

CATHODIC ELIMINATION OF COPPER ION FROM ITS AQUEOUS SOLUTION BY ACTIVATED AND OTHER TYPES OF CARBON FIBERS

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Introduction and experimental

Treatment of waste water containing copper ion is a matter of concern for manufacturers of printed circuits boards. Although activated carbon is a favorite material for decontamination of water, it adsorbs virtually no copper ion when it is simply soaked in it. However, there will be a significant economical merit if activated carbon can be made applicable in this field, since it is an inexpensive adsorbent which is capable of eliminating various unwanted contaminants simultaneously.

Against this background, we have attempted to collect copper ion in the solution with use of an activated carbon fiber (ACF) under cathodic potential. Namely, a bundle of an ACF was soaked in a 0.5 M sulfuric acid containing or not containing 127 wppm of copper ion under cathodic potentials in order to observe its elimination of copper ion from the solution. The performance was compared with that of other carbon fibers (Tab. 1) and of copper wire. The results were discussed based on the information obtained from electrochemical impedance spectrometry (EIS).

Table 1 Specimen fibers and their values of p and q

fibers	Code	Lc (nm)*	p	q
Activate	ACF	1.0	-3.1	0.82
ex-Kynol	KYN	1.0	---	---
ex-Kevlar	KEV	1.4	---	---
ex-lignin	GLY	1.2	-3.6	0.51
PAN hi-st.	PHS	2.0	-2.4	0.24
PAN hi-mod.	PHM	5.4	-3.9	0.62
ex-pitch 50T	50T	12.9	-2.9	0.30
ex-pitch 70T	70T	14.5	-3.9	0.18
copper	CUW	---	-5.3	0.53

*Size of crystallite along the c-axis

Results

The rest potentials for ACF in the copper-containing solution and in the copper-free solution shifted from ca. +400 mV (vs. Ag/AgCl electrode) with time towards the noble side. It was +460 mV when 4000 min (about 67 h) elapsed and it was still going on shifting.

Figure 1 shows chronological variation of the residual concentrations at -100 mv and -180 mV. Although inactivated carbon fibers with a comparable low L_c -value (see Tab. 1) did not eliminate copper ion even at -180 mV, ACF did so at a cathodic potential of -100 mV. A residual concentration of 1 wppm was achieved when 8.8 mg of the ACF was soaked in 15 ml of the solution and a cathodic potential of -200 mV was applied for about 90 h (not shown in Fig. 1). The reason for the performance of ACF being relatively excellent for its low L_c -value was considered to lie in a unique path of electric current endowed exclusively to ACF. According to the results of electrochemical impedance spectroscopy (Fig. 2), the path was decayed by the cathodic reaction.

For the fibers capable of eliminating copper ion, their residual concentration decreased acutely in the very initial period, and then gradually. (In some cases, the residual concentration stood almost still or even increased as the time goes on. This is considered to be caused by drop-off of the once deposited copper particles from the fiber surface into the solution, due to their excessive growth or due to mechanical shock from outside.)

In the ideal case, the relative variations of the residual concentration (C/C_0 , C_0 is the initial concentration) were considered to be approximated by

$$\log (C/C_0) = p t + \log q$$

t: elapsed time, p, q: constants.

This means that the rates of the variation were proportional to the residual concentration of copper ion in the solution. Table 1 contains the values of p and q.

The values of p little differed among the fibers, while those of q varied among the fibers. The rates of the acute decrease were so large as to control the residual concentration at the rest of the elapsed time. The rates were the smallest for ACF.

Figure 3 illustrates a relationship between $1/q$ and the capacity of the electric double layer of the fibers freshly soaked in the copper-free solution[1]. This implies that the acute decrease in the residual concentration is due to condensation of copper ion in the electric double layer formed immediately after a cathodic potential is applied.

The structure of the electric double layer of ACF (and, to a lesser extent, of GLY) appeared to be different from that of the other fibers, because the plots are located off the straight line. ACF performed less favorably than expected from its electric-double-layer capacitance.

Reference

1. I. Tomizuka et al, "Characterization of carbon fibers by EIS in sulfuric acid", *this extended abstract*.

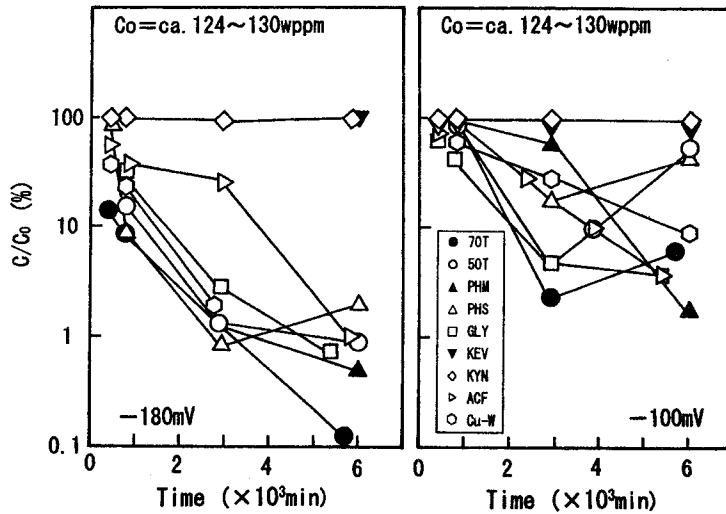


Fig. 1 Chronological variation of the residual concentration of copper ion in the solution.

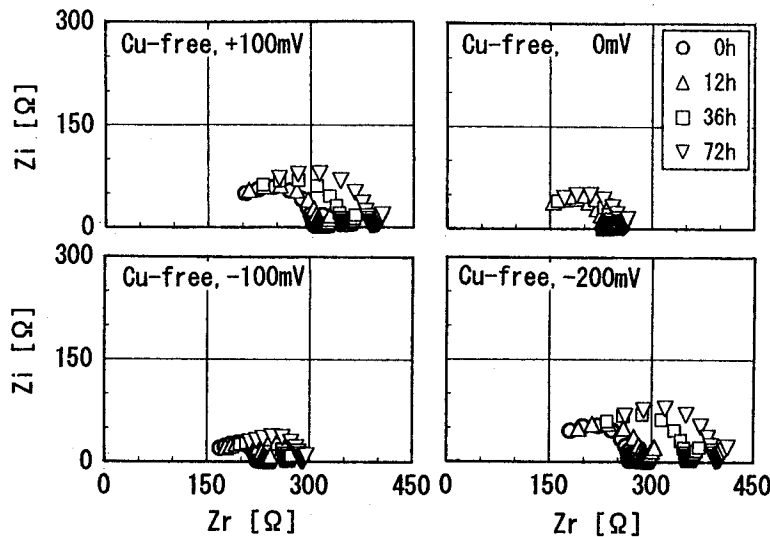


Fig. 2 Cole-Cole plots of ACF in the copper-free solution

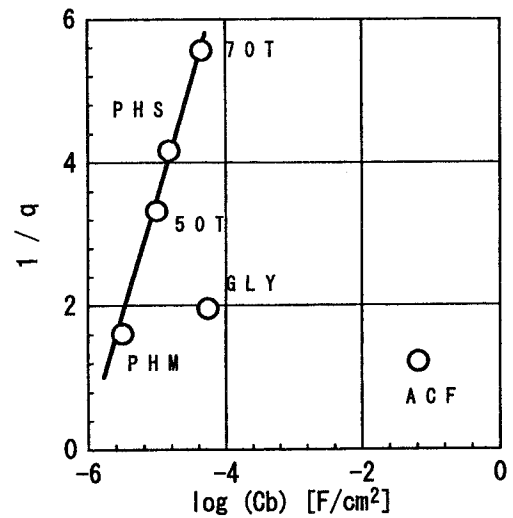


Fig. 3 Plots of $1/q$ against an electric double-layer-capacitance of the fibers in the copper free solution (C_b).