

Adsorption and surface properties of activated carbon fiber felt electrochemically deposited with metallic ions

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Metal/activated carbon fibers were electrochemically prepared with various metals such as Ag, Cu and Ni. The changes of the physicochemical properties of the activated carbon fiber felts with metallic ions were investigated depending on the treatment times. The activated carbon fiber felts were evaluated for the physicochemical properties of adsorption isotherms and surface area. The quantitative properties in the metal ion solutions were also analyzed from measurements of pH concentration and elemental analysis after the electrochemical treatment. The amount of Ag ions was abruptly decreased at the beginning of the electrochemical reaction, while the amount of Ni ions was nearly constant after the time becomes longer than 20 minute. Subsequently, the surface morphologies were studied to interpret the changes of the adsorption properties.

Key words: Metal/activated carbon fiber, Physicochemical properties, Adsorption isotherm, Surface morphology.

Introduction

Activated carbon materials have been applied most frequently as adsorbents and virtually displaced other materials in water purification, solvent recovery, gas refining, air purification, exhaust desulfurization, deodorization, gas separation and recovery. In particular, the application of activated carbon fibers (ACFs) for water treatment includes, but is not limited to decolorization of solutions like removal of color, odor, taste and other undesirable organic impurities from water, treatment of wastewater and collection and C of solutes [1].

Usually, transition metals are deposited electrochemically [2], by an ion exchange method [3] or by vapour evaporation under vacuum [4]. Activated carbon fiber and activated carbon materials can also reduce ions of higher standard potentials to elemental metals or lower valence ions [5, 6]. The applications of activated carbon fiber and activated carbon indicating electrodes in potentiometric systems showed that when these materials was in contact with metal ion (Ag^+ , Cu^{2+} , Ni^{2+} , Pd^+ etc.) solutions their electrochemical properties changed, as a consequence of spontaneous metal ion deposition on the surface of the carbon materials [7]. Such metal modified carbon electrodes can also used as antibacterial agents [8], catalysts [9], or electrocatalysts [10]. Because these metals have difference ionization tendency, Coulomb force and electrochemical behavior, the study of the properties of modified

activated carbon is very important for electrochemical treatment of metal ions. The electro-deposition of metal ions on granular activated carbon and activated carbon fiber can be used for shielding electromagnetic fields. The sorption capacity for metal ions and electrochemical behavior of activated carbon fiber with pre-adsorbed metal ions are strongly influenced by the chemical surface structure of the supported activated carbon fiber.

In this study, we investigate the changes of physicochemical properties of typical activated carbon fiber felts electrochemically deposited with metallic ions, such as Ag, Cu and Ni and the dependence on treatment times. The activated carbon fiber felts are evaluated for the physicochemical properties of adsorption isotherms and surface area, as well as the quantitative properties in terms of metal ions. Furthermore, the surface morphologies are studied to interpret the changes of the adsorption properties.

Experimental Procedure

Home-made ACFs used as a raw material were prepared from commercial PAN fibers (T-300 Amoco, USA). The elemental analysis (Ce 1110 Elemental analyzer, USA) was conducted for non-treated PAN fiber (Table 1). The fiber was burned off at 450 °C, then chemically activated with KOH and K_2CO_3 in the temperature range of 900~950 °C. For electrochemically metal treatments, AgNO_3 (Aldrich, 99+%, ACS reagent), CuCl_2 (Aldrich, 99+%, ACS reagent) and NiCl_2 (Aldrich, 99+%, ACS reagent) were used as a Ag, Cu and Ni source, respectively. The test electrodes were fabricated as follows. A working electrode consisted of a size of 20(b) × 50(h) × 5(t) mm for the felt type

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Table 1. Characteristics of the Starting Activated Carbon Fiber

	S_{BET} (m ² /g)	Volatile Matter (%)	Ash Content (%)	Elemental Analysis (%)				
				C	H	S	N	O
Activated carbon fiber felt	1920.8	1.93	0.120	95.7	0.920	0.00	1.13	2.25

activated carbon fiber, while a counter electrode was an artificial graphite rod. The electrolyte was 0.001 M metal (Ag, Cu and Ni) nitrate or chloride solution. The electrode properties were investigated by electrochemically adsorbed metal ion measurements at 0.5 mAcm⁻² at room temperature. The measured voltage was set to 4.5 V. All the measurements were conducted in a glove box containing dry argon at room temperature.

For measurements of the physical adsorption properties of the activated carbon fiber felts electrochemically treated with metallic ions, Degisorb 2500 (Micrometrics Instruments Co., USA) volumetric adsorption analyzer was used to study the nitrogen adsorption isotherm at 77 K. During the process of adsorbed volume measurements, nitrogen gas of 99.99999% (Nippon Oxygen Gas Co., Japan) was used as an adsorbent. BET specific surface area, pore volumes and pore size distribution for the felts were investigated from the measurement of nitrogen adsorption isotherms. Before the measurements, all of the felts were heated to 350°C in a high vacuum (1.0×10^{-5} torr) for 5 h as a degassing condition. Scanning electron microscopy (SEM, JSM-5200 JOEL, Japan) was used to observe the surface state and structure of metal treated ACFs and the physical state of the metals. For the elemental analysis in metal ion solutions after electrochemical adsorption, Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES, Jovin Yvon Ultima-C) was used to study the quantitative properties. A combination pH electrode (EYELA Model AR 10) was used to measure the solution pH.

Results and Discussion

The studies on the deposition of metal ions to the activated carbon fibers indicated that such a process consists of several consecutive steps [7]: transfer of the solvated ions (metal ions) from the bulk solution to the proximity of the fiber surface, adsorption of the metal ions and growth of metals on the fiber surface, surface diffusion of metal ions towards active centers, reduction of metal ions on the fiber surface, and incorporation of the metals into the fiber lattice. This method for the electrochemical treatment of metal has the merit of a homogeneous distribution of metal on the fiber surface without impurities like metal oxide compounds. The chemical industry generates wastewater that contains toxic matters like heavy metals in small concentrations so that their economic recovery is not feasible. But, the method using an activated carbon fiber electrode can be

used to separate heavy metals from wastewater.

To compare the adsorption properties after the electrochemical metal treatment, the time dependences of the adsorption isotherms for electrochemically metal-treated activated carbon fibers deposited with various amounts of Ag, Cu and Ni solution are shown in Fig. 1, 2 and 3. These isotherms can be classified as typical Type-I. From the isotherms in Fig. 1 and 3, it is noted that the amount of adsorbed N₂ is slowly increased in the region where the relative pressure is lower than 0.4, while the amount is nearly constant when the relative pressure becomes higher than 0.4. In case of the isotherms in Fig. 2, the amount of adsorbed N₂ abruptly increased in the region where the relative pressure is lower than 0.3. These phenomena are also observed as typical characteristics in microporous carbons. As shown in Fig. 1, 2 and 3, the amounts of adsorbed N₂ (ml/g) decrease with the time of the electrochemical treatment. It is supposed that the macropore, mesopore and wider micropore formed on the surface before the electrochemical treatment are transformed to micropores and narrower micropores. Therefore, it can be suggested that the structure of the electrochemically treated metal-activated carbon fibers is more microporous than meso- and macroporous. The calculated

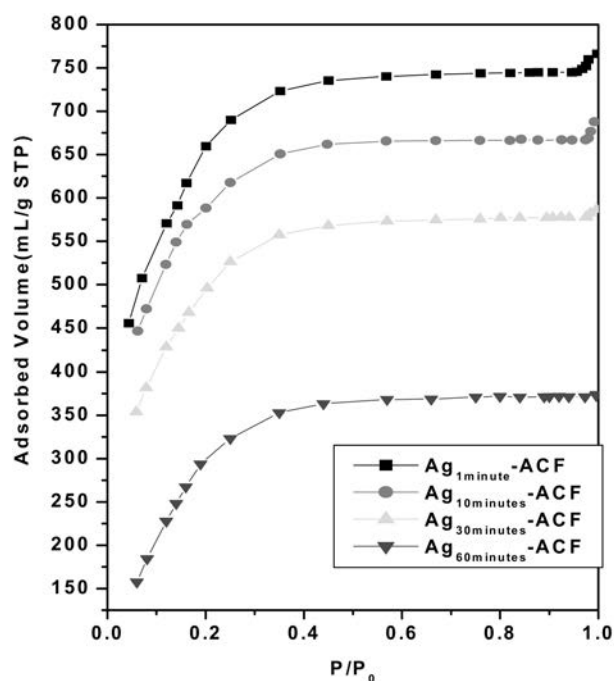


Fig. 1. Time dependence of adsorption isotherm for ACFs electrochemically treated with metallic Ag ion.

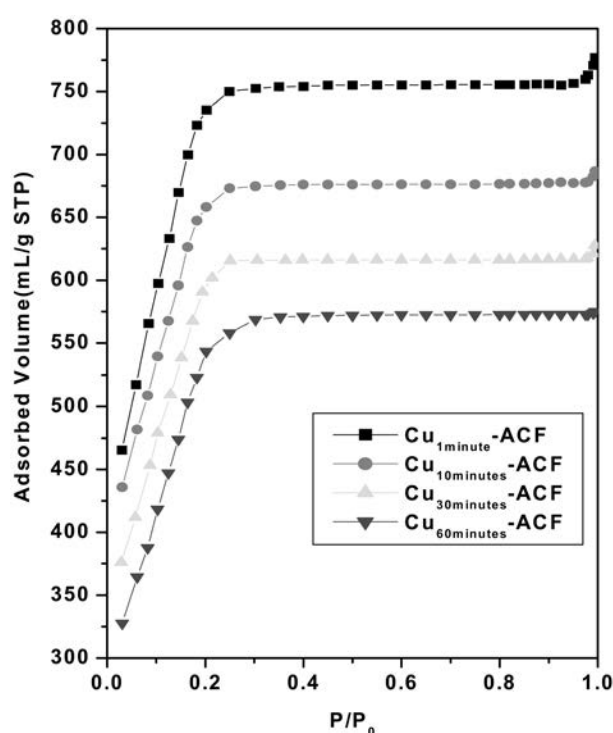


Fig. 2. Time dependence of adsorption isotherm for ACFs electrochemically treated with metallic Cu ion.

S_{BET} , micropore volume and pore radius after electrochemical treatment for Ag-ACFs, Cu-ACFs and Ni-ACFs are shown in Table 2. The areas of electrochemically treated metal-activated carbon fibers are in the range of 913.8~1642.3 m^2/g for Ag, 1365.2~1720.8 m^2/g for Cu, and 1212.6~1895.2 m^2/g for Ni, while the surface area of the starting materials was 1920.8 m^2/g .

Specific pore volumes calculated from α_s -plot are in the range of 0.56~1.12 cm^3/g for Ag, 0.75~1.15 cm^3/g for Cu, and 0.59~1.06 cm^3/g for Ni, respectively. Average pore radii are distributed in the range of 11.6~17.7 Å for Ag, 13.8~18.2 Å for Cu and 7.99~13.5 Å for Ni, respectively.

The electrochemical adsorption of metal ions as a function of pH variation in the solution was studied using activated carbon fiber as a function of time. The pH variation during the electrochemical reaction in metal solution with activated carbon fiber electrodes is shown in Fig. 4. From this Fig. 4, it is seen that the pH concentration abruptly decreased at the beginning of the electrochemical reaction, while the concentrations in the Ag and Ni solutions are nearly constant after the time becomes longer than 10 minute. The pH in the Cu solution is continuously decreased from the beginning point to the end point. It is considered that the pH is a very important factor and the reason for water pollution with increasing acidity in the industrial field. According to Bansal *et al.* [1], it is suggested that the amount of adsorption is a function of the total metal ion concentration and pH of the solution as well as the nature of the carbon used. Activated carbon and ion exchange resins have been used to remove trace metal ions from liquid waste and drinking water. From the results presented, it is proposed that the pH during removing the trace metal ions from the solution should be decreased with increasing adsorbed metal contents on activated carbon fiber electrodes. The differences in adsorption properties among the metal species are mainly due to the electrochemical behavior of metal ions in solution. Ion transference and conductivity are

Table 2. Comparison of S_{BET} , Micropore Volume and Pore Radius after electrochemical treatment (a) Ag-ACFs, (b) Cu-ACFs and (c) Ni-ACFs

(a)			
Sample	S_{BET} (m^2/g)	Specific Micropore Volume (cm^3/g)	Average Pore Radius (Å)
Ag _{1minute} -ACF	1642.3	1.12	17.67
Ag _{10minutes} -ACF	1583.6	0.93	15.98
Ag _{30minutes} -ACF	1321.7	0.70	13.40
Ag _{60minutes} -ACF	913.80	0.56	11.61
(b)			
Sample	S_{BET} (m^2/g)	Specific Micropore Volume (cm^3/g)	Average Pore Radius (Å)
Cu _{1minute} -ACF	1720.8	1.15	18.2
Cu _{10minutes} -ACF	1612.6	1.12	17.1
Cu _{30minutes} -ACF	1525.8	0.90	15.6
Cu _{60minutes} -ACF	1365.2	0.75	13.8
(c)			
Sample	S_{BET} (m^2/g)	Specific Micropore Volume (cm^3/g)	Average Pore Radius (Å)
Ni _{1minute} -ACF	1895.2	1.06	13.5
Ni _{10minutes} -ACF	1432.3	0.83	10.9
Ni _{30minutes} -ACF	1373.1	0.70	9.81
Ni _{60minutes} -ACF	1212.6	0.59	7.99

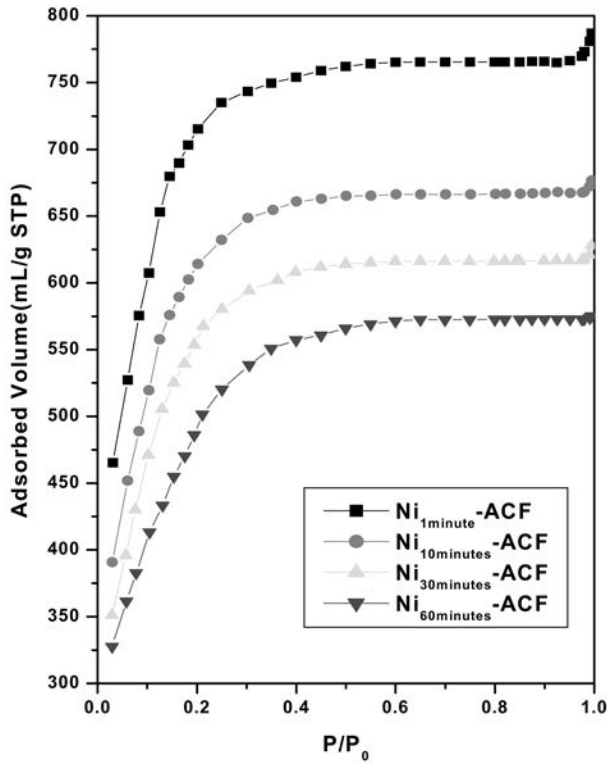


Fig. 3. Time dependence of adsorption isotherm for ACFs electrochemically treated with metallic Ni ion.

defined by

$$A = A_0 - \frac{|z_1 z_2| A^0 F^2}{12 \pi \epsilon \epsilon_0 x_A R T N_A} \frac{q}{1+q} - \frac{|z_1| + |z_2|}{6 \pi \eta N_A} x_A \quad (1)$$

where, A is the molar conductivity, A^0 is the molar conductivity extrapolated to infinite dilution, x_A is the ion layer thickness, η is the solvent viscosity, ϵ is the dielectric constant, F is the Faraday constant, N_A is the Avogadro number and z_1 and z_2 are the positive and negative ion charges, and

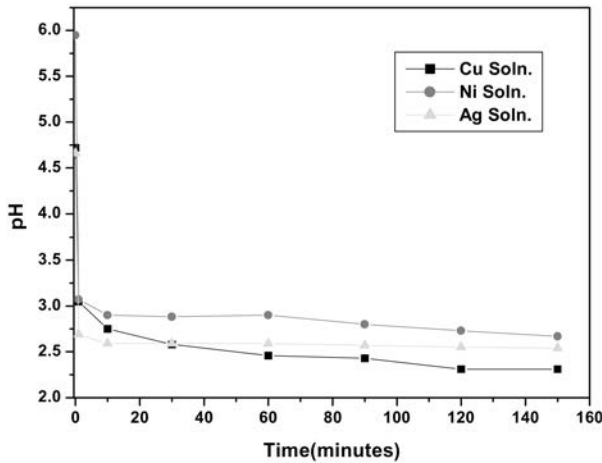


Fig. 4. pH variation in metallic ion solutions after electrochemical reaction using ACF felt.

$$q = \frac{z_1 z_2}{(z_1 - z_2)(z_1 t_1 - z_1 t_2)} \quad (2)$$

where t_1 and t_2 are the transference numbers.

The results of quantitative analysis of metal using Inductively Coupled Plasma-Atomic Emission Spectrometer after electrochemical reactions in metal solutions and the dependence on time are shown Fig. 5. The amount of all metals used decreased with increasing electrochemical treatment time. In particular, the amount of Ag ions abruptly decreased at the beginning of the electrochemical reaction, while the amount of Ni ion was nearly constant after the time becomes longer than 20 minutes. The amount of Cu ion slowly decreased from the beginning to the end of the electrochemical reaction. The trend of deposition on activated carbon fiber electrodes is concerned with ionization tendency and reactivity of metals. Before metal ions reach the fiber surface, they should diffuse from the bulk solution through the concentration boundary layer to the fiber/solution interface. This character is simply an ion transfer phenomenon, and consequently, could be well described by a simplified diffusion equation. For the fluidization, metal ions movement from the solution to the fiber surface may take place by a combination of diffusion and convection. If we assume that the weight fraction of component A (metal ion) is ω_A , the solution density ρ_f and the diffusion coefficient is D_{AB} , for a one-dimensional steady state diffusion in the y direction, the mass flux of component A with respect to stationary coordinates n_{Ay} (made up of a bulk contribution and a diffusive flux superimposed on the bulk flow) is given by

$$n_{Ay} = \frac{DM_A}{A dt} = \omega_A (n_{Ay} + n_{By}) + \rho_f D_{AB} \frac{d\omega_A}{dy} \quad (3)$$

Although the above equation is presented in terms of mass concentration units, molar units could also be

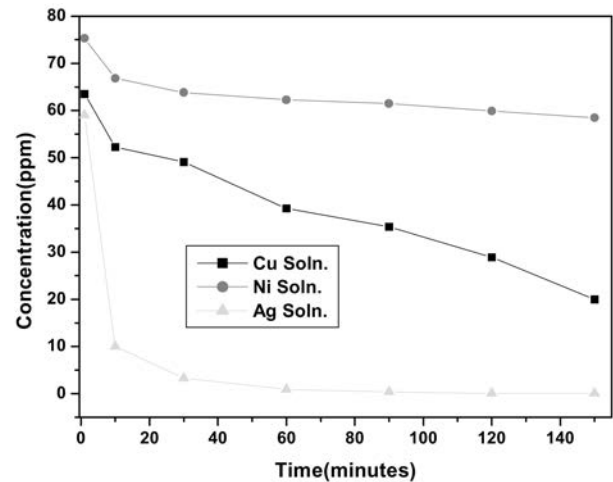


Fig. 5. Results of metallic ion analysis in solutions after electrochemical reaction using ACF felt.

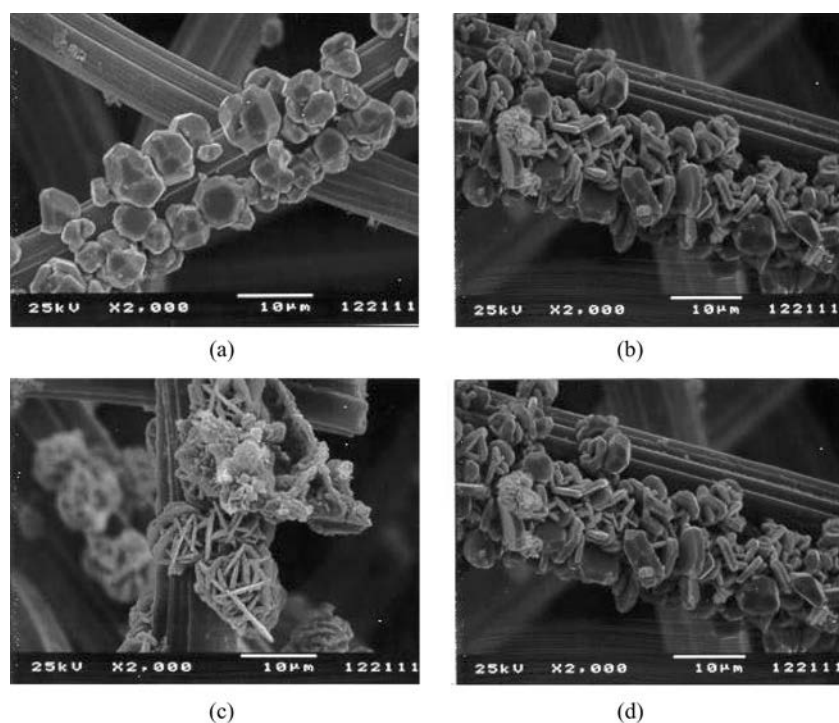


Fig. 6. SEM images after electrochemical adsorption of Ag with ACF in 0.01 M Ag solution; (a) After 1 minute, (b) After 10 minutes, (c) After 30 minutes and (d) After 60 minutes.

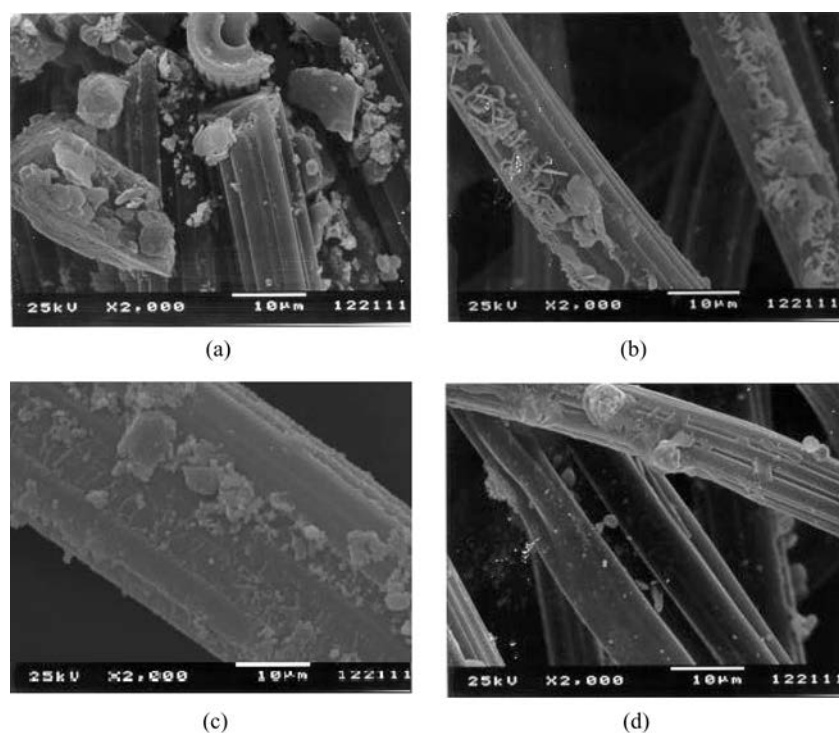


Fig. 7. SEM images after electrochemical adsorption of Cu with ACF in 0.01 M Cu solution; (a) After 1 minute, (b) After 10 minutes, (c) After 30 minutes and (d) After 60 minutes.

used.

The surface morphology and crystal grown state of metal on the fiber surface were investigated by SEM. Typical SEM images are shown in Fig. 6, 7 and 8. Fig. 6 shows the surface morphologies of the electro

chemically adsorbed Ag-activated carbon fiber. The highly developed cracks and cavities, and homogeneously distributed metals and electro chemically grown crystal particles on the fiber surface may be observed. It is considered that the cracks and cavities developed,

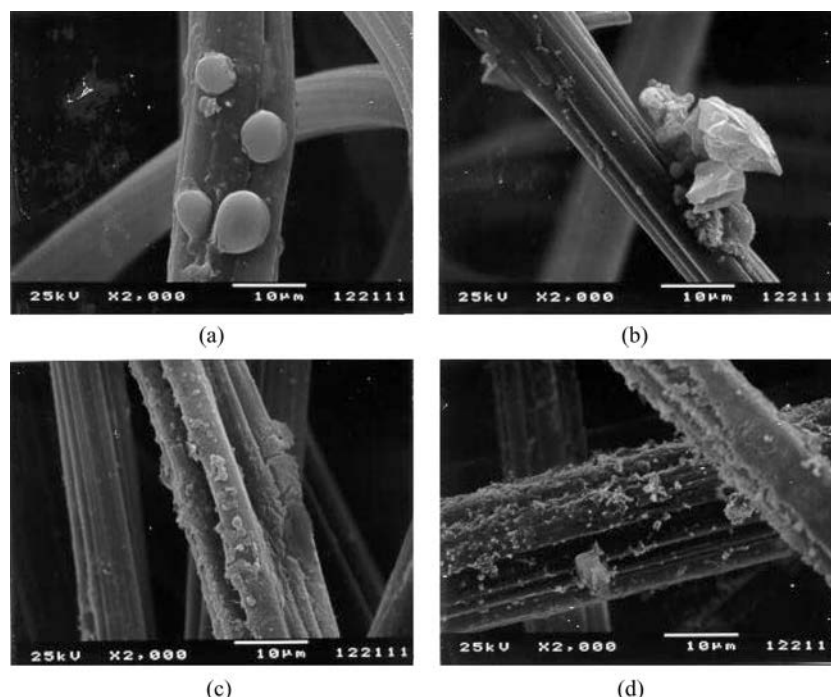


Fig. 8. SEM images after electrochemical adsorption of Ni with ACF in 0.01 M Ni solution; (a) After 1 minute, (b) After 10 minutes, (c) After 30 minutes and (d) After 60 minutes.

the distributed metal and their crystal particles are related to the pore structures like S_{BET} , micropore volume and pore radius. Fig. 7 and 8 show the surface morphologies of the electrochemically adsorbed Cu- and Ni- activated carbon fiber. The outer surface states of the activated carbon fibers are influenced by the metals treated. In the case of Cu in Fig. 7, it is shown that the Cu metal particles on the surface are dispersed heterogeneously and randomly. Almost all the particles are larger than $5\ \mu\text{m}$ in size when the treatment time was longer than 10 minutes. Since the size of particles is larger than the cavities or cracks, several metal particles are observed on blocked cavities or cracks and coated fiber surface. As the treatment time becomes longer, the particles become longer crystals. In Fig. 8, Ni metal particles on the surface are larger than $2\sim 3\ \mu\text{m}$ in size when the treatment time was longer than 30 minutes. The tendency for the electrochemical adsorption effect of Ni-ACF is very different to that of Ag- and Cu-ACFs. The difference depends on the attraction force between the electrochemically charged fiber surface and Ni^+ ions. Table 3 shows the result of Energy Disperse X-ray (EDX) analysis of metallic ion deposited activated carbon fiber felts. From the results, the amount of C, major metals (Ag, Cu and Ni), O and others are listed. The amount of carbon and major metals is richer than any other elements. The amounts of major metals (Ag, Cu and Ni) increase with treatment times. For the electrochemically treated activated carbon fiber felts for 1 minute, a nonhomogeneous distribution of metals is observed, which becomes homogeneous as the carbon surface is oxidized. This

Table 3. EDX Elemental Micro-Analysis of metal/ACFs

	Elements (%)			
	C	Metal (Ag, Cu and Ni)	O	Others
Ag _{1minute} -ACF	81.7	9.01	7.36	1.97
Ag _{10minutes} -ACF	73.0	14.8	10.9	1.39
Ag _{30minutes} -ACF	55.3	35.7	7.26	1.74
Ag _{60minutes} -ACF	9.78	87.3	2.25	0.630
Cu _{1minute} -ACF	89.8	8.56	1.04	0.560
Cu _{10minutes} -ACF	87.5	10.3	1.98	0.230
Cu _{30minutes} -ACF	60.6	36.2	1.88	1.33
Cu _{60minutes} -ACF	18.1	79.3	2.04	0.560
Ni _{1minute} -ACF	94.3	4.23	1.02	0.450
Ni _{10minutes} -ACF	87.9	9.43	2.05	0.650
Ni _{30minutes} -ACF	69.7	28.9	1.25	0.140
Ni _{60minutes} -ACF	40.5	55.4	2.34	1.76

change seem to show that the functionality of activated carbon fiber felt surfaces affects the dispersion of the metals, because the concentration of (+) charges on the activated carbon fiber felt electrode is enhanced depending on the condition with an increase of acidity in solution.

Conclusion

In conclusion, the changes of the physicochemical properties of typical activated carbon fibers deposited with Ag, Cu and Ni were investigated depending on the treatment time. The adsorption isotherms and surface

area of the activated carbon fiber felts were suggested and shown to affect the physicochemical properties, as well as the quantitative properties with the metal ions. Consequently, it is noted that the pH value during removal of the trace metal ions in solution is decreased with increasing adsorbed metal content on the activated carbon fiber electrode. In particular, the amount of Ag ions abruptly decreased at the beginning of the electrochemical reaction, while the amount of Ni ions was nearly constant after the time became longer than 20 minutes. Subsequently, the surface morphologies were suggested to affect the changes of the adsorption properties, accompanying the highly developed creases and cavities, homogeneously distributed metals and electrochemically grown crystal particles on the fiber surface.

References

1. R.C. Bansal, B.J. Donnet, and F. Stoeckli, *Active carbon*, New York; Marcel Dekker, 198 Chapter 3, p. 56.
2. E. Theodoridou, A.D. Jannakoudakis, P.D. Jannakoudakis, P. Andonoglou, and J.O. Besenhard, *Synthetic Metals* 87 (1997) 225.
3. H. Yoshitake, T. Mochizuki, O. Yamazaki, and K.I. Ota, *J. Electroanal Chem.* 361 (1993) 229.
4. P. Fauchais, A. Vavdelle, and A. Denarjean, *Surface & Coating Technology* 97 (1997) 66.
5. R.W. Fu, A.M. Zeng, and Y. Lu, *Carbon* 32 (1994) 593.
6. R.W. Fu and A.M. Zeng, *Carbon* 36 (1998) 19.
7. X. Zhang, H. Zeng, and Y. Lu, *International Symposium on Carbon Science and Technology for New Carbons - Extended Abstracts* (1998) 502.
8. W.C. Oh and W.C. Jang, *Carbon* 41 (2003) 1737.
9. S.R. de Mugual, J.I. Villa, E.I. Jablonski, O.A. Scelza, C.S.M. de Lecea, and A. Linares-Solano, *Applied catalysis a General* 232 (2002) 71.
10. W.C. Oh, B.S. Kim, and Y.S. Lee, *Proceeding of international Conf. on Carbon '02*, Beijing, China, 2002.