1. Scheme adapted from the one proposed by Danilov et al. [17] for the role of mass transport in consecutive reactions.

3. Results

As an initial characterization of the system, different potential scan rates were employed in a solution containing 0.5 mol L⁻¹ sulfuric acid and 0.1 mol L⁻¹ glycerol, with the electrode at either 0 rpm (black curve) and 400 rpm (green curve), and the results are displayed in Fig. 1.

The black curve (solid and dotted) in Fig. 1(C) displays the usual reported behavior for the oxidation of glycerol in acidic media. It is possible to distinguish one peak (with a shoulder) in the positive-going part of the scan, at ~0.8 V, related to the oxidation of glycerol and the products of its oxidation, such as glyceraldehyde and CO_{ad} [25,29]. It is noteworthy that no process takes place until the potential reaches ~0.80 V due to the coverage of CO_{ads} on the surface of the electrode. In the negative-going part of the scan, the surface is covered by platinum oxide and only at ~0.85 V some sites are freed, and the oxidation of glycerol and its products takes place. In this scenario, the oxidation processes described by peak III are increased in higher potentials than the platinum oxides reduction (yielding CO₂ and glyceric acid) and decreased at lower potentials with CO accumulation on surface [33].

An important aspect to be discussed on Fig. 1 is the appearance of a peak at ~0.55 V (peak I), in Fig. 1(C) and (D). With a stationary electrode, the process is found to be suppressed and no faradaic current can be observed until ~0.65 V, which is described thoroughly in the literature [20,30] as an inhibition caused by the

adsorption of CO. However, this process appears when the scan rates are higher than 0.01 V s⁻¹ and with an electrode. These two conditions, alongside with the use of a polycrystalline platinum electrode in acidic media, to the best of our knowledge, have not been reported elsewhere. Tests were performed to show that this new feature is not related to a contamination of the system, (see the analysis in Supplementary Information Files, Section 2) as well as the study performed by Kwon et al. [34] in which it is discarded any catalytic effect caused by traces of molecular oxygen present in supporting electrolyte. The other two peaks (peaks II and III) present in the voltammetry have their current decreased with the rotation speed and further discussion on this topic will be provided in the next section.

To understand the dependence of the electro-oxidation of glycerol on platinum with the mass transport condition, Fig. 2 brings the cyclic voltammetry responses at different rotation speeds of the electrode at 0.1 V s⁻¹.

Fig. 2 shows that the rotation speed of the electrode plays an important role in the response of the cyclic voltammetry, as it controls the mass transport of species from/to the interface. Fig. 2 (A) shows the typical response for the electro-oxidation of glycerol on polycrystalline platinum, at 0 rpm [20,30]. With rotation speeds as low as 100 rpm (Fig. 2 (B)), the new peak at ~0.55 V appears and remains present in the rotation speeds tested (Fig. 2 (C) to (F)). To classify the faradaic processes present in the voltammetry and understand their dependence with the rotation speed, a closer look into the mechanism by which glycerol is electro-oxidized is required. According to Koper and co-workers [30], there are at least 5 faradaic steps that depends on the adsorption of the reactants. HPLC analysis from samples collected during slow rate linear sweeps [25] found that glyceraldehyde and glyceric acid are the major soluble products below 1.0 V with 1,3-dihydroxyacetone being also detected, but at very low concentrations. These results agree with previous *in situ* FTIRs data that also reveals the presence of CO_{ad} in potentials below the peak II onset in quiescent solutions [27,35]. At high potential (E > 1.2 V), formic and glycolic acids are the other observed products. Thus, due to the potential region in which the peak I and II are present, the following discussion will

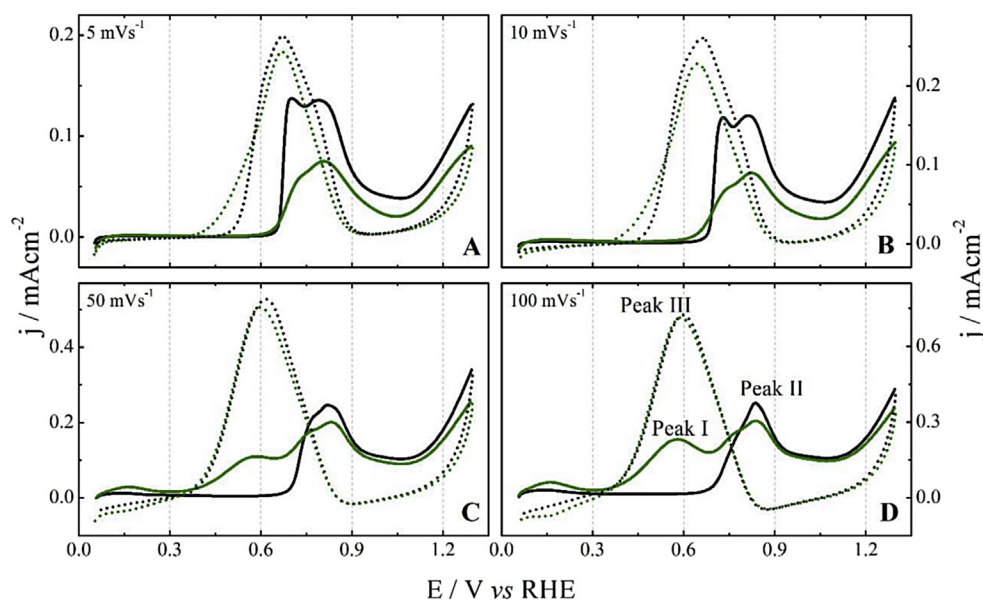


Fig. 1. Cyclic voltammograms of Pt in H₂SO₄ 0.5 mol L⁻¹ + Glycerol 0.1 mol L⁻¹ at 0 rpm (black curve) and 400 rpm (green curve) at distinct scan rates as indicated on panels (A)–(D). Solid and dotted lines represent positive and negative going scans, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

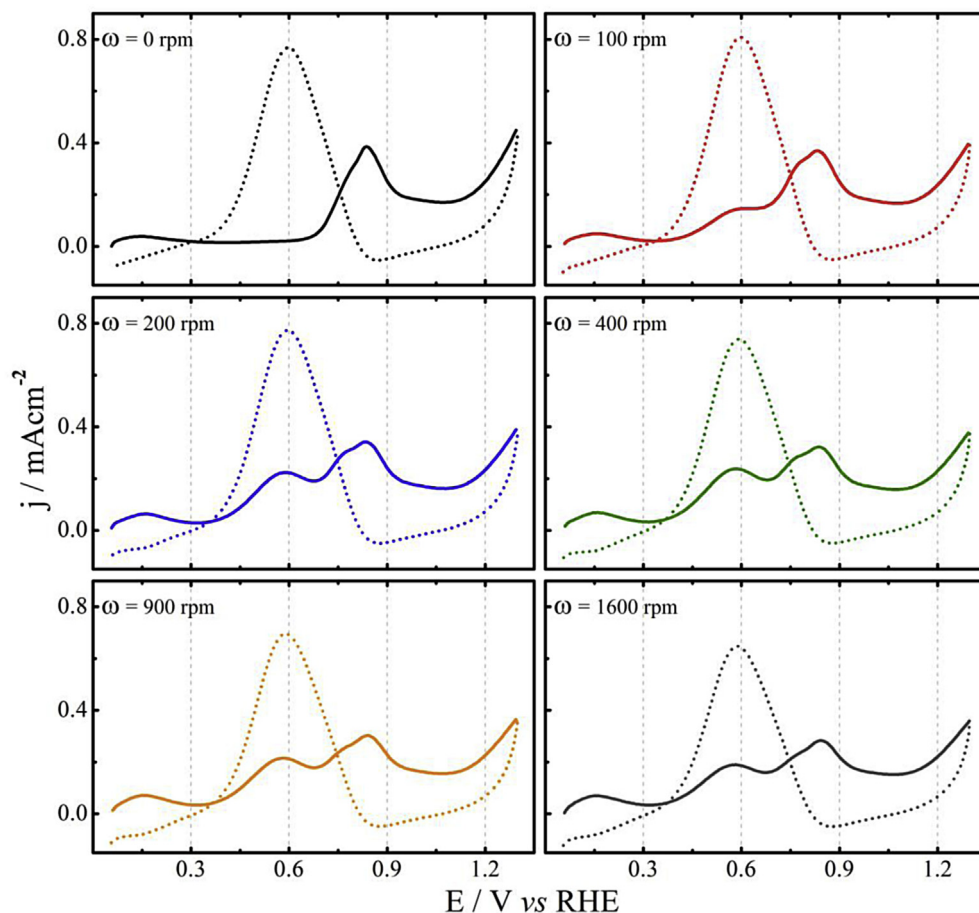
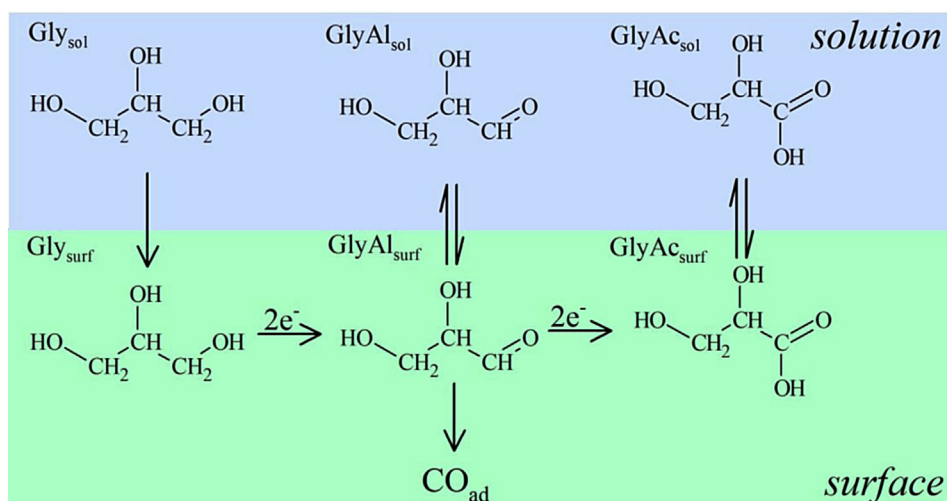


Fig. 2. Cyclic voltammograms at 0.1 V s^{-1} at different electrode rotation speeds as indicated on the panels. Electrolyte conditions are the same of Fig. 1. Solid and dotted lines represent positive and negative going scans, respectively.

consider the oxidation of glycerol yielding glyceraldehyde and glyceric acid only. In this way, Scheme 2 can be drawn to summarize the most important steps for the following discussion.

In this reaction scheme, glyceraldehyde plays the important role of re-adsorbing intermediate that can be oxidized to glyceric acid or

through a C–C bond scission yielding CO_{ad} and C_2 products. At principle, the CO_{ad} could come from glyceric acid, as suggested in previous works, but in general the adsorption of aldehydes on Pt surface results in CO_{ad} [18,36] and the selectivity of glycerol oxidation is more than 75% to glyceraldehyde below 1.0 V. Since



Scheme 2. Reaction pathways for electro-oxidation of glycerol on polycrystalline Pt at $E < 1.0 \text{ V}$. Gly, GlyAl and GlyAc represent the Glycerol, Glyceraldehyde and Glyceric Acid, respectively for the species in solution (sol) or on surface (surf).

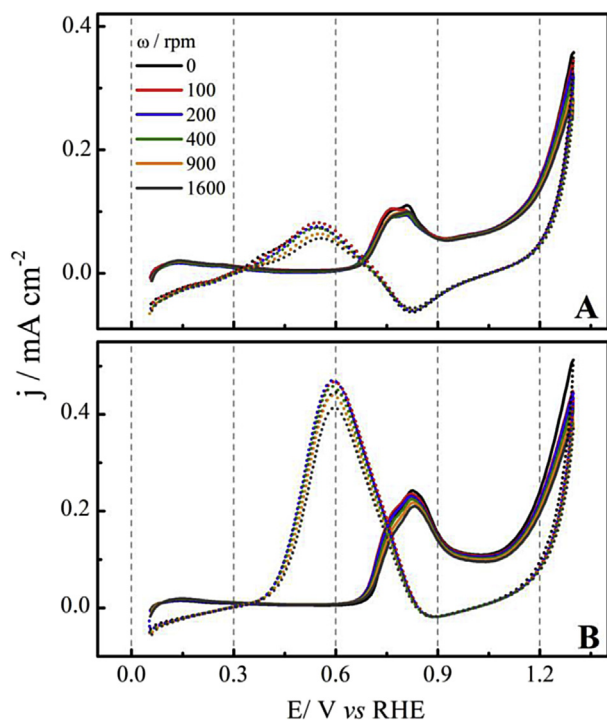


Fig. 3. Cyclic voltammograms at 0.05 V s^{-1} in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ + (A) 0.01 mol L^{-1} glyceraldehyde and (B) 0.01 mol L^{-1} glyceraldehyde + 0.1 mol L^{-1} glycerol. Solid and dotted lines represent positive and negative going scans, respectively.

glyceraldehyde is a soluble intermediate of the reaction, the mass transport will impact greatly on its concentration in the interface. To further understand the role of glyceraldehyde, Fig. 3 displays the result of a cyclic voltammetry performed in the same conditions of Fig. 2 (A) in the presence of 0.01 mol L^{-1} glyceraldehyde and (B) 0.01 mol L^{-1} glyceraldehyde + 0.1 mol L^{-1} glycerol.

It is possible to see in Fig. 3 (A) that during positive going scan, regardless of the rotation speed, no process takes place until 0.8 V , where one peak (and a shoulder) is observed for the oxidation of glyceraldehyde. The presence of only one peak is related to the higher production of CO from glyceraldehyde when compared to the production of glycerol, as it was described by Schnaidt [33]. Therefore, in Fig. 3 (B), when both molecules are present, only one peak is present, since the higher coverage of CO provided by glyceraldehyde inhibits any process below $\sim 0.7 \text{ V}$. It is also noticeable a small shoulder on the peak present in the increasing potential direction of the voltammetry, and this could be attributed to the oxidation of glyceraldehyde while the other, at higher potentials, to the oxidation of glycerol.

In order to deepen the study of the effect of intermediates on the poisoning of glycerol electro-oxidation, we employed the same strategy that Grozovski et al. [37] used for formic acid. Considering that the poison is oxidized at high potentials, a potential program composed by a pulsed voltammetry in which 1 s steps at 0.85 V are followed by 1 s steps at $E \text{ V}$ ($0.05 < E < 0.85$) (Fig. 4(a)) allows us to analyze current changes due to the poison formation at fixed potentials. The current transients can be described by Equation (2) [37]:

$$j = j_{\max} \left(\frac{1}{1 + k_{\text{ads}} t (1 - p)} \right)^{\frac{1}{p-1}} \quad (2)$$

with j and j_{\max} being the current density and current density at $\theta = 0$, respectively, t the time, p a parameter connected to the

number of surface sites necessary to the poisoning formation and k_{ads} the first order poison-formation reaction rate.

Three representative fitted transients (dotted lines) and experimental data (symbols) collected in the presence of glycerol are shown in Fig. 4(b) as well as the equation parameters j_{\max} and k_{ads} on panels (c) and (d), respectively. The same procedure was employed to glyceraldehyde (GlyAl) and glycerol + glyceraldehyde (Gly + GlyAl) solutions. The first important piece of information extracted from these experiments is the oxidation currents of glycerol or glycerol + glyceraldehyde mixtures in potentials lower than 0.7 V , when the surface is not poisoned, as described by j_{\max} values. This behavior supports the glycerol oxidation at low potential in absence of poisons (probably CO_{ad}). Secondly, the k_{ads} values and their potential-dependence are very similar in all conditions, suggesting a similar mechanism of surface poisoning, i.e. glycerol \rightarrow glyceraldehyde \rightarrow CO_{ad} . When only glyceraldehyde is present, small currents are observed because the process is almost completely inhibited. However, when both alcohol and aldehyde are present, after the CO_{ad} removal, a competition between glycerol oxidation and glyceraldehyde (mainly from the solution, since the time is too short) adsorption yielding CO_{ad} takes place on the surface and partially decreases the overall current.

To clarify the dependence of the processes presented in Fig. 2 with the mass transport condition, Fig. 5 presents the maximum of current at each separate peak, with the rotation speed of the electrode.

To understand why both peaks II and III are decreasing with an increase on the rotation speed of the electrode, one must refer to the work of Puthiyapura et al. [18]. In this work, the authors describe the same trend for methanol and ethanol oxidation on electrodeposited platinum and justify the decrease by a combination of two factors: the removal of partial oxidation intermediates, which then cannot be further oxidized, and a change in the mechanism, favoring a route that leads to more strongly adsorbed intermediate, namely CO_{ad} . The authors discuss that the second factor is only relevant for the electro-oxidation of methanol, as for ethanol the reversibility of the changes in current by the rotation of the electrode shows that no accumulation of CO_{ad} happens at the potentials investigated. For ethanol, the authors claim that the carboxylic acid is difficult to be oxidized at that potential, therefore the diffusing intermediate should be the aldehyde. A direct parallel can be drawn to the electro-oxidation of glycerol, as the evidence that glyceric acid is not oxidized at that potential [31], yielding that the diffusing species should be glyceraldehyde, following Scheme 2.

The profile found for peak I is a bit more intricate and to understand its behavior, a numerical experiment was performed based on the work of Danilov et al. [17]. For this experiment, the system is proposed to be described by two consecutive reactions, as shown in Scheme 1. Thus, by using all conditions employed in the work of Danilov et al. [17] and by only changing the value of k_1^0 from 5×10^{-5} to 1×10^{-5} , we achieved the result present in Fig. 6.

Fig. 6 presents how the individual current of each process (namely peak I, II or III) varies with the electrode rotation.

By the results presented in Fig. 6 it is possible to see the profile obtained for the currents of Peak I, II and III varying with increasing rotation speeds of the electrode. From this result it is possible to infer on the behavior of peak II, which would be the oxidation of glycerol to glyceraldehyde, but separated from any other processes, which is not experimentally feasible due to the plenitude of intermediates from this reaction. The curve for peak I shows the same behavior as the one observed for the new peak obtained experimentally, Fig. 2 – Peak I and for the peak on the reverse scan (Fig. 2 – Peak III). This fitting of the experimental data in a numerical experiment only shows that the hypothesis of the role of the

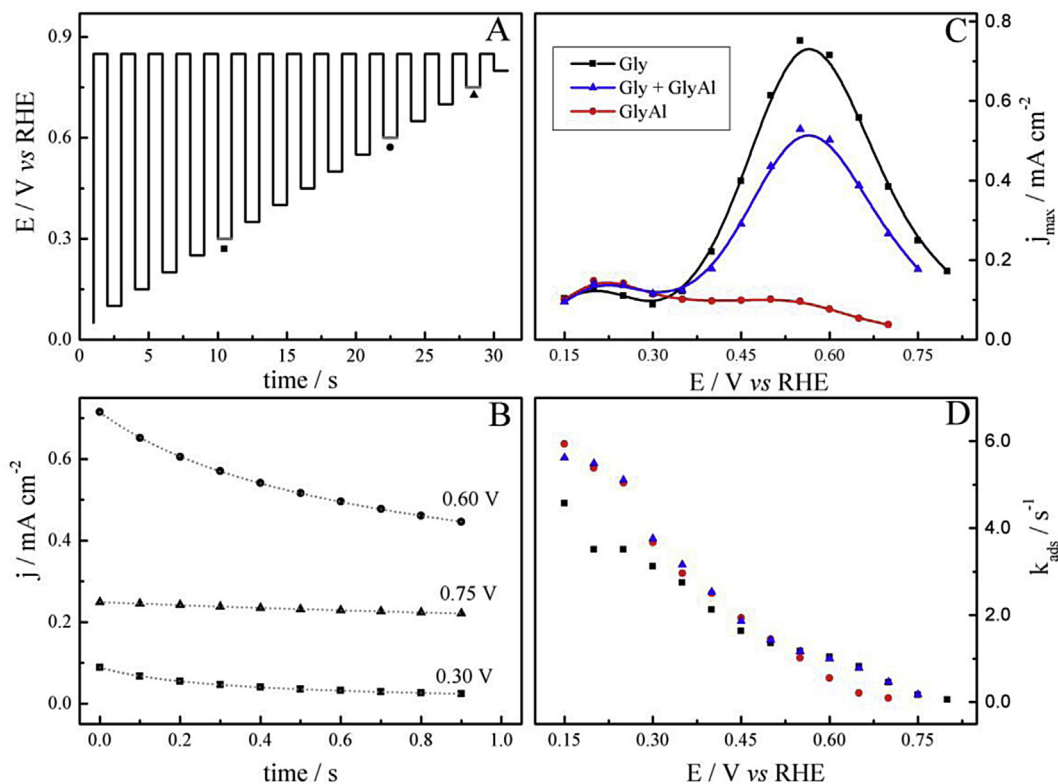


Fig. 4. (a) Potential program for the pulsed voltammetry experiments; (b) current transients obtained at select potentials as indicated on the curves and on the potential program; (c) maximum currents and (d) poison-formation reaction rate (k_{ads}) extracted after fitting the current transients using Equation (2). Experimental conditions are the same of Fig. 3 at 0 rpm.

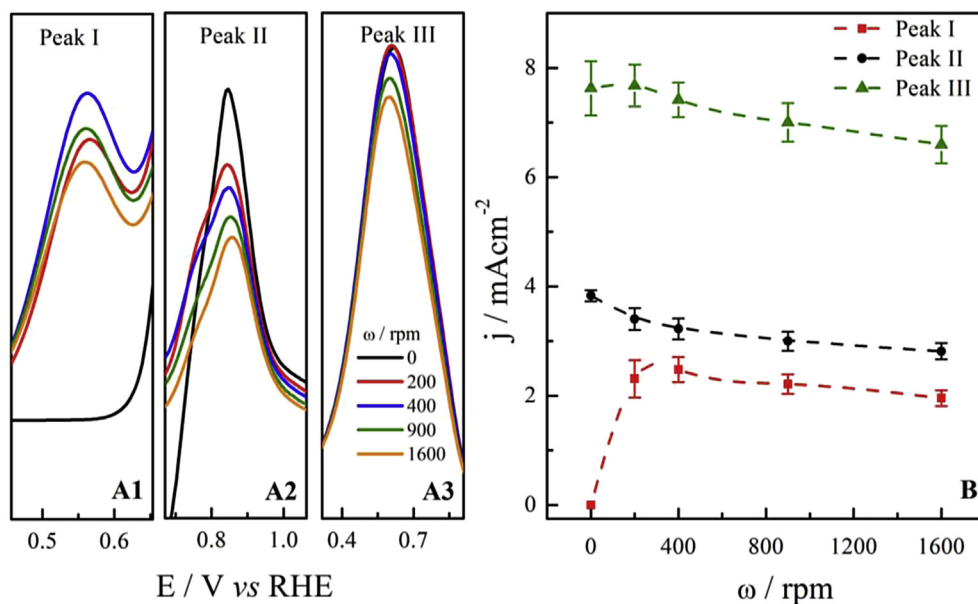


Fig. 5. (A1-A3) j - E profiles in the regions of peaks I to III extracted from Fig. 2 (B) current in the peaks in function of electrode rotations speed.

electrode rotation on the currents of each sequential step is precise. Another important factor to be considered is the absence of Peak I in Fig. 3 (A). This is caused by the chemical decomposition of glyceraldehyde at low potentials yielding CO_{ad} , which poisons the surface to the electrochemical reaction of glyceraldehyde to glyceric acid.

Performing the glycerol electro-oxidation under galvanostatic conditions, the effect of rotation speed was also observed under oscillatory conditions. Fig. 7 shows the time series at 0.13 mA cm^{-2} for four rotation speeds and for the stagnant electrolyte. The potential oscillations with (peak to peak) amplitude bigger than 200 mV are observed in stagnant electrolyte along 165 s. These

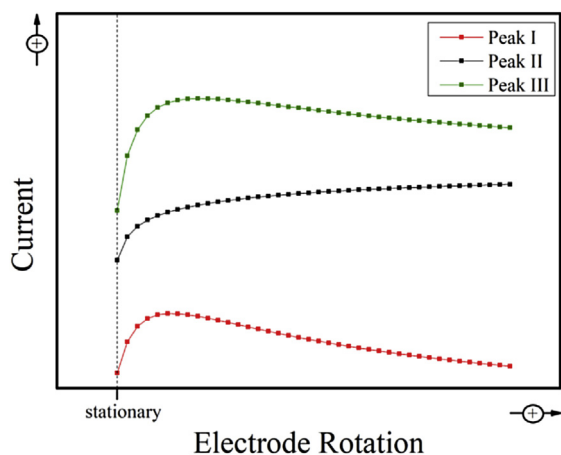


Fig. 6. Results of the numerical experiment using the conditions presented in supplementary information.

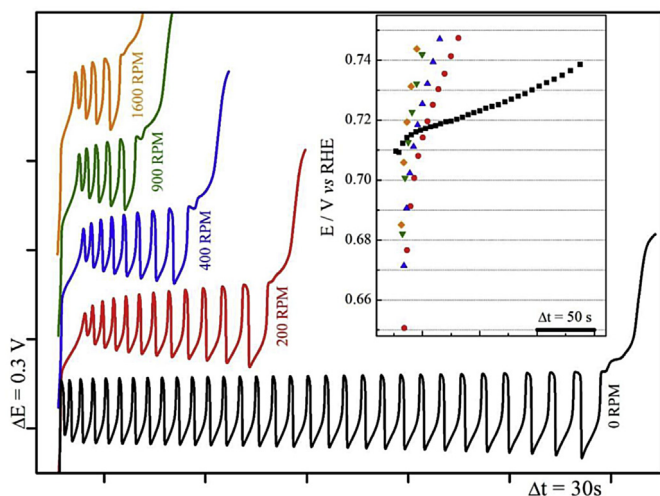


Fig. 7. Galvanostatic time-series at $j = 0.13 \text{ mA cm}^{-2}$ for distinct rotation rates. Electrolyte conditions are the same of Fig. 1. Inset: Maximum potential of each cycle of each time-series in different rotation rates.

oscillations with the so-called period one and mean oscillation frequency (ω) of $0.20 \pm 0.06 \text{ Hz}$ are in agreement with those previous reported [38] and it also occurs in the potential region between the peaks I and II described on Fig. 1 (see Support Information Files, Section 3, for time series in RHE scale). Increasing the rotation speed decreases the time-series, while the frequency ω increases slightly, yielding 0.25 ± 0.08 (200 rpm), 0.29 ± 0.09 (400 rpm), 0.3 ± 0.1 (900 rpm) and $0.3 \pm 0.1 \text{ Hz}$ (1600 rpm).

Zulke et al. [39] reported the end of oscillations during electro-oxidation of glycerol in alkaline media, when the rotation speed was increased from 0 to 1600 rpm, which the authors described as caused by an impact in the critical population of intermediates required for the oscillations to be sustained. Herein, besides the effect on frequency and oscillating time, by increasing the rotation speed, the maximum potential reached in each oscillation cycle (inset in Fig. 7) exceeds 0.74 V faster.

Oscillations in electrochemical systems are caused by the competition between the potential-dependent adsorption of species, and specifically to the electro-oxidation of alcohols, CO_{ad} appears as a key intermediate responsible for poisoning the surface

and causing an increase in the potential, in galvanostatic experiments [40]. The metal oxidation at high potential plays a dual role on oscillations i.e. firstly, it is the responsible for the CO_{ads} oxidation, causing a decrease in the potential and reestablishing a new oscillation cycle. On the other hand, it contributes to the slow formation of stable oxides that deactivates surface sites, culminating in a potential jump to $E > 1.1 \text{ V}$ [41]. Thus, the oscillations reflect not only the nature of the species at the interphase, but also their competition for surface sites. By stripping out the soluble intermediates from the interphase, by employing a rotation on the electrode, it is expected a decrease in the poisoning of the surface. Since the C3 pathway does not seem to be able to keep the oxidation current at low potentials, allowing an increase in the irreversible oxide formation, the oscillations end sooner than in the stationary condition.

4. Conclusions

In this work it was presented the effect of rotation rate during glycerol electro-oxidation at Pt surfaces. Reaction intermediates, named glyceraldehyde, appears as an active specie displaying a dual role on the electro-oxidation of glycerol, i.e. it is the precursor of glyceric acid on the oxidation C3 pathway, but its presence on the surface are responsible to increase the CO coverage at low potential. With the following discussion, a condition in which the diffusion of the species is favored is presented, which can lead to a decrease of the concentration of this molecule near the electrode, yielding the oxidation of glycerol at lower potential ($\sim 0.55 \text{ V}$). If these parameters are translated into *in operando* condition, a higher overall efficiency could be achieved for the process and the production of biodiesel would be made even more advantageous. Also, the discussion herein presented opens the perspective for the development of catalysts less active for glyceraldehyde electro-oxidation, which can produce a more efficient cell to convert glycerol into other molecules or energy.

Acknowledgements

The authors thank São Paulo Research Foundation (FAPESP) for financial support (#2013/07296-2). EGM acknowledge CDMF/FAPESP (#2017/21929-9) and GBM acknowledge CNPq/PIBIC for the scholarships granted. The authors would also like to acknowledge Sirlon Blaskiewicz for the assistance in designing the graphical abstract.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.electacta.2018.11.085>.

References

- [1] S.S. Yazdani, R. Gonzalez, Anaerobic fermentation of glycerol: a path to economic viability for the biofuels industry, *Curr. Opin. Biotechnol.* 18 (2007) 213–219.
- [2] M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi, C. Della Pina, From glycerol to value-added products, *Angew. Chem. Int. Ed.* 46 (2007) 4434–4440.
- [3] A. Behr, J. Eilting, K. Irawadi, J. Leschinski, F. Lindner, Improved utilisation of renewable resources: new important derivatives of glycerol, *Green Chem.* 10 (2008) 13–30.
- [4] D.T. Johnson, K.A. Taconi, The glycerin glut: options for the value-added conversion of crude glycerol resulting from biodiesel production, *Environ. Prog.* 26 (2007) 338–348.
- [5] J. Chaminand, L. Djakovitch, P. Gallezot, P. Marion, C. Pinel, C. Rosier, Glycerol hydrogenolysis on heterogeneous catalysts, *Green Chem.* 6 (2004) 359–361.
- [6] M. Roice, K.P. Subhashchandran, A. Gean, J. Franklin, V.N.R. Pillai, Synthesis and characterization of glycerol dimethacrylate cross-linked polymethyl methacrylate: a resin for solid phase peptide synthesis, *Polymer* 44 (2003) 911–922.

- [7] M. Simoes, S. Baranton, C. Coutanceau, Electrochemical valorisation of glycerol, *Chemosuschem* 5 (2012) 2106–2124.
- [8] Z.Y. Zhang, L. Xin, W.Z. Li, Electrocatalytic oxidation of glycerol on Pt/C in anion-exchange membrane fuel cell: cogeneration of electricity and valuable chemicals, *Appl. Catal. B Environ.* 119 (2012) 40–48.
- [9] N. Benipal, J. Qi, J.C. Gentile, W.Z. Li, Direct glycerol fuel cell with polytetrafluoroethylene (PTFE) thin film separator, *Renew. Energy* 105 (2017) 647–655.
- [10] A.M. Gomez-Marin, J.M. Feliu, Role of oxygen-containing species at Pt(111) on the oxygen reduction reaction in acid media, *J. Solid State Electrochem.* 19 (2015) 2831–2841.
- [11] A.M. Gomez-Marin, J.M. Feliu, New insights into the oxygen reduction reaction mechanism on Pt(111): a detailed electrochemical study, *Chemosuschem* 6 (2013) 1091–1100.
- [12] S.B. Adler, Factors governing oxygen reduction in solid oxide fuel cell cathodes, *Chem. Rev.* 104 (2004) 4791–4843.
- [13] A.J. Arvia, S.L. Marchiano, J.J. Podestá, The diffusion of ferrocyanide and ferricyanide ions in aqueous solutions of potassium hydroxide, *Electrochim. Acta* 12 (1967) 259–266.
- [14] E.S. Man, E.E. Farndon, S.A. Campbell, F.C. Walsh, Current versus potential studies for copper electrodeposition at a rotating disc electrode, *Trans. I Met Finish* 74 (1996) 39–44.
- [15] V.S. Protsenko, F.I. Danilov, Multistep electrochemical reactions involving transport of intermediates between the near-electrode layer and the bulk solution: a kinetics analysis based on theory of generalized variables (theory of similarity), *Russ. J. Electrochem.* 41 (2005) 108–112.
- [16] V.S. Protsenko, F.I. Danilov, Multistep electrochemical reactions involving transport of intermediates between the near-electrode layer and the bulk solution: the kinetics of two-step processes in conditions of non-steady-state diffusion, *Russ. J. Electrochem.* 41 (2005) 1274–1281.
- [17] F.I. Danilov, V.S. Protsenko, Multistage electrochemical reactions with the transfer of intermediates between near-electrode layer and bulk solution: analysis of a kinetic model and computer-aided modeling, *Russ. J. Electrochem.* 40 (2004) 1–8.
- [18] V.K. Puthiyapura, W.F. Lin, A.E. Russell, D.J.L. Brett, C. Hardacre, Effect of mass transport on the electrochemical oxidation of alcohols over electrodeposited film and carbon-supported Pt electrodes, *Top. Catal.* 61 (2018) 240–253.
- [19] R.S. Gonçalves, W.E. Triaca, T. Rabockai, The potentiodynamic electrooxidation of glycerol on platinumized platinum-electrodes, *Anal. Lett. Pt A* 18 (1985) 957–973.
- [20] C. Angelucci, J. Souza-Garcia, P. Fernández, P. Santiago, R.M.L.M. Sandrini, Glycerol electrooxidation on noble metal electrode surfaces, in: *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering*, 2017.
- [21] G.V. Kornienko, N.V. Chaenko, V.L. Kornienko, Indirect electrocatalytic oxidation of glycerol on platinum electrode in acidic electrolyte involving active oxygen forms, *Russ. J. Electrochem.* 51 (2015) 1115–1118.
- [22] P.S. Fernandez, C.A. Martins, M.E. Martins, G.A. Camara, Electrooxidation of glycerol on platinum nanoparticles: deciphering how the position of each carbon affects the oxidation pathways, *Electrochim. Acta* 112 (2013) 686–691.
- [23] J.F. Gomes, F.B.C. de Paula, L.H.S. Gasparotto, G. Tremiliosi-Filho, The influence of the Pt crystalline surface orientation on the glycerol electro-oxidation in acidic media, *Electrochim. Acta* 76 (2012) 88–93.
- [24] P.S. Fernandez, M.E. Martins, C.A. Martins, G.A. Camara, The electro-oxidation of isotopically labeled glycerol on platinum: new information on C-C bond cleavage and CO₂ production, *Electrochem. Commun.* 15 (2012) 14–17.
- [25] Y. Kwon, K.J.P. Schouten, M.T.M. Koper, Mechanism of the catalytic oxidation of glycerol on polycrystalline gold and platinum electrodes, *ChemCatChem* 3 (2011) 1176–1185.
- [26] M. Avramovic, J.M. Leger, B. Beden, F. Hahn, C. Lamy, Adsorption of glycerol on platinum in alkaline-medium - effect of the electrode structure, *J. Electroanal. Chem.* 351 (1993) 285–297.
- [27] J.F. Gomes, G. Tremiliosi-Filho, Spectroscopic studies of the glycerol electro-oxidation on polycrystalline Au and Pt surfaces in acidic and alkaline media, *Electrocatalysis* 2 (2011) 96–105.
- [28] Y. Kwon, M.T.M. Koper, Combining voltammetry with HPLC: application to electro-oxidation of glycerol, *Anal. Chem.* 82 (2010) 5420–5424.
- [29] J. Schnaidt, M. Heinen, D. Denot, Z. Jusys, R.J. Behm, Electrooxidation of glycerol studied by combined in situ IR spectroscopy and online mass spectrometry under continuous flow conditions, *J. Electroanal. Chem.* 661 (2011) 250–264.
- [30] A.C. Garcia, M.J. Kolb, C.V.Y. Sanchez, J. Vos, Y.Y. Birdja, Y. Kwon, G. Tremiliosi-Filho, M.T.M. Koper, Strong impact of platinum surface structure on primary and secondary alcohol oxidation during electro-oxidation of glycerol, *ACS Catal.* 6 (2016) 4491–4500.
- [31] R.M.L.M. Sandrini, J.R. Sempionatto, E. Herrero, J.M. Feliu, J. Souza-Garcia, C.A. Angelucci, Mechanistic aspects of glycerol electrooxidation on Pt(111) electrode in alkaline media, *Electrochem. Commun.* 86 (2018) 149–152.
- [32] E. Sitta, M.A. Nascimento, H. Varela, Complex kinetics, high frequency oscillations and temperature compensation in the electro-oxidation of ethylene glycol on platinum, *Phys. Chem. Chem. Phys.* 12 (2010) 15195–15206.
- [33] J. Schnaidt, Electrooxidation of C2 and C3 Molecules Studied by Combined in Situ ATR-FTIRS and Online DEMS, PhD Thesis, Open Access Repositorium der Universität Ulm, 2013.
- [34] Y. Kwon, S.J. Raaijman, M.T.M. Koper, Role of peroxide in the catalytic activity of gold for oxidation reactions in aqueous media: an electrochemical study, *ChemCatChem* 6 (2014) 79–81.
- [35] C.A. Martins, M.J. Giz, G.A. Camara, Generation of carbon dioxide from glycerol: evidences of massive production on polycrystalline platinum, *Electrochim. Acta* 56 (2011) 4549–4553.
- [36] M.J.S. Farias, G.A. Camara, A.A. Tanaka, T. Iwasita, Acetaldehyde electro-oxidation: the influence of concentration on the yields of parallel pathways, *J. Electroanal. Chem.* 600 (2007) 236–242.
- [37] V. Grozovski, V. Climent, E. Herrero, J.M. Feliu, Intrinsic activity and poisoning rate for HCOOH oxidation at Pt(100) and vicinal surfaces containing monoatomic (111) steps, *ChemPhysChem* 10 (2009) 1922–1926.
- [38] C.P. Oliveira, N.V. Lussari, E. Sitta, H. Varela, Oscillatory electro-oxidation of glycerol on platinum, *Electrochim. Acta* 85 (2012) 674–679.
- [39] A. Zülke, P. Perroni, E.G. Machado, H. Varela, Rrde studies of glycerol electro-oxidation: local pH variation and oscillatory dynamics, *ECS Trans.* 77 (2017) 1643–1650.
- [40] E.G. Machado, H. Varela, Kinetic instabilities in electrocatalysis, in: K. Wandelt (Ed.), *Encyclopedia of Interfacial Chemistry: Surface Science and Electrochemistry*, 2018, pp. 701–718.
- [41] R. Nagao, E. Sitta, H. Varela, Stabilizing nonstationary electrochemical time series, *J. Phys. Chem. C* 114 (2010) 22262–22268.