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Redox Processes Involving Quinones on Poly-3,4-ethylenedioxythiophene-Modified Glassy Carbon Surface

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Abstract—Redox transformations involving quinone/hydroquinone redox pair on a glassy carbon electrode (pristine and modified with poly-3,4-ethylenedioxythiophene film) have been investigated by means of cyclic voltammetry.

Keywords: quinone/hydroquinone redox pair, poly-3,4-ethylenedioxythiophene, cyclic voltammetry

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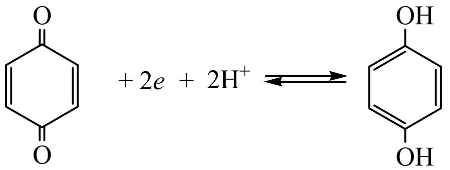
Redox transformations of quinones on dropping mercury electrode have been studied in detail. At sufficiently high positive potentials, polarograms of *o*- and *p*-quinones exhibit a two-electron wave corresponding to the quinone–hydroquinone transition [1, 2]. Much less attention has been paid to electrochemical processes involving quinones on solid and chemically modified electrodes [3–5]. The interest to redox behavior of simple and substituted quinones has been recently restored in view of promising applications as components of electrochemical energy storage systems. These compounds can be used as molecular components for organic redox batteries and species immobilized in polymeric and carbon matrices for the construction of composite materials of energy storage devices such as supercapacitors or lithium-ion batteries [6–15]. The redox activity of quinones and the charge required for redox transformations are determined by the presence of characteristic C=O groups in the aromatic ring. The key features of practical electrochemical systems are high rate of the redox processes, stability of the redox transformations during long cycling, and the absence of side processes. This is determined by the nature of the organic substrate as well as electrolyte and electrode material.

The mechanisms of the processes involving quinones may be substantially different depending on the nature of the medium and the electrode. For example, stable anionic and radical intermediate species are formed in aprotic solvents, which can interact with the components of the electrolyte and complicate the processes. Another specific feature of the quinones redox reactions in aprotic media is the formation of dimers and even polymerization on electrodes [6, 9, 10]. Quite simple voltammetric responses with a single pair of redox peaks are indicative of the process occurring via a series of intermediate steps. Far simpler mechanisms are generally observed for recharging of quinone-containing compounds in acidic aqueous solutions, where the process of the quinone group reduction includes successive protonation and electron transfer [3]:



(1)

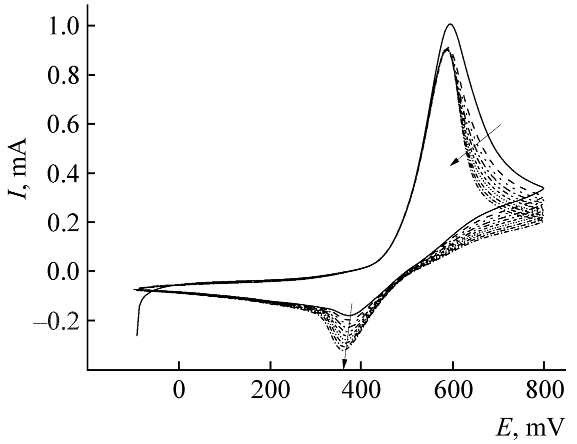


Fig. 1. CV curves for hydroquinone on the GC electrode in 0.5 M H_2SO_4, v = 10 mV/s, 8 cycles of potential scan.

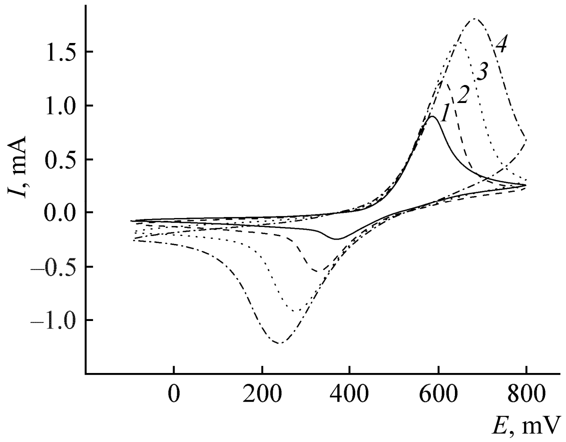
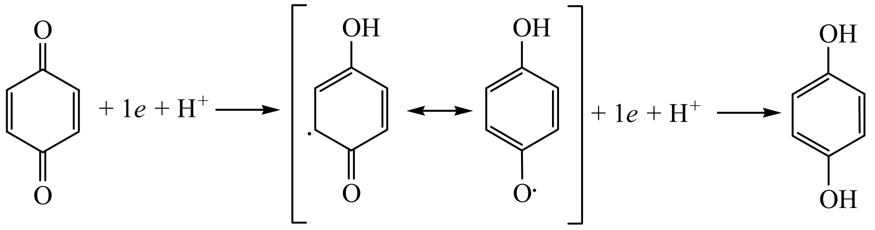


Fig. 2. CV curves for hydroquinone on the GC electrode in 0.5 M H_2SO_4 at different potential scan rates, mV/s: (*1*) 10, (*2*) 20, (*3*) 50, and (*4*) 100.



(2)

In this study, the redox transformations involving the quinone/hydroquinone redox pair were investigated by means of cyclic voltammetry (CV) on glassy carbon electrode (GC), pristine as well as modified by poly-3,4-ethylenedioxythiophene film (GC/PEDOT). The study aimed also to elucidate the conditions to perform reversible redox processes in the studied systems.

CVs for the GC electrode in 0.5 M H_2SO_4 solution in the presence of hydroquinone are shown in Figs. 1 and 2. In the absence of a redox-active components in the solution, the GC electrode demonstrated low background current due to charging of the electrode surface and redox transformations of possible admixtures (for example, dissolved oxygen). When hydroquinone (0.2 M) was introduced in the 0.5 M H_2SO_4 solution, the voltammograms on the GC electrode showed well-defined peaks, with high peak-to-peak separation values. The mean value of the formal potential of the redox process (calculated as half-sum of the potentials of the cathodic and anodic peaks) was close to 482 mV. The difference between the potentials of the anodic and cathodic peaks (ΔE) at the potential scan rate of 10, 20, 50, 100 mV/s (Fig. 2) was 216, 282, 370, and 442 mV, respectively. The prominent difference in the peak potentials suggested irreversible electrochemical process. In that case, the total reaction proceeded as two-electron process with participation of two protons. In the course of the cyclic variation of the potential, the change in the shape of voltammograms from cycle to cycle was observed, consisting in sharp decrease in the area of the cathodic peak, especially at low potential scan rates.

The ratio between the currents of the cathodic and anodic peaks was gradually changed with the increase in the cycle number (Fig. 1), and the charge disbalance for the direct and reverse processes was enhanced. In other words, instability of the oxidation and reduction currents was observed for the GC electrode, and the area under the redox peaks was decreased in the course of the cycling. After prolonged cycling of the potential (up to 50 cycles) without stirring, the formation of a “cloud” of suspended precipitate of the products of hydroquinone oxidation near the surface of the electrode was observed. Replacement of the electrolyte with a freshly prepared hydroquinone solution recovered the ratio of the cathodic and anodic peaks to the original value, indicating the influence of accumulation of the side reaction products on the redox transformations on the electrode.

The poor stability of the voltammetric response for GC electrode in the presence of quinone/hydroquinone

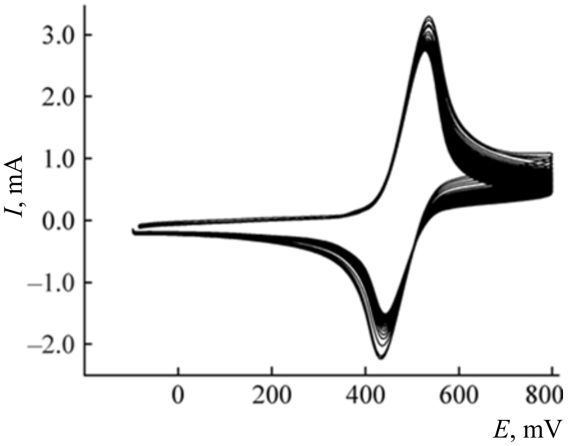


Fig. 3. CV curves for hydroquinone on the GC/PEDOT electrode in 0.5 M H_2SO_4, v = 20 mV/s, 40 cycles of potential scan.

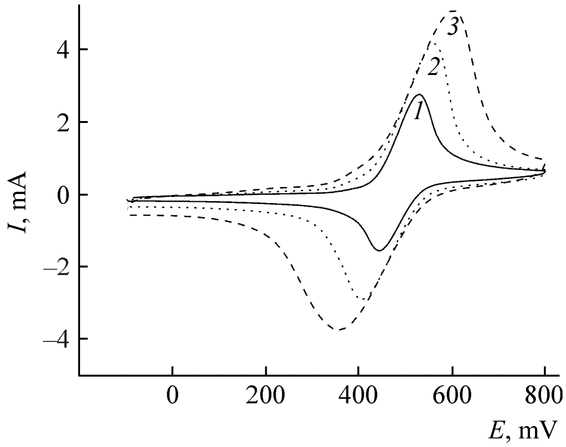


Fig. 4. CV curves for hydroquinone on the GC/PEDOT electrode in 0.5 M H_2SO_4 at different potential scan rates, mV/s: (*1*) 10, (*2*) 20, and (*3*) 50.

pair could be due to the side processes leading to the formation of intermediate oxidation products which possessed, as followed from the experiment, low solubility, and hence precipitated. According to the discussion in [1, 2], such product could contain poorly soluble dimeric and oligomeric products of hydroquinone oxidation [in particular, quinhydrone compounds, Eq. (2)].

In the case of the modified GC/PEDOT electrode in 0.5 M H_2SO_4 solution in the presence of 0.2 M of hydroquinone, we also observed a single pair of distinct redox peaks, the average value of the formal potential of the redox process being close to 470 mV. Cathodic and anodic redox peaks exhibited noticeably smaller separation in the potential scale in comparison with the GC electrode (ΔE = 86 mV at v = 20 mV/s) (Fig. 3), increasing with the increase in the potential scan rate (ΔE was 154 mV at v = 50 mV/s and 245 mV at v = 100 mV/s) (Fig. 4). That was indicative of substantial catalytic effect of the conducting polymer coating on the rate of the processes involving hydroquinone. Apparently, the reaction of the quinone molecules with the surface groups of the conducting polymer resulted in the increase in the rate constant of the quinone redox reactions. Those interactions might stabilize the transition states of the product formed at the reaction stage (*2*) on the surface of the polymer and prevent the dimerization reaction. Most probably, those interactions involved the π–π interactions between the aromatic and pseudo-aromatic rings of quinones and the conducting polymer as well as possible the formation of hydrogen bonds between the oxygen-containing groups of quinone and surface oxygen and sulfur atoms of the conducting polymer. Reliable elucidation of the nature of the interactions required *in situ* measurements on the electrodes during the process which were beyond the scope of the study.

Besides the decrease in the cathodic and anodic peak potentials, surface modification of the electrode with the conductive polymer led to substantial increase in the peak currents, possibly due to the increase in the electrode surface area accessible for redox transformations of hydroquinone molecules, owing to high porosity of the polymeric film. Therefore, notable acceleration of the process of charge transfer in the quinone/hydroquinone pair on the surface of the GC electrode modified with conducting polymer PEDOT was observed as compared to pristine GC electrode, as well as the increase in selectivity of quinone reduction with respect the final product, hydroquinone. Those data demonstrated the possibility of sharp increase in the redox capacity of the polymeric film in the presence of electroactive component (quinone) in the electrolyte.

The peak currents increased with the potential scan rate (Fig. 4), but the initially proportional growth was gradually slowed down, evidencing the change in the process kinetics and diffusion limitation of the current related to slow transfer of quinone molecules to the electrode surface. It could be suggested that the formation of diffusion layers with the altered concentration of quinone originated from the bulk of the film (where the mass transfer process was slower in the porous structure) and then the diffusion layer with the varied quinone concentration was developed closer to the electrode surface.

The stability of the electrochemical response could be judged from the dependence of the relative area under the anodic peak on the cycle number. It was clearly seen that the amount of electricity consumed decreased over first several cycles but then became constant. The initial decrease in the amount of consumed charge was probably due to the development of the steady-state regime of the mass transfer to and from the electrode surface under the conditions of non-stirred solution, including mass transfer in the bulk of the film. Further stabilization of the response indicated good reversibility of the redox processes involving quinones on the surface of poly-3,4-ethylenedioxythiophene film.

In summary, we found that the modification of glassy carbon electrode with poly-3,4-ethylenedioxythiophene resulted in substantial increase in reversibility of redox transformations of the quinone/hydroquinone pair in 0.5 M H_2SO_4 solutions. In both cases, two-electron redox transition took place. The instability of the electrochemical response observed for the GC electrode in the presence of quinone was related to dimerization of intermediate products of quinone reduction. The improved reversibility and stability of the electrochemical response in the case of GC/PEDOT electrode was ascribed to stabilization of intermediate reduction products adsorbed on the polymer surface. It was shown that the use of redox-active component might substantially increase the electrode capacity, which can be used in the field of energy storage materials.

EXPERIMENTAL

3,4-Ethylenedioxythiophene (Aldrich), anhydrous lithium perchlorate (“chemical pure” grade), anhydrous acetonitrile (abcr GmbH, Germany), hydroquinone (“chemical pure” grade) and sulfuric acid (“extra pure” grade) were used. The solutions for electrochemical testing were prepared using deionized water obtained from Millipore Direct-Q UV (Millipore Corp., USA) purification system.

Glassy carbon disc electrode was used as the working electrode (GC-2000, $S = 0.07\ cm^2$). Before coating, the surface of the GC electrode was thoroughly polished with aluminum oxide (particle size 1–3 μm) and washed with deionized water.

Electrochemical synthesis of poly-3,4-ethylenedioxythiophene films was performed under galvanostatic conditions (current density $1\ mA/cm^2$) in a solution containing 0.05 M of 3,4-ethylenedioxythiophene (EDOT) and 0.1 M of $LiClO_4$ in acetonitrile.

Electrochemical measurements were performed in a three-electrode glass cell with a platinum counter-electrode at room temperature (20±2°C). The measured potentials were given with respect to silver chloride electrode in saturated NaCl solution. CV measurements were performed using a GAMRY Interface 1000 potentiostat-galvanostat (Gamry, USA). The potential scan rate was varied within 10–100 mV/s range.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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