

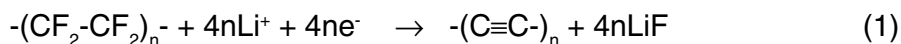
LITHIUM ION DOPING AND DEDOPING BEHAVIOR OF CARBYNE-LIKE CARBON FILM ELECTRODE

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Introduction

Carbyne is a linear chainlike (one dimensional) carbon allotrope. This characteristic carbon structure consists of *sp*-hybridized carbon atoms, so carbyne can be considered to have two kinds of poly-yne type $-(C\equiv C)_n-$; α carbyne) and cumulene type $=(C=C)_n=$; β carbyne). Both of the two kinds of carbyne contain two conjugated π electrons per one carbon atom, so carbyne can be expected as a new functional materials, such as super conductor, magnetic material, rechargeable battery anode, etc. Many researchers have tried to synthesize carbyne with various physical or chemical methods, but the physicochemical properties have not been clarified yet. The reason is that carbyne have less chemical stability through cross-linking of carbon chain. Kavan, et al., 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 carbyne-like carbon[1]. The authors also found to obtain the similar structure of carbyne-like carbon by the direct defluorination of PTFE with Li metal foil at room temperature [2]. The reaction scheme is explained as follows.



The product obtained by the above method has electronic or ionic conductivity [1]. The stoichiometry is estimated to be CLi_x ($x = \sim 0.2$) by titration [1]. These properties give us the interests about electrochemical doping and dedoping of Li^+ . However, the product is very fragile and unstable in oxygen and moisture, so it is difficult to measure electrochemical properties. Recently, we have found that the PTFE film coated with gold thin layer can be electrochemically defluorinated to produce the carbon thin film composed of carbyne-like structure in nonaqueous electrolyte of Li^+ ion. This method makes it possible to measure “*in-situ*” electrochemical behavior the carbyne-like structure without change of electrolyte

or sample transfer from the preparation system. In this paper, the electrochemical behavior of doping/dedoping of Li^+ will be reported for the carbyne-like carbon film prepared by the above procedure.

Experimental

The electrochemical defluorination of PTFE goes through the gold layer as shown in Fig.1(a). The electrochemical reduction in nonaqueous electrolyte of Li^+ causes the defluorination of PTFE by the charge transfer of Li^+ and electron to form the carbyne-like structure and LiF nano-particles.

The test electrode was prepared by the sputtering gold (~ 100 nm) on PTFE film (Good Fellow, $10\ \mu\text{m}$ thickness, density is $2.2\ \text{gcm}^{-3}$). The photograph of the gold layer-coated PTFE film electrode was shown in Fig.2. The electrochemical reaction proceeds on 1×1 cm square of the gold-layered part. The other gold part works as current collector.

Propylene carbonate solution containing $1.0\ \text{mol dm}^{-3}$ LiClO_4 ($1.0\text{M LiClO}_4/\text{PC}$) was used as electrolyte. The electrochemical operation was conducted by three-electrode system in pure argon atmosphere. The electrochemical reduction was performed under potentiostatic method ($0\ \text{V}$ vs. Li/Li^+ , 84 h).

The electrochemical doping of Li^+ also goes during the defluorination step by the electrochemical reduction as shown in Fig.1(b). The doped Li^+ can be electrochemically extracted (dedoped) by the electrochemical oxidation, which was conducted under galvanostatic method ($0.05\ \text{mA}$, cut off potential is $4\ \text{V}$ vs. Li/Li^+) in this paper.

Results and Discussions

Fig.3 shows the Raman spectra of the PTFE film and the electrochemical defluorinated PTFE film electrode. The measurement was conducted under pure argon atmosphere by using the sealed sample holder with quartz window. The difference in both spectra indicates the activity of PTFE on the electrochemical reduction. Two peaks were observed in the defluorinated samples. The broad peak around $2000\ \text{cm}^{-1}$ is attributed to the carbyne-like structure, and that around $1200 \sim 1600\ \text{cm}^{-1}$ is the $s\text{p}^2$ type amorphous carbon structure [1,3]. The latter can be considered to be the decomposed products of carbyne-like structure due to cross-linking. The length of carbon chain in the carbyne-like structure was estimated to be $n = 6.5$ by Kastner's equation [4].

Fig.4 is the chronopotentiogram (potential-time curve) at the electrochemical oxidation after the electrochemical reduction of the PTFE film electrode. The electrode potential

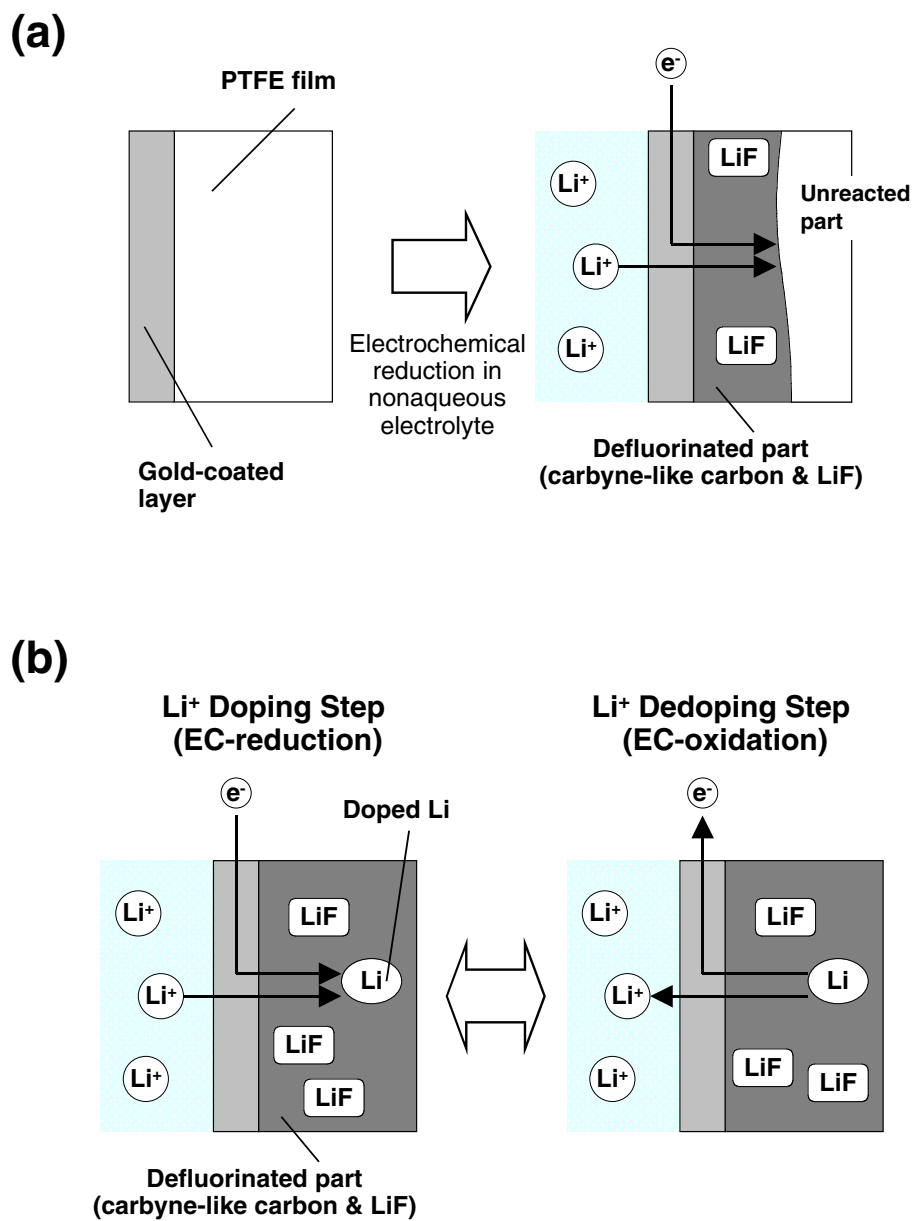


Figure 1 Schematic illustration of the concept for (a) defluorination of the gold-layer coated PTFE film by electrochemical reduction in nonaqueous electrolyte and (b) Li⁺ doping/dedoping by electrochemical reduction/oxidation.

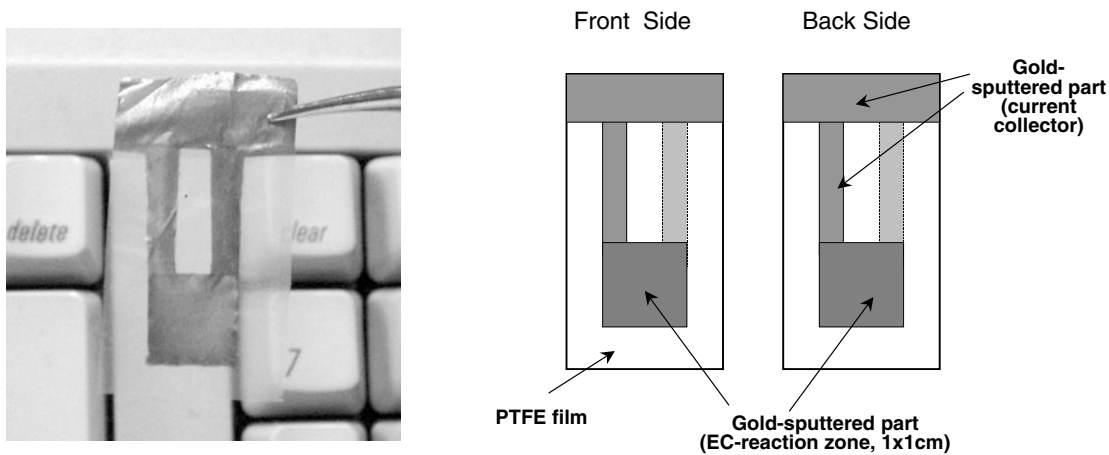


Figure 2 (a) Photograph of the gold-layer coated PTFE film electrode and (b) schematic illustration of the electrode.

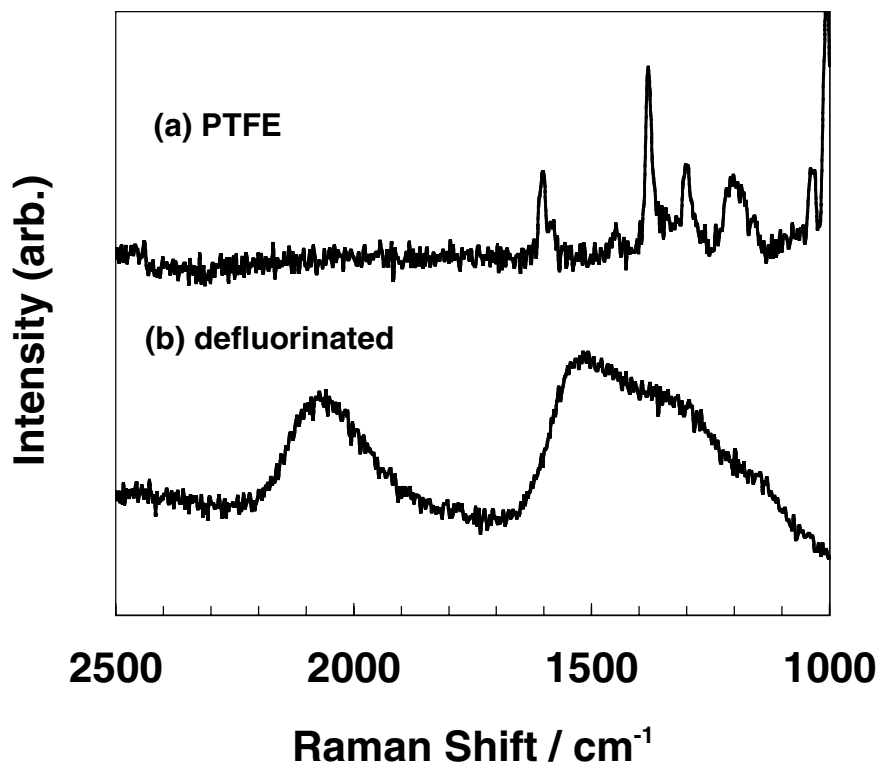


Figure 3 Raman spectra of (a) the PTFE film electrode and (b) the defluorinated PTFE film electrode by the electrochemical reduction (excited laser: 532 nm, 3.75mW, 2 μ m spot).

gradually goes up with the passed electricity by the electrochemical oxidation. The blank experiment of the gold-layer coated polypropylene film electrode indicated no potential plateau and no significant behavior. These results suggest that the behavior in Fig. 3 originates from the Li⁺ dedoping ($\text{CLi}_x \rightarrow \text{C} + x\text{Li}^+ + xe^-$). The initial short three step around 0 ~ 0.2 C might be due to the Li⁺ dedoping from the coated gold layer, because gold is known to form the alloy with Li by the electrochemical reduction. The amount of the passed electricity up to 4 V vs. Li/Li⁺ reached around 2.4 C. Assuming all doped Li⁺ can be dedoped, it indicates the stoichiometry of the carbon part is $\text{CLi}_{0.57}$ ($\text{C}_{1.8}\text{Li}$), which corresponds to ~ 1300 mAh/g-C of capacity as lithium ion battery anode. Comparison with graphite anode suggested large amount of Li doping per carbon atoms for the carbyne-like structure. We are now investigating the dependence of the amount of doped/dedoped Li on the experimental condition at the electrochemical reduction and the doping/dedoping cycle-ability.

Acknowledgment

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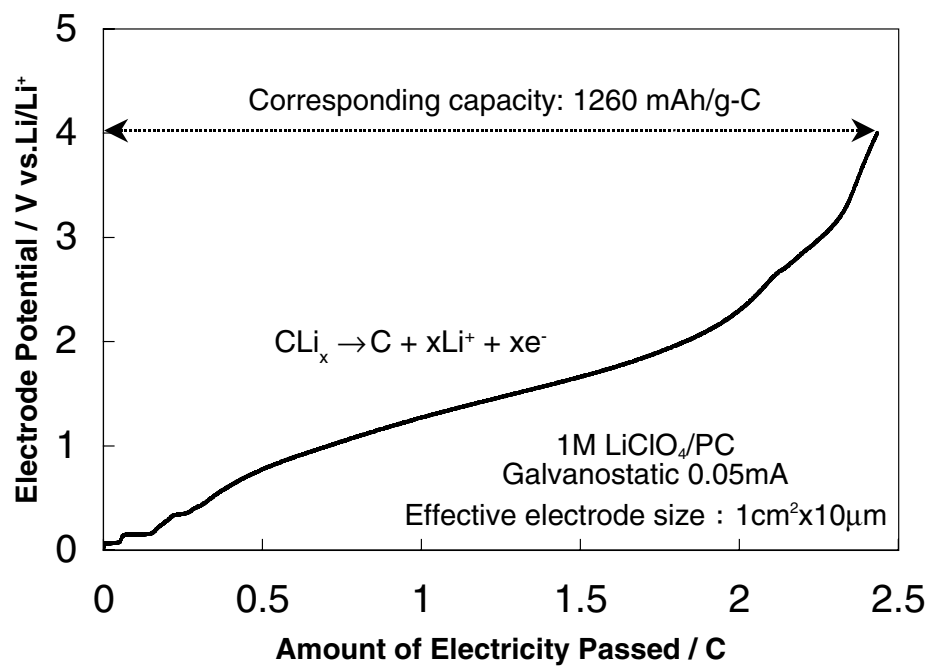


Figure 4 the chronopotentiogram (potential-time curve) at the electrochemical oxidation (galvanostatic, 0.05 mA) after the electrochemical reduction (potentiostatic, 0V vs. Li/Li⁺, 84h) of the PTFE film electrode. Electrolyte : 1.0 M LiClO₄/PC.