

Electrochemical Lithium Ion Doping and Undoping Behavior of Carbyne-like Carbon Film Electrode

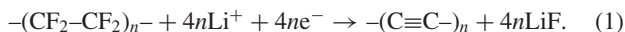
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Carbyne is one of the allotropes of sp-carbon with a one-dimensional chain, but its physicochemical properties have not yet been clarified. We produced a carbyne-like carbon (carbon containing sp bond) electrode by electrochemical reduction in an organic electrolyte (1.0 mol dm⁻³ LiClO₄/propylene carbonate) using a poly(tetrafluoroethylene) (PTFE) film electrode coated with a thin gold layer. The Li⁺ ion can be doped/undoped in the carbyne-like carbon film by electrochemical reduction/oxidation. The stoichiometry of the electrochemically reduced PTFE is estimated to be CLi_{0.48}·2LiF which corresponds to a lithium ion battery negative electrode with ≈1100 mAh g⁻¹ (of carbon) capacity.

Carbyne is a chain-like (one-dimensional) carbon allotrope consisting of sp-hybridized carbon atoms of the polyynic type (-(C≡C)_n-; α carbyne) or cumulene type (=C=C=C_n=; β carbyne). Both of these two kinds of carbynes contain two conjugated π electrons per one carbon atom, so the carbyne is expected to be a new functional material by chemical/electrochemical reactivity or soliton/polaron generation, such as a super conductor, magnetic material, rechargeable battery electrode, etc. Many researchers have tried to synthesize carbyne by various physical or chemical methods, but its physicochemical properties have not yet been clarified.¹ The reason is that the carbyne had a reduced chemical stability through crosslinking of the carbon chain. Kavan reported that the defluorinated (carbonized) product of poly(tetrafluoroethylene) (PTFE) with lithium amalgamate in a vacuum system had a micro/nano domain structure of lithium fluoride and the carbyne-like carbon.² The authors also obtained a structure similar to the carbyne-like carbon by the direct defluorination of PTFE with Li metal foil at room temperature.³ The reaction scheme is described as follows.



The defluorinated product has an electronic or ionic conductivity.² The stoichiometry of the product by the amalgamate-defluorination is estimated to be CM_{≈0.2}·2LiM (M = Li, Na, and K) by titration.² These properties attracted our interest in the electrochemical doping and undoping of Li⁺. However, the product is very fragile and unstable in oxygen and moisture; therefore, it is difficult to measure its electrochemical properties. Recently, we have found that a PTFE film coated with a thin gold layer can be electrochemically defluorinated to produce the carbyne-like structure in a nonaqueous electrolyte containing Li⁺ ions. This method makes it possible to measure electrochemical behavior of the carbyne-like carbon without any sample transfer from the preparation system. In this paper, the electrochemical behavior of the doping/undoping of Li⁺ is reported for the carbyne-like carbon film.

The electrochemical defluorination of PTFE goes through

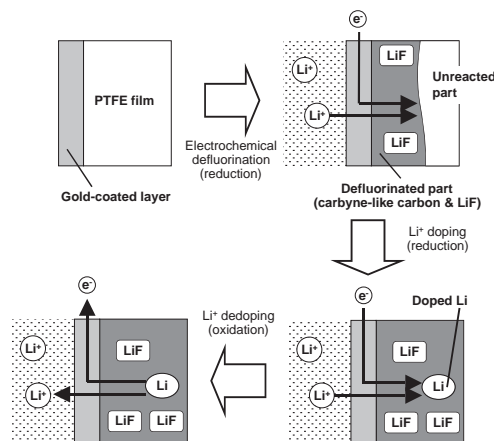


Figure 1. Schematic illustration of the concept for defluorination of the gold-layer coated PTFE film by electrochemical reduction in nonaqueous electrolyte and Li⁺ doping/undoping by electrochemical reduction/oxidation.

the gold layer as shown in Figure 1. The electrochemical reduction in a nonaqueous Li⁺ electrolyte causes the defluorination of PTFE by the charge transfer of Li⁺ and an electron to form the carbyne-like structure and LiF nanoparticles. The test electrode was prepared by sputtering gold (≈100 nm) on both sides of the PTFE film (Good Fellow, 10 μm thickness, density is 2.2 g cm⁻³). The electrochemical reaction proceeded on a 1 × 1 cm² area of the gold-coated electrode.

A propylene carbonate solution containing 1.0 mol dm⁻³ LiClO₄ (1.0 M LiClO₄/PC) was used as the electrolyte. The electrochemical reaction was conducted using a three-electrode system in a pure argon atmosphere. The electrochemical reduction was performed under potentiostatic control (0 V vs Li/Li⁺, 84 h). The electrochemical doping of Li⁺ follows the defluorination during the electrochemical reduction step as shown in Figure 1. The doped Li⁺ can be electrochemically extracted (undoped) by the electrochemical oxidation, which was conducted under galvanostatic control (0.05 mA, cut-off potential is 4 V vs. Li/Li⁺). The potential and current profiles obtained in this study are shown in Figure 2.

Figure 3 shows the Raman spectra of the PTFE film and the defluorinated PTFE. The measurement was conducted under a pure argon atmosphere using the sealed sample holder with a quartz glass window. The difference in both spectra indicates the activity of PTFE during the electrochemical reduction. Two peaks were observed in the defluorinated sample. The peak around 2000 cm⁻¹ is attributed to the sp-bond, indicating the presence of the carbyne-like structure.²⁻⁴ The length of the carbon chain (-(C≡C)_n-) was estimated to be n = 6 using Kastner's equation.⁵ The broad peak around 1200–1600 cm⁻¹ is assigned to the sp²/sp³ type amorphous carbon, which can be

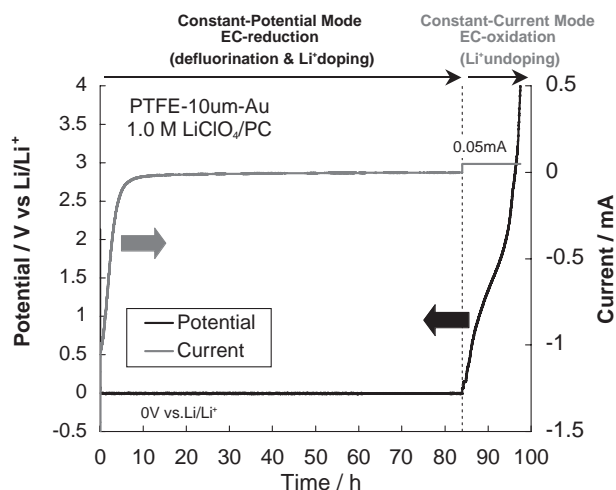


Figure 2. Potential and current profile of Au-coated PTFE electrode during electrochemical reduction (84 h, 0 V vs Li/Li⁺) and oxidation (0.05 mA) in 1.0 M LiClO₄/PC.

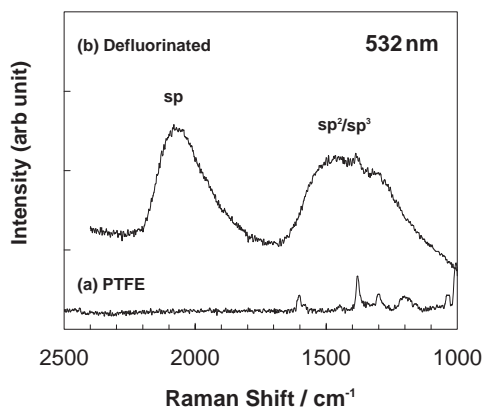


Figure 3. Raman spectra (532 nm, 3.75 mW, 4 μm spot) of (a) PTFE film and (b) electrochemically defluorinated PTFE electrode. The electrode back was not Au-coated and the Raman spectrum was observed through the back face unreacted.

considered to be the decomposed products of the sp-bonded carbons due to crosslinking.^{2,3}

In the XRD pattern (not shown here), the very broadened diffraction lines of LiF were observed in the defluorinated PTFE. The Raman and XRD analyses indicated that the defluorinated PTFE electrode is composed of well-dispersed LiF nanocrystals and sp/sp²/sp³ carbon. This structure corresponds to that reported by Kavan.²

Figure 4a is the potential profile for the electrochemical oxidation after the electrochemical reduction of the PTFE film electrode. The electrode potential gradually increases owing to the electrochemical oxidation. These results suggest that the electrochemical behavior of the PTFE electrode is due to the Li⁺ undoping (CLi_x → C + xLi⁺ + xe⁻) from the lithiated carbon matrix. The initial short plateaux around 0–0.2 C might be due to the Li⁺ undoping from the lithiated gold layer, because gold is known to form a Li-alloy by the electrochemical reduction. The control experiment (Figure 4b) using the gold-coated nickel plate electrode, which indicated a drastic potential in-

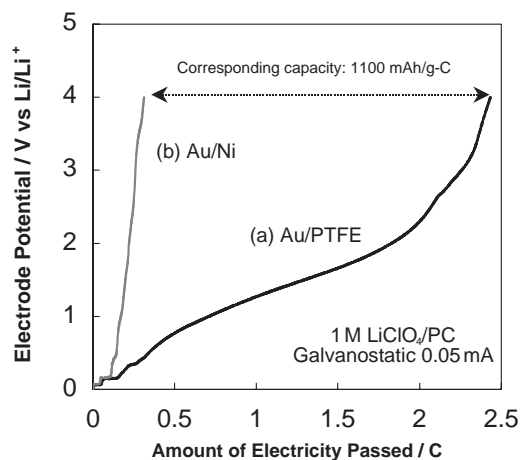


Figure 4. Potential change during electrochemical oxidation (in 1.0 M LiClO₄/PC, 0.05 mA) of the Au-coated electrodes. (a) PTFE film electrode (carbyne-like carbon electrode) or (b) Ni electrode (control test). Both electrodes were electrochemically reduced (0 V vs Li/Li⁺, 84 h) before the oxidation.

crease after the corresponding short plateaux, confirms the Li⁺ undoping capacity of the reduced PTFE electrode. Assuming that all the doped Li⁺ can be undoped and then subtracting the contribution of the gold coating to the Li⁺ undoping, the stoichiometry of the electrochemically reduced PTFE is estimated to be CLi_{0.48}·2LiF which corresponds to a lithium ion battery negative electrode with an ≈1100 mAh g⁻¹ (of carbon) capacity. A comparison with the graphite negative electrode (CLi_{0.17}, 372 mAh g⁻¹) suggested a large amount of Li doping per carbon atom for the carbyne-like structure although a wide potential scan of 0–4 V Li/Li⁺ is necessary for complete undoping. The low-crystalline carbons such as soft carbon are well known to have a high Li⁺ doping capacity (>600 mAh g⁻¹);⁶ therefore, the electrochemical behavior might also be correlated to the crystallinity. We are now investigating the doping/undoping cycling-performance and the interaction of the carbon triple bond with the doped Li⁺.

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