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Injection of electrons in hexamethylphosphoric triamide solutions at moderate cathodic potentials

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The electrochemical emission of solvated electrons from nanostructured electrodes of different morphology was revealed by ESR spectroscopy at moderate cathodic potentials.

The electrochemical generation of solvated electrons is well known.[1–3] It was of no further interest to carry out electrode processes in such a way. The latest related article[4] was published in 1995. This seems to be due to that cathodic generation of e_s^- was observed only at very high cathodic potentials ($E \leq -3$ V s.c.e.), which required expensive and toxic high-purity solvents. However, generation potential can become considerably positive for nanostructured carbon electrodes.[5,6] An increase of current was explained[6] by electron emission from atomically sharp parts of a nanopaper electrode containing single-walled nanotubes (SWNT) when a solvated electron acceptor (N_2O) was added to aqueous solution. This assumption is based on the analogy of the existence of experimentally established autoelectron emission into a vacuum from different nanostructured materials.[7–9]

The goal of this work was to verify experimentally the hypothesis[6] of the electron emission from nanostructured electrodes in hexamethylphosphoric triamide (HMPA) solutions.

The method of SWNT fabrication was described elsewhere.[10] In this study, we used nanopaper, whose physico-chemical properties were similar to those reported previously.[11]

Carbon filaments were composed of a SWNT covered by an outer shell. The SWNT form a channel along the full length of a filament (3–5 mm) with a diameter of ~2–4.5 nm. The outer shell was built of a disordered carbon material.[12]

Column structures consisted of highly ordered parallel columns ~50 μm in diameter with hemispherical tops. SWNT with a diameter of 20–30 nm and a length of ~1 μm are located on these tops. The scanning electron microscopy images of all of the used structures and the technology of preparation of the electrodes were reported elsewhere.[13]

Some experiments were performed on electropolished copper and sharpened tungsten electrodes.

ESR measurements were performed on a standard 9 GHz spectrometer (Poland) at 77 K. Purification of HMPA, background electrolyte, and the control of solvent purity were carried out using a published procedure.[14] The potentials were measured with respect to an aqueous saturated calomel electrode.

For all the above carbon electrodes in HMPA solutions of 0.2 M $NaClO_4$ the current increase accompanying by an intense blue coloration of solution was observed in voltammograms under potential shift to the cathodic range. Both processes started even at $E = -(1.0–1.4)$ V. Such a characteristic coloration was found[1–4] to be unequivocally due to the existence of e_s^- and was never observed in other cases. The dark blue solution formed near the nanopaper electrode at $E = -1.2$ V was introduced into a quartz vessel, which was then placed in the resonator of an ESR-spectrometer. The ESR signal from the frozen dark blue HMPA solution consists of a narrow singlet with $\Delta H = 0.58$ mT and $g = 2.0024$ (Figure 1) coinciding with the g value of free electron.[15,16] Similar signals were observed[16] in HMPA solutions using three different methods of electron generation: chemical, electrochemical and radiochemical. Thus, the given experimental facts suggest the emission of solvated electrons from nanostructured carbon at moderate cathodic potentials.

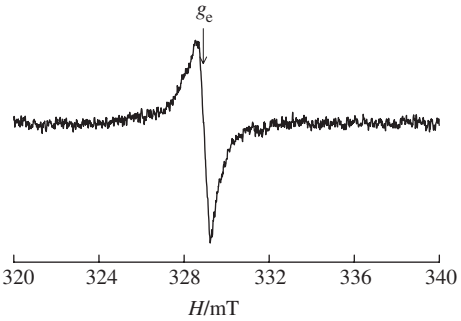

Figure 1 ESR spectrum of electrons generated from carbon nanostructured electrodes in HMPA + 0.2 M $NaClO_4$ at 77 K, $E = -1.2$ V.

The voltammograms of the electrodes in HMPA solution are shown in Figure 2. Since absolute current values (I) are from 10^{-4} (for nanopaper) to 10^{-9} A (for filament electrodes), current densities are represented in Figure 2. We estimated the electrode area contacting with electrolyte from current values in the –(0.2–0.6) V potential range. The current value is proportional to the scan rate within the range 0.01–0.5 V s^{-1}. Specific capacities of an electrochemical double layer were supposed to be approximately equal (accurate to within a factor of 2) for various carbon structures and metallic electrodes.[17] The relationships between emission current at $E = \text{const}$ and measurable values of capacity are given in the inset of Figure 2. It is obvious that, for nanopaper and column electrodes, there is linear correlation between these values. The data in the inset of Figure 2 are presented for the samples having a mean capacity value (C_E). On the contrary, such a correlation is not observed for filament structures. The current–voltage characteristic of the sample with the lowest value of the I/C_E ratio is given for this reason. Even provided that the dependencies in Figure 2 have rather

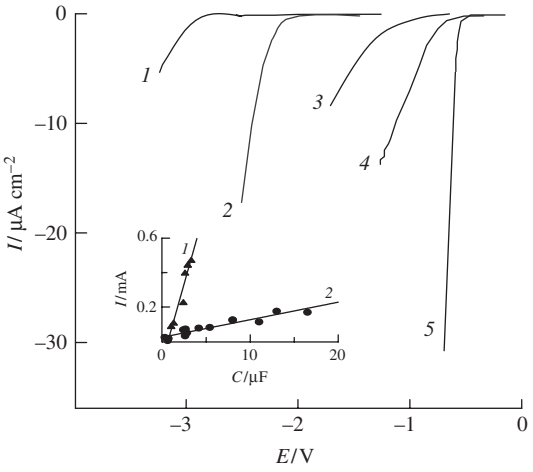

Figure 2 Voltammograms of (*1*) copper, (*2*) tungsten, (*3*) nanopaper, (*4*) column and (*5*) filament electrodes in HMPA + 0.2 M $NaClO_4$. Scan rate is 0.05 V s^{-1}. Inset shows the *I*–*C* relations for (*1*) nanopaper and (*2*) column electrodes at $E = -1.2$ V (The current value for column electrodes is multiplied by 20).

qualitative than quantitative character because of proximity of the assumption, they allow us to conclude that the most effective emitter of e_s^- (*i.e.*, having a maximum number of emission centres per unit area), is the filament structure and the least active cathode is nanopaper. The voltammograms were recorded on electrochemically sharpened tungsten electrodes to reveal a correlation between surface morphology and current value of solvated electrons emission (Figure 2). The overvoltage decrease of electron emission was observed for a tungsten edge to be accompanied by a dark blue colouration near the electrode surface in contrast to polished metallic electrodes. However, *I* and blue colour intensity on sharpened electrodes were unstable and monotonically lowered with time in comparison with carbon electrodes. It is accorded with published data[8,9] where auto-electron emission centres were shown to be located on the tips of nanotubes. Thus, the given experimental data indicate that a considerable decrease of the overvoltage of solvated electrons emission into HMPA solutions is independent of electrode nature and is defined by the presence of atomically sharp parts of its surface. It is possible to interpret qualitatively the results for carbon nanostructures in terms of differences in their morphology: each sharp part of filament structure is available to a solution, and for nanopaper the access of electrolyte is limited to SWNT edges bound in bundles. SWNT located on hemispherical tops of column structures are more available to a solution than nanopaper parts.

Experimental results are direct evidence of the generation of solvated electrons from nanocarbon structures in HMPA in a moderate cathodic potential range. Though the establishment of physical principles of solvated electrons injection into a solution is of indisputable interest and demands further research, its existence allows one to govern a cathodic reaction mechanism regardless of emission physical nature.

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