Carbon nanotube coating silicon doped with Cr as a high capacity anode

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Abstract

Effects of dopant and coating carbon nanotube on anodic performance of Si were studied for metallic anode Li ion rechargeable battery with large capacity. Although the large Li intercalation capacity higher than $1500 \, \text{mAh g}^{-1}$ is exhibited on pure Si, it decreased drastically with increasing cycle number. Increasing the electrical conductivity by doping Cr or B is effective for increasing the initial capacity and the cycle stability of Si for Li intercalation. Coating semiconductive Si with the carbon nanotube by decomposition of hydrocarbon is effective for increasing the cycle stability, though the initial Li intercalation capacity slightly decreased. Conducting binder is also important for increasing the cycle stability and it was found that Li intercalation capacity higher than $1500 \, \text{mAh g}^{-1}$ can be sustained by using poly vynliden fruolide. Consequently, reversible Li intercalation capacity of $1500 \, \text{mAh g}^{-1}$ was successfully sustained after 10th cycles of charge and discharge by doping Cr and coating with carbon nanotube.
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1. Introduction

Graphitic carbon is widely used for the anode of Li ion rechargeable battery [1]. At present, one of the most important issues for anode materials in Li ion rechargeable battery is to elevate the capacity for Li intercalation. Development of alternative anode material to graphitic carbon anode is highly demanded. In the previous study, we investigated the Li intercalation into graphitic carbon nanotube which is obtained by decomposition of CH_4 and it was found that the carbon nanotube obtained by the decomposition of CH_4 over Ni catalyst exhibits a good anodic property and usable as the anode for Li ion rechargeable battery [2–4]. However, theoretical capacity of such graphitic carbon anode is $372 \, \text{mAh g}^{-1}$ and further larger capacity is required. From the viewpoints of capacity, metal anode is attracting much interest. However,

the metal anode such as Sn has a disadvantage of low cycle stability. Among the metal anode reported so far, silicon is one of the most interesting materials because of the extremely large capacity for Li intercalation, ca. $4000 \, \text{mAh g}^{-1}$ for the theoretical capacity [5]. In order to improve the cycle stability, there are several attempts reported. It is reported that Si film prepared by DC spattering or vacuum deposition method exhibits almost theoretical capacity for Li intercalation [6,7]. However, Si thin film prepared by DC spattering method is not suitable for the mass production and the thickness of the film is limited. Therefore, development of Si powder with high cycle stability is strongly required. Yoshio and co-workers reported that the cycle stability of Si was much improved by coating with carbon [8,9]. We also found that coating Si with carbon nanotube is effective for elevating cycle stability of Si [10]. However, effects of carbon coating on the cycle stability of Si for Li intercalation are not studied thoroughly. In addition, it is well known that electrical conductivity of Si can be controlled by using small amount of dopant. In spite

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of this, effects of dopant on anodic property of Si are not studied in detail. In this study, the electrochemical intercalation property of Li into semiconductive Si powder doped with Cr, P or B was studied. In addition, the effects of coating carbon nanotube on anodic performance of semiconductive Si powder were further studied.

2. Experimental

High purity Si powder (Wako, 99.99%) and p-type Si powders with Cr or B doped or n-type one with P were used in this study for Si anode. Cr doped Si was obtained by ball-milling of n-type Si wafer (Toshiba Ceramics Co. Ltd.) and P or B doped samples were also obtained by ball-milling of the block-like Si which is synthesized with a molten method by Shinetsu Chem. Co. Ltd. Coating of carbon nanotube was performed by decomposition of CH_4 by using Ni for catalyst at temperature of 1073 K for 6 h. Ni loaded (10 wt.%) graphitic carbon fiber (Petoka FM16) was first mixed with Si powder (Ni/C:Si = 3:7 wt.%) with planetary ball mill (200 rpm, 2 h) in stainless steel pot (100 ml in volume) and nylon coated iron ball (10 mm in diameter). Ni/carbon catalyst was obtained by impregnation of $Ni(NO_3)_2$ in aqueous solution. Decomposition of CH_4 into carbon was performed with the conventional fixed bed reactor. SEM observation was performed by using SEM (Hitachi, type 2400S) at an accelerated voltage of 25 kV. Anodic performance of carbon nanotube was measured by applying the constant current (0.4 mA cm^{-2}) in the potential window of 1.5–0.0 V by using computer controlled DC source (Nagano BTS 2004). For the counter electrode, Li metal was always used and the details of the used cell were described in our previous paper [2]. Each sample was mixed with ethylene–propylene–dimethyl–monomer (EPDM) in cyclohexane or poly vinylidene fluoride in *n*-methyl pyrrolidone for conducting binder and then pressed into a stainless-steel grid on the stainless-steel plate as an anode. Polypropyrene (PP) was used as separator and ethylene carbonate (EC)–dimethyl propionate (DMC) (1:2) dissolved with 1 M $LiPF_6$ (Ube Kosan Co. Ltd.) were used for electrolyte.

3. Results and discussion

3.1. Anodic performance of semiconductive Si

It is considered that one reason for low cycle stability of Si is low electrical conductivity, which lead to the decomposition of electrolyte [11]. The electrical conductivity of Si can be controlled by doping aliovalent cation. In this study, effects of dopant on Li intercalation performance of Si were studied. Fig. 1 shows the XRD patterns of doped Si used in this study. It is obvious that all diffraction peaks from Cr, P or B doped Si can be assigned to those from Si and no peaks form impurity phase was observed. Although the observed diffrac-
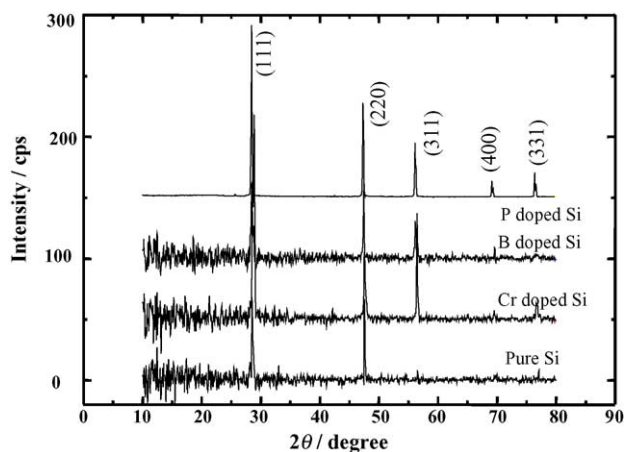

Fig. 1. XRD patterns of Cr, B, and P doped Si and pure Si powder.

tion peaks are different between the doped and undoped Si and also different from the powder diffraction database, all peaks can be assigned to the diffraction peaks from Si powder in powder diffraction database. Therefore, this difference could be explained by the orientation of crystals. This is because the Si powder used in this study is obtained from single like crystal. In addition, diffraction angle of each peak was shifted by dopant. Therefore, it is considered that all dopants successfully formed solid solution with Si.

Fig. 2 shows the charge–discharge curves of pure Si and Cr, P or B doped one. It is seen that extremely large capacity for the electrochemical Li intercalation, which is larger than 1000 mAh g^{-1}, was observed on all samples at the initial charge step. Although the de-intercalation of Li is observed at the potential of 0.45 V, it is obvious that the reversibility of Li intercalation was quite low on all samples and the capacity for the de-intercalation of Li becomes lower than 500 mAh g^{-1}. Comparing with pure Si powder, Cr or B doped one exhibited the larger capacity for the initial Li intercalation and de-intercalation. On the other hand, reversible capacity became much smaller than that of Si in case of P doped
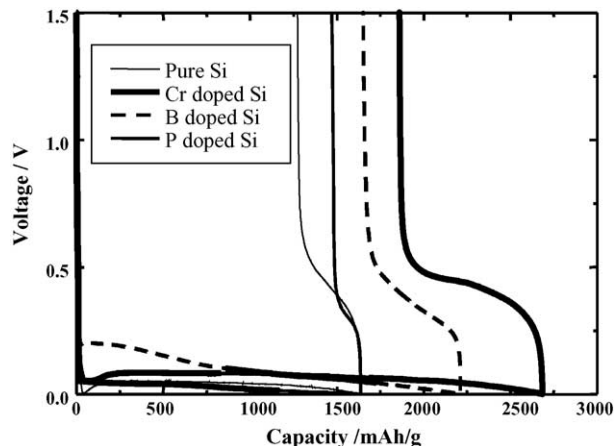

Fig. 2. Charge–discharge curves of pure Si and Cr, P or B doped one.
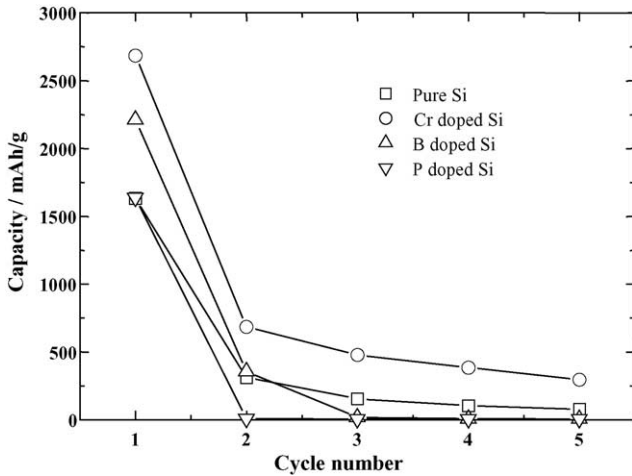
Fig. 3. Cycle stability of Li intercalation on Si or Cr, P or B doped one.

Fig. 4. Cyclic voltammetry of Si and Cr doped Si.

one. Therefore, dopant effects were varied depending on the dopant.

Fig. 3 shows the cycle stability of Li intercalation on Si or doped ones. It is seen that the capacity of Si for Li intercalation faded away drastically with the cycle number of charge and discharge, and after fifth cycle, capacity for Li intercalation is negligible. On the other hand, it is clear that doping Cr or B is effective for increasing the initial capacity. In addition, it is seen that Cr doping is effective for the cycle stability. Although the large irreversible capacity was also observed at the initial Li intercalation and de-intercalation cycles, the capacity after second cycle in Cr doped one is much larger than that in pure Si. After fifth cycle, the capacity for Li intercalation was sustained a value of 250 mAh g^{-1} in case of Si powders doped with Cr. However, in case of P or B doped Si, capacity fading is much larger comparing with that of non-doped one. Therefore, it is seen that cycle stability is also strongly dependent on the dopant.

Table 1 summarized the chemical analysis results of dopant amount, electrical conductivity at room temperature and Li intercalation capacity on the doped Si. Since we used the commercially available semiconductive Si, the concentration of dopant is different. In accordance with the different concentration, the electrical conductivity is also greatly varied with dopant. As shown in Table 1, the larger capacity is achieved on Si anode with higher electrical conductivity. However, in case of B doped sample, the electrical conductivity is much higher than that of Cr doped one but the reversible capacity for Li intercalation is small. Therefore, high
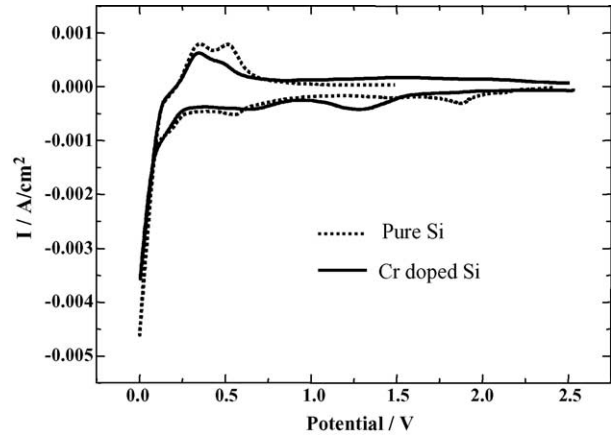
conductivity is important for the large capacity, but it seems like that the chemical compatibility of dopant and Li is also important for high reversible capacity. However, at present, details of the chemical interaction between dopant and Li are not clear. Among the investigated doped Si, Cr doped one exhibits the largest capacity and cycle stability and studied in further detail in this study.

In order to study the improved capacity of Cr doped Si, cyclic voltammetry was performed and comparison of cyclic voltammetry of pure Si and Cr doped one was shown in Fig. 4. In case of pure Si, there are two peaks observed for intercalation of Li at 2.0 and 0.5 V and also two for de-intercalation at 0.25 and 0.5 V versus Li/Li$^+$. Therefore, it is seen that two different intercalation steps exist for Si. On the other hand, in case of Cr doped one, two peaks were also observed for intercalation and de-intercalation. However, obviously, the peak at 2.0 V for Li intercalation shifted to lower potential and that at 0.5 V for Li de-intercalation becomes smaller. Therefore, by doping Cr, Li intercalation at higher potential may be easier and increase the cycle stability as discussed. In any case, it is seen that Cr doped Si exhibits the highest capacity and cycle stability among the studied Si based samples. Further improvement in the anodic property of Cr doped Si was studied.

3.2. Effects of carbon coating of Cr doped Si on anodic property

Since the formation of oxide on the surface of Si is one reason for large irreversibility of Li intercalation in Si [11], it

Table 1
Effects capacity of Si of dopant on the electrical conductivity and Li intercalation

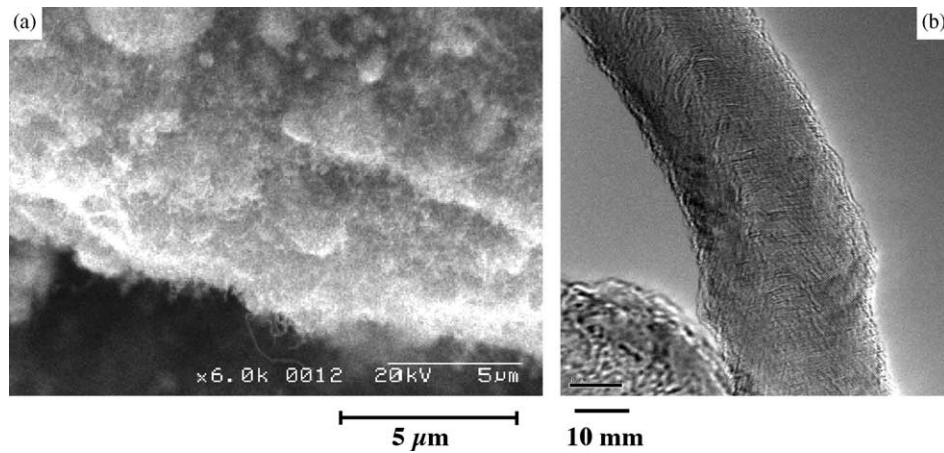|	Amount of additive	Conductivity σ (S cm^{-1})	Intercalation capacity (mAh g^{-1})	Reversible capacity (mAh g^{-1})
Pure Si	None	8.83×10^{-2}	1631	357
Cr doped Si	0.02%	4.71×10^{-1}	2684	822
B doped Si	0.3%	1.64×10^{3}	2213	562
P doped Si	0.08%	1.22×10^{-4}	1638	165

Fig. 5. SEM (a) and TEM (b) image of the sample after deposition of carbon nanotube at 973 K.

can be expected that further improvement in cycle stability is expected by coating Si with carbon. Yang et al. reported that Li diffuses to Si through surface carbon and surface carbon is effective for preventing the direct contact with electrolyte or lithium oxide [12]. In this study, effects of carbon coating for Cr doped Si were further studied. Since the large volumetric change occurs during Li electrochemical intercalation, we considered that coating the surface with fiber like carbon is effective for increasing the cycle stability of Si powder comparing with the dense film like carbon coat, which is reported by Dimov et al. [8,9]. Fig. 5 shows the SEM and TEM image of the sample after deposition of carbon nanotube at 973 K. The sample powder after ball-milling consist of submicrometer sized Si and carbon particles. On the other hand, it is seen that there are many thin carbon fibers covered on the surface of Si powders. Further detail observation of the formed carbon with TEM suggest that the formed carbon is the tubular shape and the size is around 40–50 nm in diameter. Therefore, it is seen that the carbon nanotube coated Si powder was successfully synthesized in this study.
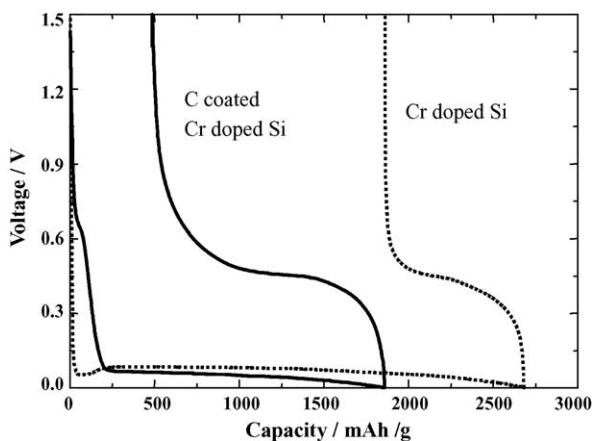
Fig. 6 shows the charge and discharge curve of Si coated with carbon nanotube. In all Si samples, de-intercalation of Li was observed at 0.5 V. Therefore, intercalation of Li is mainly occurred on Si and contribution of Li intercalation on carbon filament may not be large in the carbon filament coated Si. On the other hand, typical peak to graphitic carbon nanotube was observed at 0.8 V at the first intercalation step. Although the similar peak is also observed on the carbon mixed Si sample, the content of carbon power is negligibly small and large part of carbon in the present sample is surface carbon nanotubes. Therefore, SEI layer may form on the surface carbon nanotubes at the first electrochemical intercalation like the graphitic carbon anode and the formed SEI layer may prevent the surface oxidation between Si and organic electrolyte.

Binder compound is also important in order to achieve the high reversibility. Fig. 7 shows the effects of binder on the cycle stability of carbon coated Si doped with Cr. Comparing with EMPD for binder, initial capacity of carbon coated Si is almost the same as that using PVDF for binder. However, it

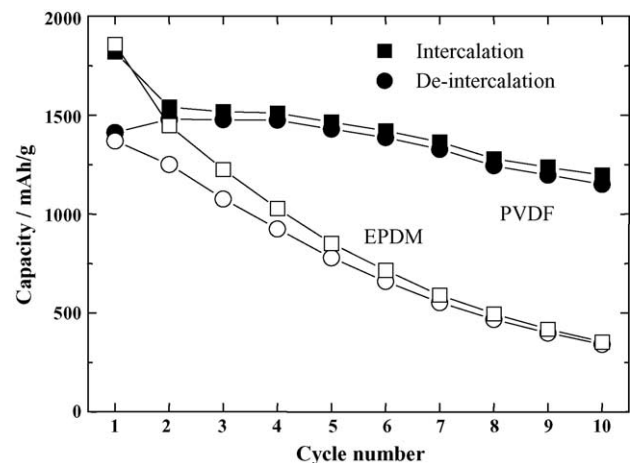Fig. 6. Charge and discharge curve of Si coated with carbon nanotube.

Fig. 7. Effects of binder on the cycle stability of carbon coated Si doped with Cr.

was obvious that the cycle stability was much improved when PVDF was used for binder and after eight cycles of charge and discharge, the reversible capacity can be sustained a value higher than 1500 mAh g^{-1}, which is almost three times larger than that of the current graphitic carbon anode. Therefore, it can be said that PVDF is more suitable for binder for Si anode. Since it is well known that PVDF exhibits Li ion conductivity, the positive effects of PVDF could be explained by uniform intercalation of Li into Si through PVDF. In any case, this study reveals that the reversibility of Li intercalation into Si could be improved by increasing conductivity and reversible capacity of 1250 mAh g^{-1} was sustained after 10th charge and discharge cycles.

4. Conclusion

Although the large initial capacity for Li intercalation was observed on Si, cycle stability was quite low and after few cycles for charge and discharge, Li intercalation capacity was hardly observed. However, it was found that the cycle stability of Si could increase drastically by elevating electrical conductivity. This study reveals that increase in electrical conductivity by doping Cr, coating carbon tubes from CH$_4$, and using PVDF for binder is quite effective for increasing the cycle stability of Si coated with carbon nanotubes. On this optimized sample, reversible capacity of 1250 mAh g^{-1} was sta-

bly sustained after 10th charge–discharge cycles. Therefore, semiconductive Si coated with carbon nanotube is highly interesting from alternative anode for Li ion rechargeable battery.

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