Journal of Electroanalytical Chemistry 780 (2016) 391–395

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Insights of glycerol electrooxidation on polycrystalline silver electrode

Nina Y. Suzuki, Patrícia V.B. Santiago, Thalita S. Galhardo, Wagner A. Carvalho,
Janaina Souza-Garcia *, Camilo A. Angelucci *

Universidade Federal do ABC, Centro de Ciências Naturais e Humanas, Av. dos Estados, 5001, Bairro Bangu, 09210-580 Santo André, SP, Brazil

ARTICLE INFO

Article history:
Received 20 July 2015
Received in revised form 23 November 2015
Accepted 11 February 2016
Available online 13 February 2016

Keywords:
Glycerol
Electrooxidation
Silver

ABSTRACT

This work presents a detailed study of silver electrode activity toward glycerol electrooxidation reaction (GEOR) in alkaline media. The effect of pH and glycerol concentration on GEOR kinetics was investigated by cyclic voltammetry technique. It has been found that hydroxyl ions concentration leads to an oxidation current increase, which indicates that glyceroxide could be the active species for GEOR. The presence of silver oxide layer inhibits the glycerol oxidation process, reaching maximum current densities of 2.3 mA cm^{-2} (1 M glycerol in 1 M NaOH). HPLC studies indicate that formic, glycolic and glyceric acids are the main products.

1. Introduction

Nowadays the demand for fossil and pollutant energy sources substitutes is growing fast. Biodiesel is an important alternative on this scenario with its production increasing each year. Biodiesel is produced by transesterification process of renewable biological sources, such as vegetable oils and animals fats, with a simple alcohol (ethanol or methanol) in acidic or alkaline media. During the biodiesel production, glycerol (GlyOH) is obtained as a byproduct on a proportion of 10:1. Even with a large number of applications, glycerol produced from biodiesel industries cannot be totally used and it has become a surplus on the market. This issue could be mitigated by using glycerol as feedstock in reactions targeted to produce higher value chemicals and the electrooxidation process presents a potential tool to this goal. Several works have been done in order to identify the best electrocatalyst. The most studied materials are gold [1–4], platinum [1,2,5–7] and palladium [8,9]. Some investigations using silver containing electrodes, such as AuAg [10], PdAg [9] and PtAg [11] showed promising results, however, only few works using pure Ag electrodes have been reported [10,12].

Avramov-ivić et al. [12] investigated the activity of bulk Ag electrodes toward glycerol electrooxidation reaction (GEOR). They observed higher oxidation currents compared to those obtained by methanol and ethylene glycol oxidation in the same potential range. The results showed that the GEOR takes place only in the oxide formation region. They also observed that the current decreases with the scan rate, however no investigation on the charge of the process was carried out [12]. On the other hand, Gomes et al. [10], using Ag nanoparticles as electrocatalyst, did not observe any currents related to GEOR.

In order to better understand the reactional mechanism of the GEOR on silver electrode, this work investigated the influence of the pH on the activity of bulk Ag electrodes for this reaction.

2. Experimental

The experiments were performed with an AutoLab potentiostat. The working electrode was a Ag small sphere prepared by melting the edge of silver wire (99,999%), as described by Clavilier et al. [13]. At this point the material is slowly cooled producing a polyoriented single crystal. The reference electrode used was a reversible hydrogen electrode (RHE) and a platinum wire was used as a counter electrode. All recorded current signals are presented in current density. The silver electrode was flame annealed before each experiment. The procedure was carefully done to avoid the melting and oxidation of the electrode. The different pH electrolytes were prepared from Sigma-Aldrich suprapur (99.99%) NaOH and ultrapure water (Millipore-MiliQ, 18.2 MΩ). The ohmic drop was compensated for each experiment [14]. The electrochemical cell was kept free from oxygen with Ar (5.0 analytical) atmosphere.

The electrolysis was carried out in pH 13 electrolyte and glycerol 0.1 M for 14 h. The working electrode was a 2.5 × 2.5 cm silver gauze, as well as the counter electrode. The potential applied was 1.125 V, which corresponds to the maximum current potential. The products' analysis was carried out using a HPLC chromatograph (Agilent 1220) equipped with ultraviolet (UV) and refractive index (RI) detectors. The reactant and the products were separated on an ion-exchange column (Hi-Plex H 7.7 × 300 mm – Agilent) heated at 338 K. The eluent

---

* Corresponding authors.
E-mail addresses: janaina.garcia@ufabc.edu.br (J. Souza-Garcia), camilo.angelucci@ufabc.edu.br (C.A. Angelucci).

http://dx.doi.org/10.1016/j.jelechem.2016.02.020
1572-6657/

was a solution of H_2SO_4 (0.005 M) and 20 μL of the sample was analyzed.

3. Results and discussion

3.1. Silver electrode electrochemical characterization

Prior the GEOR studies on silver, we performed an electrode characterization in the electrolyte solution with absence of glycerol species. Cyclic voltammetry technique is a useful tool to gather information of metal–solution interface and provide important data to understand the overall GEOR response on electrode surface.

The characteristic voltammetric behavior of Ag electrode in 0.1 M NaOH is presented in Fig. 1. Changes in the upper limit potential show the dependence of the reduction peaks, observed at 1.34 and 0.95 V (here identified as C1 and C2, respectively) with the oxidation processes from peaks A1, A2, A3 and A4 (at 1.16, 1.23, 1.36 and 1.71 V, respectively). Comparing the oxidation and reduction charges (Fig. 1c), it can be seen that peak C1 is related to the reduction of part of species oxidized in peak 4, but complete reduction can only be seen after reduction peak C2. These results are in agreement with previous reports that deeply investigated the behavior of Ag in alkaline media [15–23].

Sheng-li Chen and coworkers [20], using electrochemical quartz crystal microbalance (EQCM), showed that peaks A1, A2 and A3 correspond to the formation of Ag_2O, first in the superficial layer (A1), then in the layers below (A2 and A3). The authors did not identify the formation of AgOH during peak A1 as other authors suggest [15–18], however, they did not discard the possibility of its formation and fast conversion to Ag_2O. They also demonstrated that during peak A2, along with Ag_2O formation, there is the dissolution of a very small amount of Ag atoms, probably in the $Ag(OH)_2^-$ form. The process of peak A4 corresponds to the formation of AgO/Ag_2O_2 species [15–18,22,24].

During the experiments presented in Fig. 1 it was possible to observe some changes on the electrode surface and its behavior when it was submitted to potentials higher than 1.4 V, leading to the formation of AgO. Once this potential was applied, the electrode does not return to its original appearance and performance (it becomes opaque and yellowish), even after the complete reduction of the surface (peaks C1 and C2). These changes affected the electrode performance resulting on unstable voltammograms. If the electrode is continuously cycled until potentials higher than 1.4 V, an increase in the current density is observed due to the variation in the electrode active area because of structural surface changes by formation of silver oxides. The same behavior was observed by Kunze et al. [22].

In this work, despite the fact that high oxidation currents were observed in the oxide region (Figure SI-1), the upper limit potential was settled at 1.35 V, before the bulk oxidation, to guarantee the stability of the electrode surface. Working in this potential region allows the observation of oxidation currents that can be masked when cycling to more positive potentials because of the high currents from oxide formation.

3.2. Glycerol electrooxidation on silver electrodes

Fig. 2 presents the cyclic voltammograms (CV) of silver electrodes in different glycerol concentration. For the sake of comparison the CV in the absence of glycerol is displayed. As can be seen, the effect of glycerol concentration is directly evidenced in the current density response. The general features observed during the positive scan seem to be not influenced by GlyOH species increase. The GEOR onset (~0.7 V *vs.* RHE) as well as the peak potential (1.125 V *vs.* RHE) keep unaltered regarding the GlyOH concentration changes. In spite of the oxidation rates increase, around 1.2 V, the current densities response show a similar trend of peak A3 (blank CV), probably indicating the inhibition of GEOR in detriment of oxide silver formation.

During the negative scan, the current response of GEOR is overlapped with silver oxide reduction process as observed by the presence of the C2 peak. Followed by a faster current density increase and, from about 1 V, the negative scan matches the positive.

Observing the voltammograms, some questions regarding the relationship between peak A1 (formation of Ag_2O in the superficial layer) and the first glycerol oxidation peak may arise. In order to better understand this process, a new potential window was settled. An upper limit potential of 1.17 V was used, the end of the oxidation process of peak A1. Fig. 3 shows the voltammograms at this condition for three different glycerol concentrations as well as in the absence of glycerol.

Evaluating the data from Figs. 1 and 3, it is possible to see that there is a relationship between the end of the process of peak A1 and glycerol oxidation current decrease at all glycerol concentrations.

Since glycerol reacts with hydroxyl groups adsorbed at the electrode surface, based on data from Ag(111) Pourbaix diagram calculated by Hansen and coworkers [24], it is possible to suggest that, even if the existence of AgOH species is brief [20], it is enough to allow the oxidation of glycerol. After the first Ag_2O monolayer is complete, the GEOR is inhibited. At this point, there are no available sites for glycerol adsorption and subsequent oxidation, or the presence of OH adsorbed species, justifying the decrease of the glycerol oxidation current as shown on Fig. 3. This conclusion may seem different from that obtained by Avramov-Ivić et al. [12], however, the potential region studied by the authors is different from the one used here. In that case, the authors did not observe any activity for GEOR at lower potentials, possibly because the high bulk oxidation currents hid the glycerol oxidation currents. The

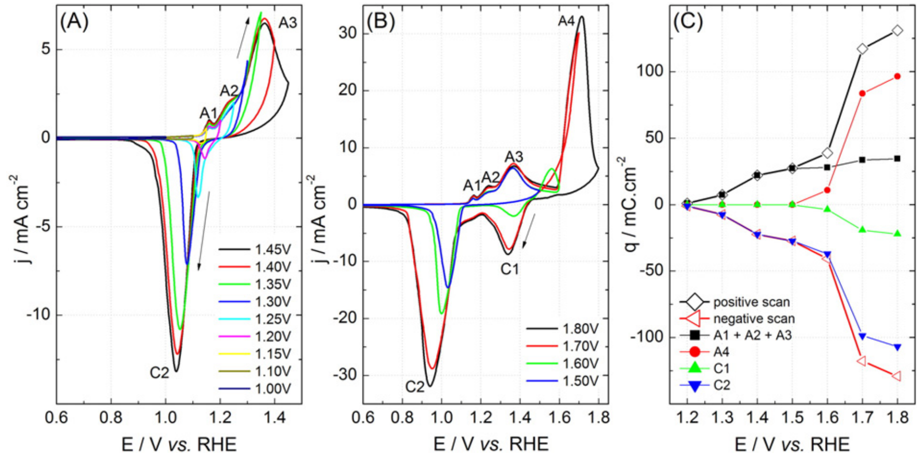

Fig. 1. Cyclic voltammogram of Ag electrode in 0.1 M NaOH, at 50 mV s^{-1}, with different upper limit potentials: 1.0–1.45 V (A), 1.5–1.8 V (B); (C) calculated charge for each cycle from (A) and (B).