Electrochemical behavior of diamond-like carbon film electrodes in aqueous electrolutes

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The problem of electrode material for realization a wide spectrum of reactions is an old problem of electrochemistry. It remains to be actual up today. The electrode must have high electrocatalytic activity and stability of working characteristics, and also the desired properties: corrosive inertness, selectivity and availability of initial materials. The electrodes based on diamond and diamond-like materials meet most of indicated requirements. The films of amorphous carbon, so-called a-C films, being inexpensive material keep all advantages of conducting diamond electrodes – high corrosion resistance, wide range of ideal polarizability in the background electrolytes, sensitivity to the small concentrations of depolarizer. There are available, inexpensive methods of obtaining a-C films with high performance characteristics. The results of study electrochemical properties of a-C films, deposited on conducting substrates (including ones with formation of transitional layer of carbide phase for the improvement of adhesion) are presented in this work. The electrochemical activity of a-C films was estimated from data of cyclic voltammetry in solutions of the systems $[Fe(CN)_6]^{3-/4-}$, $Ce^{4+/3+}$, the resistance of electrodes – from data of impedancemetry in the solution of 0,5 M H_2SO_4.

Experiment.

The a-C films were deposited on substrates of different materials (Si, Cr, Mo, Pt, galssy carbon) by the method of magnetron sputtering of graphite target [1,2]. Some films were doped with the boron or nitrogen during the deposition. Films of thickness 1÷1,5 μm and 50 nm (only on Si substrate) were used. Ohmic contacts to the films were realized with the help of silver glue, an inoperative surface of electrode was insulated by the cleared paraffin. Voltampere curves of oxidation of $[Fe(CN)_6]^{4-}$ or Ce^{3+} and of electroreduction of $[Fe(CN)_6]^{3-}$ or (Ce^{4+}) were obtained by potensiostat Pi-50-1.1 with the linear scanning of potential rate V=2÷500 mV/s. The concentrations of the Red-Ox forms of depolarizators were varied in the range of $1*10^{-4} – 2*10^{-2}$ mol/l. For the impedance measuring in the range 0,1÷20 kHz and for the cyclic voltametry at the rapid potential scanning the computerized measuring system Unilab was used.

Results and Discussion

Low background currents < 10 μA/cm^2 were recorded in the potential range (–1,2÷+1,7) V vs Ag/AgCl in the system 0,5 M H_2SO_4 on the a-C film electrodes and this range did not depend on film thickness and doping level. The cyclic voltamperograms of the systems $[Fe(CN)_6]^{3-/4-}$ and $Ce^{3+/4+}$ have a classic form with peaks of anode (I_{pa}) and cathode (I_{pc}) currents. The values of I_p and E_p of voltammograms of the systems under investigation vary depending on the potential scanning rates according to the theory of voltammetry [3] (Figs.1, 2). The difference of potential peaks ($\Delta E_P = E_{pa} – E_{pc}$) is 0,2 V for the first and 0,68 V for second Red-Ox systems. It is known that ΔE_P =59 mV for one-electron reversible electrochemical reaction, but in the systems under examination the electrode reactions occur irreversibly. Kinetic characteristics [4, 5], calculated for these reactions from the plots in Figs 1, 2, substantially differ from data, obtained for metallic electrodes (Pt): for $[Fe(CN)_6]^{3-}$ α =0.37; β= 0.4; $k^0= 7*10^{-5}$ cm/sec; $D= 1{,}42*10^{-5}$ cm^2/sec. The resistance of investigated films was estimated by the impedancemetry and direct current measurements: the obtained data are in the limits - 0,1÷ 1 Ohm cm.

Present investigation and comparison of results obtained by us earlier and by other authors [6] have shown that electrochemical behavior of a-C films and diamond (film, monocrystalline) electrodes is generally the same.

This research has been partly supported by the STCU project 1622

[1] L.R.Shaginyan, A.A.Onoprienko, V.F.Britun, V.P. Smirnov , Influence of different physical factors on microstructure and properties of magnetron sputtered amorphous carbon films, Thin Solid Films, v.397, 2001, p.288-295

[2] V.Kulikovsky, P.Bohac, F.Franc, A.Deineka, V.Vorlicek, L.Jastrabik, Hardness, instrinsic stress and structure of the a-C and a-C:H films preparated by magnetron sputtering, Diamond and Related Materials,v.10,2001, p.1076-1081.

[3] Z. Galus, Theoretical foundation of electrochemical analysis, Moscow: Mir,1974, 552 p .

[4] I.Novoselova, O.Fedoryshena, A.Onoprienko, E.Panov, Electrochemical behavior of the boron-doped amorphous carbon films, Ukr.Chim.Zurn.,2002,v.68,№9, p.32-36

[5] O. Fedoryshena, V.Kulikovskij, E.Panov, I. Novoselova, M.Olijnik Visnyk of the Lviv University, 2002, N 42, Part.1, p.105.

[6] Yu.V. Pleskov. Synthetic Diamond in Electrochemistry, Uspekhi Khimii (Russian Chemical Reviews) (in Russian), 1999, v. 68, N 5, p. 416 – 429.

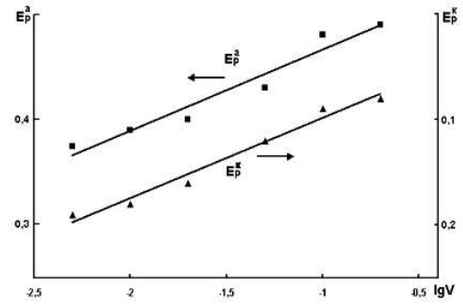

Fig. 1. Dependenses of $E_{pk}$and E_{pa} on potential scannng rates in the solution 1M KCl+$2{,}5*10^{-3}$[$Fe(CN)_6$]$^{3-/4-}$

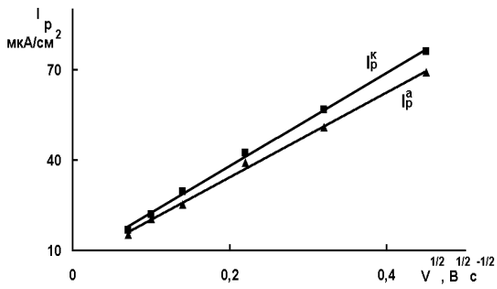

Fig.2. Dependenses of I_{pk} and I_{pa} on potential scanning rates in the solution 1M KCl+$2{,}5*10^{-3}$[$Fe(CN)_6$]$^{3-/4-}$