

Controlling Factor of Electrocatalytic Activity of Iron-containing Carbon Materials

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Iron-containing carbons were prepared from mixtures of ferrocene and poly(furfuryl alcohol) by varying their preparation conditions. The electrocatalytic activity of the carbons was assessed with $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ redox reaction, and was revealed to be strongly affected by the fraction of a turbostratic carbon structure (Ts-phase) in the material determined by X-ray diffraction.

Carbon material is a commonly used electrode material for electrochemical analyses because of its chemical stability, wide ranges of available potential in aqueous solutions, and easiness for surface modification.¹ However, nevertheless of its importance in electrochemical field, very few studies focused on the preparation of carbon intending improvements of the electrocatalytic activity of carbons insofar as we know.

In the course of our studies of preparing electronically functional carbons by controlling carbonization, the iron-containing carbons made from mixtures of ferrocene-poly(furfuryl alcohol) or of ferrocene-resol resin were revealed to have heterogeneous electron transfer rates as high as platinum, when the materials were used as working electrode in an aqueous solution of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ redox couple.^{2,3} The remarkable characteristics of these materials are follows: they include partially organized graphite-like (turbostratic carbon) constituent, of which appearance was fur-like structure under scanning electron microscope. In addition, the iron incorporated in the materials was identified as α -Fe, γ -Fe and Fe_3C by Mössbauer spectroscopy measurements.⁴ We consider the high heterogeneous electron transfer rate would be brought about by the presence of the turbostratic structure. In this study, we prepared iron-containing carbon with various contents of the turbostratic structure and studied the relation between the content and the electrocatalytic activity of the materials.

Addition of a small amount of HCl at 80 °C initiated the polymerization of furfuryl alcohol mixed with a predetermined amount of ferrocene (2 wt% Fe in the starting polymer). Polymerization was completed by keeping the mixture at 80 °C for 72 h. The ferrocene-poly(furfuryl alcohol) mixture was subjected to heating in a He flow at a rate of 3 °C min⁻¹ up to 700 °C, and then were held at the temperature for 1-15 h followed by cooling to room temperature at various rates (0.5-250 °C min⁻¹). The samples are referred by their preparation conditions if necessary, for example Fe(2)700-1-250 stands for the sample carbonized at 700 °C for 1 h and followed by cooling at 250 °C min⁻¹. The carbonized samples were pulverized into powder to pass through a 150-mesh sieve. Then, they were bonded to stainless current collector with a Teflon suspension as a binder to be subjected to electrochemical measurements. Electrolyte used was an aqueous solution of 6 mol dm⁻³ $\text{K}_3[\text{Fe}(\text{CN})_6]$ with 1 mol dm⁻¹ KNO_3 as a supporting electrolyte.

Figure 1 shows typical X-ray diffractograms of the obtained material. When no ferrocene was added to the polymer (Figure 1 (a)), only halo diffraction was observed in the present

diffraction angle region. The nominal d_{002} was 3.7~3.9 Å. Figure 1 (b) is a typical diffractogram for the iron-containing carbons prepared here. It can be seen that a defined peak is superimposed on a broad amorphous scattering. The peak position of the former diffraction corresponds to (002) reflection of turbostratic structure ($d_{002} \sim 3.4$ Å). We separated the two contributions in the manner illustrated in the figure, and defined a parameter to indicate the contents of the turbostratic structure with a formula: $f_T = A_T / (A_T + A_{\text{amorphous}})$, where A stands for the area of the diffractogram of each component. Heat treatment of Fe(2)700-1-250 at 2800 °C gave no signs of graphitization. This is a characteristic feature of the Ts-phase (thermally stable turbostratic phase),⁵ hence we concluded the iron-containing carbons prepared in this study are composed of an amorphous phase and the Ts-phase. No separated (100) and (101) peaks were observed, but only a broad (10) peak was observed instead. This observation indicated no regular stacking took place in the material. The crystallite size, L_a , calculated from the line width of the (10) peak increased with f_T .

Electrocatalytic activity of the materials was assessed by the

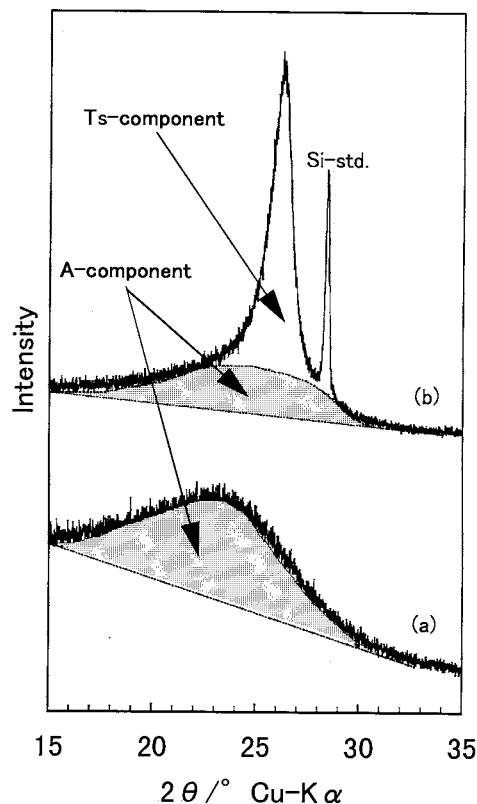


Figure 1. Illustrations of the X-ray diffractograms of the carbons in this study. (a) polyfurfuryl alcohol without iron, (b) Fe(2)700-3-250.

separation between the oxidative and reductive peaks in cyclic voltammograms, which was recorded at a scan rate of 5 mV sec^{-1} . Hereafter the peak separation is referred to ΔE_p . Figure 2 shows the relation between ΔE_p and f_T . With the increase in f_T , ΔE_p gradually decreased down to 60 mV, which is close to the theoretical value for one-electron reversible case, 59 mV. The obtained smooth relation indicated that the component responsible for the electrocatalytic activity should be the Ts-phase. Therefore, we conclude that the content of the Ts-phase is the controlling factor of the activity.

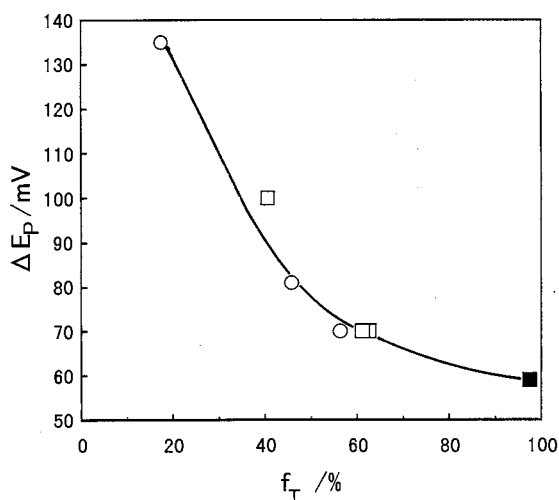


Figure 2. Relation between ΔE_p and f_T of the iron-containing carbons prepared in this study. \circ : Fe(2)700-1-r ($r = 0.5$ – $250^\circ\text{C min}^{-1}$), \square : Fe(2)700-t-250 ($t = 3$ – 15 h), \blacksquare : heat treated Fe(2)700-1-250 at 2800°C .

Arising questions are what properties of the Ts-phase can relate the electron transfer at the interface between the carbon and the electrolyte, and how it promotes the electron transfer. Electrocatalytic activity of carbon materials is influenced by the presence of some specific surface functional groups or by the crystallographic orientation of the plane facing to the electrolyte solution.¹ As mentioned above, the Ts-phase is not an usual carbon in the respect of resisting to graphitization. So, this

phase is expected to have particular surface structures promoting the electron transfer at the interface. We are undergoing surface chemical approaches to investigate the surface of the iron-containing carbons.

Let us consider the gradual decrease of ΔE_p in the lower f_T region than 40%. A possible explanation for this is based on the difference in the electrical conductivity of the iron-containing carbons. Recently, we have found that the electrical conductivity of the carbon with Ts-phase was higher than the carbon without Ts-phase.⁴ When materials with different electrical conductivity are mixed, the conductivity of the mixture should vary dramatically as a function of the mixing ratio.⁶ Therefore, the electrical conductivity of the iron-containing carbon is expected to vary as a function of f_T . We should remember that the potentiostat regulate the potential of the current collector rather than that of the surface of the bound carbon samples on to the collector. So, the actual potential of the surface of the electrode is different from the potential set by the potentiostat because of an IR drop occurring across the carbon layer. The potential difference should be smaller, when a carbon with higher conductivity is used as the working electrode material. While, the difference would be significant for the carbons with lower conductivity. In the latter case, a broadened cyclic voltammogram will be obtained. In the manner mentioned above, ΔE_p is inferred to vary with f_T . Electrical conductivity measurements on the composites are being studied in our laboratory.

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References and Notes

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