



# Process of phenol electrooxidation on the expanded graphite electrode accompanied by the *in-situ* anodic regeneration



P. Krawczyk\*, T. Rozmanowski, B. Gurzęda, M. Osińska

Poznan University of Technology, Institute of Chemistry and Technical Electrochemistry, ul. Berdychowo 4, 60-965 Poznań, Poland

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## ABSTRACT

The investigations reported in this paper, were devoted to electrochemical regeneration of spent expanded graphite (EG), carried out *in-situ* during the process of electrochemical oxidation of phenol. The electrochemical process of phenol oxidation followed by the anodic regeneration of EG electrode was investigated by cyclic voltammetry technique in electrolytes composed of 0.1 M phenol dissolved in 0.5 M and 6 M KOH. The obtained results undoubtedly revealed that, owing to the considerable potential lowering of electrochemical decomposition of water, the anodic oxidation of phenol in 6 M KOH partially proceeded within the potentials of violent oxygen evolution. The active oxygen and/or hydroxyl radicals, generated during oxygen evolution, impacted both as phenol oxidation supporting oxidants and as *in-situ* synthesized regenerating agents of spent electrode material. Owing to this feature, the established process may be continued during the consecutive cycles. The enhanced level of electrochemical activity of EG remains almost unchanged during the initial 3 cycles of voltammetric process of phenol oxidation. On farther scanning, the EG activity decreases reaching in tenth cycle activity on significantly higher level compared to the process performed in 0.1 M phenol in 0.5 M KOH. The higher activity of EG demonstrated in 0.1 M phenol in 6 M KOH is proved by the higher decline in phenol concentration and lower value of total organic carbon. It cannot be excluded that partial damage to the EG structure is responsible for the noted decrease.

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## 1. Introduction

It is widely known that phenol can be electrochemically oxidized to final products – CO<sub>2</sub> and water [1,2]. Taking into account the efficiency of process of phenol electrooxidation, the key step is the step in which, the tearing of aromatic ring accompanied by the formation of carboxylic acids takes place [2]. On the other hand, the formation of passive, insoluble and electrode surface covering, oligomeric film is widely recognized as a disadvantageous effect of electrochemical phenol oxidation on various types of electrodes [3–8]. The oligomeric layer hinders phenol access to active sites on electrode surface, disturbing the process or, in some cases, leading to its interruption. Since the process of oxidation cannot be continued, a regeneration of the spent electrode should be taken into consideration as an alternative solution for its effective reuse.

Among the methods, used for regeneration of carbon materials coated with phenols, electrochemical processes are also known [9–11]. Zhou and Lei revealed that active carbon loaded with p-nitrophenol, can be recovered by electrochemical decomposition of p-nitrophenol [9]. Highly effective regeneration was obtained due to the presence of

active agents, such as OH• radical and HClO, electrochemically generated in NaCl-containing electrolyte [10,11].

Our previous works have shown that the electrochemical methods can be considered for effective regeneration of spent expanded graphite (EG) electrodes without introduction of any additional chemical compounds, such as chlorine ions. Due to the reactions, occurring between evolved hydrogen [12] and oxygen [13] with oligomer coating of the electrode surface, the electrochemical activity of EG was restored and even considerably improved. The reported improvement has been explained in terms of the physical and chemical modification of the EG surface by KOH electrolyte, used for regeneration. The main disadvantage of the described method appears to be the necessity of the regenerated electrode to be moved from a regeneration reactor to a reactor for electrooxidation of phenol. The mentioned operation may be associated with the risk of partial deactivation of unstable species created on the electrode surface during its regeneration.

Therefore the purpose of the present work was to study the process of phenol electrooxidation, carried out in conjunction with *in-situ* performed anodic regeneration of expanded graphite electrode. The electrochemical investigations were conducted by the cyclic voltammetry technique in KOH solutions of different concentrations. The interpretation of electrochemical properties of EG was supported by an examination of

\* Corresponding author.

E-mail address: [piotr.krawczyk@put.poznan.pl](mailto:piotr.krawczyk@put.poznan.pl) (P. Krawczyk).

its structural properties (BET surface) and its surface chemical composition (XPS and FTIR analysis).

## 2. Experimental

### 2.1. Electrode material

The investigated expanded graphite (EG) was synthesized by thermal exfoliation of a stage-4 graphite intercalation compound with sulfuric acid (H<sub>2</sub>SO<sub>4</sub>-GIC). The exfoliation was performed in the air for 4 min at the temperature of 800 °C.

### 2.2. Electrochemical measurements

Processes of phenol electrooxidation with simultaneous regeneration of EG electrode were carried out by the cyclic voltammetry method in 0.1 M phenol, dissolved in 0.5 (sample EG-F-0.5) and of 6 M KOH (sample EG-F-6). Prolongation the potential scanning to 10 cycles allowed the examination of long-term electrochemical stability of *in-situ* regenerated EG (sample EG-F-6 × 10). The processes were conducted within the potential range:  $E_R \leftrightarrow 0.8$  V with a scan rate of 0.1 mV s<sup>-1</sup>. A three-compartment cell was composed of powder type EG electrode as a working electrode, Hg/HgO/0.5 M KOH electrode as a reference electrode (0.117 V vs. NHE) and graphite rod (5 mm in diameter) as a counter electrode. The mass of the working electrode was 15 mg. In order to examine the influence of KOH concentration on the electrochemical features of EG, measurements were performed in phenol-free KOH electrolyte under the above-mentioned conditions. The details of the working electrode construction can be found in our previous papers [12–15]. Electrochemical measurements were carried out, using an AUTOLAB potentiostat-galvanostat (model PGSTAT 30).

### 2.3. The properties of the EG electrode after phenol electrooxidation

Morphological properties of EG electrodes after the process of phenol electrooxidation was studied by scanning electron microscopy (SEM) (S-3400N, Hitachi microscope) using a voltage acceleration of electron beam equal to 15 keV.

Chemical composition of EG surface before and after phenol oxidation were determined by FTIR and XPS spectroscopy. FTIR measurements were performed with a BRUKER-model 113 V IR spectrometer, using the KBr technique, whereas the XPS investigations were conducted with VSW-Vacuum Systems Workshop Ltd. England, using a non-monochromatized Al K $\alpha$  radiation (1486.6 eV) operated at 15 kV and 200 W. Mathematical analysis of the achieved XPS spectra were calculated using XPSpeak 41 computer software. The binding energy scale was corrected by referring to the graphitic peak at 284.6 eV.

Specific surface area of EG before and after the processes of phenol electrooxidation were determined from the isotherms obtained by N<sub>2</sub> adsorption at 77 K with ASAP 2010 apparatus and calculated using the BET equation.

The decline in phenol concentration and total organic carbon determined in electrolyte after the electrochemical processes were the source of information on efficiency of phenol degradation. The examination of phenol concentration and soluble by-products were performed on HP5890II gas chromatograph using capillary column MXT-5 (Restek) 30 m × 0.28 mm × 0.25  $\mu$ m and flame ionization detector (FID), whereas the total organic carbon (TOC) was determined by TOC-L analyser (Shimadzu).

## 3. Results and discussion

### 3.1. Electrochemical oxidation of phenol

Cyclic voltammograms depicting the electrooxidation of 0.1 M phenol, dissolved in 0.5 M KOH at the EG electrode are presented in our

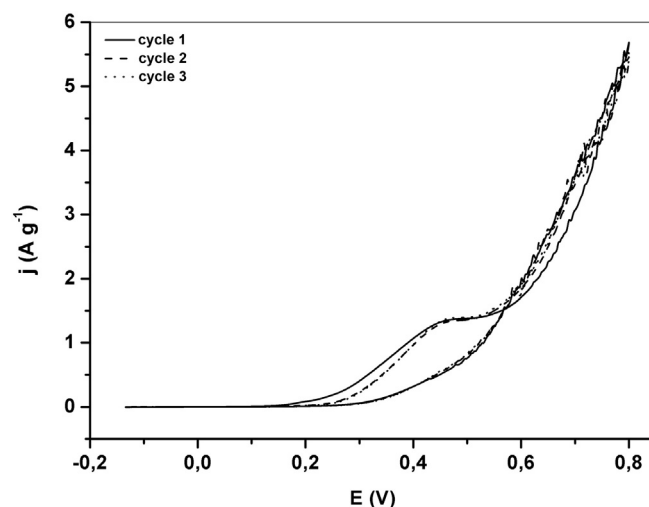


Fig. 1. Voltammetric curves recorded for EG in 0.1 M solution of phenol in 6 M KOH (1–3 cycles). Potential range:  $E_R \leftrightarrow 0.8$  V vs. Hg/HgO/0.5 KOH. Scan rate 0.1 mV s<sup>-1</sup>.

previous works [12,13]. As seen from these works, the peak intensity, as well as the current charge, fell down markedly after the first oxidation cycle, indicating a dramatic loss of EG electrochemical activity. For the first cycle, the peak charge was equal to 15.3 C, whereas for the second cycle, it was 7.8 C. The oligomer products of incomplete phenol oxidation, due to its features (electrochemical inactivity, very low conductivity), should be considered responsible for the deteriorating EG activity [12–15].

Our previous paper clearly showed the possibility to regenerate and even considerably improve the electrochemical activity of spent EG electrode [12,13]. In order to enhance the electrochemical activity of regenerated EG, the reactions between oligomer film and active oxygen, generated during anodic regeneration of spent EG were necessary [13]. The process of anodic regeneration depends on applied potential and concentration of KOH, used as the regenerating electrolyte. A high potential (1.3 V) as well as high concentration of KOH (6 M) appeared to be the proper conditions for violent oxygen evolution. Such a behavior facilitates an active oxygen and/or hydroxyl radicals production thus enhancing the efficiency of EG/oligomer regeneration [13].

In order to simplify the procedure of EG regeneration and to omit the risk of electrode deactivation, due to electrode movement after its regeneration, our present investigations were focused on phenol

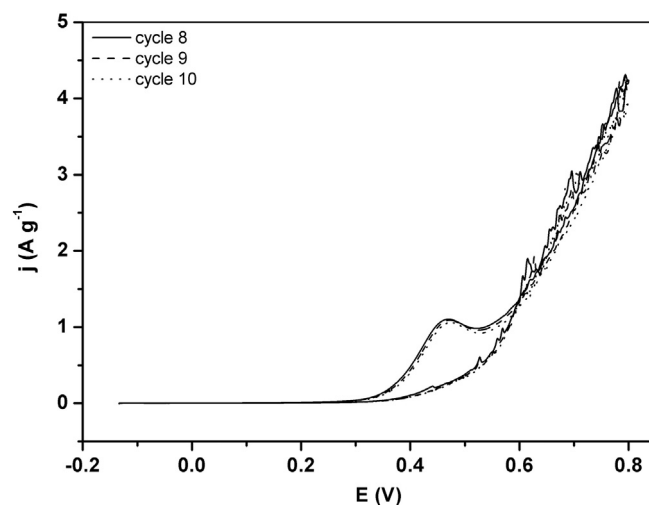


Fig. 2. Voltammetric curves recorded for EG in 0.1 M solution of phenol in 6 M KOH (8–10 cycles). Potential range:  $E_R \leftrightarrow 0.8$  V vs. Hg/HgO/0.5 KOH. Scan rate 0.1 mV s<sup>-1</sup>.

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