

ELIMINATION OF COPPER ION FROM ITS DILUTE AQUEOUS SOLUTION BY VARIOUS CARBON FIBERS UNDER APPLIED CATHODIC POTENTIALS

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Keywords: carbon fiber, waste water treatment, copper ion

SYNOPSIS

A series of carbon fibers were dipped in an acidic aqueous solution containing copper ion. Cathodic potentials were applied to them. Chronological variation of residual concentration was observed. The behavior was discussed based on electrochemical impedance spectrometry. The ultrahigh modulus carbon fiber performed the best under the condition most favorable for it. Poorly crystallized activated carbon fiber was not much behind. A carbon fiber with a high electro-conductivity and covered with prism planes of the graphitic layer over the surface would perform much better, if such a fiber were available.

INTRODUCTION

Elimination of copper ion from acidic waste water is a problem to be solved for manufacturers of print-circuit boards. The ion is eliminated by non-recycling processes or by recycling ones. Non-recycling ones are cheaper but dubious from environmental point of view. The reverse is the case for the recycling ones. This research is intended to develop a new, more economical recycling process on the basis of electrochemical deposition of the metal.

The material for the electrode for this purpose must be electro-conductive, chemically stable and of a large surface area. Carbon fibers are considered to satisfy these requirements to a reasonable extent. In order to specify the most appropriate fiber, we compared performance of a series of carbon fibers and discussed the behavior based on electrochemical impedance spectrometry (EIS).

EXPERIMENTAL

Employed carbon fibers are tabulated in Table 1. They cover fibers of a wide range of crystallinity, starting from a virtually-amorphous fiber from phenol resin, terminating at an ultrahigh modulus fiber (UHMF) from pitch. They include an activated carbon fiber from phenol-resin based carbon fiber (ACF). A wire of fine copper filaments was also used as a reference. This wire comprises 45 filaments of 170micrometers in diameter. Any fiber carries no coating and no sizing except for ACF, whose surface treatment is not disclosed.

Chronological variation of residual concentration of copper ion was observed with use of a cell depicted in Fig.1, together with details of the connecting section from the metallic terminal pipe to carbon fiber. The free length of the fiber was 40mm. Bottom 35mm of the fiber was dipped in a 15ml of 0.5M of sulfuric acid containing 124wppm of copper ion. A potential of -180mV or -100mV was applied to the terminal (as measured against an Ag/AgCl reference electrode. Also -200mV, 0mV and +100mV for ACF). Separate experiments were performed for each intended time of dipping. Neither mechanical stirring nor gas-bubbling was performed, because these actions might cause detachment of once-deposited metallic copper, which was weakly bonded to a fiber. Numbers of monofilament were approximately 3000 - 4500. Exact number varied depending on the specimen, because some fibers were in a form of yarn, and because their exact counting was not practical. Residual concentration was determined by an atomic absorption spectrum.

EIS was observed in an ordinary cell containing 500ml of the solution. The free length of the fiber was 25mm, and its bottom 5mm was dipped in the solution. The number of monofilament was approximately 2100 for ACF and 2000 for UHMF. Impedance was observed at in the frequency range between 100kHz through 100mHz at each increment of 0.2 of its logarithmic value. A bias voltage was selected from -200mV, -180mV, -100mV, 0mV and +100mV, as appropriate. Perturbation voltage was 10mV(0-p value). The impedance was calculated from integrated values of 1000cycles.

RESULTS AND DISCUSSION

Variation of the residual concentration

In the case of ACF, a nominal potential more cathodic than -100mV was required for elimination of copper ion. Variations of residual concentration of the ion at nominal potentials of -100mV and -180mV are illustrated in Fig. 2 for selected fibers. Tentatively the data are cited in as-observed values, not normalized by the surface area or another, because it is not certain what type of normalization makes sense. Amount of deposited metal varied along the fiber axis and/or among filaments. UHMF performed the best (whether normalized or not). But the other fibers, including those not shown here, were not much behind it.

The trends of the variation were almost identical for most of the cases. The variation in the first 12 hours (the initial period) was more or less different from what followed thereafter (the later period). The amount of the variation in the initial period varied considerably with fibers and applied potentials. For poorly-crystallized fibers it was almost always nil or a moderate decrease. For well-crystallized one, it was a drastic decrease at -180mV, while it was almost nil at -100mV. In the later period, logarithm of the residual concentration decreased almost linearly against time for most fibers, especially at -180mV. In the other words, the variations

were reasonably approximated with an equation of the type

$$\log(C) = p \cdot t + \log(q) \quad (1)$$

C: residual concentration, t: time, p,q: constants.

This means that the rate of the elimination is roughly proportional to the residual concentration. The values of p were not much different among most of the fibers for a given potential. As the pattern of the variation was such that the performance of a fiber was controlled largely by the value of q, especially at -180mV .

A taper-off of the rate of the elimination or even an increase in the residual concentration was observed for certain high-performance fibers in a very later stage of their dipping. A likely cause for it is that some of excessively-grown metallic copper particles detached off the fiber and re-dissolved into the solution. They were found to be bonded to a fiber very weakly.

Electrochemical Impedance Spectrometry (EIS)

Shape of the Cole-Cole plots varied considerably from one fiber to another. Most of them were composed of two arcs, although some appeared to comprise a single arc or three arcs. Three cases of two fibers are discussed in this preprint.

Cole-Cole plots for ACF, one of the most poorly crystallized fibers, are shown in Fig.3. They are typical of two arc plots. They contain a large (apparent) solution resistance and two arcs, respectively of various sizes. The right arc, which is made from impedance seen in the lower frequency side (less than 1Hz) is understood to come solely from reaction(s) across the fiber/solution interface. The left arc, made from impedance in the region larger than 1kHz, is difficult to handle, because a signal of impedance was observed even when EIS was observed in air in this frequency range. It is understood to include impedance with the fiber.

Characteristic values of the right arcs of the plots shown in Fig.3 were evaluated by assuming an equivalent circuit shown in Fig. 4. R_{sol} , C_1 & R_{11} , and C_2 & R_2 stand for (apparent) solution resistance, characteristic values for the left arc and those for the right one.

Results of the right arcs are shown in Fig. 5 (the values are based on the values of impedance observed at 0.25Hz). The values of charge transfer impedance are low. Both C_2 and R_2 decreased with time until a considerable amount of solid copper deposited on the fiber in the cases of the copper-containing solution, while only C_2 decreased in the cases of copper-free solution. This implies deposited copper making an active center. The values of R_{sol} , R_{11} , R_2 and their sum (which would be an approximate value of resistance when direct potential is applied) are summarized in Fig. 6. This chart reveals that a significant part of the total resistance goes to R_{sol} . The values of R_{sol} increased with time. Copper ion in solution diminishes R_{11} even when metallic copper does not deposit.

Fig. 7 illustrates Cole-Cole plots of UHMF, the most crystallized fiber, at a nominal potential of -100mV . Although they appeared to be composed of two arcs, they are of three. This is revealed from the plots of impedance against frequency (not shown). An arc at the high frequency end is too small to be seen in Fig. 7. This fiber shows a very small solution resistance. This chart includes plots for a copper wire observed when it was dipped in the same solution and in the copper-free sulfuric acid of the same molality. Although a chart like Fig. 5 or 6 cannot be prepared since the arcs are not well resolved, two facts are easily noticed. The first is that the initial impedance of UHMF in the copper containing solution is far higher than that of the copper wire. This means that UHMF is initially a semiconductor, if not an insulator. The second is that the shapes of the plots of UHMF approach with time to those of the copper wire in the copper-free solution.

Model of the Behavior of the Two Fibers.

ACF: Smaller value of R_2 estimated from EIS for the fiber suggests that a large number of active sites are present over the fiber surface. That is an advantage of poorly crystallized fiber. That will be the reason why poorly-crystallized fibers perform not far behind the well-crystallized fibers. Most of high R_{sol} of poorly crystallized fibers is considered to emanate, not from genuine solution resistance, but from resistance of the carbon fiber, because it is much smaller for UHMF. This means that the potential difference across the fiber/solution interface is considerably lower than the nominal voltage applied by the potentiostat, (especially when current is large i.e. in the initial period), now that cathodic nature wanes along the fiber axis towards the free end of the fiber. This will be the reason why the performance is not so excellent in spite of the large number of active sites over the surface of this fiber. The larger values of R_{sol} result in a lower power efficiency.

UHMF: The initial high impedance across the fiber/solution interface of UHMF suggests that the surface acts initially as a capacitor. The large decrease in residual concentration seen in the initial period for this fiber at -180mV is likely due to enrichment of copper ion in or near the electrochemical double layer. The enrichment will be high, because the potential difference across the fiber/solution interface is large. The large potential difference over the whole interface is enabled by a low electric resistance along the fiber axis, which is evident from the low (apparent) solution resistance. This effect is small at a lower cathodic potential, say at -100mV .

After finishing the initial period, main mechanism of the elimination shifts from a capacitive nature to a depositing nature. Metallic copper will deposit and grow on the active sites, now possibly on the already-deposited copper particles. This will make the mechanism of the elimination more akin to that for the copper wire. This will be the reason why the EIS of UHMF approaches to that of copper wire (in the copper-free solution, because the solution

is diluted with time). The initial high impedance of UHMF suggests also that only a limited number of active sites are present over the surface. This is a disadvantage in terms of electric deposition. This will be the reason why UHMF performs not far ahead of the other fibers in the later period in spite of its high potential difference across the fiber/solution interface.

Conclusions

A pitch-based ultrahigh modulus (and some other high modulus) fiber performed better in the condition most favorable for it. But poorly crystallized (activated or ordinary) fiber performed not too bad. Their mechanisms appear to be based on different advantages. The advantage of the former group is their high electrical conductivity along the fiber axis. This makes whole surface evenly effective. Low electrical conductivity across their surface is advantageous in the initial stage at a deep cathodic potential, but it is rather disadvantageous otherwise, especially when the cathodic potential is shallow. Directions of the high and the low electrical conductivity are mutually replaced for the latter group. The low conductivity along the fiber axis and high conductivity across the surface are their disadvantage and advantage, respectively. It is likely that a carbon fiber with a high electrical conductivity covered by prism layers of graphitic layer over the surface would perform better than those examined in this work, when such a fiber is materialized.

Acknowledgement:

The authors acknowledge valuable contribution from Prof. Ohta, Prof. Toki, both of Yokohama National University, and Mr. Kuwagaki of Hokuetsu Tanso Co.

Table 1. Employed carbon fibers.

Code	In Fig.2	Manufacturer	Features
Activated C.F.	ACF	Toyo Boseki	Commercial product.
Ex-Kynol		Home-made	Virtually amorphous.
Ex-Kevlar		Home-made	Poorly crystallized, but oriented.
Ex-lignin	GLY	Nippon Chemicals	Poorly crystallized.
PAN High-strength		Toho-Rayon	Commercial grade.
PAN High-modulus	No.2	Toho-Rayon	Commercial grade.
Ex-Pitch 70ton	UHMF	Petca	Ultrahigh modulus, well-crystallized
Ex-pitch 50ton		Petca	High modulus, next to above.
Copper wire	Wire	-----	Commercial wire with vinyl cover.

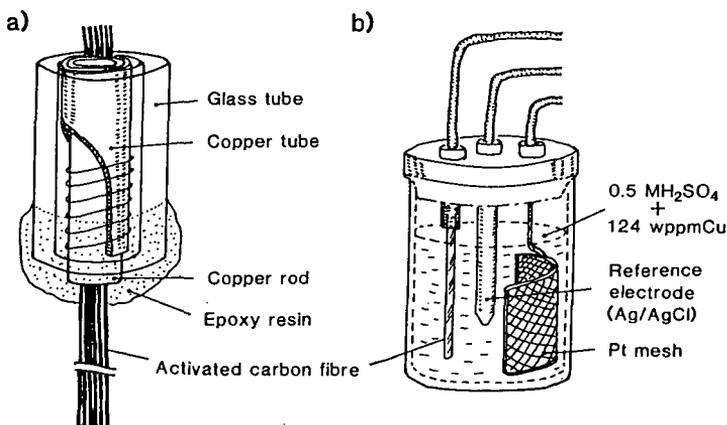


Fig. 1 Schematic illustration of the cell used for observation of residual concentration of copper ion.

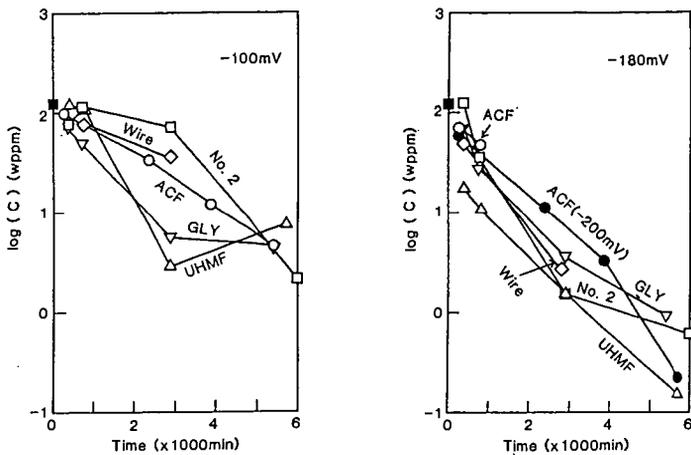


Fig. 2 Chronological variations of residual concentration of copper ion for ACF.

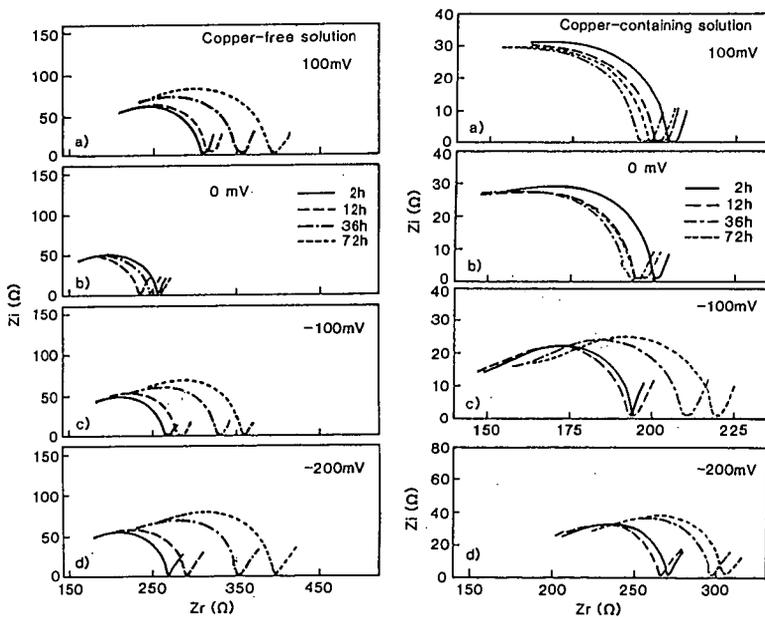


Fig. 3 EIS for ACF

Fig. 4 Equivalent circuit used for analysis of EIS of ACF

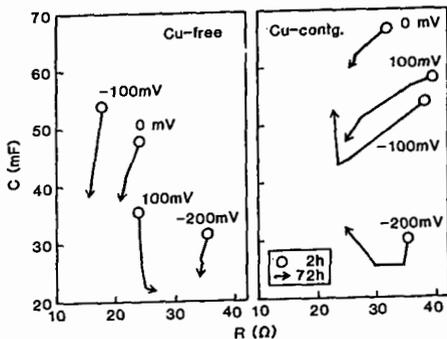
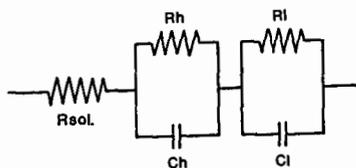


Fig. 5 Values of C_1 and R_1 for the right arcs shown in Fig. 3.

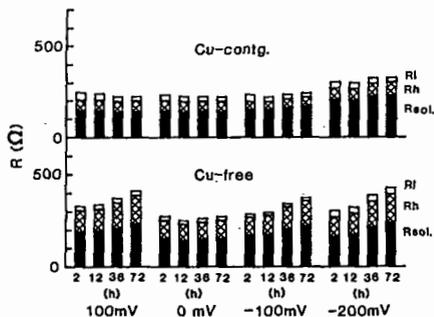


Fig. 6 Estimated contents of resistances under direct current for ACF

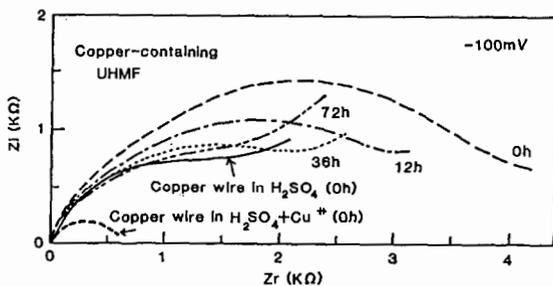


Fig. 7 Cole-Cole plots of UHMF together with those of copper wire.