Effect of Anodic Pretreatment on the Performance of Glassy Carbon Electrode in Acetonitrile and Electrooxidation of Para-substituted Phenols in Acetonitrile on Platinum and Glassy Carbon Electrode

László Kiss[1,2*], Sándor Kunsági-Máté[1,2,3]

[1] Department of General and Physical Chemistry, University of Pécs, H-7624 Pécs, Ifjúság street 6, Hungary
[2] János Szentágothai Research Center, Pécs H-7624, Ifjúság útja 20, Hungary
[3] Department of Pharmaceutical Chemistry, University of Pécs, H-7624 Pécs, Rókus street 2., Hungary
* Corresponding author, e-mail: kissl@gamma.ttk.pte.hu

Abstract

In the first part of the work electropolymerisation of phenol was studied at glassy carbon electrode. Rapid fouling of its surface indicated the formation of coherent poly(phenyleneoxide) layer which was demonstrated by the repeated cyclic voltammetric scans. Effect of anodic pretreatment potential in acetonitrile solvent was also investigated and the results showed that at potentials higher than 2 V glassy carbon electrode becomes deactivated. Preanodisation of glassy carbon electrode at 3 V in acetonitrile resulted in diminished anodic peak currents by phenols. It was due to the partial deactivation of electrode surface and its extent increased with the pretreatment time. The electrooxidation of para-substituted phenols (p-Cl-phenol, p-NO$_2$-phenol, p-tertbutylphenol, p-methoxyphenol) in acetonitrile resulted in no fouling layer on platinum electrode and the peak currents were significantly higher than in the first scan of unsubstituted phenol in the same concentration. Glassy carbon deactivated continuously by repeating the scans due to the solvent and bonding of products on the surface.

Keywords

phenols, acetonitrile, polymerization, electrochemistry, oxidative coupling

1 Introduction

There are a large number of articles focusing at the pretreatment of glassy carbon electrode but mainly in aqueous solutions. Preanodisation and precathodisation changes its surface as oxygen containing functional groups will be present on it [1-5]. These modifications enhance the usefulness of the electrode as the detection limit can be lowered significantly. A few reports can be found in the literature aiming the exploration of the effects of electrochemical pretreatment of glassy carbon electrode in dry nonaqueous solvents [6]. As acetonitrile is an appropriate solvent for characterizing the electrooxidation of a vast number of compounds due to its wide potential window, the use of platinum electrode is suitable in these investigations due to its stability in nonaqueous media. The different carbon based electrodes perform in many cases identical behavior so glassy carbon was investigated in this work in acetonitrile polarized to higher anodic potentials

in case of some selected electroactive compounds, especially phenols.

It is generally observed that most of one hydroxyl group containing phenols deactivate the surface of commonly used electrodes in most of the solvents [7-14]. It is interesting in many respects for example electrodes can be modified according to the application like size exclusion properties and corrosion protective layers. On the other hand, their voltammetry is markedly different in the different solvents and on electrodes made from different materials. Their electrochemical behavior can be significantly different depending on the number of hydroxy groups. In case of many quinones, only oxidative dehydrogenation reaction occurs. The steric hindrance caused by larger substituents alters the electrochemical behavior of phenols with one hydroxy group due to the prevention of the undesired coupling of radicals which form continuously during the anodic oxidation of substrate.

2 Experimental

All experiments were carried out at ambient conditions. The solvent acetonitrile (water content around 10^{-4} M) and the other chemicals used were analytical grade. The working electrode was a 1 mm disc shaped glassy carbon and platinum electrode sealed in polyetheretherketone (eDAQ) whose potential was quoted to a silver wire reference electrode. A platinum wire was also embedded in the solutions serving as counter electrode. Tetrabutylammonium perchlorate (TBAP) served as supporting electrolyte. Before all experiments the electrodes were polished on a polishing cloth with different particle size alumina powder (1 and 0.05 μm, respectively). It was followed by thorough washing with tap water and distilled water. The equipment used by the electrochemical experiments was a potentiostat (DropSens, Spain).

3 Results and discussion

3.1 Voltammetric oxidation of phenol in acetonitrile on glassy carbon electrode

In some earlier works phenol showed quick fouling in acetonitrile on platinum and indium tin oxide electrodes [15, 16]. In an earlier work electrooxidation of phenol was investigated on platinum electrode with cyclic voltammetry between 0 and 2 V which fouled quickly due to the formation of a coherent poly(phenyleneoxide) on its surface [12]. In order to see the electrooxidation of phenol on glassy carbon electrode five repetitive cyclic voltammograms were taken in acetonitrile also with it between 0 and 2 V (Fig. 1) and phenol concentration was 50 mM. Similarly to the platinum electrode, glassy carbon electrode fouled quickly, already in the first voltammogram. The shape of peak and magnitude of the peak current in the first scan around 1.6 V is very similar to that obtained with platinum electrode in our previous work where phenol was studied in aprotic nonaqueous solvents and the peak potential was also something over 1.5 V in the earlier experiments.

3.2 Extension of the potential window to 3 V

In an earlier work where substituted acetophenones were examined in acetonitrile between 0 and 4 V it was found that the oxidation peaks of acetophenones appeared only in the first scan due to the solvent [17]. By increasing the electrode potential to extreme values might result in undesired reactions which take place at the electrode/solution interface being due to the diminished solvent and/or electrode stability. Five cyclic voltammograms were recorded in acetonitrile containing 0.1 M TBAP supporting electrolyte
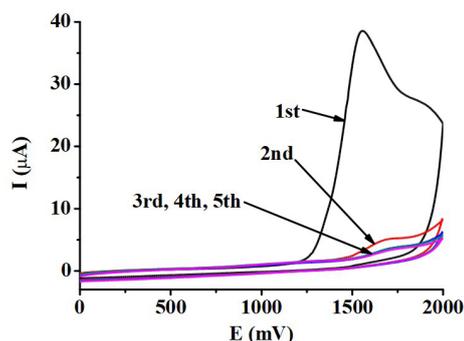

Fig. 1 Cyclic voltammetric curves of phenol in acetonitrile on glassy carbon electrode (scan rate: 0.1 V/s, c=50 mM, supporting electrolyte 0.1 M TBAP)

between 0 and 3 V (Fig. 2). The curves show a remarkable deactivation of the electrode surface extending the potential window to 3 V. At around 2.4 V an anodic peak appeared due to electrooxidation of solvent. The significant difference in currents between the first and second scan indicates that between 2 and 3 V the products of solvent electrooxidation quickly modify the surface. This finding also suggests that the behavior of glassy carbon is not affected considerably by the solvent between 0 and 2 V.

3.3 Preanodisation of glassy carbon electrode in acetonitrile at 3 V

An important feature of glassy carbon electrode is its behavior in study of selected electroactive compounds after the applied pretreatment method. In order to assess the effect of preanodisation 3 V steady potential was imposed to the glassy carbon electrode in acetonitrile containing 0.1 M TBAP supporting electrolyte. This potential was appropriate to deactivate the glassy carbon electrode as shown in the earlier Subsection 3.2. The surface of the electrode was sanded off with fine emery paper and then polished before all preanodisation to renew it completely. The effect of preanodisation time was investigated in the
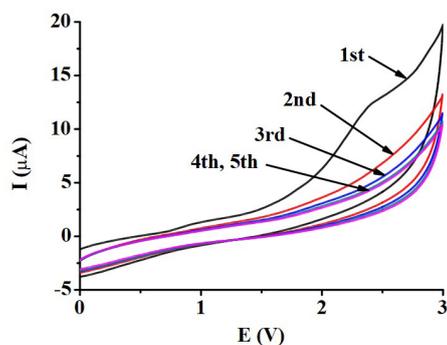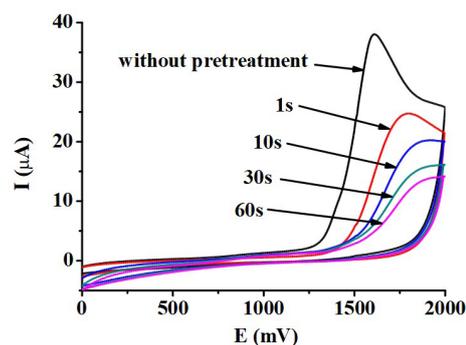

Fig. 2 Cyclic voltammograms in acetonitrile taken with glassy carbon electrode (scan rate 0.1 V/s, supporting electrolyte 0.1 M TBAP)

electrooxidation of phenol in 50 mM solution prepared with acetonitrile (Fig. 3). The curves show that by increasing the pretreatment time at 3 V the height of voltammetric peaks diminished drastically. On the other hand, the peak potentials shifted significantly to more positive values. Similar behavior was observed also by the selected para-substituted phenols but the extent of current decrease was less significant. The results suggest that during the preanodisation a highly resistive layer forms which is the product of acetonitrile electrooxidation. The surface of glassy carbon is usually covered by phenolic and oxo functional groups and they can bond substrate and product molecules through hydrogen bounds in acetonitrile leading to diminished currents after the first scan which was verified in the investigation of quinones [18]. At higher potentials acetonitrile can be oxidized also on its methyl group and the formed radicals can couple with the surface phenolic hydroxyl groups making less accessible the electrode surface for the substrate molecules. In this situation, this is the predominant cause for the observed deactivation process. The fouling by polyphenol is accelerated as a few active sites are accessible on the deactivated surface.

To get more insights into the observed deactivation process voltammograms were also taken in 5 mM aqueous solutions of two redox probes 1,4-dihydroxybenzene and $K_4[Fe(CN)_6]$ commonly used as model compounds in electrochemistry containing 50 mM KCl supporting electrolyte. The potential of glassy carbon was kept at 3 V for 60 seconds in acetonitrile solution used previously which was the preanodisation step. Small anodic peak current was obtained compared with that recorded with the untreated electrode in case of 1,4-dihydroxybenzene facilitating the presence of low conductivity surface layer. For $[Fe(CN)_6]^{4-}$ ion, the peak was negligibly small indicating that species with larger size are kept more effectively away from the glassy carbon surface due to the passivating film.

The potential dependence of preanodisation in acetonitrile was studied at several anodic potentials between 1 and 3 V changing it by 0.5 V steps with the redox probe 1,4-dihydroxybenzene. The anodic peak currents recorded with the preanodised electrode were compared with that of the bare electrode taking their ratio into consideration. The obtained results showed that at potentials higher than 2 V the electrode deactivated significantly showing that use of glassy carbon electrode is limited in the anodic potential range in acetonitrile. These observations are in accordance with the previous results.
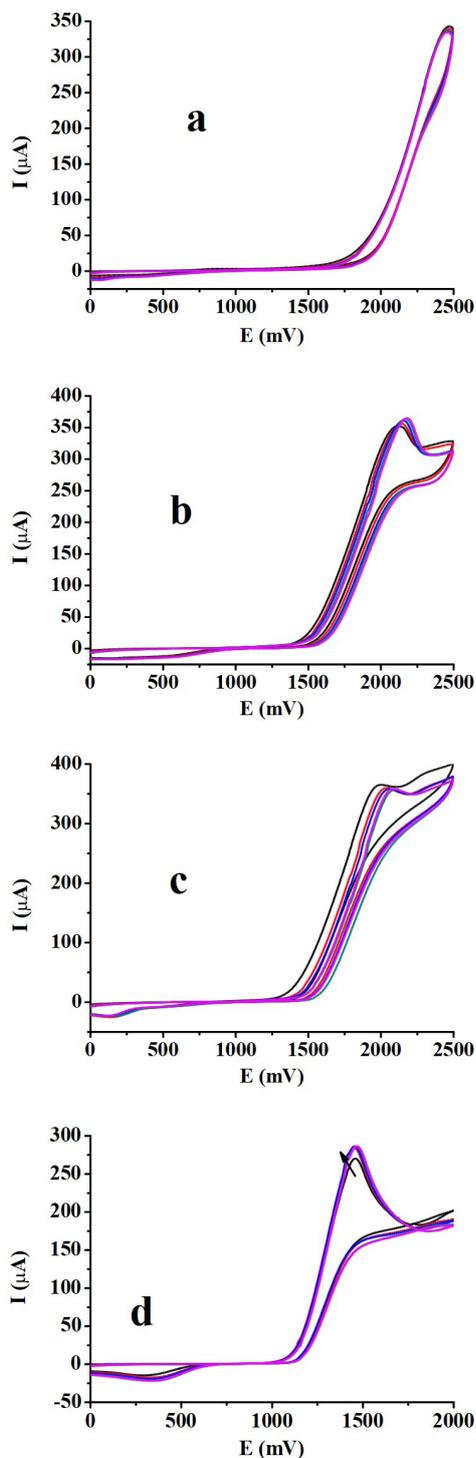

Fig. 3 Cyclic voltammetric curves of 50 mM phenol in acetonitrile on glassy carbon electrode by different preanodisation times in acetonitrile (scan rate: 0.1 V/s, supporting electrolyte 0.1 M TBAP)

### 3.4 Studies with the para-substituted phenols in acetonitrile

The para-substituted phenols were investigated in acetonitrile in 50 mM concentration by taking five subsequent cyclic voltammograms between 0 and 2.5 V (v=0.1 V/s). As the outlined para-substituted phenols have not been investigated in 50 mM concentration their electrooxidation was studied also on platinum electrode and moreover the results can be compared with results obtained with 50 mM phenol. On the other hand, the identical behavior of glassy carbon can be highlighted using a stable electrode as standard and platinum was appropriate in this respect. The reason is that contrarily to phenol the products of the anodic oxidation of para-substituted derivatives did not deactivate the platinum electrode (Fig. 4) showing that the presence of substituents in the para position causes a steric hindrance for the entrapment of other phenolic units into the electrochemically formed radicals. One of the most stable position for the unpaired electron is the para, oligomers formed being able to dissolve in the solvent. The nature of substituent has an additional effect on the results as in case of *p*-nitro-phenol its peak potentials are remarkably more positive than that of the other three para substituted derivatives. The nitro group has a very strong electron withdrawing effect particularly if it is present in the para position of the benzene ring. The potential window was between 0 and 2 V for *p*-methoxyphenol as its oxidation peak appeared at less positive potential than 2 V. It shows that the methoxy group significantly activates the benzene ring. Its voltammograms were reproducible, however the height of the first one is a little smaller than that of the other ones indicating that the surface of platinum was cleaned electrochemically in the first scan which was also observed by other electroactive materials in acetonitrile

on platinum electrode [17]. As a matter of fact *p*-methoxyphenol is the monomethyl ether of 1,4-dihydroxybenzene which can be oxidized similarly to 1,4-dihydroxybenzene producing a protonated species similar to *p*-benzoquinone in aprotic nonaqueous solvents.

In contrary, the peak currents decreased continuously in case of glassy carbon electrode (Fig. 5) indicating remarkably the deactivation of the carbon surface which was mainly due to the solvent as it was discussed in Subsection 3.2. The *p*-methoxyphenol was an exception

Fig. 4 Subsequent cyclic voltammograms of *p*-NO₂-phenol (a), *p*-Cl-phenol (b), *p*-tert-butyl-phenol (c) and *p*-methoxyphenol (d) on platinum electrode (scan rate 0.1 V/s, *c*=50 mM, supporting electrolyte 0.1 M TBAP)
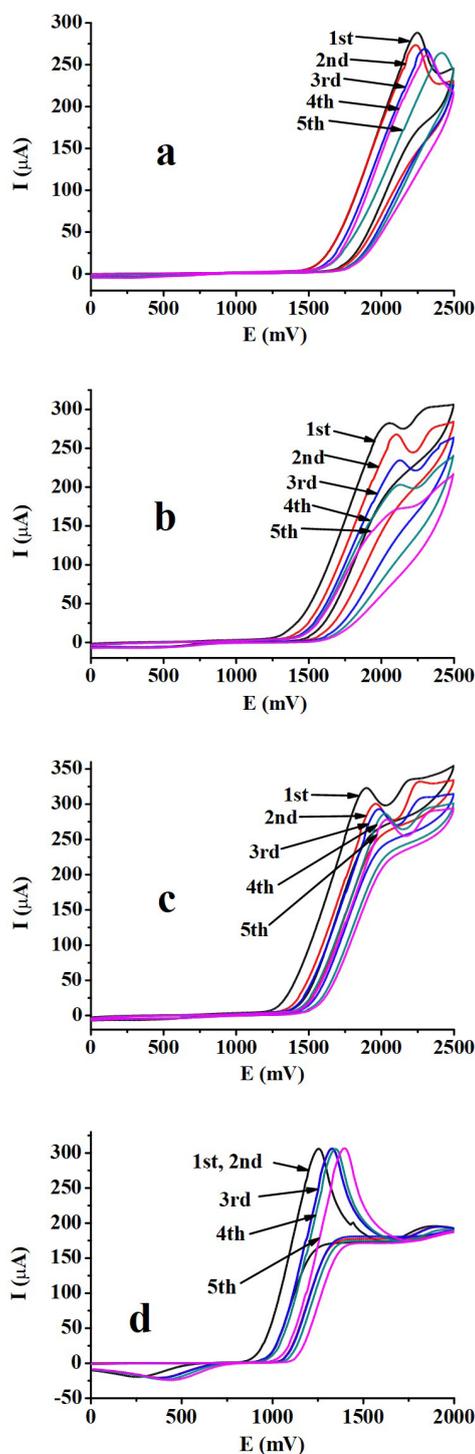
Fig. 5 Subsequent cyclic voltammograms of *p*-NO₂-phenol (a), *p*-Cl-phenol (b), *p*-tertbutyl-phenol (c) and *p*-methoxyphenol (d) on glassy carbon electrode (scan rate 0.1 V/s, *c*=50 mM, supporting electrolyte 0.1 M TBAP)

as the heights of its peaks did not decrease but shifted a little to more positive potentials probably due to the small increase of surface resistance during the recording of curves. The reason for the good reproducibility of peak current heights is that the anodic peaks appeared below 2 V and scanning to 2.5 V was not essential for the appearance of its anodic peak thus avoiding the electrode deactivation due to the solvent at higher potentials than 2 V.

The oxidation peak positions in voltammograms of para substituted phenols taken with both electrodes shifted to significantly more positive potentials relative to that of phenol. The other remarkable difference is the magnitude of peak currents which were several times higher in case of the phenol derivatives than that measured by phenol at the same concentration. It also shows that phenol fouls very effectively the electrode surfaces while the other phenols do not. The other reason for the high current differences might be that the potential window was extended to 2.5 V while in case of phenol 2 V was enough as upper limit to see its oxidation peaks. By comparing the initial stages of the oxidation peaks they begin around the same potential both in case of phenol and its derivatives. It suggests that the very efficient fouling caused by unsubstituted phenol electrooxidation stops the development of

the higher oxidation peak already below 2 V. The formed phenoxy radicals couple on both electrodes in acetonitrile through the benzene ring as it was shown with other substituted phenols in acetonitrile [19, 20]. These dimers then dissolve in the bulk.

4 Conclusions
Results obtained by investigating the behavior of glassy carbon electrode highlight the need of considering the usefulness of acetonitrile as solvent for electrochemistry at extremely high potentials or its contribution should be taken into consideration during investigation of selected compounds. Moreover, it can be solely responsible for the observed deactivation. Our future plan is to study the behavior of glassy carbon electrode in other commonly used solvents keeping its potential at higher values. On the other hand, the presence of substituents in the phenolic ring highly influences the structure of the forming oligomers and their solubility during electrooxidation of monomers.

References
[1] Engstrom, R. C., Strasser, V. A. "Characterization of electrochemically pretreated glassy carbon electrodes", Analytical Chemistry, 56(2), pp. 136–141, 1984.
https://doi.org/10.1021/ac00266a005

[2] Ilangovan, G., Pillai, K. C. "Mechanism of activation of glassy carbon electrodes by cathodic pretreatment", Journal of Solid State Electrochemistry, 3(6), pp. 357–360, 1999.
https://doi.org/10.1007/s100080050167

[3] Engstrom, R. C. "Electrochemical pretreatment of glassy carbon electrodes", Analytical Chemistry, 54(13), pp. 2310–2314, 1982.
https://doi.org/10.1021/ac00250a038

[4] Dai, H. P., Shiu, K. K. "Voltammetric studies of electrochemical pretreatment of rotating-disc glassy carbon electrodes in phosphate buffer", Journal of Electroanalytical Chemistry, 419(1), pp. 7–14, 1996.
https://doi.org/10.1016/S0022-0728(96)04875-9

[5] Gunasingham, H., Fleet, B. "Effect of pH on the response of glassy carbon electrodes", Analyst, 108(1284), pp. 316–321, 1983.
https://doi.org/10.1039/AN9830800316

[6] Ranganathan, S., Kuo, T., McCreery, R. L. "Facile Preparation of Active gGlassy Carbon Electrodes with Activated Carbon and Organic Solvents", Analytical Chemistry, 71(16), pp. 3574–3580, 1999.
https://doi.org/10.1021/ac981386n

[7] Ahmed, S., Ahmad, M., Butt, S. B. "Electrooxidation of chloro, nitro, and amino substituted phenols in aqueous medium and their heterogeneous kinetics", Research on Chemical Intermediates, 38(3-5), pp. 705–722, 2012.
https://doi.org/10.1007/s11164-011-0410-z

[8] Ureta-Zañartu, M. S., Bustos, P., Berríos, C., Diez, M. C., Mora, M. L., Gutiérrez, C. "Electrooxidation of 2,4-dichlorophenol and other polychlorinated phenols at a glassy carbon electrode", Electrochimica Acta, 47(15), pp. 2399–2406, 2002.
https://doi.org/10.1016/S0013-4686(02)00043-9

[9] Dulal, S. M. S. I., Won, M., Shim, Y. "Carbon fiber supported platinum nanoparticles for electrooxidation of methanol and phenol", Journal of Alloys and Compounds, 494(1-2), pp. 463–467, 2010.
https://doi.org/10.1016/j.jallcom.2010.01.083

[10] Fino, D., Jara, C. C., Saracco, G., Specchia, V., Spinelli, P. "Deactivation and regeneration of Pt anodes for the electrooxidation of phenol", Journal of Applied Electrochemistry, 35(4), pp. 405–411, 2005.
https://doi.org/10.1007/s10800-005-0799-4

[11] Kiss, L., Bősz, D., Kovács, F., Li, H., Kunsági-Máté, S. "Electrooxidation of phenol in alcohols and establishment of the permeability of the electrodeposited films", Polymer Bulletin, 76(1), pp. 215–226, 2019.
https://doi.org/10.1007/s00289-018-2372-4

[12] Kiss, L., Bősz, D., Kovács, F., Li, H., Nagy, G., Kunsági-Máté, S. "Investigation of phenol electrooxidation in aprotic non-aqueous solvents by using cyclic and normal pulse voltammetry", Polymer Bulletin, 76(1), pp. 1–6, 2019.
https://doi.org/10.1007/s00289-019-02678-2

[13] Skowroński, J. M., Krawczyk, P. "Electrooxidation of phenol at exfoliated graphite electrode in alkaline solution", Journal of Solid State Electrochemistry, 8(6), pp. 442–447, 2004.
https://doi.org/10.1007/s10008-003-0483-8

[14] Tessensohn, M. E., Hirao, H., Webster, R. D. "Electrochemical Properties of Phenols and Quinones in Organic Solvents are Strongly Influenced by Hydrogen-Bonding with Water", Journal of Physical Chemistry C, 117(2), pp. 1081–1090, 2013.
https://doi.org/10.1021/jp311007m

[15] McCarley, R. L., Irene, E. A., Murray, R. W. "Permeant molecular sieving with electrochemically prepared 6-nm films of poly(phenylene oxide)", The Journal of Physical Chemistry, 95(6), pp. 2492–2498, 1991.
https://doi.org/10.1021/j100159a071

[16] Rhodes, C. P., Long, J. W., Doescher, M. S., Fontanella, J. J., Rolison, D. R. "Nanoscale Polymer Electrolytes: Ultrathin Electrodeposited Poly(Phenylene Oxide) with Solid-State Ionic Conductivity", Journal of Physical Chemistry B, 108(35), pp. 13079–13087, 2004.
https://doi.org/10.1021/jp047671u

[17] Kiss, L., Kunsági-Máté, S. "Voltammetric oxidation of acetophenone derivatives and benzophenone in acetonitrile on a platinum and glassy carbon electrode", Comptes Rendus Chimie, 22(4), pp. 316–320, 2019.
https://doi.org/10.1016/j.crci.2019.01.007

[18] Staley, P. A., Newell, C. M., Pullmann, D. P., Smith, D. K. "The Effect of Glassy Carbon Surface Oxides in Non-Aqueous Voltammetry: The Case of Quinones in Acetonitrile", Analytical Chemistry, 86(21), pp. 10917–10924, 2014.
https://doi.org/10.1021/ac503176d

[19] Abidi, M., Derbel, N., Hkiri, R., Sbihi, H. M., Said, H., Morallon, E., Besbes-Hentati, S. "Electrodeposition of 4,4′-di-tert-butylbiphenyl peroxide from the anodic oxidation of p-tert-butylphenol in an alkaline acetonitrile solution", Journal of Applied Electrochemistry, 47(4), pp. 507–516, 2017.
https://doi.org/10.1007/s10800-016-1041-2

[20] Marková, E., Kucerová, P., Skopalová, J., Barták, P. "Electrochemical Oxidation of 2,4,6-Tribromophenol in Aqueous-Alcoholic Media", Electroanalysis, 27(1), pp. 156–165, 2015.
https://doi.org/10.1002/elan.201400412