

Voltammetric Comparison of the Electrochemical Oxidation of Toluene on Monolithic and Reticulated Glassy Carbon Electrodes in Aqueous Medium

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Abstract

The electrochemical oxidation of toluene in aqueous-acid medium was studied on monolithic and reticulated glassy carbon electrodes using cyclic voltammetry. The oxidation potential was 1.7 V for both electrodes. However, the normalized oxidation currents were higher on reticulated glassy carbon, showing more catalytic activity than on the monolithic glassy carbon. To normalize the obtained anodic current values, a method for the determination of the electrodes effective area was used, which consists in the underpotential deposition of a copper monolayer.

Keywords: electrochemical oxidation, toluene, aqueous-acid medium, monolithic and reticulated glassy carbon, effective area.

Introduction

The electrochemical oxidation of toluene on glassy carbon has been performed in organic medium and in aqueous-organic medium [1,2]. The effect of adding water to the organic solvent causes a cathodic shift in the oxidation peak; therefore, it favors the reaction of electro-oxidation. To counter the limitations of space-time low efficiency obtained in the electrochemical processes with two dimensional electrodes (monolithic glassy carbon (MGC)), three-dimensional electrodes have been used [3]. One of the most widely used three-dimensional electrodes is the reticulated glassy carbon (RGC), whose "honeycomb" structure of open pore allows it to have a high volume vacuum, high surface area and low flow resistance [4]. These features, along with the high electrical conductivity of

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the material allow the RGC to be an attractive electrode material for use in flow systems, where the volume of the cell, the electrode geometry and the time of experimentation are key variables to improve the efficiency of oxidation processes. Among the various electrochemical applications of this material, one of the best known is the generation of hydrogen peroxide via Fentons reagent for the treatment of industrial wastewater [5].

This paper presents the voltammetric study of the electrochemical oxidation of toluene in aqueous-acid medium on MGC and RGC electrodes. This comparison will allow evaluating the catalytic effect of both electrodes, as well as the effect of the effective area on the space-time efficiency in order to use a system in a state of flux. To test this, it is proposed a method to determine real areas, which consists of depositing a monolayer of copper at underpotential on the surface of the electrodes.

Methods and materials

Reagents

Analytical grade toluene 99.7% purity was used to the saturation concentration of 5 mM in 0.5 M H₂SO₄ (95-97% purity) as supporting electrolyte. The CuSO₄ was prepared at a concentration of 2×10^{-3} M in 0.1 M H₂SO₄. All solutions were prepared in ultrapure water (18 M Ω) and deoxygenated with N₂ before each experiment.

Cells and electrodes

Electrochemical studies were performed in a one compartment glass cell (16 cm³ capacity) at room temperature (22 ° C). A monolithic glassy carbon disk and a rectangular reticulated glassy carbon sheet were used as working electrodes, whose characteristics and properties are shown in Table 1. The reference electrode was Ag/AgCl (KCl saturated) and a platinum wire was used as counter electrode.

Table 1. Characteristics and properties of monolithic and reticulated glassy carbon used as working electrodes.

Electrode	Dimensions	Level of porosity (ppi)	Composition in weight *	Atomic composition *
Monolithic GC	Radius = 9 mm Geometric area = 0.636 cm ²	0	C : 93.26 % O : 6.74 %	C: 94.85 % O: 5.17 %
Reticulated GC	2.72 x 0.93 x 0.34 cm Geometric area = 279.52 cm ²	500	C : 80.43 % O : 19.57 %	C: 84.56 % O: 15.44 %

*The data of composition were determinate by X-ray dispersion spectroscopy (EDAX).

Instrumentation

The electrochemical measurements were done using a potentiostat / galvanostat coupled to a computerized system for data processing.

Voltammetric study of the electrochemical oxidation of toluene on glassy carbon electrodes

The electrochemical oxidation voltammograms of toluene 5 mM in 0.5 M H₂SO₄ were obtained at a scan rate of 10 mV/s with a potential window from 0 to 2000 mV vs. Ag/AgCl in both electrodes. The MGC was polished with alumina 0.5 micrometers and subjected to ultrasound for 10 min before each run. The RGC is soaked in pure ethanol for 2 hours to remove organic contaminants, and then stoked in concentrated H₂SO₄ for 2 hours and subsequent washing with ultrapure water between each stage. Before the run, the cleaning was complete with a cyclic voltammetry between +1000 and -1000 mV for 10 min; this allows removing adsorbed material and functional saturated groups. Finally, a -900 mV pulse for 10 minutes helps to reduce remaining traces of oxygen that are left at the electrode [6].

Determination of the effective area of glassy carbon electrodes. Deposition of a monolayer of copper at underpotential

The underpotential deposition of copper can take place on glassy carbon surface by different mechanisms depending on the glassy carbon type [7]. Herein the deposition of copper at underpotentials was carried out in both electrodes using a solution of CuSO₄ 2 x 10⁻³ M in H₂SO₄ 0.1 M. After purging the solution with N₂ for 5 min, the electrodes were polarized to 300 mV for 60 seconds to avoid having copper on the electrode surface at the moment of the deposition starting, then the potential is turned to a deposition potential (-60 mV) for 200 seconds to form the monolayer of copper, followed by a linear voltammetry of stripping from the deposition potential until it reaches 300 mV at 5 mV/s. It allows to oxidize the monolayer of copper deposited at underpotential [8]. The charge associated with the oxidation peak corrected with the charge adjusted to the background (H₂SO₄ 0.1 M) allows to calculate the effective area of the MGC electrode using the charge/area relation for a monolayer copper deposited on this material, which value is approximately 2 x 10⁻⁴ C/cm² according to Schmidt [9]. This procedure is repeated in the RGC and the charge associated to the oxidation peak allows to obtain a relation of charges between the two electrodes (Q_{RGC}/Q_{MGC}) which is equivalent to the effective area ratio (A_{RGC}/A_{MGC}), thus allowing to calculate the effective area of the RGC.

Results and discussions

Voltammetric study of the electrochemical oxidation of toluene on glassy carbon electrodes

Fig. 1 shows the corresponding voltammograms of the electrochemical oxidation of toluene in both electrodes. In both cases the observed peak potential is 1.7 V and for the oxidation wave on MGC and RGC respectively. This value is lower than the one reported by D'Elia L.F [1] in a mixture 70% aqueous - 30% organic with a value of oxidation potential 1.95 V. This confirms that water causes a cathodic shift in the oxidation potential of toluene, favoring the reaction of

electrooxidation. The absolute current of oxidation observed in the RGC is 65 times higher than in the MGC.

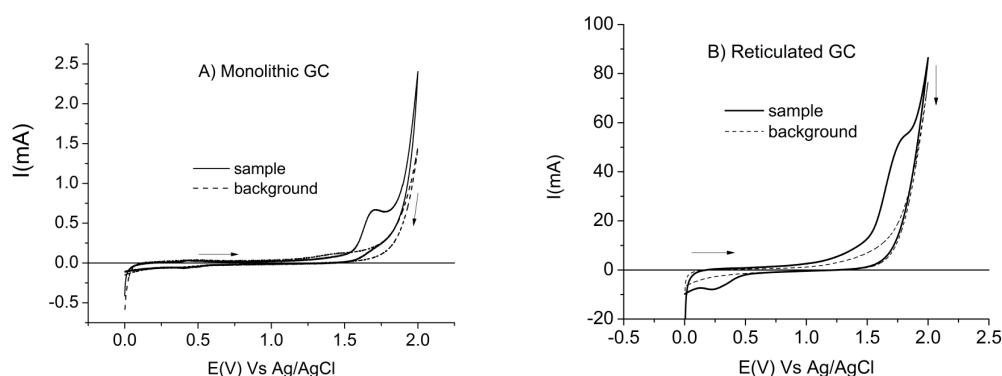


Figure 1. Voltammetric response of monolithic (A) and reticulated (B) glassy carbon electrode in toluene 5 mM dissolved in H_2SO_4 0.5 M. Scan rate 10 mV/s.

If we compare the ratio of geometric areas of both electrodes (439 times), it should be expected a current ratio similar to that value, so we can infer that normalizing currents with the geometrical area would not be appropriate, besides, there are diffusional limitations of the electroactive species to the entire electrode surface and the roughness of them also plays an important role in the effective area (see micrographs in Fig. 2 A and B). Therefore, it is necessary to develop a method that allows estimating the effective area, thus proving the catalytic effect of both electrodes. However, one can conclude that the use of RGC can oxidize the most quantity of toluene for the same cell volume (16 cm^3) and thereby improving space-time efficiency of the oxidation process, thus becoming a promising material for the oxidation of toluene in flow systems.

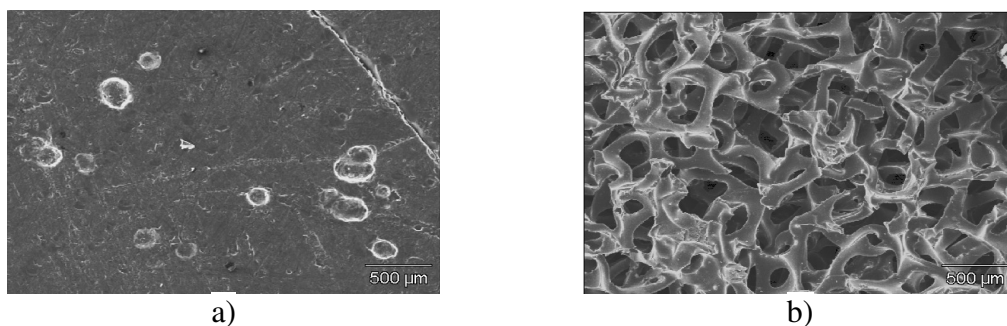


Figure 2. Electronic scanning micrographs of monolithic (a) and reticulated (b) glassy carbon. 500 μm approach.

Determination of the effective area of glassy carbon electrodes. Deposition of the monolayer of copper at underpotential

The voltammograms of Fig. 3 show the reduction peak of the copper deposit on the surface of both electrodes at -80 mV ; it is also noted the clear differences in the values of peak current, i.e., -0.17 mA and -13 mA , for the monolithic and reticulated glassy carbon, respectively, due to the differences in their effective

areas. In the backward scan it is shown the oxidation peak of the layers of stripped copper.

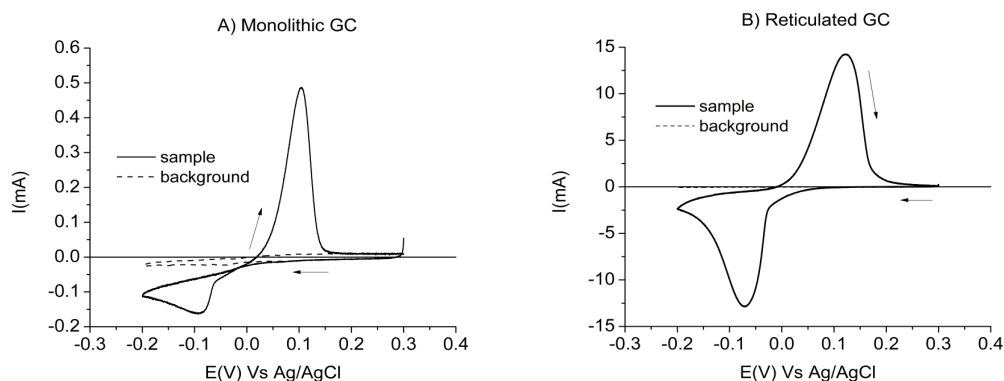


Figure 3. Voltammetric response of monolithic (A) and reticulated (B) glassy carbon electrode in CuSO_4 2×10^{-3} M dissolved in H_2SO_4 0.1 M. Scan rate 5 mV/s.

Effect of the underpotential deposition on the extent of copper in the electrode surface

Our purpose is to deposit a monolayer of copper at underpotential, so there is no possibility of three-dimensional growth of copper mass deposits. It is evidently clear that at potentials lower than -80 mV, the massive deposition of copper takes place. Between -70 mV and -60 mV the charge does not change in the monolithic glassy carbon, and between -80 mV and -40 mV in reticulated glassy carbon, indicating that the monolayer of copper is completely formed over the entire surface of the electrode and there is no contribution of mass deposit of copper. At potentials higher than -60 mV (monolithic GC) and -40 mV (reticulated GC) the charge is less, indicating that the monolayer is not fully formed (see Fig. 4).

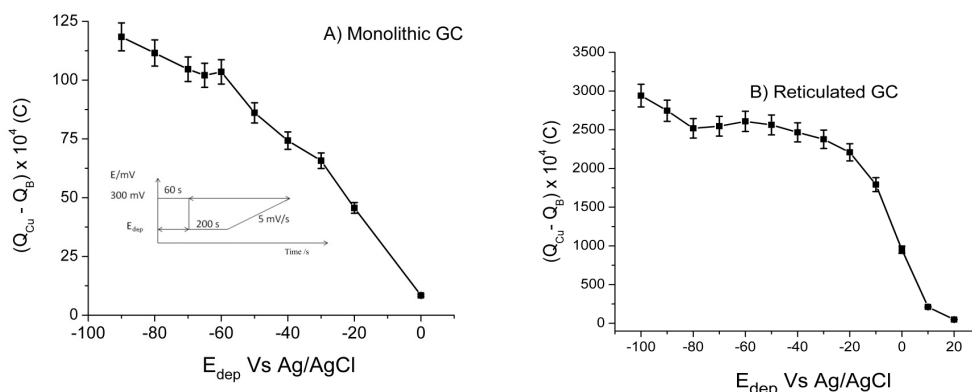


Figure 4. Total charge of oxidation of stripped copper as a function of deposition potential. A) on monolithic and B) on reticulated glassy carbon in CuSO_4 2×10^{-3} M diluted in H_2SO_4 0.1 M. Scan rate 5 mV/s. The insert shows the potential pulse program and stripping applied.

Effect of deposition time on the coverage of Cu in the electrode surface

The monolayer of copper is not deposited instantaneously and may require some time to be fully formed, so it is necessary to study the effect of deposition time on the total coverage of the monolayer. At short time is observed (Fig. 5) a significant increase of the charge of oxidation of copper deposited more intensely in the RGC than in the MGC, indicating the presence of more adsorption sites in the first. At long times, the charge remains constant indicating that the deposition process has been completed. In the MGC it has been reached a maximum charge of 102.08×10^{-4} C at 170 s, and in the RGC the maximum charge reached was 2113.06×10^{-4} C at 70 s. These charge values allow estimating the effective area of both electrodes which are shown in Table 2. With these data of effective area the oxidation currents of toluene can be normalized on both electrodes presented in the voltammograms of Fig. 1.

Table 2. Charges of oxidation of copper and real effective area of MGC and RGC electrodes.

Electrode	Charge $\times 10^{-4}$ (C)	Relation of charges (Q_{RGC}/Q_{MGC})	Real effective area (cm^2)
Monolithic GC	102.08	20.7	51.04
Reticulated GC	2113.06		1056.53

According to Fig. 6, the RGC electrode is more catalytic than MGC for the electrochemical oxidation of toluene in aqueous acid.

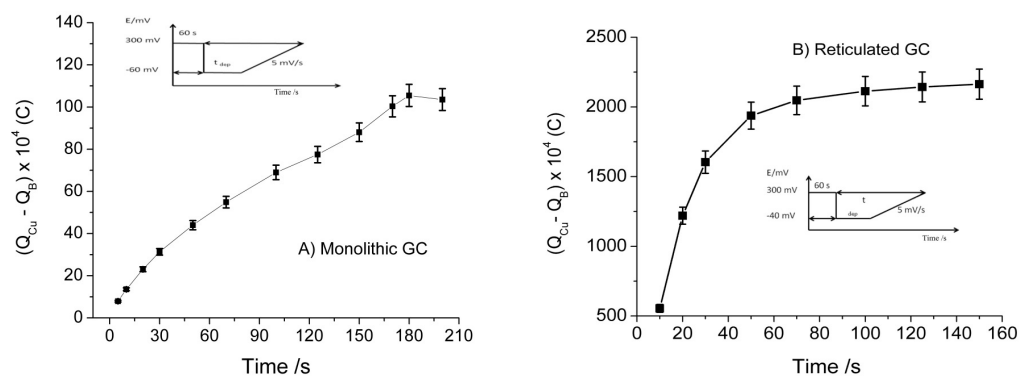


Figure 5. Total oxidation charge of stripped copper as a function of deposition time. A) on a MGC (potential of deposition -60 mV) and B) on RGC (potential of deposition -40 mV) in CuSO_4 2×10^{-3} M dissolved in H_2SO_4 0.1 M. Scan rate 5 mV/s. Insert shows the potential pulse and stripping programs implemented in both electrodes.

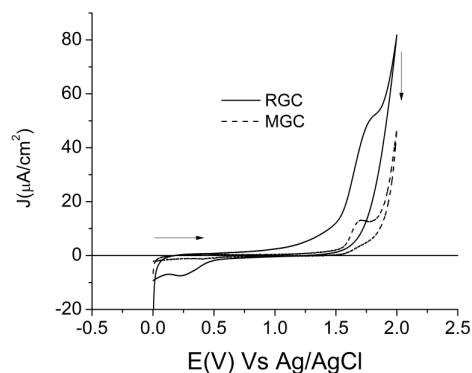


Figure 6. Voltammetric response of MGC and RGC electrodes in toluene 5 mM dissolved in H_2SO_4 0.5 M. Scan rate 10 mV/s. The current density was estimated using the real effective area of the electrodes. The real effective areas were 51.04 cm^2 for the MGC and 1056.53 cm^2 for the RGC.

Conclusions

The electrochemical oxidation of toluene in aqueous acid over MGC and RGC electrodes occurs at lower potential (1.7 V) in aqueous-organic systems. The large surface area of the RGC allows to oxidizing greater quantities of toluene per unit of reactor volume, thereby improving the efficiency of space-time process. The proposed method for determining the effective areas suggests that the RGC is more catalytic than the MGC for toluene oxidation in this medium.

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