CHARACTERIZATION OF CARBON FIBERS BY ELECTROCHEMICAL IMPEDANCE SPECTROMETRY IN SULFURIC ACID

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Introduction

In recent time electrochemical impedance spectroscopy (EIS) is being introduced to the field of metallurgy, especially of corrosion, to study characteristics or structures of surfaces and interfaces of materials.

Although chemical or physical significance of the information obtained from EIS is not yet fully understood, this technique is utilized not only in laboratories but also in factories and fields which are connected with corrosion, firstly because the spectra reflect delicate difference of a specimen and/or of a reaction, and secondly because versatile instruments are available at cost-effective prices. In line with the trend, a large progress has been achieved with regards to interpretation of the obtained data.

As far as the carbon fibers are concerned, however, information from EIS is highly scarce. Even the spectra are not well known. Considering these situations, we have conducted research work on carbon fibers based on EIS.

Experimental

Eight fibers were selected for the current research. They are classified into 4 types:

i) Stretched fibers, which comprise two experimental pitch-based fibers (70T and 50T), a commercial high-modulus PAN-based fiber (PHM) and a commercial high-strength PAN-based fiber (PHS). Their L_c-values (sizes of crystallite) ranged from 2.0 through 14.5 nm.

ii) Low-temperature fibers, which were prepared in our laboratory by heating bundles of commercial Kevlar fiber(KEV), and Kynol fiber(KYN) in argon atmosphere up to 700 °C at a rate of 0.5 °C/min. Their L_c-values ranged from 1.0 through 1.4 nm.

iii) Sodium-doped fiber(GLY), which was an experimental fiber prepared by carbonizing a precursor spun from lignin mixed with polyvinyl alcohol. GLY contained 140 wppm of sodium. Its L_c-value was 1.2 nm.

iv) Activated carbon fiber (ACF), which was a commercial product manufactured by Toyobo Co. The internal surface area is reported to be 1400 m^2/g. Its L_c-value was 1.0 nm.

EIS was performed in a quiescent condition open to atmospheric air in a solution of 500 ml of 0.5 M sulfuric acid at a cathodic potential (-100 mV) and at an anodic potential (+1000 mV, respectively against Ag/AgCl reference electrode)). An end of a bundle of approximately 2000 filaments was inserted into a copper tube and firmly fixed by a piece of matching copper rod inserted in the tube. The free length of the fiber extending from the end of the copper tube was 25 mm, whose top 5 mm was dipped in the solution. The perturbation voltage was ± 10 mV(0-p). Its angular velocity (ω) ranged from $10^{5.8}$ rad/s (100 kHz) through $10^{-0.2}$ rad/s (100 mHz).

Results and conclusions

Figure 1 illustrates whole views of Cole-Cole plots (CCP, anodic plots only) based on the crude impedance observed 0, 12, 36 and 72 h after the start of the run. In almost all cases, the CCP comprised three arcs, a-arc, b-arc and c-arc, which were located at around $\omega=10^2$ rad/s, at $\omega<10^1$ rad/s and at $\omega>10^4$.Relative size of each arc was different depending on the fibers and sometimes on the elapsed time. The c-arc was very small for the stretched fibers, while it was large for the low-temperature fibers. Judged from the values of ω, the c-arcs are likely to come from the internal impedance of the fiber.

The values of the components of impedance were assessed by assuming Randel's model or similar equivalent circuits. The obtained values of the resistivity and the capacity of the a-arc and of the b-arc are illustrated in Figs. 2 and 3. The reason for the presence of the two types of the arc is not clear, although it has been confirmed that both of them are originated from the fiber electrode. We are suspecting inhomogeneity of the electrode surface.

Each type of the fibers is characterized as follows.

i) Stretched fibers have a small solution resistance and a small internal resistance together with a-arcs of a capacity of 4 $\mu F/cm^2$ and a resistivity of less than 1 $k\Omega cm^2$, and b-arcs of a capacity of 14 $\mu F/cm^2$ and a resistivity of 150

$k\Omega cm^2$. The L_c-value was not a good parameter to predict the impedance.

ii) The low-temperature fibers were large in the internal impedance (c-arc's impedance) and in the capacity of the b-arc.

iii) The sodium-doped fiber was large with respect to the capacity of the both arcs.

iv) The activated carbon fibers was characterized by a smaller internal resistance than expected from its amorphous structure, as well as by much larger capacity and by much smaller resistivity than the other fibers, although part of its anomalous behavior might be caused by the procedure for assessing the surface area (based on the external surface area).

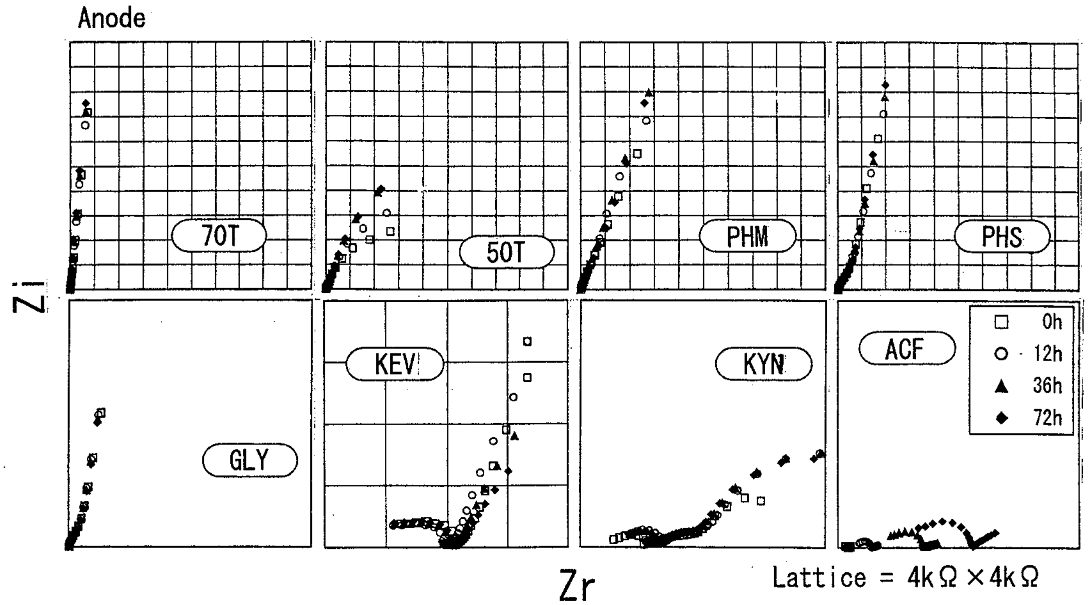

Fig. 1 (above) Cole-Cole plots of various carbon fibers. (anodic plots only).

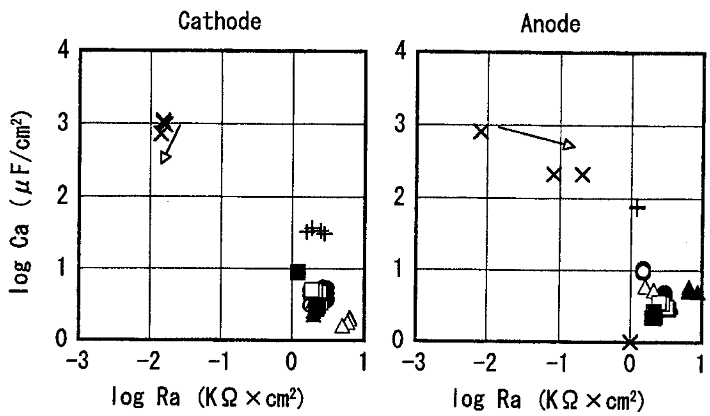

Fig. 2 (left) Values of capacity against those of resistivity for the a-arcs.

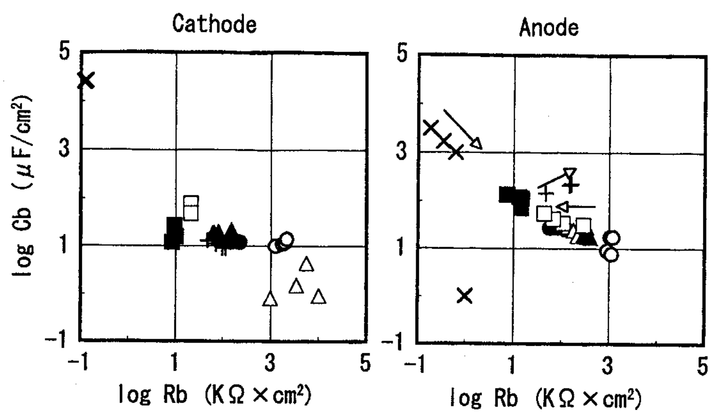

Fig. 3 Values of capacity against those of resistivity for the b-arcs.