

Short Communication

Synthesis of hydroquinone with co-generation of electricity from phenol aqueous solution in a proton exchange membrane fuel cell reactor



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ABSTRACT

In a proton exchange membrane fuel cell (PEMFC) an aqueous solution containing 100 mg L⁻¹ of phenol was oxidized at the anode using PtRu/C as catalyst while oxygen gas was reduced at cathode using Pt/C as catalyst. The use of a fuel cell as a flow reactor allowed obtaining hydroquinone, an important compound much used in medicine and cosmetic industry, as product with the co-generation of electricity. A conversion of 20% of phenol with the formation of 16 mg L⁻¹ of hydroquinone (80% of selectivity) was observed after 240 min of fuel cell operation at 80 °C.

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1. Introduction

Fuel cell power systems have received increased attention in recent years because of their potential for high fuel efficiency and lower emissions. Actually, the proton exchange membrane fuel cell (PEMFC) is an attractive energy conversion device. However, fuel cell type reactor for chemicals–energy cogeneration has become one of the new applications of PEMFC since it can be used as a reactor for selective hydrogenation/oxidation of organic compounds [1–4].

Selective oxidation is one of the most important reactions for fine chemical's synthesis. However, the designs of catalysts and reactor for selective oxidation are difficult because generally the complete oxidation is preferred instead of the selective one [5]. In this way, authors have used fuel cells as selective oxidation reactor for the partial oxidation of organic compounds as methane [2,3,5] and, sometimes, the reactor is possible to convert the energy of oxidation into electric power. Then, in such cases, there is a bi-functional reaction system and it is regarded as one of the chemicals–energy co-generation systems [5].

Tagawa et al. [5] used a solid oxide fuel cell system to the selective oxidation of methane. As this reactor could also convert the oxidation energy into electric power, they call it a chemical energy co-generation. Ishihara et al. [2] used the same reactor proposed by Tagawa et al. [5] for the simultaneous generation of synthesis gas and electric power.

Taking into account the partial oxidation, phenol is one of the most common organic water pollutants, produced in a large number of applications and its global production is estimated to reach 6 million tons per year [6–8]; however, while phenol is considered as a pollutant, hydroquinone, a product of the phenol partial oxidation, is an important chemical material and organic synthesis intermediate widely used in many fields such as in medicines, cosmetics, pesticides flavoring agents, among others [9–11].

Hydroquinone was first obtained in 1820 by Pelletier and Caventou by dry distillation of quinic acid [12] and until now it is widely used in the fields of medical, food, dye and photography chemicals [13]. Hansen et al. [14] proposed a new route to aromatic chemicals involving intermediacy of polyhydroxyaromatics derived from glucose. In their study, the centerpiece of the strategy was the discovery that catalytic hydrogenation of polyhydroxybenzenes followed by acid-catalyzed dehydration of the dihydro intermediates leads to loss of one oxygen atom from the starting polyhydroxy-benzene and the result was a new benzene-free synthesis of hydroquinone.

Accordingly to Shi et al. [15] and Yang et al. [16] catalytic hydroxylation of phenol is the most appropriate way for producing catechol and hydroquinone and compared to the homogeneously catalyzed reaction, the heterogeneously catalyzed hydroxylation with solid catalysts has attracted more interest due to favorable properties. Therefore, new heterogeneous catalysts are one of the most important current topics researches [15].

Many studies have revealed that noble metals such as Pd, Pt and Au supported on different supports possess high catalytic activities in a number of oxidation reaction. Thus, monometallic catalysts can be

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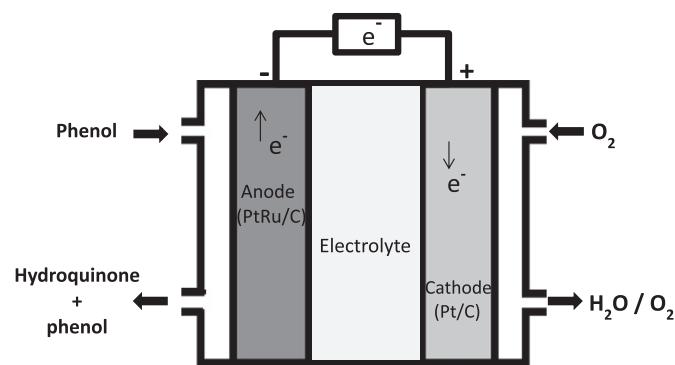


Fig. 1. Scheme of the fuel cell used as flow reactor to produce hydroquinone.

modified by adding a second metal in order to improve the oxidation of hydrocarbons [15,17].

Aiming the selective oxidation of phenol to hydroquinone and also the production of electricity, this paper proposes the use of a selective reactor, a PEMFC. It is important to stress that this is an example of chemicals–energy co-generation system since the generation of the hydroquinone will also produce electricity. For this study a Pt/C BASF® and a PtRu/C BASF® were used as cathode and anode of the PEMFC, respectively.

2. Experimental

The phenol conversion in hydroquinone was taken in a fuel cell with an area of 5 cm² used as flow reactor. The temperature was set at 80 °C for the fuel cell and 85 °C for the oxygen humidifier. All electrodes contained 1 mg of Pt per cm² in the anode or in the cathode. In these experiments, commercial Pt/C (20 wt.%) from BASF® was used in the cathode and PtRu/C atomic ratio 1:1 (20 wt.%) from BASF® was used in the anode. The electrocatalyst was painted over carbon cloth in the form of a homogeneous dispersion prepared using Nafion® solution (5 wt.%, Aldrich) and isopropanol (J.T. Baker). After the preparation, the electrodes were hot pressed on both sides of a Nafion® 117 membrane at 125 °C for 5 min under a pressure of 247 kgf cm⁻². Prior to use, the membranes were exposed to 3 wt.% H₂O₂, washed with distilled water and treated with 0.5 mol L⁻¹ H₂SO₄. The 100 mg L⁻¹ of phenol aqueous solution was delivered at 2.0 mL min⁻¹ through the anode and the oxygen flow was regulated at 500 mL min⁻¹ through the

cathode. The partial oxidation of phenol was taken using a potentiostat/galvanostat PGSTAT 302N Autolab and the chronoamperometry mode at 0 V for 4 h.

The phenol partial oxidation to hydroquinone was monitored using high performance liquid chromatography (HPLC) analysis. For HPLC analysis, the samples were first filtered through a Millipore 0.45 mm Durapore PVDF filter and then analyzed immediately following collection from the reactor (fuel cell). The phenol concentration was monitored using a HPLC Shimadzu 20A equipped with a monolithic C-18 column (100 mm × 4.6 mm, Phenomenex) at 40 °C, a mobile phase composed of methanol: 1% acetic acid solution (30:70, v/v) and a flow rate of 1 mL min⁻¹. The injection volume was 20 μL and the detection wavelength, 280 nm (PDA SPD-20A) [30]. The phenol and the hydroquinone concentrations were calculated by previously constructed analytical curves.

3. Results and discussion

Fig. 1 shows the scheme of the fuel cell used as flow reactor. By this figure the phenol was inset into the PtRu/C anode and the oxygen was inset into the Pt/C cathode. The flow of the electrons was taken by the anode to the cathode.

It is known from the literature that platinum is the best electrocatalyst for the oxygen reduction reaction [18–21] and it is also known that PtRu/C electrocatalysts present oxygenated species [18,22–25] that could contribute to the addition of the hydroxyl radicals into the phenol molecule and then to the electrogeneration of hydroquinone.

Fig. 2 shows the chromatograms of the aliquots taken during the four-hour period of the chronoamperometry realized at 0 V. By this figure it is possible to observe a peak at 2.9 min attributed to phenol and as the reaction proceeds, just one more peak appears (at 2.1 min) and gets more intensity during the 4 h experiment. Thus, the chromatograms suggest the formation of just one product, in other words, suggests a selective electro-synthesis.

Considering the literature about phenol oxidation it is known that phenol has an OH group in its structure which activates the *ortho* and *para* positions in the aromatic ring, however, the position *para* is preferred and in a medium containing hydroxyl radicals, hydroquinone and benzoquinone could be formed [26]. Then, in order to distinguish which product was formed during phenol partial oxidation, hydroquinone and benzoquinone were purchased from sigma and injected in the HPLC system at the same conditions. From this experiment it was possible to observe that benzoquinone yield a peak at 2.4 min, while

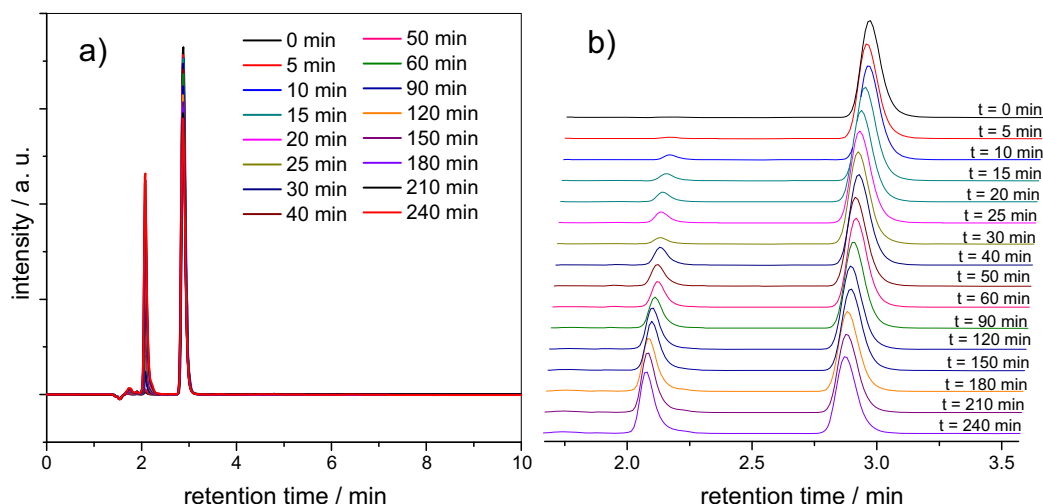


Fig. 2. a) Chromatograms of the different aliquots taken in the different times during the chronoamperometry. b) Zoom of the region between 1.5 and 3.5 min.

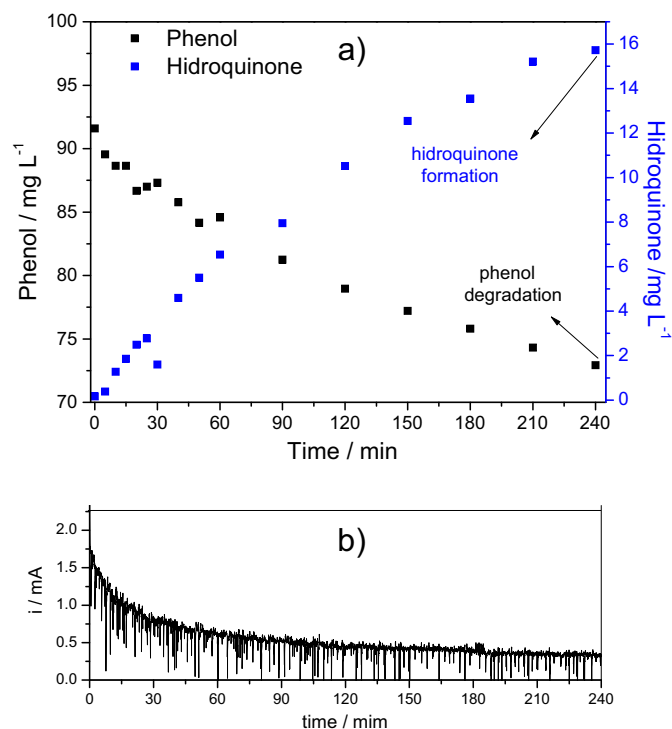


Fig. 3. a) Phenol degradation with the hydroquinone production during the 4 hour experiment. b) The electricity co-generation during the hydroquinone production.

hydroquinone yields a peak at 2.1 min. Then, the compound obtained during the phenol partial oxidation was just the hydroquinone.

Yoshida et al. [27] during the characterization of the microbial hydroxylation of hydrocarbon, found that some n-alkane-assimilating bacteria could hydroxylate not only aliphatic hydrocarbons but also aromatic compounds such as benzene or phenol. Moreover, they observed that when phenol was used as substrate, only hydroquinone was formed. Moreover, Sundaram et al. [28] observed that electrochemical reaction of phenol on carbon nanotubes modified glassy carbon electrode in neutral pH followed phenoxyl radical reaction mechanism along with generation and mobilization of hydroquinone.

Fig. 3a shows the phenol degradation with the hydroquinone production during the 4 hour experiment. Fig. 3b shows the electricity generation during this process. From Fig. 3a it is possible to observe the oxidation of phenol with the production of hydroquinone. Using the PtRu/C in the anode it was possible to observe the conversion of 20% of the phenol injected while 16 mg L⁻¹ of hydroquinone was produced yielding also electricity, as can be seen from Fig. 3b.

With this experiment we proposed a new methodology to produce hydroquinone from phenol selective oxidation. It is important to highlight that hydroquinone is a value-added product most used in medicine and cosmetics, while phenol is one of the most common organic water pollutants. Moreover, with the production of hydroquinone there was also the production of electricity. Most of the proposed ways to clean water uses energy [26,29–31] while using the fuel cell as selective reactor we could clean water producing energy.

4. Conclusions

In this work we described a new method to produce hydroquinone, a value-added compound much used in medicine and cosmetics, by the selective phenol oxidation using a PEMFC as reactor. This system can

also be called a chemical–energy co-generation since the production of hydroquinone generates electricity. Using the PtRu/C as anode it was possible to observe the conversion of 20% of the phenol with the formation of 16 mg L⁻¹ of hydroquinone yielding also electricity. This is a new methodology to reduce the contamination of industrial effluent generating a value-added product, hydroquinone, with also the co-generation of energy. Further studies are necessary to improve the generation of hydroquinone using different catalyst, improving also the power density of fuel cell used as reactor. This work opens the studies of co-generation of value-added products and energy, using the fuel cell as reactor.

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Appendix A. supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.catcom.2014.09.048>.

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