Influence of surface chemical structure of active carbon on its electrochemical behaviour in the presence of silver

S. BINIAK[1]*, M. PAKULA[2] and A. ŚWIĄTKOWSKI[3]

[1]*Faculty of Chemistry, Nicolaus Copernicus University, 87-100 Toruń, Poland;*
[2]*Polish Naval Academy, 81-919 Gdynia, Poland;*
[3]*Military Technical Academy, 01-489 Warsaw, Poland*
(*author for correspondence)

Abstract

Cyclic voltammetric studies of the influence of surface chemistry on the electrochemical behaviour of powdered active carbon electrodes were carried out in the presence of silver both in bulk solution and pre-adsorbed on carbon. Surfaces with a variety of chemical properties were obtained through the modification of carbon samples by heat treatment under vacuum, oxidation with concentrated nitric acid and annealing in an ammonia atmosphere. The surface area (BET), acid–base neutralization capacities and sorption capacity towards Ag^+ ions were estimated in the samples obtained. The states and relative amounts of deposited Ag species were estimated using XPS. The influence of the surface chemistry of the powdered carbon material in terms of its electrochemical properties and the mechanism of silver adsorption and deposition is discussed.

1. Introduction

It has been shown that active carbon materials not only have excellent adsorption capabilities but also outstanding reduction properties. They are capable of reducing ions of higher standard potentials to adsorbed elemental metals or lower valence ions [1–7]. In prolonged contact with Ag(I) ion solution, carbon materials acquire a large percentage of zero-valence silver on the surface and in the near-surface region [3–7]. The following phenomena may occur on the carbon surface: (i) cation exchange and/or complex formation of metal ions, (ii) spontaneous reduction of cations connected with carbon surface oxidation, (iii) diffusion and/or intercalation of metal, and (iv) growth of hemispherical silver nuclei on the surface. All these phenomena have occurred to varying extents on different carbon materials [3–16].

The reduction property of active carbon was expected to be potentially useful in the concentration, ecovery or separation of precious metals and in the treatment of toxic solutions or gases. Hiskey and Jiang [13] investi-gated the loading of gold onto carbon in chloride solutions and found that Au(III) is reduced to metallic gold on the carbon surface; the rate of reduction is controlled by boundary layer diffusion.

The electrodeposition of silver on carbon electrodes has been investigated, particular attention being given to the study of the initial stages leading to the formation of metallic centres [14–16]. Because carbon materials appropriately modified with silver can be used not only in electrocatalysis [7] and catalysis [8] but also as antibacterial agents [9, 10], the study of the properties of these materials is highly significant in theory and practice. However, ways of controlling the size distribution of the deposited silver particles need to be found before any practical applications can be embarked upon.

This paper examines the relationship between the sorption capacity towards Ag^+ ions, the electrochemical behaviour of powdered active carbon materials with pre-adsorbed silver and the chemical structure of the active carbon surface.

2. Experimental details

2.1. *Materials and their properties*

Three samples of de-ashed (conc. HF and HCl) and chemically modified commercial active carbon D-43/1 (Carbo-Tech, Essen, Germany) were studied. Oxidation with concentrated HNO_3 (D–O), as well as annealing in an ammonia atmosphere at 1170 K (D–N) and under vacuum at 1000 K (D–H), were used as modification procedures. The chemical properties of the modified carbon surface were estimated by standard neutralization – titration with HCl, NaOH (0.1 M in water) and $NaOC_2H_5$ (0.1 M in ethanol). Additionally, the pHs of carbon slurries in 0.1 M $NaNO_3$ were determined. The results are presented in Table 1. Information about the surface chemical structure of the carbon samples used is given elsewhere [17].

2.2. *Adsorption and cyclic voltammetric measurements*

The extent of Ag^+ ion adsorption on three modified active carbons from aq. $AgNO_3$ (0.05 M, pH 3.20) were measured. The active carbon samples were immersed in the solution in dark bottles for 2 h, after which the Ag^+ concentration and the pH of the solutions were determined. The Ag^+ concentration was determined by titration with KSCN using Fe^{3+} as indicator. The adsorbed Ag^+ ions were partially removed from the carbon surface by washing in dil. HNO_3 (0.01 M). The results are listed in Table 2.

The carbon samples obtained with both adsorbed and partially removed Ag^+ ions were milled and then used as powdered active carbon electrodes in the cyclic voltammetric studies. The measurements were performed using the typical three-electrode system and cell described earlier [18, 19].

2.3. *XPS measurements*

XP spectra were obtained with an EscaLab 210 (V. G. Scientific Ltd.) photoelectron spectrometer using non-monochromatized AlK_α radiation (1486.6 eV), the source being operated at 15 kV and 34 mA. Prior to XPS measurement, the carbon samples with preadsorbed silver were dried for 2 h at 373 K. The vacuum in the analysis chamber was always better than 5×10^{-10} Pa. The high-resolution scans were performed over the 365–376 eV range (Ag 3d spectrum) with the pass energy adjusted to 20 eV. In order to obtain an acceptable signal-to-noise ratio the spectral region was scanned 200 times. After subtraction of the base line (Sirley-type), curve fitting was performed using the nonlinear least-squares algorithm and assuming a gaussian/lorenzian mix of variable proportion peak shape. This peak-fitting was repeated until an acceptable fit was obtained (error 5%). The positions of deconvoluted peaks were determined in accordance with literature data [20–22] and empirically derived values.

3. Results and discussion

The results of the physicochemical investigations are set out in Table 1. The surface chemical structure of the active carbon materials tested were highly diverse and depended on the modification procedure used. The oxidized carbon (D–O) exhibits the presence of acidic groups (neutralised with NaOH) and neutral surface oxides (difference between NaOH and $NaOC_2H_5$ consumption). Annealing, especially heating in ammonia (D–N), enhances the basic properties of the carbons at the expense of their acidic properties. Annealing under vacuum (D–H) also creates basic properties on the carbon surface. According to some authors [23–26], the existence of pyrone-like structures incorporated in the carbon matrix is partly responsible for the carbon's basicity. As pyrones are very slightly basic ($pK_b \sim 13$), the recorded pH values of carbon suspension (near 10) indicate the presence of relatively strong basic sites with pK_b about 4. These sites may be the result of the adsorption of molecular oxygen and the form of superoxide ions O_2^-, which can act as a strong Brönsted base [27]. The more pronounced basic properties of ammonia-treated carbon (D–N) result from the presence of additional basic sites, probably nitrogen structures incorporated into the carbon matrix [28]. The surface modification procedures applied to

Table 1. Selected physicochemical properties of the carbon tested

Carbon sample	Apparent surface area, S_{BET}/m^2 g^{-1}	pH*	Acid–base neutralization capacity/mmol g^{-1}		
			HCl	NaOH	$NaOC_2H_5$
D–H	1133	10.7	0.42	0.13	0.22
D–O	1071	3.08	0.13	1.66	2.05
D–N	1178	10.4	0.63	0.09	0.32

*In 0.1 M $NaNO_3$ (blank pH = 6.68)

the tested carbon change its surface area only slightly (Table 1). The nearly 10% differences in apparent surface area (S_{BET}) do not explain the marked differences in adsorption capacity towards silver cations (Table 2).

The contact of active carbon materials with an aqueous solution containing silver ions leads to cation adsorption and the formation of an imperfect metallic electrode sensitive to these ions. Silver films on platinum and carbon electrodes immersed in a solution of silver ions have already been observed [29]. In addition, carbon electrodes show a well-known redox sensitivity similar to any other inert redox electrode [30]. The amount of silver taken up by active carbon depends closely on the immersion time [11], and the precipitation of metallic silver seems to predominate after the first two hours of contact. In order to measure the exchange capacity for Ag^+, the relatively short immersion time (2 h) was used and the amounts of Ag^+ ions eluted with dilute. nitric acid were determined (Table 2). The amount of silver deposited during the first 2 h of immersion depends on the chemical nature of the sorbent and was highest for D–H, intermediate for D–N and nearly 2.5 times smaller for D–O carbon. Adsorption of silver is accompanied by an increase in hydrogen ion concentration (in relation to pH of carbon slurries in $NaNO_3$ solution, see Tables 1 and 2) as a result of ion exchange and/or spontaneous oxidation of the carbon surface (with the participation of water molecules).

The cyclic voltammograms of Ag deposition/solution on the powdered active carbon electrodes (PACEs) tested in aqueous solutions with different Ag^+ concentrations are shown in Figure 1. Figure 1(a) shows CVs recorded in a 0.05 M $NaNO_3$ + 0.01 M $AgNO_3$ solution. The cathodic wave at these electrodes occurs at higher potentials than at a platinum electrode [12]; however, the positive shift is highest for the oxidised carbon (D–O) and lowest for D-N carbon. This means that the presence of surface oxides facilitates reduction in contradistinction to nitrogen-containing functional groups (Brönsted bases). At low Ag^+ concentrations only the anodic response for the D–O carbon (curve 2, Figure 1(a)) is observed ($E_{p,a1} \cong +0.45$ V). Additionally,

Table 2. Ag^+ ion adsorption and desorption data

Carbon sample	Ag^+ ions adsorption		Ag^+ ions eluation with 0.01 M HNO_3
	/mmol g^{-1}	pH	/mmol g^{-1}
D–H	1.120	3.60	0.180
D–O	0.484	2.45	0.182
D–N	0.872	3.66	0.242
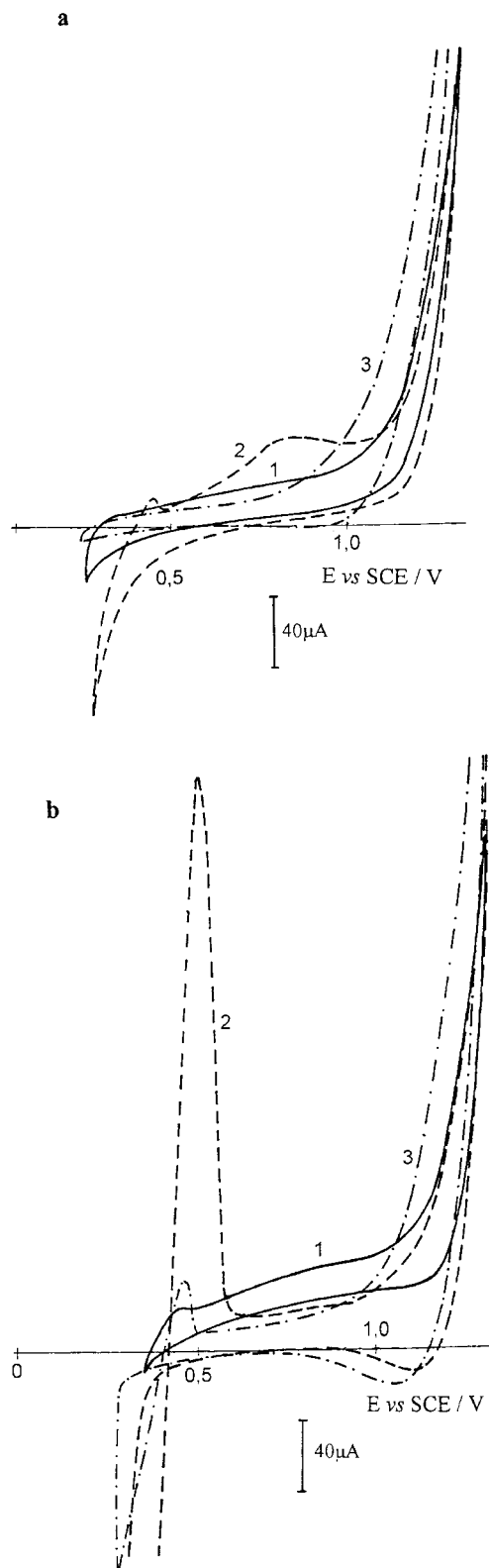
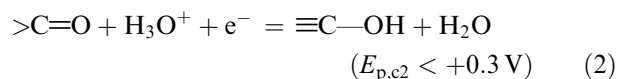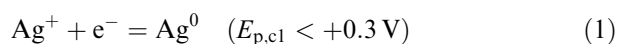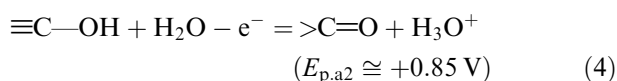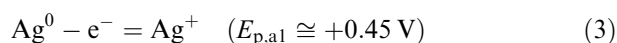*Fig. 1.* Cyclic voltammograms for the PACEs ((1) D–H, (2) D–O, (3) D–N)) recorded after 2 h in (a) 0.05 M $NaNO_3$ + 0.01 M $AgNO_3$, (b) 0.05 M $NaNO_3$ + 0.05 M $AgNO_3$; ($v = 10^{-2}$ V s^{-1}).

the presence of a broad anodic peak on this cyclic curve in the 0.8–0.9 V potential range ($E_{p,a2} \cong +0.85$ V) can be described by the oxidation of electroactive functional groups. Some reactions explaining the observed peaks and waves are as follows:
cathodic (waves):

$$Ag^+ + e^- = Ag^0 \quad (E_{p,c1} < +0.3\,\text{V}) \tag{1}$$

$$>\!C\!=\!O + H_3O^+ + e^- = \equiv\!C\!-\!OH + H_2O$$
$$(E_{p,c2} < +0.3\,\text{V}) \tag{2}$$

anodic (peaks):

$$Ag^0 - e^- = Ag^+ \quad (E_{p,a1} \cong +0.45\,\text{V}) \tag{3}$$

$$\equiv\!C\!-\!OH + H_2O - e^- = >\!C\!=\!O + H_3O^+$$
$$(E_{p,a2} \cong +0.85\,\text{V}) \tag{4}$$

The cathodic processes (1 and 2) create a cathodic wave whose half-wave potentials depend on the pH values of the electrolyte in the near-electrode electrolyte layer. No anodic response for nonoxidized carbons (D–H and D–N) and the weak response for oxidized carbon (D–O) suggests that silver ion reduction is electrochemically irreversible. The shape of the cyclic curves in Figure 1(a) indicates that for carbons with a basic surface (D–N, D–H) and a low silver ion concentration, all the ions in the near electrode layer (volume of powdered electrode) undergo reduction to an electrochemically inactive metallic form. Furthermore, electrooxidation of silver on these carbons is probably inhibited.

This emerges clearly from Figure 1(b), which shows CV curves recorded in a 0.05 M AgNO$_3$ + 0.05 M NaNO$_3$ solution. At higher Ag$^+$ ion concentrations a strong anodic peak for oxidized carbon (D–O), a very weak anodic peak for heat-treated carbon (D–H) and an intermediate peak for D–N carbon were recorded. The shape of the CV curves and, hence, the electrochemical equilibria for D–N and D–H carbons are established very quickly; there is hardly any difference between the first and subsequent cycles. For D–O carbon the anodic peak during the first 2 h of cyclization decreases in size (Figure 2) and correlates well with the silver adsorption equilibrium on this carbon. Nearly 40% of the adsorbed silver can be removed from this carbon surface with dilute acid (Table 2), which indicates that cation exchange took place on this carbon, and that the cation exchanger can be reactivated by reduction according to the scheme proposed by Theodoridou et al. for noble metal ions [31]:
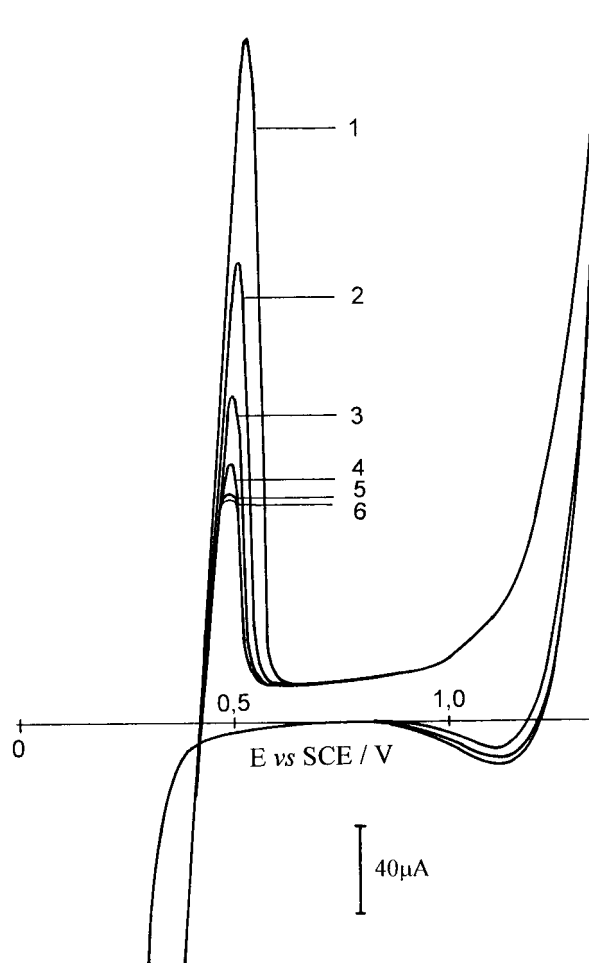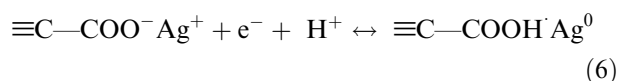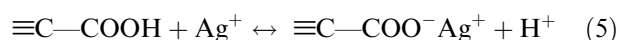

Fig. 2. Cyclic voltammograms for D–O carbon in 0.05 M NaNO$_3$ + 0.05 M AgNO$_3$ during cyclization: (1) 15, (2) 19, (3) 23, (4) 27, (5) 75 and (6) 135 min. (steady state); ($v = 10^{-2}$ V s^{-1}).

$$\equiv\!C\!-\!COOH + Ag^+ \leftrightarrow \equiv\!C\!-\!COO^-Ag^+ + H^+ \tag{5}$$

$$\equiv\!C\!-\!COO^-Ag^+ + e^- + H^+ \leftrightarrow \equiv\!C\!-\!COOH\,Ag^0 \tag{6}$$

The cyclic voltammograms obtained for powdered electrodes prepared from carbons with deposited silver are shown in Figure 3. The CV recorded in neutral blank solution (0.05 M NaNO$_3$) (Figure 3(a)) for D–H carbon (curve 1) shows the presence of a pair of broad peaks ($E_{p,c} = +0.10$ V, $E_{p,a} = +0.65$ V) that can be described as surface oxide functional groups created as result of the spontaneous oxidative action of silver ions during deposition:

$$\equiv\!C\!\cdot + Ag^+ + H_2O = \equiv\!C\!-\!OH\,Ag^0 + H^+ \tag{7}$$
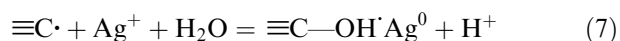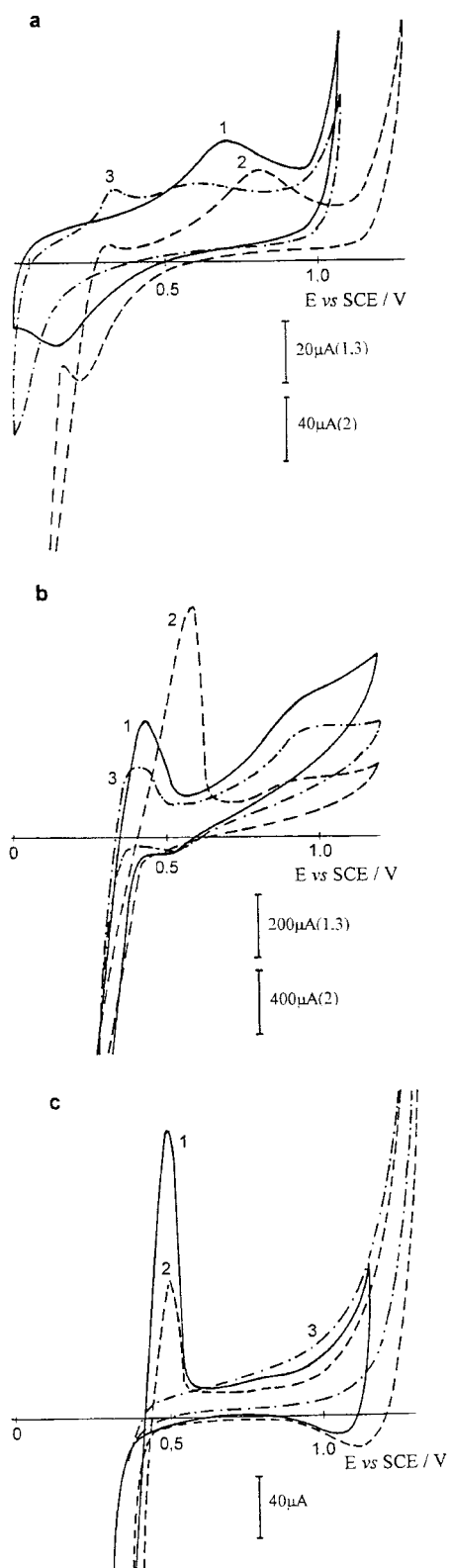
where $\equiv\!C\!\cdot$ is the Lewis base centre.

Fig. 3. Cyclic voltammograms for the PACEs ((1) D–H, (2) D–O, (3) D–N)) with preadsorbed silver recorded in (a) 0.05 M NaNO$_3$, (b) 0.05 M HNO$_3$, (c) 0.05 M NaNO$_3$ + 0.05 M AgNO$_3$; ($v = 10^{-2}$ V s^{-1}).

The absence of silver oxidation and/or reduction peaks is evidence for the electrochemical inactivity of the silver deposited on this carbon (in the form of metallic crystallities). The cyclic voltammogram recorded for the D–O carbon (curve 2) exhibits two anodic peaks ($E_{p,a1} = +0.27$ V, $E_{p,a2} = +0.77$ V) due to the oxidation of adsorbed silver and surface hydroquinone-like groups, respectively. A single cathodic peak ($E_{p,c1} = +0.16$ V) is due to the reduction of quinone-like surface groups according to scheme (2). The large cathodic reduction wave confirms the presence of adsorbed silver cations and their reduction according to scheme (6). For D–N carbon (curve 3) the anodic silver oxidation peak ($E_{p,a1} = +0.30$ V) is indicative of the presence of electroactive silver (e.g. isolated ion/atom couples) adsorbed on the surface. This can be explained by the presence of nitrogen atoms (Brönsted bases) in the surface structures of D–N carbon and their participation in the adsorption thus:

$$>N{-}H + Ag^+ = >N^{\cdot}Ag^0 + H^+ \tag{8}$$

$$>N^{\cdot} + Ag^+ = >N^{\cdot}Ag^+ \tag{9}$$
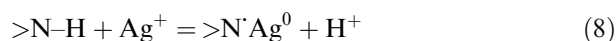
Weakly marked and broad, the second anodic peak shows that the D–N carbon surface contains the smallest amount of electroactive oxides what points on its resistance to oxidation during silver ion adsorption. This peak positive shifting can be caused by higher pH of near electrode layer of solution.

The cyclic voltammograms of all the carbons carrying preadsorbed silver, recorded in dil. nitric acid solution (Figure 3(b)), exhibit a Ag$^+$/Ag^0 couple (cathodic wave $< +0.4$ V and an anodic response in the $+0.40$–0.60 V potential range), as well as an electroactive quinone/hydroquinone-like surface system ($E_{p,c} \cong +0.50$ V; $E_{p,a2} \cong +0.90$ V). The presence of distinctly shaped anodic silver oxidation peaks indicates the partial solution of sorbed (deposited) metal. An almost six-fold higher anodic peak for D–O carbon confirmes the partially ionic form of the adsorbed silver.

The cyclic voltammogram of Ag deposition/solution on carbons with preadsorbed silver in the 0.05 M NaNO$_3$ + 0.05 M AgNO$_3$ solution is shown in Figure 3(c). In relation to the initial carbons (Figure 1(b)) a taller silver oxidation peak for the D–H carbon and a shorter one for the D–O are recorded; however, in the case of the D–N carbon, this peak almost completely disappears. This indicates that silver deposition on D–H carbon is easier if this has previously been covered with a metallic silver layer. This behaviour is a typical example of the nucleation and growth of electrodeposition. The different behaviour of the D–N carbon is

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indicative of another kind of interaction between silver
and this carbon surface.

All carbon samples have been studied by XPS method
in powdered form before and after silver uptake. Some
peaks attributable to carbon, oxygen, nitrogen and
silver (for samples after adsorption) are observed. The
surface composition estimated from XPS data for each
sample are shown in Table 3. The amounts of surface
silver correlated strongly with Ag$^+$ ion adsorption
(Table 2). Figure 4 shows the high resolution silver 3d
spectra from the studied carbon samples. There were
marked differences between experimental (dots) and
sythesized (continous) lines in all the spectra. The
positions of fitted peaks (dashed lines) were determined
according to literature data [21, 22], as well as to
empirically derived values. Table 3 shows the results
obtained from the curve-fitting of the Ag $3d_{5/2}$
(364–370 eV region) spectra of silver deposited on the
carbons. The binding energy (BE), the full width at half
maximum (FWHM) and the relative peak area (r.p.a.)
for separate peaks were estimated and collected. The
XPS results show that the main peak (BE = 367.9 eV),
due to the deposition of metallic silver, is the largest for
D–H carbon. Comparison of these peaks with the $3d_{5/2}$
peaks obtained from metallic Ag and solid AgO/Ag$_2$O
samples [22] shows them to be correlated to some extent.
The BE shift of the $3d_{5/2}$ peak from Ag metal
(BE = 368 eV) to AgO (BE = 367.3 eV) is negative,
which is the opposite of what is expected between a
metal and its oxides [21]. This effect was explained by
differences between Ag^0 and AgO other than electro-
negativity, such as lattice potential, work function
changes, and extra-atomic relaxation energies [22].
Another difference between the $3d_{5/2}$ spectrum obtained
from metallic silver and silver oxides is that the oxide
peak is much broader (FWHM = 1.9 eV) compared to
that of Ag^0 (FWHM = 1.15 eV). Therefore, the broad
peak obtained from the silver adsorbed on the carbons
(BE = 367.0 eV) may be due to the ionic form of the
metal. The next broad peak with BE = 369.3 eV is
probably caused by the presence of isolated zero-valence
silver atoms deposited on the carbon surface.
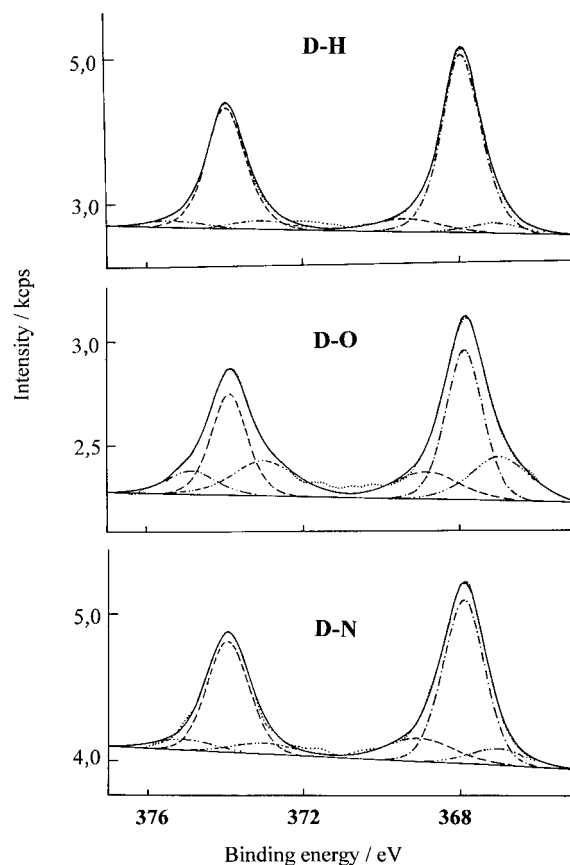

Fig. 4. High-resolution XP spectra of Ag 3d region of carbon samples
after Ag$^+$ ion adsorption.

The XPS results presented in Table 4 confirm the
adsorption/desorption data and electrochemical deposi-
tion/dissolution observation. The smallest amount of
adsorbed metallic silver (in lattice form) and the highest
quantity of ionic silver on the oxidised carbon surface
confirms the partial ion-exchange nature of the adsorp-
tion process for this material. Moreover, the highest

Table 3. Surface composition (at %) of active carbons in ground form

Carbon sample	C	O*	N	Ag
D–H	96.88	2.72	0.40	–
D–H/Ag	94.60	3.77	0.47	1.15
D–O	88.70	10.10	1.20	–
D–O/Ag	88.98	9.42	1.12	0.48
D–N	90.81	6.20	2.91	–
D–N/Ag	90.18	6.38	2.76	0.67

*Oxygen from water excluded

Table 4. Ag $3d_{5/2}$ peak parameters deduced from XPS spectra

Carbon sample	Peak Ag $3d_{5/2}$ parameters		
	BE/eV	r.p.a./%	FWHM/eV
D–H	369.3	10.1	1.93
	367.9	84.5	1.20
	367.0	5.4	1.62
D–O	368.9	20.0	2.01
	367.9	59.4	1.13
	366.9	21.6	1.80
D–N	369.0	16.8	2.09
	367.9	74.5	1.30
	367.0	8.7	1.71

number of isolated silver atoms on this carbon (r.p.a. = 20%) shows that reduction of metal ions took place after sorption on surface functional groups. The ionic and isolated atomic forms of adsorbed silver exhibit electrochemical activity (see Figure 1(b) and 3(b)) and can be eluted with dil. nitric acid (see Table 2). The relatively high participation of metallic silver (both latticed and isolated) in the total XPS signal for D–N carbon is indicative of the different nature of the interaction between nitrogen-containing surface functional groups and adsorbed silver species. Coordination of silver ions with nitrogen probably disperses the silver on the carbon surface, which prevents crystallite formation.

4. Conclusions

(i) The electrochemical behaviour of powdered carbon electrodes in aqueous electrolytes depends on the chemical nature of the surface of the carbon used.

(ii) The surface chemistry of the electrode material strongly influences the Ag^+/Ag^0 redox process: (a) spontaneous and rapid reduction of silver on D–H carbon (Lewis-base) causes silver crystallites to be deposited on the carbon surface, which results in electrode deactivation; (b) the interaction of silver ions with surface oxygen- or nitrogen-containing functional groups (on the D–O and D–N carbons) results in the appearance of an anodic response, a peak due to the oxidation of isolated silver atoms.

(iii) The preadsorption of silver on carbons alters the electrochemical behaviour of the electrodes: (a) electroactive redox surface centres appear on the D–H carbon as a result of oxidation with Ag^+ ions (probably quinone–hydroquinone-like surface forms); (b) the anodic response (the silver oxidation peak) occurs in acidic solution for all the carbon materials studied.

Acknowledgements

References

1. P.A.M. Teirlinck and F.M. Petersen, *Separation Sci. Technol.* **30** (1995) 3129.
2. Yu. A. Tarasenko, A.A. Bagreev, and B.B. Yatsenko, *Russ. J. Phys. Chem.* **67** (1993) 2099.
3. R.-W. Fu, H.-M. Zeng, and Y. Lu, *Carbon*, **31** (1993) 1089.
4. R.-W. Fu, H.-M. Zeng, and Y. Lu, *ibid.* **32** (1994) 593.
5. N.S. Marinkovic, A. Dekanski, Z. Luaševic, B. Vučurović, M. Luašević and J. Stevanović, *Vacuum*, **40** (1990) 95.
6. A. Dekanski, N.S. Marinkovic, J. Stevanovic, V.M. Jovanovic, Z. Luaševic and M. Luašević, *ibid.* **41** (1990) 1772.
7. G.A. Ragoisha, V.M. Jovanovic, M.A. Avramov-Jvic, R.T. Atanasoski and W.H. Smyrl, *J. Electroanal. Chem.* **319** (1991) 373.
8. P.G. Hall, P.M. Gittins, J.M. Winn and J. Robertson *Carbon* **23** (1985) 353.
9. A. Oya, S. Yoshida, J. Alcaniz-Monge and A. Linares-Solano, *ibid.* **34** (1996) 53.
10. Ch. Y. Li, Y.Z. Wan, J. Wang, Y.L. Wang, X.Q. Jiang and L.M. Han, *ibid.*, **36** (1998) 61.
11. A. Swiatkowski, G. Szymanski, and S. Biniak, *in* 'Fundamentals of Adsorption', edited by M.D. LeVan (Kluwer Academic Publishing, Boston, 1996), p. 912.
12. E. Theodoridou, A.D. Jannakoudakis, J.O. Besenhard, and R.F. Sauter, Extend. Abstr. International Conference 'Carbon'86', Baden-Baden (1986) p. 632
13. J.B. Hiskey and X.H. Jiang, *Gold* **90** (1990) 369.
14. A. Serruya, B.R. Scharifker, I. Gonzalez, M.T. Oropeza and M. Palomar-Pardave, *J. Appl. Electrochem.* **26** (1996) 451.
15. B.U. Yoon, K.-C. Cho and H. Kim, *Anal. Sci.* **12** (1996) 321.
16. J.P. Sousa, *J. Electroanal. Chem.* **372** (1994) 152.
17. S. Biniak, G. Szymanski, J. Siedlewski and A. Swiatkowski, *Carbon* **37** (1997) 1799.
18. M. Pakula, A. Światkowski and S. Biniak, *J. Appl. Electrochem.* **25** (1995) 1038.
19. A. Światkowski, M. Pakula, and S. Biniak, *Electrochim. Acta* **42** (1997) 1441.
20. M. Pakula, S. Biniak and A. Świątkowski, *Langmuir,* **14** (1998) 3089.
21. J.F. Moulder, W.F. Stickle, P.E. Sobol and K.D. Bomben, 'Handbook of X-ray Photoelectron Spectroscopy', edited by J. Chastain, (Perkin-Elmer Corporation, Eden Praire, Minnesota, USA, 1992).
22. J.F. Weaver and G.B. Hoflund, *J. Phys Chem.* **98** (1994) 8519.
23. H.P. Boehm and M. Voll, *Carbon* **8** (1970) 227.
24. M. Voll and H.P. Boehm, *ibid.* **9** (1971) 481.
25. H.P. Boehm, *ibid.* **32** (1994) 759.
26. C.A. Leon y Leon, J. Solar, V. Calemma and L.R. Radovic, *ibid.* **30** (1992) 797.
27. J. Zawadzki and S. Biniak, *Polish J. Chem.* **62** (1988) 195.
28. D. Mang, H.P. Boehm, K. Stanczyk and H. Marsh, *Carbon* **30** (1992) 391.
29. P.L. Allen and A. Hickling, *Anal. Chim. Acta* **11** (1954) 467.
30. V. Majer, J. Vesely and K. Stulik, *Electroanal. Chem. Interface. Electrochem.* **45** (1973) 113.
31. E. Theodoridou, A.D. Jannakoudakis, P.D. Jannakoudakis, N. Pagalos, J.O. Besenhard, C.I. Donner and M. Wicher, *Electrochim. Acta,* **38** (1993) 793.