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EFFECTS OF HEAT-TREATMENT ON ELECTROCHEMICAL BEHAVIOR

Polyacenic semiconductive (PAS) electrode for Li ion battery*

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Abstract

The polyacenic semiconductive (PAS) material is a typical amorphous carbon prepared by pyrolysis of phenolformaldehyde resin, and is actually utilized as anode of high-capacity rechargeable batteries. In this work, change in the discharging amount of Li^+ before and after heat-treatment of the PAS electrodes at the various doping level was examined in detail. As a result, the doped Li can be classified into two types: (i) heat-resistant Li-dopant (or Li-dopant with high diffusion coefficient) and (ii) heat-fragile Li-dopant (or Li-dopant with low diffusion coefficient). The latter Li-dopants are generated above the doping level of 30% ($[Li]/[C]\geq0.3$) and is considered to be the origin of high-capacity of PAS anode compared with that of graphite anode. This aspect is also supported by the ESR, ^{7}Li-NMR, and XPS observation results.

Keywords: amorphous carbon, charge-discharge characteristics, electrochemistry, heat-treatment, Li ion battery

Introduction

The substance obtained by heat treatment of organic compounds, for instance, polymers at temperatures less than 1000°C has a typical amorphous structure and is generally called amorphous carbon (a-C). Of these a-C, what is prepared by heat treatment of phenolformaldehyde resin at about 700°C under non-oxidative atmosphere has been named polyacenic semiconductor (PAS) materials [1] after their structural resemblance to so-called one-dimensional graphite or polyacene, as shown in Fig. 1. The structural feature that PAS is abundant with pores of miscellaneous sizes [2] facilitates doping with large amount of lithium. We have shown for the first time [3] that PAS can be electrochemically doped with Li up to the molar ratio of C_2Li

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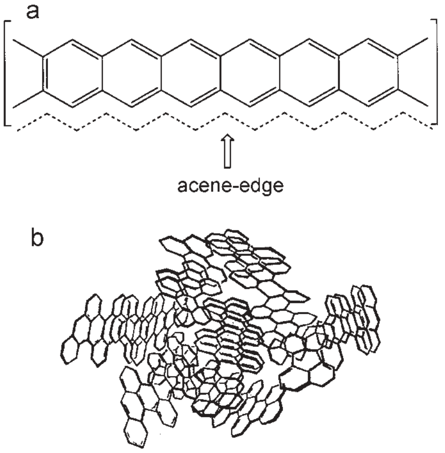

Fig. 1 An illustrative model structure of a – polyacene and b – PAS

([C]/[Li]=2 or charging level of 1100 mAh g^{-1}, being approximately three times larger than graphite [4]. This enables us to fabricate a high-capacity anode for Li-ion rechargeable batteries and, actually, we have commercialized many kinds of rechargeable batteries employing PAS [5].

It is obvious that more attention on the safety of the PAS anode should be paid from the commercial point of view. One of the most embarrassing factors is safety of batteries is self-heat-generation, mainly caused by the reaction between the electrolyte and the anode. In order to estimate the generated heat, it has been examined that the calorific value accompanied with reaction between the Li-doped PAS anodes and the electrolyte in comparison with some Li-doped graphite electrodes on the basis of the differential scanning calorimetry (DSC) measurements [5]. Consequently, the calorific value of the Li-doped PAS anode was found to be small, despite of containing more Li than the graphite anodes. Note that the observed exothermal reaction occurs at about 150°C. Although it was confirmed that the Li-doped PAS anode has the small calorific value as mentioned above, it has not been examined yet whether the discharging characteristics of the Li-doped PAS anode remain unchanged after the heat-treatment at higher than 150°C.

In this article we electrochemically measured the amount of discharging (Li-dedoping) for the Li-doped PAS anode after heat treatment at 150 and 200°C. The change in the discharging amount is discussed in comparison with the electron spin resonance (ESR), ^{7}Li nuclear magnetic resonance (^{7}Li-NMR), and X-ray photoelectron spectroscopy (XPS) observation results [6–9].

Experimental

The PAS sample employed here was made by pyrolysis of phenolformaldehyde resin at 680°C under non-oxidative atmosphere, the details of which have been reported elsewhere [1]. This sample had the [H]/[C] molar ratio of 0.26 similar to that employed in our previous electrochemical [6], ESR [7], ^{7}Li-NMR [8], and XPS [6, 9] studies. After milling PAS powder with particle diameter of 4 μm through the jet milling machine, the powder sample was finished in a sheet form for the electrochemical operation by mixing of 10 mass% poly(vinylidene fluoride) (PVdF) as binder.

The electrochemical Li doping was carried out at a constant current (1.7 mA cm^{-2}) for each sample in a rectangular polypropylene cell incorporating the PAS sheet (working) and Li (counter and reference) electrodes using a charge-discharge unit (Hokuto HJ-201B). 1 M LiPF$_6$ solution in carefully purified propylene carbonate (PC) was used as electrolyte. The Li-doing amount, x (%), was controlled by the coulometry according to the following equation:

$$x(\%)\equiv\frac{[\mathrm{Li}]}{[\mathrm{C}]}100=\frac{3.6Q(12+r)}{96500}100 \qquad (1)$$

where Q (in mAh g^{-1}) is the amount of transferred charge during a doping process and r the [H]/[C] molar ratio of the PAS sheet employed (0.26 in the present study).

After the doping process, the portion of the sample with electrolyte solution was heat-treated for 10 min at a specific temperature (150 and 200°C) on a hot-stage under dry Ar atmosphere (heating rate 10°C min^{-1}). Finally, a constant current dedoping (0.33 mA cm^{-2}) was carried out in order to check the discharging characteristics of both the heat-treated and non-heat-treated samples.

Results

Figure 2 illustrates the relationship between the amount of the charging (Li-doping) before heat treatment and that of the discharging (Li-dedoping) after heat-treatment for the PAS electrode. The result for the non-heat-treated PAS electrode is also depicted in Fig. 2 for comparison. As is evident from these plots, the discharging behav-

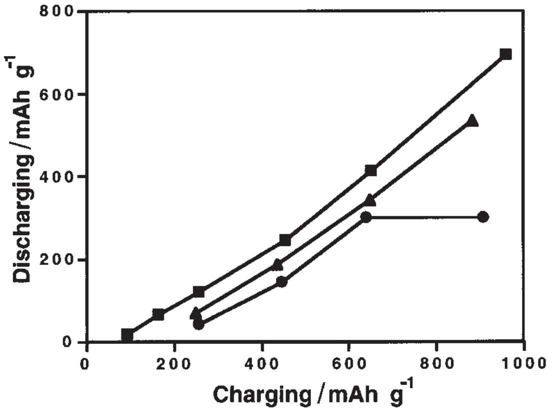

Fig. 2 Relationship of charging (Li-doping) – discharging (Li-dedoping) for the PAS electrode. Each doped electrode was heat-treated between the charging and the discharging operations: at 150°C (solid triangle), 200°C (solid circle), and without heat-treatment (solid square)

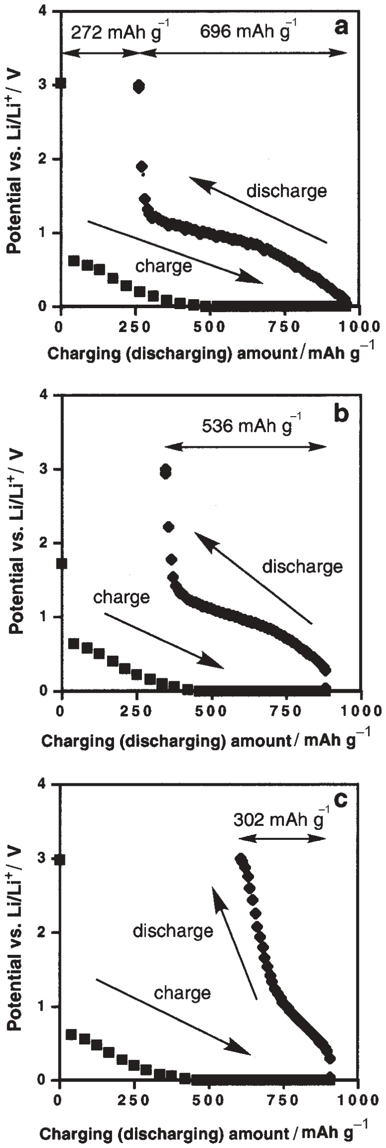

Fig. 3 Relationship between the electrode potential and the discharging (Li-dedoping) amount of the highly charged (deeply Li-doped) PAS electrode after heat-treatment: a – non-heat-treatment, b – 150°C, and c – 200°C

ior of the sample heat-treated at 150°C is similar to that of the non-heat-treated sample, except for slight decrease in the amount of discharging. Note that the exothermic reaction between the PAS electrode and the electrolyte takes place at about 150°C [5]. On the other hand, distinct change in the amount of discharging was seen in the highly charged regime (600–900 mAh g^{-1}) when heat-treated at 200°C. The discharging amount is suppressed to almost a constant value (ca 300 mAh g^{-1}) when charged to more than 600 mAh g^{-1}. As a whole, the present result indicates, that the discharging behavior of the deeply Li-doped PAS electrode changes abruptly at a certain heat-treatment temperature between 150 and 200°C.

In Fig. 3, the charging process before heat-treatment and the discharging process after heat-treatment for the deeply Li-doped PAS electrodes (850–950 mAh g^{-1}) are shown in order to examine the discharging process after heat-treatment in detail. In the charging process, the PAS electrode potential dropped rapidly and the Li-doping proceeds at a constant potential of ca 0 V *vs*. Li/Li^+. On the other hand, at the beginning of discharging, the electrode potential for all the samples increased monotonously. Subsequently, a potential plateau appeared at about 1.0 V in the range from 300 to 600 mAh g^{-1}, suggesting different Li-dedoping process from the early one up to 300 mAh g^{-1}. More noteworthy is that such a potential plateau is no more observable for the sample heat-treated at 200°C. This indicates that there exist two kinds of Li-dopants: one is easily dedopable heat-resistant lithium and the other hardly dedopable heat-fragile-lithium.

Discussion

Let us discuss here the change in discharging behavior of the Li-doped PAS electrode depending on the heat-treatment temperature. As has been reported in our previous works [3, 6], the process of Li-doping into the present PAS sample is supposed to be inhomogeneous due to possible irregular doping into miscellaneous sites in contrast to graphite [10, 11].

From the ESR measurements, the single Lorentzian spectra are observed for the Li-doped PAS electrodes [7]. The change in peak-to-peak linewidth (ΔH_{pp}) upon the amount of doped Li at room temperature is shown in Fig. 4. It is clearly seen that the ΔH_{pp} remains almost unchanged up to about 10%-doped regime (~220 mAh g^{-1}) and then increases monotonously. As will be described later, the constant ΔH_{pp} at the early

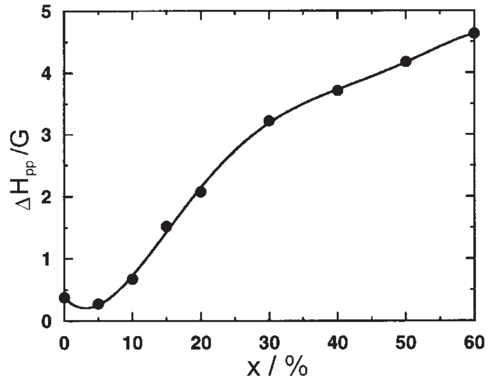

Fig. 4 Change in the peak-to-peak linewidth (ΔH_{pp}) of the ESR lineshape of carbon π-radical spins in the PAS electrode depending on Li-doping amount at 293 K. The line is a guide for eye

Li-doping stage is closely related to the fact that so-called irreversible capacity equivalent to ca 10%-doped Li is observed even in the non-heat-treated sample. At the first charging, the Li-dopants are mainly consumed by decomposition of the electrolyte on the surface of PAS associated with the formation of passivation layer [9]. Hence the electronic state of the PAS electrode remains rather unchanged, leading to the constant ΔH_{pp}. On the other hand, increase in the ΔH_{pp} upon Li-doping can be regarded as development of the spin-lattice relaxation based on the spin-orbit interaction between the conduction electrons in PAS and the Li-dopants [7]. More importantly, a slight change in the slope of the ΔH_{pp} *vs*. x plot is seen at x=30% (~660 mAh g^{-1}). This slight decrease in the slope suggests that the spin-orbit interaction begins to saturate above the 30% doping range. This phenomenon is explainable by the assumption that the Li-dopants become more and more metallic above the 30%-doping range. Actually, a conduction electron should hardly hop onto metallic-like lithium atoms due to electrostatic repulsion.

In order to investigate the Li-doping process from change in the electronic states of Li-dopant, we have carried out ^{7}Li-NMR measurements for the Li-doped PAS electrode [8]. As a result, all the samples showed a broad signal at 0–9 ppm with respect to that of LiCl reference. Figure 5 shows the ^{7}Li-NMR shift plot *vs*. Li-doping amount. In accordance with the ESR measurements, in the initial doping stage (x<10%), it is considered that scavenging of the impurity spins of PAS by Li-dopants and decomposition of the electrolyte leads to the fully ionized Li atoms (~0 ppm). Moreover, the electronic state surrounding the Li nucleus considerably changes in the 10–30% doping range and finally it becomes unchanged above 30%. The Knight shift upon Li-doping indicates that charge of the doped Li changes from Li^+ to $Li^{\delta+}$ ($0<\delta<1$). This tendency is in good accordance with that in the ESR measurements above mentioned.

As far as the charge of Li-dopant according to the doping level is concerned, the XPS is a powerful tool After Ar sputtering on the Li-doped PAS electrode, the XPS spectra of the Li_{1s} and C_{1s} were measured and, as a result, it was seen that the binding energies of the Li_{1s} peak for the dopant Li were 56.5, 56.2, and 55.9 eV, respectively, at 10% (~220 mAh g^{-1}), 30% (~660 mAh g^{-1}), and 46% (~730 mAh g^{-1}) doping levels [6, 9]. The

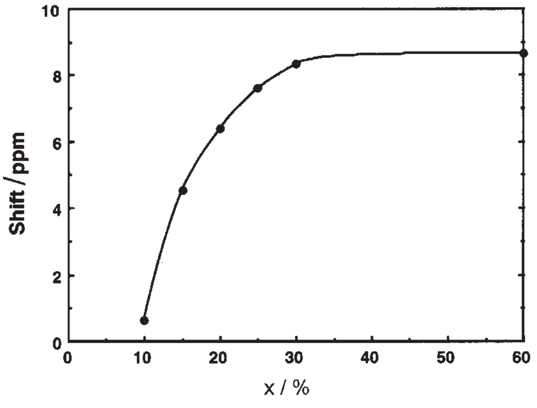

Fig. 5 Knight shift of the ^{7}Li-NMR spectra for the Li-doped PAS electrode plotted *vs*. Li concentration, x (%). The line is a guide for eye

observed binding energies are higher than metallic lithium (55.2 eV) but lower than that of ionic lithium in, e.g., $LiBF_4$ (58.0 eV). It is apparent that the more deeply lithium is doped, the more metallic it becomes. In contrast, the binding energies of the C_{1s} peak for the PAS electrode itself remained mostly unchanged (~285 eV).

The discharging behavior can now be interpreted with the above-mentioned background. First of all, the initial Li doping curve cannot be fully reproduced as is easily deduced in Fig. 3a for the non-heat-treated PAS sample, once it has experienced a charging–discharging process. This feature comes from the remaining Li that cannot be dedoped, which causes irreversible capacity. This quantity amounts to 12%-doped Li (262 mAh g^{-1}) being in good agreement with the ESR and ^{7}Li-NMR results. Next, in the discharging process of the sample heat-treated at 200°C, the potential plateau at about 1.0 V is not observed at all during discharging the amount of 302 mAh g^{-1} as seen in Fig. 3c. On the other hand, the discharging process of the non-heat-treated and 150°C-treated PAS electrodes has the potential plateau and the amount of discharge corresponds to that of 696 and 536 mAh g^{-1} for non-heat-treated (Fig. 3a) and 150°C-treated (Fig. 3b) samples, respectively. Therefore, it is considered that the difference (394 mAh g^{-1}) in the amount of released Li-dopants between the non-heat-treated and 200°C-treated samples is somehow lost by the very heat-treatment at 200°C.

From the ESR and ^{7}Li-NMR studies, it is obvious that the electronic states of the Li-dopant and the PAS electrode begin to change at the 30%-doped stage. These facts strongly suggest that there exist two kinds of Li-dopants, one of which has charge close to that of ionic lithium and another to metallic lithium. This picture also coincides with the theoretical comparison of the ionicity of the intercalated and adsorbed Li-dopants [12]. According to this theoretical analysis, the lithium doped above the 30%-doping level mainly resides on the acene-edge (Fig. 1a) and loosely bound to PAS, indicating that it has partial ionic character. Furthermore, from the relaxation time (T_1) in the ^{7}Li-NMR measurements the Li atoms doped in the PAS electrode are expected to be mobile as compared with those in the graphite electrode and rapidly exchange each other [8]. Therefore, the observed spectra can be averaged into a single spectrum in the observation time scale of ^{7}Li-NMR, in spite of existence of two kinds of Li-dopants. Synthesizing all these results, the metallic-like Li-dopants can feasibly react with the electrolyte at an elevating temperature. Therefore, the partially ionic Li-dopants result in the fragility against heat-treatment above 200°C. Hence, heat-treatment at 200°C leads to decrease in the discharging amount of the PAS electrode when charged beyond the 30%-doping level (656 mAh g^{-1}) due to (i) decomposition of the metallic-like Li-dopants. As a result, the discharging amount for the 200°C-treated PAS electrode remains constant (about 300 mAh g^{-1}) after the charging above 600 mAh g^{-1} (Fig. 2).

On the other hand, the lithium doped to less than 30%-doping level is alive even after heat-treatment, that is, heat-resistant. This amount happens to be similar to theoretical maximum capacity of 372 mAh g^{-1} (18%-doping level) for the graphite electrode. These heat-resistant Li-dopants have ionic character and are probably accommodated in graphitic fragments of PAS [13], which results at most in the formation of the C_6Li configuration.

Conclusions

We have examined the change in the discharging amount after heat-treatment (150 and 200°C) of the charged (Li-doped) PAS electrode. After the heat-treatment at 150°C, the amount of discharging was almost linear to that of charging, showing the similar behavior with the non-heat-treated PAS electrode. After heat-treatment at 200°C, however, it was found that the amount of discharging is flattened at about 300 mAh g^{-1} for the deeply doped electrode. This strongly suggests that there exist two kinds of Li-dopants. On the basis of the ESR, ^{7}Li-NMR, and XPS measurements, one is attributed to heat-resistant lithium with ionic character and the other to heat-fragile lithium with metallic character. Moreover, the former is formed at the early doping stage (less than 600 mAh g^{-1}) and the latter at the deeply doped stage (above 600 mAh g^{-1}). Lastly, it should be noted that the irreversible capacity generated by heat-treatment can also be interpreted by the Li-dopants with low diffusion coefficients as well as by decomposition of the metallic-like Li-dopants. However, at the present stage, it is yet difficult to identify the origin of this new irreversible capacity. For this purpose, ^{7}Li-NMR studies for the heat-treated Li-doped PAS electrodes are in progress and will be reported elsewhere.

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