Nanotechnology in the electrochemical sensors development

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Electrochemical sensors included several main types as conductometric (CS), potentiometric (PS) (pH and ion selective sensors), chronoamperometric (CAS) and big group of voltAmmetric (VA) sensors. In recent time, the VA is practically one of main electrochemical methods because of VA high sensitivity and selectivity in both inorganic and organic chemistry. The VA method is also one of main methods of analysis in broad range from high concentrations up to metals traces and organics traces. It is reason we focus on these VA sensors. One of the first applications of electrochemical kinetics to analysis of micro concentration of metals is the pioneering work suggested about long time ago by Ja. Heyrovsky. Professor Heyrovsky suggests and developed VA mercury drop electrode (MDE). The electrode has unique stability, reproducibility and sensitivity. After short time, the Heyrovsky MDE electrode starts to working in USA and Europe metallurgy and car industry. Results of the work of Heyrovsky are pointed Nobel prize [1]. The VA sensors on Hg-drop electrodes are received a broad application in next decades. At the same time, it was found some drawbacks these electrodes. One of the main disadvantages of mercury electrode is big amount of Hg (up to several kg Hg in one mercury drop electrode). Well known that mercury (especially vapor of Hg) is strong poison. It forced chemists focus on searching of electrodes with min (or without) mercury.

Next step in VA achieved by the appearance of new mercury-thin film (MF) electrode. The MF electrode allows not only increasing VA method sensitivity of 2-3 orders and also decreasing Hg quantity to mg level and less. Low mercury level is important also for staff working with the MF electrode. The MF electrode and method of stripping voltammetry (SVA) suggested in earlier 60-es by TM Florence [2] and XZ Brainina [3]. The method based on carbon electrode plated with thin film of Hg. In the SVA method, first stage is Men+ cathodic deposition from solution into C/Hg° film (Me° electro concentration) and then second stage - anodic dissolving. Anodic current peak (analytical signal) is proportional of metal bulk concentration. Method SVA found broad applications in both technology and environmental investigations. In our laboratory was improved MF technology. It developed long-term MF electrode. In brief, the technology included electrode preparation by cold press method from mix carbon powder+plastic binder with (0.3% to 3.0%) HgX additives (where X-haloid). Next step-polishing of electrode working surface. The bulk modified long-term electrode (MPE) shows high stability at least of 12 months. The MPE applied not only to heavy metal traces detection and also to organics (nitroaromatics, aliphatic and aromatic thiols) [4].

In general, one of main demands to the sensors is sensitivity (S): A relation between analytical signal (S_a) and blank signal (S_b). $S=S_a/S_b$. In VA methods sensitivity determined as relation between current peak value (I_p) to background current (I_{bg}). Practically for solid electrode $I_{bg}=I_{dl}$, where Idl-current of double layer capacitor. The I_{dl} linear depended from electrochemically active surface (S_a) of electrode. In general $S_a=A*r$, (where A-geometry area of sensor surface; r-roughness factor). And sensitivity $S= I_p/I_{dl}$. For sensor optimal sensitivity: Ip - → max, and I_{dl} -- → min. For Pt, Au and GC electrodes, demand of I_{dl}- → (min) is realized with polishing of electrode surface. Searching of new electrode based on carbon materials based on materials with min roughness factor [5].

Effective and sensitive MF electrode included small amount of mercury. Now in electrodes mercury application practically forbidden with Environmental agencies. The fatal disadvantage of MF electrodes forced to search of new "mercury dry" materials.

Classical electrode materials now are noble metals (Au, Pt and Pt-group) and relatively new material such as appeared in 70-es glassy carbon (GC), (see for example 5) Advantage of these electrodes is high mechanical stability and chemical (electrochemical) resistance, stability in broad range of potential (broad electrochemical "window"). One of main advantage of solid electrodes is possibility of creating long-term miniature sensor systems. Disadvantage is that (in contrast to Hg-drop and Hg-film electrodes) for solid electrodes reproducibility of sensor active surface (S_a) is challenge. For these solid electrodes, stability of S_a at high anode potentials or in the presence of surface-active components is serious problem. Other words it is problems of corrosion or passivation of active surface of the electrode

According to Randles-Shevchik equation [6] analytical signal-peak current (I_p) is proportional to concentration of electro active compound (Co) in assumption that S_a=const: Ip=k' Co. It means that instability of active electrode surface lied to increasing of detection error. For the case of VA solid electrode, it is important goal to develop electrode with reproducible S_a (roughness factor).

Systematical search in the field of electrode materials in our laboratory was allowing suggest a new prospective carbon material-carbon paper (CP) [7,8]. The advantage of CP electrode is combination of low background current and high analytical signal. A drawback of this material is not satisfactory mechanical stability. The drawback was overcoming by means of electrode design, such as putting CP sensor element in miniature flexible hermetic plastic frame.

We suggested a method of preparing CP nano-carbon electrode surface (with controlled roughness factor). In brief, the pretreatment method is to use cyclic voltammetry in background (b_g) solutions (pH-0.5 to 1.5) during 150-200 cycles. Both carbon oxides is gaseous, it means that electrode surface is clean (no surface solid oxides). In these treatment processes electrode surface is covered with ensemble of nano particles of carbon. These data was directly used for control active electrode surface (roughness factor-re). In general active electrode surface is proportional to double layer capacity (Cdl-e). The calculation of double layer capacitance carried out by next procedure: $C_{dl\text{-}e}=(\Delta I_{dl\cdot t})/\Delta E$, where: Δ_{Idl}-current in double layer range of potentials, t-time of the current measurement, ΔE-interval of potential in the range. Roughness factor value calculated from next equation: $re=C_{dl\text{-}e}/C_{dl\text{-}sp}$, where $_{Cdl\text{-}sp}$-double layer capacity by r_{st}=1.0. For this and similar carbon materials value of r_{st}=7-10 μF/cm^2 [9].

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This CP electrode applied to study of electrochemical behavior of nitroaromatic compounds (NA) and of cyclic nitroamines group (NOM) compounds (explosives). Concentration of the NA and NOM compounds in air is very low. It forced researchers search about new ways to increasing of sensitivity of detection these compounds. One of these methods is study interacting of nitro-group with active amino-groups (Meisenheimer complex) on the electrodes surface. As to our knowledge first article about detection of TNT with electrode chemically modified with amino-group (CME-Am) published I. Wilner group (T. Bourenko) [10]. The first application to TN_t detection on nano-wires electrode suggested Patolsky et al. [11]. The CME-Am electrode allows increasing TNT detection sensitivity at least of two-three orders. We improved this technology and developed long-term CME-Am electrode sensitive not only to TNT and also to RDX and PETN. It was developed new sensors to detection traces of these NA and NOM compounds in single cycle of measurement [12].

The CP electrodes technology we applied to another group of explosives to organic peroxides. Well known that dangerous explosives based on organic peroxides can be easy prepared in home conditions. One of main such peroxide is triacetone triperoxide (TATP). In this high dangerous explosive, there is no nitro group. It means that standard method explosives detection based on reduction of nitro group is not useful in the case. In our laboratory developed a different method based on decomposition of peroxide molecule and registration of signal (peak current) products of the decomposition [13].

This is only some of examples that show highly large possibilities of application of Nano-technology in electrochemical methods. It is clear that main challenge in all electrochemical sensors technology is methods of creating stable and well definited active nano-surface of solid electrodes our laboratory continue work in the direction and ask researchers to combine efforts in this important field.

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