Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2009, **19**, 317–319

Mendeleev Communications

Effect of organic adsorbates on the electrochemical behaviour of carbon nanostructures

Alexander G. Krivenko,*[a] Natal'ya S. Komarova,[a] Elena V. Stenina[b] and Liana N. Sviridova[b]

[a] *Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 496 522 3507; e-mail: krivenko@icp.ac.ru*
[b] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*

DOI: 10.1016/j.mencom.2009.11.007

The effect of camphor, cryptand [2.2.2] and sodium cryptate adsorption on the differential capacitance of carbon nanostructures has been studied. A 2–4-fold increase in the differential capacitance of these materials in the potential range from –1.0 to 0 V has been discovered and explained by the Rehbinder effect.

Starting from 1996 when the first study on the electrochemistry of nanotube electrodes appeared, the number of both fundamental and applied studies on electrodes from nanostructured carbon materials was increasing. Current attention is focused on various effects resulting from the adsorption of organic molecules on electrodes containing nanostructured carbon.[1,2]

Interest in these problems is primarily due to the discovery of electrocatalytic effects of the adsorbate on the electrode reactions that occur at the nanotube electrode–solution interface.[3,4] However, the results of the majority of studies are scattered, hard to systematize, and actually provide little information on the adsorption processes on such electrodes. For this reason, it seems expedient to study electrodes based on well-characterised carbon nanostructures with various morphologies, in solutions of adsorbates comprehensively studied before on smooth metal electrodes. The following adsorbates were chosen: camphor, cryptofix (cryptand [2.2.2]) and its cationic complexes (cryptates). These surface-active compounds have very high surface activity that manifests itself as complete surface coverage by the adsorbate even at very small volume concentrations of surfactants (10^{-4}–10^{-5} mol dm^{-3}) in almost the entire range of adsorption potentials. To a considerable extent, this is due to the high value of attraction constant a, which characterises the lateral interactions of adsorbate particles, in the Frumkin isotherm, which most adequately describes adsorption phenomena on mercury-like electrodes. The highest value ($a \sim 6$) among the selected compounds belongs to camphor, which forms a two-dimensional condensed layer on electrodes from mercury, zinc, tin and bismuth; this is one of the strongest layers among those known to date. It is known that the presence of a two-dimensional condensed camphor layer decreases the rate of electron transfer in the $[Fe(CN)_6]^{3-/4-}$ redox reaction on Au[5] and inhibits the electrochemical reduction of the persulfate ion on Hg.[6]

Note that, even for traditional carbon materials, such as graphite, pyrographite, glass carbon, carbon black, carbon fibres, activated carbon, *etc.*, no unambiguous experimental data have been obtained concerning the effect of adsorption of organic compounds on the differential capacitance (C) and the electron transfer rate. In particular, published data for glass carbon show differently directed changes in electrochemical characteristics, which depend on the preparation method, sample preparation for the measurements and nature of the adsorbate.[7,8]

The adsorption properties of materials from carbon nanotubes primarily depend on the number of individual adsorption sites.[9] In turn, this parameter is determined by the conditions under which van der Waals interactions facilitating the association of nanotubes into bundles operate; the material surface becomes unequally accessible as a result of this association.

This study deals with the effect of adsorption of camphor, cryptand [2.2.2] and sodium cryptate on the value of C and electrode reaction currents on nanostructured carbon of various morphologies in aqueous electrolyte solutions. We chose the following model electrode processes: the $[Fe(CN)_6]^{3-/4-}$ redox reaction, which is often used for testing nanostructured electrodes, and the previously discovered[10,11] electroreduction reactions of various depolarisers (N_2O, NO_2^-, NO_3^-) due to injection of solvated electrons into the electrolyte solution from atomic-sharp surface areas in the cathodic potential region.

Three types of carbon structures were used for electrode preparation: nanopaper, columnar and filament structures. The preparation techniques and full characteristics of these structures are given elsewhere.[10,12,13] Nanopaper consisted of single-walled nanotubes (SWNT) with characteristic diameters of 1.2–1.6 nm (> 98–99 wt%) associated into bundles by van der Waals forces; the bundles consisted of ~100–5000 nanotubes and, in turn, constituted larger carpet-like aggregates up to hundreds of micrometers in size. The apparent working surface area of these electrodes was ~0.1–0.05 cm^2.[10] Columnar structures were represented by column-like elements consisting of amorphous carbon flakes up to 2–3 mm long with a diameter of about 50 μm. The hemispheric apexes of these structures contain multiple-walled nanotubes 20–30 nm in diameter and ~1 m in length. The third structure consists of SWNTs 2–4 nm in diameter and 0.5–1.5 mm in length, coated with a shell 50–130 nm in diameter consisting of unordered graphite-like carbon.

Differential capacitance was measured by cyclic voltammetry and impedance method on electrodes based on the structures described above, in the presence and in the absence of adsorbates. Measurement results show that, for nanopaper and columnar structures, the capacitance increases in sodium sulfate solutions containing 10^{-4} mol dm^{-3} of camphor in the entire range of potentials covered, in comparison with solutions containing no adsorbate. An increase in the camphor concentration by an order results in a further increase in capacitance of the structures specified above. A similar situation is observed for cryptofix and sodium cryptate. The increase in C of the nanopaper structure upon addition of adsorbates is shown in Figure 1.

Since the measurements were carried out at a high AC frequency (1117 Hz) and Faraday currents were not detected in the potential range of –(0.7–0.1) V, the contribution of pseudocapacity to the measured C values is insignificant. The observed

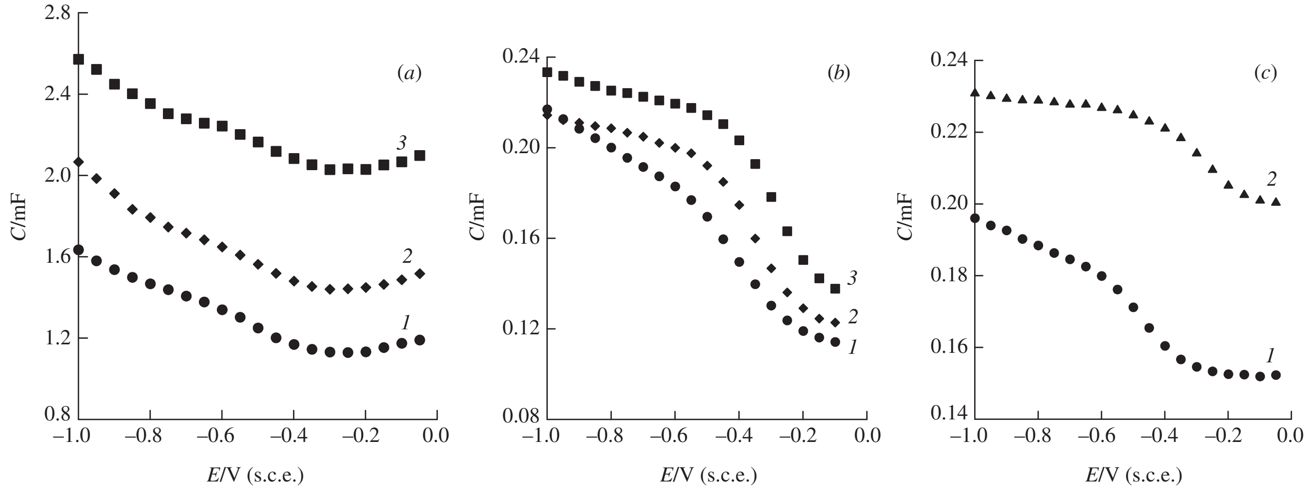

Figure 1 $C(E)$ curves on a nanopaper electrode (*a*) in (*1*) 0.1 M Na_2SO_4, (*2*) 0.1 M Na_2SO_4 + 10^{-4} M camphor and (*3*) 0.1 M Na_2SO_4 + 10^{-3} M camphor solutions; (*b*) in (*1*) 0.1 M Na_2SO_4, (*2*) 0.1 M Na_2SO_4 + 10^{-4} M sodium cryptate and (*3*) 0.1 M Na_2SO_4 + 10^{-3} M sodium cryptate solutions; (*c*) in (*1*) 0.01 M $MgSO_4$ and (*2*) 0.01 M $MgSO_4$ + 10^{-2} M cryptofix solutions. Surfaces of electrodes are different for (*a*), (*b*) and (*c*).

effect of capacitance increase is unusual because C is expected to decrease upon adsorption of surface-active compounds on electrodes. The discovered experimental fact of capacitance increase upon adsorption of surface active compounds on the electrodes can only be explained by a considerable increase in the electrode surface accessible to the electrolyte. Taking into account the morphology of nanopaper and columnar electrodes,[9,14] it can be assumed that the increase in differential capacitance is caused by an increase in the surface due to a partial fragmentation of bundles into which SWNTs are consolidated by van der Waals forces during the synthesis, while for columnar electrodes this effect may be due to splitting of carbon ‘flakes’ that form highly oriented columnar structures. The surface of a nanopaper electrode increased in the presence of camphor by a factor of 10–15.

In our opinion, the discovered increase in differential capacitance of nanostructured carbon electrodes in the presence of surface-active compounds suggests that their surface undergoes loosening, which is a specific form of the Rehbinder effect. The essence of this effect lies in the plasticising effect of environments, solutions of surface-active compounds in particular, on solid materials. Note that the thermodynamic Rehbinder effect results from a decrease in work for the formation of new surface upon deformation due to a decrease in free surface energy of a solid exposed to the environment. The molecular nature of this effect lies in the facilitation of breakdown and cleavage of intermolecular (interatomic, ionic) bonds in a solid in the presence of adsorption-active but sufficiently mobile foreign molecules (atoms, ions).[14] A similar effect was observed previously in the electrochemically initiated incorporation of alkali metal ions into SWNT bunches followed by their partial splitting.[15]

Under the same measurement conditions, the capacitance of the filament structure decreases insignificantly, *viz*., by a factor of 1.2–1.3. This also implies some growth in the accessible electrode surface, which should have resulted in an increase in capacitance, but this effect is almost eliminated by the decrease in capacitance due to the adsorption of the surface-active compound. Based on the morphology of this structure, it can be stated that the filament structure is the least susceptible to loosening upon adsorption of organic compounds.

A study on the effect of adsorption of the surface-active compounds on electrode reactions at the nanostructured electrode/solution interface revealed that the presence of the adsorbates results in a noticeable inhibition of injection currents in the cathodic range of potentials starting from a concentration of 10^{-4} mol dm^{-3}. These adsorption layers similarly affect the electroreduction of nitrate and nitrite ions on nanopaper and columnar structures. Conversely, a noticeable decrease in the peak amplitudes for the $[Fe(CN)_6]^{3-/4-}$ redox reaction on the nanopaper electrode occurs only at camphor or sodium cryptate concentrations of $\geq 10^{-3}$ mol dm^{-3}. Consolidated experimental data on the effect of camphor, sodium cryptate and cryptofix on the differential capacitance and electrode reaction currents on nanostructured electrodes are presented in Table 1.

Thus, we found that the effect of adsorbates on differential capacitance is opposite for nanostructured electrodes (with highly developed surface) and smooth ones and is almost similar as concerns the inhibition of electrode reactions. It is assumed that, owing to the high surface activity of surface-active compounds used in the study, the formation of adsorption layers is accompanied by at least partial disintegration of carbon nanoforms, which explains the increase in the differential capacitance

Table 1 Effect of adsorbates on differential capacitance (C_d), injection currents (I_i) and reduction of $K_3[Fe(CN)_6]$ (I_R) on carbon nanostructures.

Electrode type	Camphor (10^{-4} M)/(10^{-3} M)			Sodium cryptate (10^{-4} M)/(10^{-3} M)			Cryptofix (10^{-2} M)	
	C_d	I_i	I_R	C_d	I_i	I_R	C_d	I_i
Nanopaper	Increased by a factor of (2–3)/(3–4)	Inhibited by a factor of (1.5–1.7)/(2.0–2.5)	Unchanged/inhibited by a factor of (1.4–1.6)	Increased by a factor of (2–3)/(3–4)	Inhibited by a factor of (2–3)/(completely)	Unchanged/inhibited by a factor of (1.4–1.5)	Increased by a factor of (1.3–1.4)	Inhibited by a factor of (1.2–1.3)
Columnar	Increased by a factor of (2–3)/(3–4)	Inhibited by a factor of (1.3–1.4)/(2.3–2.6)	Unchanged/inhibited by a factor of (1.3–1.5)	Increased by a factor of (3–4)/(7–8)	Inhibited by a factor of (1.05–1.10)/(1.2–2.8)	Inhibited by a factor of (2–3)/(3–4)	Increased by a factor of (1.1–1.2)	Inhibited by a factor of (4.5–5.0)
Filament	Inhibited by a factor of (1.3–1.5)	—	—	—	—	—	—	—

that is not observed for smooth electrodes. On the other hand, the effects of inhibition of electrode reactions upon adsorption of surface-active compounds are similar for smooth and nanostructured electrodes.

References

1 N. S. Lawrence and J. Wang, *Electrochem. Commun.*, 2006, **8**, 71.

2 C. E. Banks, A. Crossley, Ch. Salter, Sh. J. Wilkins and R. G. Compton, *Angew. Chem.*, 2006, **45**, 2533.

3 R. H. Baughman, C. Cui, A. A. Zakhidov, Z. Iqbal, J. N. Barisci, G. M. Spinks, G. G. Wallace, A. Mazzoldi, D. De Rossi, A. G. Rinzler, O. Jaschinski, S. Roth and M. Kertesz, *Science*, 1999, **284**, 1340.

4 M. L. Pedano and G. A. Rivas, *Electrochem. Commun.*, 2004, **6**, 10.

5 J. Oslonovitch, Y.-J. Li, C. Donner and K. Krischer, *J. Electroanal. Chem.*, 2002, **541**, 163.

6 N. V. Fedorovich, B. B. Damaskin, E. V. Stenina and C. M. Beniaminova, *Elektrokhimiya*, 1979, **15**, 1226 (*Russ. J. Electrochem.*, 1979, **15**, 1413).

7 M. Danckwerts, J. Oslonovitch, B. Pettinger and K. Krischer, *J. Phys. Chem. B*, 2004, **108**, 14398.

8 M. R. Tarasevich, *Elektrokhimiya uglerodnykh materialov* (*Electrochemistry of Carbon Materials*), Nauka, Moscow, 1984, p. 251 (in Russian).

9 A. V. Eketskii, *Usp. Fiz. Nauk*, 2004, **174**, 1191 (*Phys. Usp.*, 2004, **47**, 1119).

10 A. G. Krivenko, V. I. Matyushenko, E. V. Stenina, L. N. Sviridova, A. V. Krestinin, G. I. Zvereva, V. A. Kurmaz, A. G. Ryabenko, S. N. Dmitriev and V. A. Skuratov, *Electrochem. Commun.*, 2005, **7**, 199.

11 A. G. Krivenko, N. S. Komarova and N. P. Piven', *Electrochem. Commun.*, 2007, **9**, 2364.

12 B. P. Tarasov, V. E. Muradyan, Yu. M. Shul'ga, E. P. Krinichnaya, N. S. Kuyunko, O. N. Efimov, E. D. Obraztsova, D. V. Schur, J. P. Maehlen, V. A. Yartys and H.-J. Lai, *Carbon*, 2003, **41**, 1357.

13 N. A. Kiselev, A. V. Krestinin, A. V. Raevskii, O. M. Zhigalina, G. I. Zvereva, M. B. Kislov, V. V. Artemov, Yu. V. Grigoriev and J. L. Hutchiso, *Carbon*, 2006, **44**, 2289.

14 P. A. Rehbinder, *Izbrannye trudy* (*Selected Works*), Nauka, Moscow, 1978, p. 368 (in Russian).

15 S. Agnihotri, J. P. Mota, M. Rostam-Abadi and M. J. Rood, *J. Phys. Chem. B*, 2006, **110**, 7640.

Received: 15th May 2009; Com. 09/3337