

A TRIAL OF ELECTROCHEMICAL SYNTHESIS OF CARBON FROM ACETYLENE IN NONAQUEOUS ELECTROLYTES

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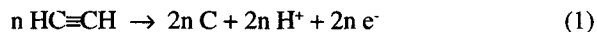
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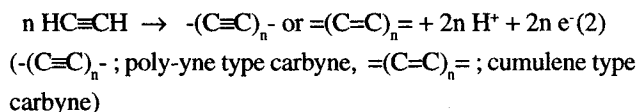
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Introduction

In general, artificial carbonaceous materials have been synthesized by the carbonization reaction of organic polymers or condensed aromatic compounds with heat treatment. However, there are some reports about the methods of carbonization without heat treatment. This is called "electrochemical carbon" [1], which is obtained by the electrochemical reduction or oxidation of organic compound or organic polymer at room temperature. For example, an electrochemical carbon is prepared from the reductive defluorination reaction of poly-tetrafluoroethylene (PTFE) with alkali amalgam. Moreover, it has been known that the carbon has unique chemical and physical structure. Kavan's group reported that it contains the triple bond chain of carbon atoms like carbyne structure [1]. On the other hand, acetylene gas can be considered as source of carbonaceous materials. In fact, acetylene gas has been used as sources when a carbonaceous film is prepared by CVD methods. Abe's group suggests that this CVD film is composed of amorphous carbon structure and that it can be applied to anode of Lithium Ion Battery [2]. However, these methods have to need the complicated vacuum system, and it is difficult to control the reaction condition to obtain the materials. Kijima's group already reported the condensation of acetylene by electrochemical oxidation to obtain carbonaceous materials [3]. However, this reaction needs a Cu-complex catalyst and a large amount of reaction products has not been obtained. Therefore, in our study, electrochemical synthesis of carbon was tried to develop a more facile preparation of new carbonaceous materials from acetylene at room temperature. The carbonization reaction is based on the electrochemical oxidation of acetylene with dehydrogeneration, as follows (equation (1))



Moreover, if acetylene can be considered as minimum unit of carbyne (a linear allotrope: $-(\text{C}\equiv\text{C})_n-$), the electrochemical oxidation of acetylene can be expected as a new method of synthesis of carbyne (equation (2)).



Therefore, the possibility of formation of carbyne is also discussed with characterization of the product compounds in this study.

Experimental

Electrochemical carbonization of acetylene was conducted with a standard electrochemical three-electrode cell. Acetone (Ac) containing 0.2 mol dm^{-3} tetrabutylammonium perchlorate ($(\text{C}_4\text{H}_9)_4\text{NClO}_4$; TBAP) was used as the base electrolyte. The saturated electrolyte with acetylene was prepared by bubbling of pure acetylene gas into the base electrolyte for 20 min. The substrate electrode was polycrystalline gold plate (2cm^2). The counter electrode was platinum plate, and the reference electrode was Ag/Ag⁺ reversible system (acetone containing 0.2 mol dm^{-3} TBAP and 0.01 mol dm^{-3} AgClO₄ was used as the electrolyte for the reference electrode). The electrochemical condition at the carbonization was performed by the potential sweep method or potentiostatic method. All procedures above were conducted in a pure argon dry box at room temperature.

Results and Discussion

Figure 1 shows the potential sweep voltammogram on the gold substrate electrodes in the TBAP/Ac electrolyte without acetylene or containing saturated acetylene. The oxidation current rapidly increased at 1.5 V vs. Ag/Ag⁺ when the

electrolyte does not contain acetylene. On the other hand, when the TBAP/Ac electrolyte was saturated with acetylene, the drastic increment of oxidation current was already observed at 0.8 V vs. Ag/Ag⁺. When the oxidation current was started up, the electrodes' color turned from golden yellow to shiny black. This result indicates that oxidative compounds were deposited on the substrate electrode. After the oxidation, the whole of the electrode was covered with many deposits with submicron size, as shown in Fig.2 (a). These deposits were accumulated smoothly on the surface. Figure 3 shows the Raman spectra of the electrochemical oxidation deposits obtained on the gold electrode in TBAP/Ac containing acetylene. In the spectrum, a peak around 1560 cm⁻¹ can be attributed to conjugated C=C bond. In general, the Raman peak around 1580 cm⁻¹ for carbon materials is assigned to the G line which is derived from the stretching (E_{2g}) mode of conjugated bond of carbons in the graphene sheet, so the peak at 1560 cm⁻¹ in Fig.3 may correspond to the G line. Moreover, a small and complicated peak was observed in the region around 1200-1400 cm⁻¹. This may be assigned to the lattice defects in the graphene sheet such as edge of graphite crystallite (the D line). So, these peaks in Fig. 3 suggest the formation of carbonaceous materials on the electrode. However, no peaks attributed to C≡C bond (2000 -2100cm⁻¹) were observed in the Raman spectrum. Thus, it was concluded that the carbyne structure cannot be produced in this experimental condition at the electrochemical oxidation of acetylene. At the present time, we are looking for the experimental condition (for example, substrate electrode, electrolyte composition, acetylene derivatives, etc.) to get carbon materials containing the carbyne structure.

References

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3. Ohmura K, Kijima M, and Shirakawa H. Synthesis of conducting polymers with conjugated carbon-carbon triple bonds by electrochemical condensation of acetylene derivatives catalyzed by copper complex. *Synthetic Metals* 1997 ; 84 : 417-418.

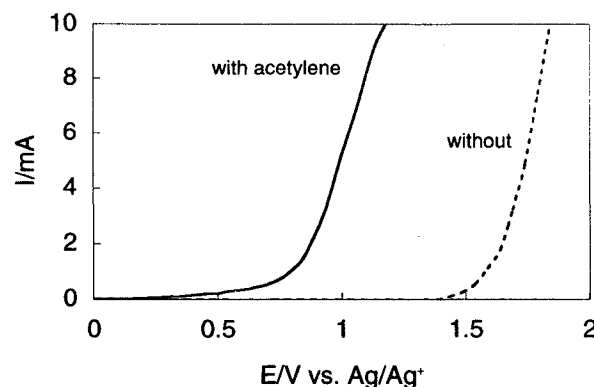


Figure 1 Potential sweep voltammograms on gold substrate electrode in 0.2 M TBAP/Ac.

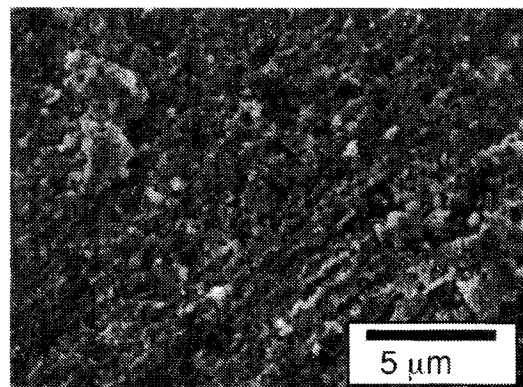


Figure 2 Scanning electron microscopic image of the electrochemical oxidation deposits obtained on the gold electrode in 0.2 M TBAP/Ac containing saturated acetylene. The electrochemical oxidation was conducted at 1.0 V vs. Ag/Ag⁺ for 5 min.

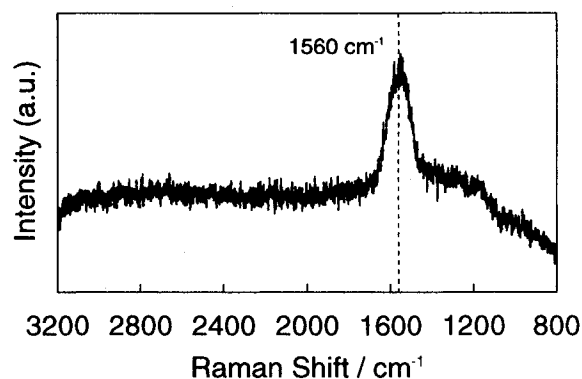


Figure 3 Raman spectrum of the electrochemical oxidation deposits obtained on the gold electrode in acetone containing 0.2 M TBAP/Ac containing saturated acetylene. The electrochemical oxidation was conducted at 1.0 V vs. Ag/Ag⁺ for 5 min.