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J. M. Skowroński · P. Krawczyk

Electrooxidation of phenol at exfoliated graphite electrode in alkaline solution

Abstract The present paper reports on exfoliated graphite (EG) used for the cyclic electrochemical process of phenol oxidation in alkaline solution. It is shown that the electrochemical activity of anode-produced EG decreases considerably in the second cycle due to the deposition of an oligomer film, composed of the products of phenol oxidation, on the EG surface. Thermal treatment of the inactive graphite anode in air at 500 °C provided a regenerated material of activity three times higher for the first cycle and 2.6 times higher for three cycles as compared to the original anode. The reason for such a behavior is assigned to a carbon film formed on the EG surface during the carbonization/oxidation processes involving the products of phenol oxidation. Comparative studies showed that electroactivity of the original EG can also be enhanced if before the process of phenol oxidation the original EG is activated by heat treatment. Unfortunately, the electrochemical activity of the product of such a treatment is higher only for the first cycle of phenol oxidation and drops dramatically in the following cycles.

Introduction

Exfoliated graphite (EG) is a product of the process of exfoliation of graphite intercalation compounds (GICs). Exfoliation of GICs can occur due to the phase transition

J. M. Skowroński (✉) · P. Krawczyk
Institute of Chemistry and Technical Electrochemistry,
Poznań University of Technology,
ul. Piotrowo 3, 60-965 Poznań, Poland
E-mail: jan.skowronski@put.poznan.pl
Tel.: +48-61-6653641
Fax: +48-61-6652571

involving the thermal decomposition of intercalate layers in GICs by evaporation of intercalate, and the process of exfoliation results an expansion of up to a hundred times of graphite along the c axis. In addition to the most often used thermal method [1], EG can also be easily obtained using electrochemical [2, 3] and chemical methods [4]. The physicochemical features of EG are significantly different, as compared to the properties of the host GIC used for exfoliation. The modified porosity, high adsorption capability, high temperature resistance and low density are the properties that make EG so attractive in many areas of science and industry. If part of the intercalate persists in the graphite structure after the process of exfoliation, the compound obtained is called an exfoliated graphite intercalation compound (EG-GIC) [4]. The physicochemical features of EG-GIC are derivative properties of both the original GIC used for exfoliation and pure exfoliated graphite. Owing to its properties, exfoliated graphite is applicable in many technical fields, such as high temperature gaskets, seals, packing, fire extinguisher agents, thermal insulators and composite filler [5, 6]. Recently, a very important application of EG has been found in ecology, e.g., as sorbents of heavy oils and other heavy hydrocarbons from waste water [7, 8, 9, 10, 11].

The process of phenol oxidation is very interesting from the ecological point of view. Waste waters from industries, such as petrochemical, chemical and pharmaceutical and others, which contain phenolic compounds are the most dangerous, especially for human life. There is a need to develop effective method of purification of phenolic waste water. Among various methods used for the removal of phenol from aqueous wastes, oxidation techniques, involving electrochemical oxidation, seems to be effective and economically attractive [12, 13, 14, 15, 16, 17, 18, 19]. During the process of phenol electrooxidation a passive layer, composed of polymer products of phenol oxidation, forms on the electrode surface and its presence gives rise to a significant decrease in electrode activity. This phenomenon has been observed for many kinds of

electrodes, e.g., platinum [12, 13, 14], platinum/gold [15], carbon fiber [18] and glassy carbon [19].

Recent studies concerning the regeneration of carbon materials, mostly active carbons covered with adsorbed organic species, have dealt with thermal methods of regeneration [20, 21, 22, 23, 24, 25, 26, 27]. It has been pointed out that, under optimized conditions of regeneration, the original characteristics of carbon materials can easily be restored and even improved. Depending on the temperature at which the regenerations are performed, the removal of adsorbed compounds from carbon materials involves such processes as evaporation of water, thermal desorption of volatile compounds, pyrolysis and the formation of carbon char (carbonization). Besides the thermal regeneration of carbon materials, chemical [20, 21, 22, 23, 24, 25, 26, 27], catalytically assisted chemical methods [24, 27], photocatalytic [24, 28] and electrochemical methods [24, 26] have also been reported.

Our preliminary investigations on the electrochemical properties of exfoliated graphite have shown [29] that this material can be considered as an active electrode material for the anodic oxidation of phenol. However, as in the above examples, a passive layer composed of oligomer compounds is formed on the EG surface during the first oxidation step. The presence of non-active and adhesive film brings about an abrupt decrease of its electrochemical activity, and its activity in subsequent steps of phenol oxidation is very poor. A similar effect of deactivation has been reported earlier for electrochemical oxidation of phenol with the use of a platinum electrode [12, 13] and a glassy carbon electrode [19].

In this work, the process of electrochemical oxidation of phenol on thermally regenerated EG, previously covered with oligomer products of phenol oxidation, is investigated. The electrochemical removal of phenol from alkaline solutions occurring on an exfoliated graphite electrode followed by its thermal regeneration is for the first time examined. The intention of this work is not to determine the activity of exfoliated graphite in comparison with other materials, especially active carbons, but to show how thermal treatment of exfoliated graphite used in the process of phenol oxidation enhances its activity considerably over that of the starting EG, and simultaneously provides a composite material of higher resistance to deactivation. The anodic charge calculated from voltammetric curves recorded in the potential range of phenol oxidation was taken as a
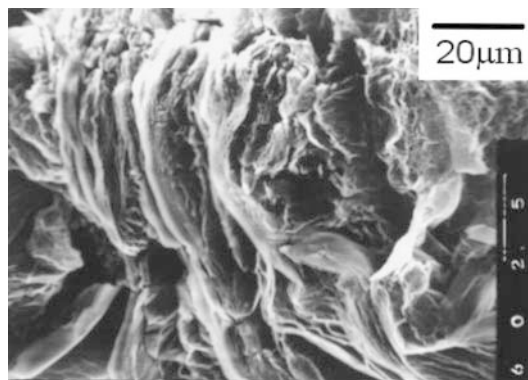

Fig. 1 SEM micrograph of exfoliated graphite

measure of the electrochemical activity of the EG electrode. This method allowed us to assess the changes in electrochemical activity arising from thermal treatment of electrode material.

Experimental

Exfoliated graphite used as the electrode material was prepared by thermal decomposition of graphite intercalation compound with sulfuric acid (H_2SO_4-GIC) at 800 °C for 5 min. A scanning electron micrograph of exfoliated graphite is presented in Fig. 1. H_2SO_4-GIC was synthesized by anodic oxidation of graphite in 18 M H_2SO_4, according to the procedure described earlier [30]. H_2SO_4-GIC was rinsed with water and subjected to decomposition. The specific surface area and average pore diameter of exfoliated graphite (before and after electrochemical and thermal treatments) were determined from the isotherms obtained by N_2 adsorption at 77 K. The data obtained are given in Table 1.

Cyclic voltammetry measurements with a scan rate 0.1 mV/s were performed in the potential range from the rest potential of electrode (E_R) to 0.8 V using a 0.5 M aqueous solution of KOH containing 0.1 M phenol. Similar to experiments reported in [12, 13, 14, 15], a relatively high concentration of phenol was used to avoid the influence of the change in phenol concentration at the electrode–electrolyte interface on the kinetics of the electrochemical process upon cycling. Because preliminary experiments showed that for a chosen concentration of phenol stirring the solution had no effect on the character of voltamograms recorded during three cycles, further measurements were performed in stationary electrolyte. After starting the measurements, the potential was swept from E_R in the positive direction. Voltammetric curves shown in Fig. 5 were carried out in a blank 0.5 M aqueous solution of KOH in the potential range $-0.8 \leftrightarrow 0.5$ V. To reveal the reactions arising from surface functional groups originally present on the EG particles, after starting the measurements at E_R, the potential was varied in the negative direction. All the potentials on the presented voltammograms are referred to the Hg/HgO/0.5 M KOH

Table 1 Specific surface area and average pore diameter of examined samples

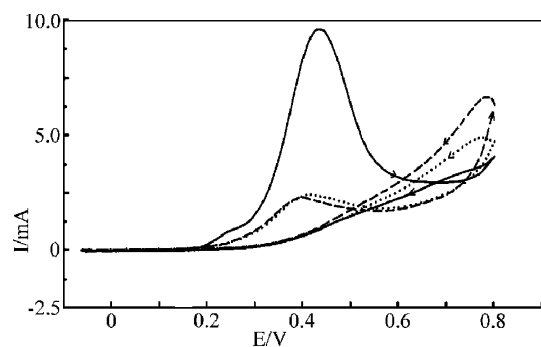|	Original EG	EG after phenol oxidation	EG regenerated for 1 h at 500 °C	EG regenerated for 2 h at 500 °C	EG activated for 1 h at 500 °C
Surface area (m^2/g)	30.9	7.5	29.5	30.1	35.8
Average pore diameter (nm)	9.0	9.2	10.6	10.0	9.2

electrode. In each case the mass of the working electrode was equal to 30 mg. The powder type working electrodes were prepared according to the following procedure. Exfoliated graphite was placed in a pocket made of porous polymer material, in which a graphite rod (5 mm in diameter), playing the role of current collector, had previously been inserted. The contribution of the graphite rod to the oxidation charge of phenol is negligibly small compared with that of a complete electrode containing the EG particles. A similar graphite rod was used as a counter electrode. The reference electrode was connected to the solution under investigation by a Luggin capillary. Before starting measurements the working electrode was equilibrated at an opened circuit for 1 h. After the electrochemical process of phenol oxidation, the EG sample was removed from the electrolytic cell, rinsed with distilled water and air dried. Electrochemical measurements were performed using an AUTOLAB potentiostat–galvanostat (model PGSTAT 30). Phenol used as reagent was purchased from LACHEMA (puriss. > 99.5 wt.%).
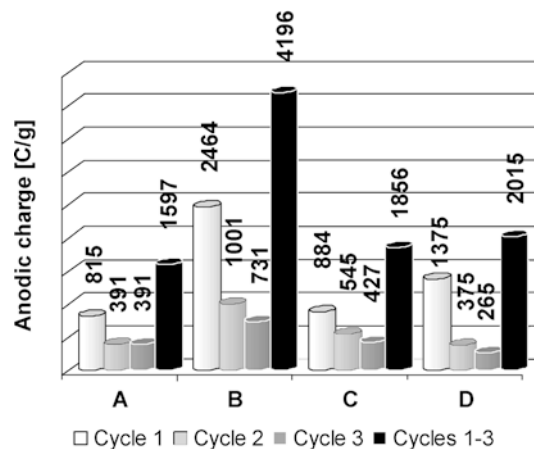
Thermal regeneration of exhausted EG was carried out in muffle furnace at a temperature of 500 °C in air. The process of regeneration was started after EG was inserted into the cold furnace and sample was kept at the chosen temperature for 1 and 2 h. For comparison, the original EG was heat treated in the same temperature in air.

Results and discussion

Figure 2 displays cyclic voltammograms recorded in a 0.1 M solution of phenol in 0.5-M KOH for the original EG. For the first cycle, a large peak with anodic charge 815 C/g, corresponding to phenol oxidation is observed at the potential around 0.43 V. The amounts of anodic charges recorded during electrochemical phenol oxidation for the original and modified EG anodes are also gathered in Fig. 3. As can be seen in Fig. 2, an abrupt decrease in intensity of the current peak observed for the second and third cycle can be related to the loss of electrochemical activity due to the formation of a passive oligomer film on the EG surface during the first oxidation cycle. Such an explanation agrees with the fact that no reduction peak is recorded after the polarization direction is reversed. As reported earlier [12, 13, 14, 15, 18, 19], phenol electrooxidation can result in the formation of passive polymer products which makes the electrode inactive. The formation of such a layer is proven here by a four-fold decrease in the BET surface

Fig. 3 Comparison of anodic charges recorded during electrochemical phenol oxidation for the original and modified EG anodes. **A** the original EG; **B** EG regenerated at 500 °C for 1 h in air; **C** EG regenerated at 500 °C for 2 h in air; **D** EG activated at 500 °C for 1 h in air
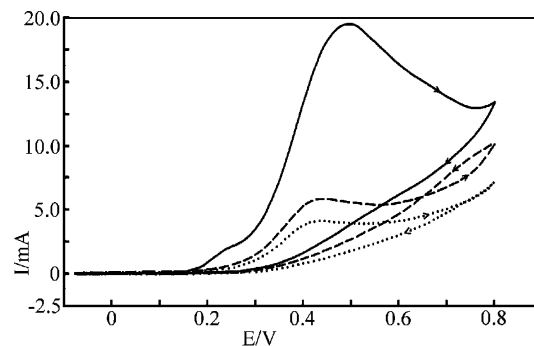
Fig. 4 Cyclic voltammograms recorded in 0.1 M phenol in 0.5 M KOH for the exhausted EG treated at 500 °C for 1 h: —, cycle 1; ---, cycle 2; · · ·, cycle 3. Potential range: $E_R \leftrightarrow 0.8$ V

area measured for the EG after one cycle of phenol oxidation (Table 1). The presence of a non-conductive layer on the EG surface may account for the worsening of electrochemical activity in the second cycle. A considerable decrease of the anodic peak at 0.43 V for the second cycle, and the appearance of an anodic peak at 0.78 V for the second and third cycle during the negative run, suggest that the electrochemical properties of EG are markedly altered after the first cycle of phenol oxidation. The peak at 0.78 V is associated with both the consecutive reactions of phenol oxidation and the oxidation reaction of oligomer products formed on the EG surface during the first cycle of phenol oxidation. Because the oligomer film gives rise to a drastic decrease in electrochemical activity of EG in the process of phenol oxidation, before reuse of EG its regeneration must be performed.

Figure 4 displays cyclic voltammograms recorded in phenol-containing electrolyte for EG regenerated at 500 °C for 1 h. Before thermal regeneration EG was

Fig. 2 Cyclic voltammograms recorded in 0.1 M phenol in 0.5 M KOH for the original EG: —, cycle 1; ---, cycle 2; · · ·, cycle 3. Potential range: $E_R \leftrightarrow 0.8$ V
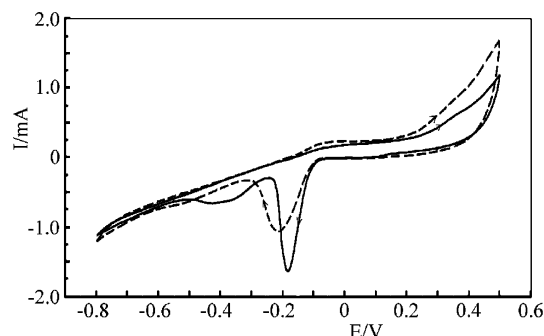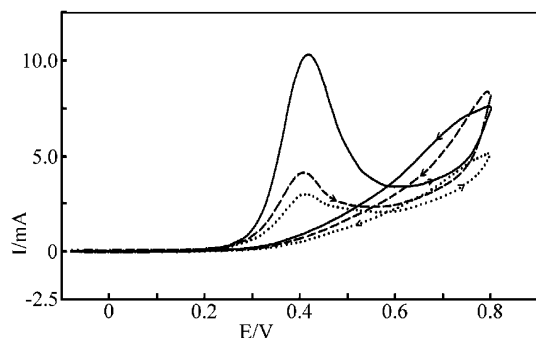
Fig. 5 Cyclic voltammograms recorded in 0.5 M KOH in the potential range for EG regenerated at 500 °C for 1 h in air (—) and for EG activated at 500 °C for 1 h in air (---). Potential range: $-0.8 \leftrightarrow 0.5$ V

used as the working electrode in the process of phenol oxidation carried out for one complete cycle ($E_R \leftrightarrow 0.8$ V). As seen in Table 1, the oligomer film formed on the EG surface during one cycle of phenol oxidation resulted in a decrease in surface area from 31 m^2/g for the original EG to 7.5 m^2/g for the EG/oligomer composite. It is known that the process of phenol electrooxidation can proceed according to two possible pathways: (a) the formation of passive polymer products, which make the electrode inactive, and (b) the formation of quinonic compounds, which undergo a subsequent oxidation giving final products CO_2 and water [12, 13, 14, 15, 26]. Contrary to the results of studies performed at low pHs, where processes start from the formation of phenoxy radicals, the formation of phenolate ions is the first step of the process occurring in alkaline solutions. From a comparison of voltammograms presented in Figs. 2 and 4, recorded for the original EG and EG regenerated at 500 °C, respectively, some differences in the mechanism of phenol oxidation can be seen. For the first cycle the maximum of the current peak corresponding to the phenol oxidation on the regenerated EG electrode (Fig. 4) is positioned at about 0.5 V and is shifted toward positive potentials, as compared to the peak recorded for the original EG electrode (Fig. 2). After thermal regeneration a large anodic peak associated with phenol oxidation is broader and asymmetric. It suggests that changes in chemistry and porosity at the EG surface resulting from heat treatment of the EG/oligomer composite determine the mechanism of reactions. Such an assumption is supported by voltammograms obtained in KOH solution free of phenol for activated and regenerated EG (Fig. 5). Cathodic peaks recorded instantly after starting the measurements in the negative direction can simply be attributed to the reduction of oxygen functional groups present on the graphite surface. As can be seen from this figure, the peak observed for the regenerated EG is narrower and positioned at more positive potential (-0.19 V) as compared to that arising from the reactions proceeding on the activated EG (-0.21 V). In addition, a broad cathodic peak at a potential of about -0.4 V is observed only for the regenerated EG. A high activity

noted for regenerated EG may be related to an enriched amount of active sites of lowered activation energy for the reaction of phenol oxidation. Because the reduction peak at -0.4 V appears only on voltammograms for the regenerated EG, it is reasonable to infer that oxygen groups are formed on the EG surface during heat treatment due to the decomposition of oligomer film.

The differences in electrochemical activity of the original and regenerated EG can be easily demonstrated by comparison of the peak charges in Figs. 2 and 4. The charge of the peak at 0.5 V for regenerated EG (2,464 C/g) (Fig. 4) is three times higher than that measured for the original EG (815 C/g) (Fig. 2). The enhancement of electrochemical activity after the regeneration process is also observed for the subsequent cycles (Fig. 3). As seen from this figure, the peak charge for the third cycle of regenerated EG even exceeds the total charge collected for the second and third cycle of the original EG. This observation indicates that during heat treatment of the EG/oligomer composite at 500 °C the decomposition of the oligomer film occurs with simultaneous modification of the EG surface. It is very likely that such a modification results in the increased amount of surface oxygen groups produced due to simultaneous oxidation of the exfoliated graphite substrate and carbon film formed on the EG surface due to carbonization of the oligomer film. It is well known that the process of carbonization occurs when carbon materials filled with organic compounds are subjected to heat treatment at about 500 °C [20, 23, 24, 27]. Shter et al. [27] have reported that during thermal treatment at temperatures up to 400 °C in air, phenol-covered activated carbon fibers undergo such processes as phenol desorption from the outer surface of fibers, the formation of heavier intermediate non-volatile compounds (oxidative coupling reactions), whereas above 400 °C complete combustion occurs. Contrary to this behavior, instead of phenol adsorbed on activated carbon, during our investigations EG is covered with oligomer products of phenol oxidation and the composite obtained is subjected to thermal regeneration. A high resistance of EG to oxidation made the use of higher temperatures possible. As seen from Table 1, the surface area of EG regenerated for 1 h at 500 °C remained close to that for the original EG, but noticeable increase in average pore diameter took place after regeneration. This change may be related to the presence of carbon film formed on the EG surface.

The influence of the regeneration time on the electrochemical activity of regenerated EG in the process of phenol oxidation can be revealed by comparison of Figs. 4 and 6. Figure 6 shows cyclic voltammograms recorded in phenol-containing electrolyte for EG regenerated at 500 °C for 2 h. From comparison of Figs. 4 and 6, one can infer that the anodic charge related to phenol oxidation decreases significantly as the regeneration time is expanded from 1 to 2 h. The charge of the oxidation peak measured for the first cycle of EG regenerated for 2 h (884 C/g) is similar to that noted for the original EG (815 C/g) and is 2.8 times lower than
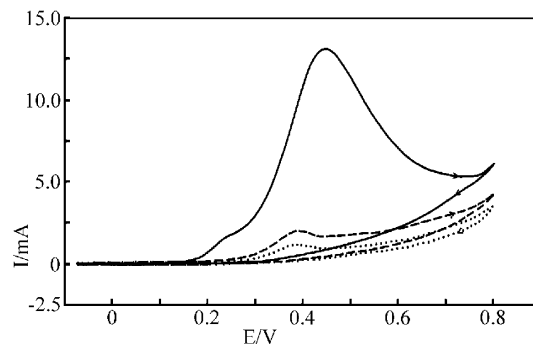
Fig. 6 Cyclic voltammograms recorded in 0.1 M phenol in 0.5 M KOH for the exhausted EG treated at 500 °C for 2 h: —, cycle 1; ---, cycle 2; · · ·, cycle 3. Potential range: $E_R \leftrightarrow 0.8$ V

Fig. 7 Cyclic voltammograms recorded in 0.1 M phenol in 0.5 M KOH for the activated EG treated at 500 °C for 1 h: —, cycle 1; ---, cycle 2; · · ·, cycle 3. Potential range: $E_R \leftrightarrow 0.8$ V

that for the EG regenerated for 1 h (2,464 C/g). It shows that 2 h of regeneration is too long to preserve the carbon film on the EG surface in an oxidizing atmosphere.

To ascertain the influence of carbonized oligomer film on the improvement of electrochemical activity of regenerated EG, before the reaction of phenol oxidation, the original EG was heat treated at 500 °C for 1 h in air and after such an activation was examined electrochemically in the electrolyte containing phenol. Voltammograms obtained for activated EG are illustrated in Fig. 7. The results summarized in Fig. 3 show that the anodic charge calculated for the first cycle of activated EG is 69% greater then that for the original EG. To understand this increase in electrochemical activation it is reasonable to note that heat treatment of the original EG gives rise to a 16% development of surface area (Table 1). On the other hand, it must be emphasized that for the first cycle the anodic charge of activated EG is only 56% of that for regenerated EG (Fig. 3). A great drawback of activated EG is that its activity declines the most rapidly upon cycling. From the view of a long-term use of EG, the total anodic charge measured for three cycles of phenol oxidation is the highest for EG regenerated for 1 h. The electrode prepared from this graphite is 2.6 and 2.1 times more active than the electrode prepared using the original EG and activated EG, respectively.

The above discussion leads to the conclusion that the oligomer film formed on the EG surface is responsible for an enhancement of electrochemical activity of regenerated EG. Its electrochemical activity can be attributed to an increased amount of oxygen functional groups present on the surface of the carbon/carbon composite. From the results obtained it is evident that the chemical structure of oxygen functional groups following electrochemical activity depends on whether or not the process of phenol oxidation was performed before heat treatment of exfoliated graphite. This conclusion is consistent with differences in voltammograms obtained in the electrolyte free of phenol for the regenerated and activated EG (Fig. 5). It is worth noting that during the regeneration of exhausted EG for 1 h a significant increase in average pore diameter took place

(Table 1). This structural parameter changed in the following order: regenerated EG > activated EG > original EG. The higher value of average pore diameter for the regenerated EG makes the access of phenol molecules to active sites easier.

Conclusions

Taking into account the fact that oligomer products are formed on the electrode surface during phenol oxidation in alkaline solution, in the present work phenol electrooxidation was examined on a new type of electrode made of exfoliated graphite and the process of regeneration of exhausted electrode material was carried out by heat treatment at 500 °C in air. As a result of this process, the electrochemical activity of regenerated EG samples not only attained that of the starting material but exceeded it by up to three times. The improvement was noted both for the first cycle of phenol oxidation and for the three cycles examined. This result shows the material examined and the regeneration method to be worthy of further study to understand the mechanism of the regeneration process and, as a consequence, to improve the electrode material. An insight into the crystalline, porous and chemical structure of the product of regeneration allows one to reveal the factors responsible for enhanced activity of regenerated EG. At this stage of investigations, it is reasonable to assume that the increase in electrochemical activity of regenerated EG over that of the original EG is associated with the formation of a carbon/carbon composite composed of the EG substrate coated with an active carbon layer produced by carbonization of the oligomer film. Comparative studies showed that the electroactivity of the original EG can also be enhanced if before the process of phenol oxidation the original EG is activated by heat treatment in air. Unfortunately, the activity of such a material is higher only for the first cycle of phenol oxidation and drops dramatically in the following cycles.

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