Short communication

Highly reversible carbon–nano-silicon composite anodes for lithium rechargeable batteries

Qin Si, K. Hanai, N. Imanishi, M. Kubo, A. Hirano, Y. Takeda*, O. Yamamoto

Department of Chemistry, Faculty of Engineering, Mie University, 1577 Kurimamachiya-cho, Tsu, Mie 514-8507, Japan

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ABSTRACT

A high-performance carbon–Si composite anode for lithium rechargeable batteries was developed. Si powder was coated with amorphous carbon by pyrolyzing polyvinyl chloride and chlorinated polyethylene at 900 °C for 2 h. The electrochemical performance of the carbon–Si composite anode depended on the Si particle size and the carbon content of the composite. A carbon–nano-size Si (average size 50 nm) composite with 48 wt.% carbon showed an excellent performance. The coulombic efficiency in the first cycle was 69.2% and the second cycle reversible discharge capacity of 970 mAh g^{-1}. The capacity fade on cycling was 0.24% per cycle during the first 40 cycles. The carbon–micron-sized Si (average size 4 μm) composite showed a high coulombic efficiency of 78.6% in first cycle, but with poor cycling performance. The capacity fade within 30 cycles was 1.7% per cycle. The effect of the chlorine content in the precursor on the cycling performance was not detectable.

1. Introduction

The energy density of the widely used lithium-ion secondary batteries with the carbon anode and the LiCoO$_2$ cathode has been improved by two times in the past decade. The energy density of the batteries of small size is as high as 200 Wh kg^{-1}. Recently, higher energy density large size batteries have been required in the fields as hybrid electric vehicles (HEVs) and electric vehicles (EVs). One approach to improve the energy density of lithium ion batteries is to substitute the carbon anode for a new material. The theoretical lithium insertion capacity of graphite is 372 mAh g^{-1}, which is only about one-tenth of Li. Unfortunately, the use of lithium metal as the anode in the electrolyte solution was difficult, because of the dendrite formation on the lithium anode surface [1]. Lithium metal alloys have been studied as the alternative anodes in lithium reversible batteries for many years. Among the lithium metal alloy, silicon shows a high theoretical capacity of 1967 mAh g^{-1} Li$_{4.4}$Si (4200 mAh g^{-1} Si) [2]. Although Si has a high lithium insertion capacity, a huge volume change (maximum 320%) is accompanied by the insertion of lithium into Si, which leads to a strong mechanical stress of the crystallites and thus to the loss of the electrical contact [3]. The mechanical stress results in the rapid loss of the reversible capacity upon prolonged cycling. Especially, a large irreversible capacity over 50% was found during the first cycle.

Many approaches have been reported to reduce the first cycle irreversible capacity and the capacity fade during the cycling [4]. A reduction of the particle and crystalline size into the nanometer scale showed a reduction of first cycle irreversible capacity and the improvement of cycling behavior. Li et al. [5] reported that a charge capacity of 2775 mAh g^{-1} and a discharge capacity of 2097 mAh g^{-1} could be obtained for a nano-Si anode during the first cycle, giving 76% coulombic efficiency. Its reversible capacity in the 10th cycle was 1729 mAh g^{-1}. The capacity fade during cycling was as high as 1.75% per cycle. While particle size reduction can reduce the volume change to a certain degree, it cannot completely eliminate capacity fade upon cycling. Another approach to obtain a high-performance Si anode is to use a Si–C composite anode. Various methods have been employed for preparing Si–C composite anodes. A high reversible capacity was obtained for nano-Si on fine particle graphite (KS-6), where 10–20 nm Si particles were deposited on the graphite by thermal vapor deposition of silane [6,7]. This anode showed initial charge and discharge capacities of 1350 and 1000 mAh g^{-1}, respectively, and after 100 cycles, a reversible capacity over 900 mAh g^{-1} is retained. However, this preparation method is a little complicate for the commercial application.

Liu et al. [8] found a low irreversible capacity in the Si–C composite anode, where carbon was deposited on fine Si particles (<1 μm) by thermal decomposition of polyvinylchloride (PVC). The composite anode showed a high first cycle coulombic efficiency of 82% and a high reversible capacity of about 1000 mAh g^{-1}. However, the capacity degradation rate during cycling was as high as 0.93% per cycle. In this study, several sizes of silicon particles were coated

* Corresponding author. Tel.: +81 59 231 9421; fax: +81 59 231 9419.
*E-mail address:* takeda@chem.mie-u.ac.jp (Y. Takeda).

with carbon by thermal decomposition of PVC and chlorinated polyethylene (CPE), and the effect of size of silicon particles and the Si–C ratio of the Si–C composite anode on the electrochemical performances was examined. The carbon–nano-Si composite showed a high revertible capacity and an excellent cycling performance.

2. Experimental

The carbon–silicon composites were prepared by the method reported in the previous paper [8]. The silicon powders of 10 μm and 4 μm size were purchased from High Purity Chemicals, Japan, that of 0.7 μm size from Kinsei Matec, Japan, and 50 nm size from Aldrich. CPE with the different content of chlorine was supplied by Kureha Elastmer, Japan, and PVC was supplied by Aldrich. PVC (or CPE) was mixed with the silicon powders in tetrahydrofuran (THF), and dried at 60 °C for 5 h, then the mixed powders were heated at 900 °C for 2 h in 2% H_2–Ar. Elemental analysis of Si and C contents in the Si–C composite was performed using a Yanaco MT-2 CHN corder.

The electrochemical tests of the carbon–Si composite electrodes were carried out with a two-electrode coin-type cell. The working electrode was composed of 60 wt.% carbon–Si, 20 wt.% acetylene black (AB), and 20 wt.% poly(vinylidene fluoride) (PVDF). The carbon–Si composite and AB were mixed in a 0.02 g ml^{-1} PVDF/1-methl-2-pyrrolidone solution, and the viscous mixture was casted on a 300-μm thick nickel foam, which was served as a current collector. The electrode was further dried at 120 °C under vacuum for 1 h followed by pressing at 400 kgf cm^{-2}. The geometric area of the electrodes was about 0.8 cm^2 and the typical thickness was about 220 μm. The 2025 coin-type cells were assembled in an Ar-filled glove box using 1 M LiClO$_4$ in ethylene carbonate (EC) and diethylene carbonate (DEC) (1:1 in volume) as the electrolyte and metallic lithium foil (20 μm in thickness) as the counter electrode. The electrochemical performance of the composite anode was evaluated using constant current (0.1 C rate) charge–discharge cycling in the voltage range 20–1500 mV at room temperature. The electrode capacity was calculated from the weight of active material, e.g. Si–C weight.

X-ray diffraction (XRD) patterns were obtained using Rigaku Rotaflex RU-200B with Cu Kα radiation. The morphology of the composite electrode was examined with a help of scanning electron microscopy (SEM) (Hitachi SEM S-4000) and transmission electron microscopy (TEM) (Hitachi TEM H900). Raman spectroscopy was used to characterize the deposited carbon using a RNANOR T64000MI with 488 nm laser. Thermal properties of PVC and CPE were measured using a Rigaku Thermo Plus TG8120.
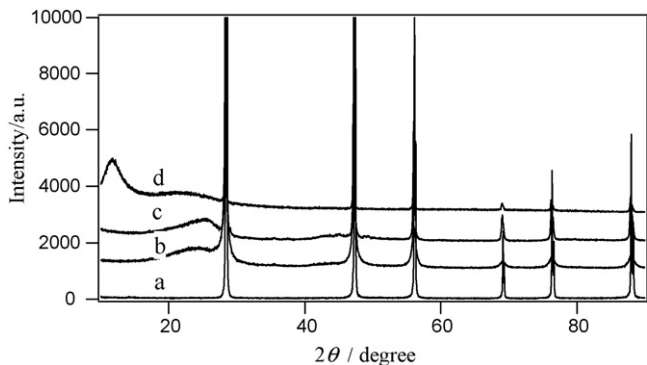
Fig. 1. XRD patterns of carbon–Si composite prepared by pyrolysis of (a) pure Si (4 μm), (b) Si (50 nm)–PVC (10:90 in weight), (c) Si (0.7 μm)–PVC (10:90 in weight), and (d) Si (4 μm)–PVC (10:90 in weight).
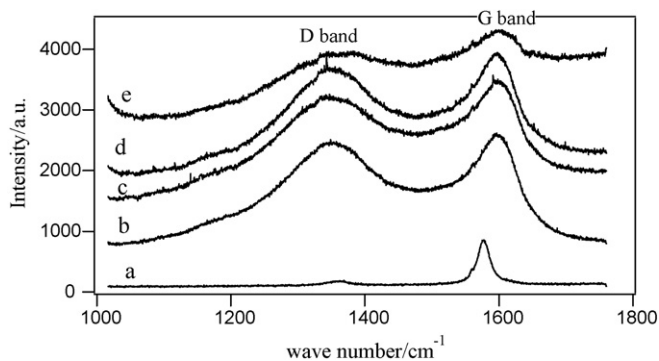
Fig. 2. Raman spectra of (a) MCMB, and carbon–Si composite prepared by pyrolysis of (b) Si (50 nm)–PVC (10:90 in weight), (c) Si (50 nm)–CPE (chlorine 70%) (10:90 in weight), and (d) Si (50 nm)–CPE (chlorine 39.5%) (10:90 in weight), and (e) Si (50 nm)–CPE (chlorine 25.5%) (10:90 in weight).

3. Results and discussion

The carbon–Si composites were prepared by pyrolyzing the mixtures of the different sized Si powder and PVC (or CPE) with the different Si:PVC (or CPE) ratios. Fig. 1 shows the typical XRD patterns of the carbon–Si composite, where the different sized Si powder and PVC mixtures (10:90 in weight) were heated at 900 °C for 2 h. The carbon content in the carbon–Si composite was slightly different with the different particle Si sizes and is around 50 wt.%. The XRD patterns show sharp Si peaks while the carbon peak is broad, which suggests that the carbon of the composite is amorphous. Fig. 2 shows Raman spectra of the carbon–Si composite, where carbon was coated on nano-Si powder (50 nm) by pyrolyzing PVC and CPE with the different chlorine contents with a 10/90 weight ratio of Si/polymer. Two main peaks are observed at around 1350 and 1580 cm^{-1}, which are designated as the D band and the G band, respectively [9]. The G band is associated with crystalline graphite, while the D band is attributed to amorphous graphitic materials. The relative intensity ratio of the D and G bands, I_G/I_D, gives information about the perfection of the graphite layered structure [10]. The I_G/I_D ratios are listed in Table 1. The effect of the chlorine content in CPE on the I_G/I_D is not clear, but the I_G/I_D ratio of meso-carbon microbeads (MCMB) is almost 11 times higher than that of pyrolyzed carbon, suggesting the pyrolyzed carbon is highly disordered. SEM and TEM images of the carbon–Si composite show the homogenous carbon distribution over the Si matrix and no deposition on the special spaces of Si matrix as shown in Fig. 3.

The anode performance of the carbon–Si composite by pyrolyzing PVC and CPE has been examined and its dependence on the Si size and the pyrolyzing conditions has been investigated. The charge and discharge curves of the carbon–50 nm Si and carbon–4 μm Si are shown in Fig. 4, where the Si and PVC mixture (10:90 weight ratio) was pyrolyzed at 900 °C for 2 h. In the first discharge capacities (intercalation of lithium into the Si–C electrode) are 1335 mAh g^{-1} for the 50 nm Si–C electrode and 1815 mAh g^{-1}

Table 1
The relative intensity ratio of the D and G bands (I_G/I_D) of the carbon-coated Si prepared by pyrolysis of CPE (or PVC) and Si (10:90 in weight)

| Samples	Carbon content (wt.%)	I_G/I_D
CPE (chlorine 25.5 wt.%)	3	1.00
CPE (chlorine 39.5 wt.%)	13	0.83
PVC (chlorine 56.8 wt.%)	48	0.85
CPE (chlorine 70 wt.%)	62	0.82
Graphite (MCMB)	100	11.00
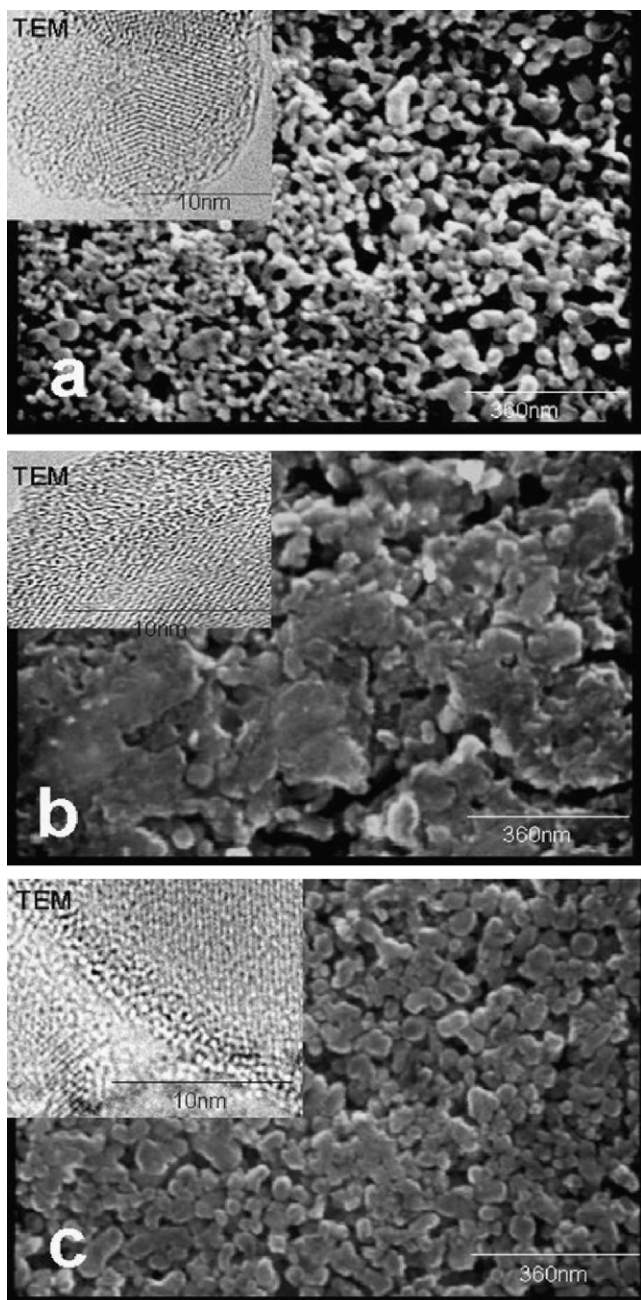
Fig. 3. TEM and SEM images of (a) nano-Si (50 nm), and carbon–Si composite prepared by pyrolysis of (b) Si (50 nm)–PVC (10:90 in weight) and (c) Si (50 nm)–PVC (50:50 in weight).

for the 4 μm Si–C electrode, while the charge capacities (deinter-calation of lithium from the Si–C electrode) are 923 mAh g^{-1} for the 50 nm Si–C electrode and 1426 mAh g^{-1} for the 4 μm Si–C electrode. The coulombic efficiency in the first cycle for the 50 nm Si–C electrode is 69.2%, while it is much higher for the 4 μm Si–C electrode (78.6%). The irreversible capacity can be attributed in part to the formation of solid electrolyte interphase (SEI) on the Si and carbon surfaces [11]. This passivation layer is expected to form through a reaction of the lithium with the solvent (EC and DEC) and the salt (LiClO$_4$) of the electrolyte. The amount of the SEI depends on the surface area. It is likely that the large surface area of nano-Si is partially responsible for the higher first cycle irreversible capacity. However, the reversible capacity of carbon-coated Si (large size)
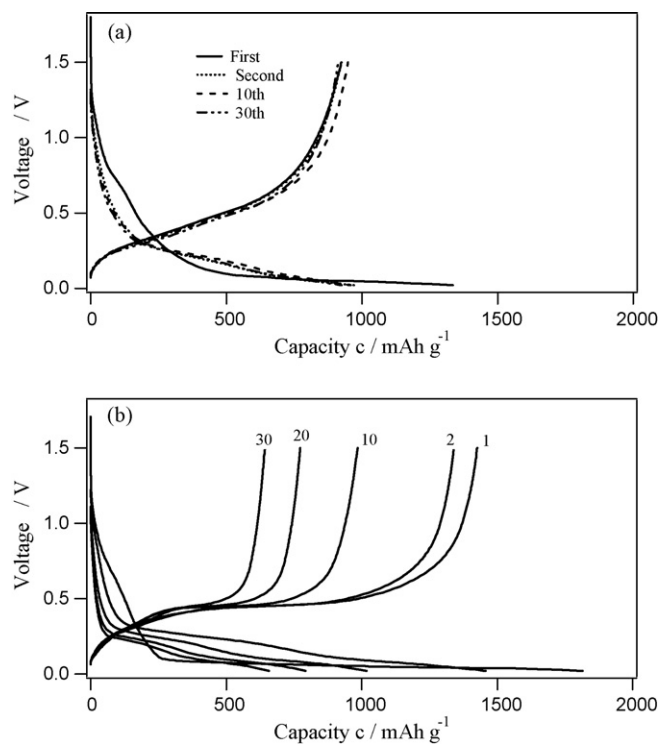
Fig. 4. The charge–discharge curves of carbon–Si composite prepared by pyrolysis of (a) Si (50 nm)–PVC (10:90 in weight) and (b) Si (4 μm)–PVC (10:90 in weight).

decreases rapidly with cycling. Fig. 5 shows the dependence of the Si size in the carbon–Si composite electrode on the charge–discharge cycling at room temperature, where Si and PVC weight ratio was 10:90. The content of carbon in the Si–C composite slightly depends on the Si particle size from 58 to 48 wt.%, which is listed in Table 2. The initial discharge capacities of the Si–C composites with large particle size Si are high. However, the discharge capacity fade upon cycling is very fast for the large size Si. The discharge capacity of the carbon–4 μm Si composite decreases from 1815 mAh g^{-1} in the first cycle to 657 mAh g^{-1} after 30 cycles. On the other hand, the carbon–50 nm Si shows a stable cycling performance. A discharge capacity of 1335 mAh g^{-1} in the first cycle decreases to 880 mAh g^{-1} in the 40th cycle. The carbon-large size Si as 10 μm composite shows a high first discharge capacity of 1674 mAh g^{-1} and the capacity decreases quickly to 344 mAh g^{-1} in the 30th cycle. The carbon–nano-Si composite by pyrolyzing PVC shows a high reversible capacity of about 900 mAh g^{-1}, a high coulombic
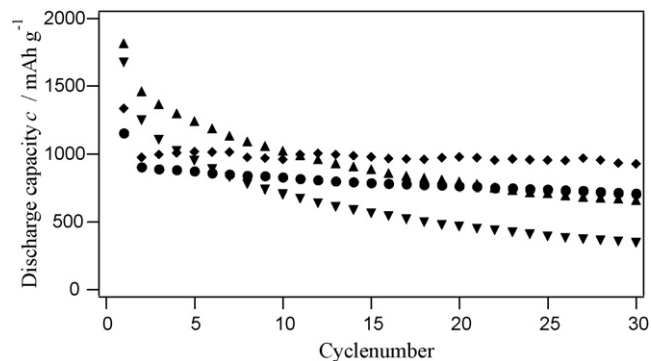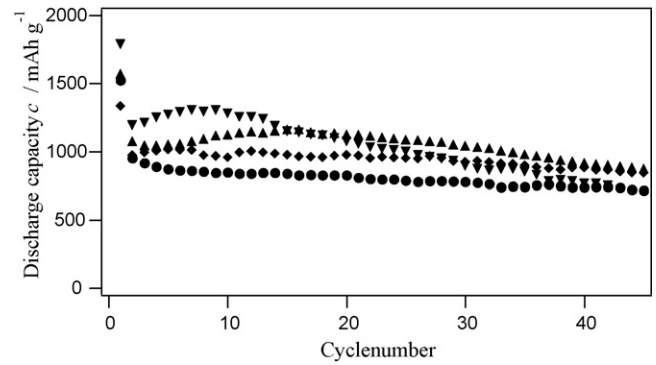

Fig. 5. Cycling performance of carbon–Si composite prepared by pyrolysis of Si–PVC (10:90 in weight) as a function of Si particle size. Cut-off voltage: 20–1500 mV. (♦) 50 nm, (●) 0.7 μm, (▲) 4 μm, and (▼) 10 μm.

Table 2
Electrochemical performance of the carbon-coated Si prepared by pyrolysis of PVC and CPE

Starting materials			Si/polymer weight ratio	Carbon content in Si–C (wt.%)	Coulombic efficiency in the first cycle (%)	Second cycle discharge capacity (mAh g⁻¹)	Capacity fade on cycling (% per cycle) (cycle number)
Polymer	Chlorine content in polymer (wt.%)	Si particle size					
CPE	25.5	50 nm	10/90	3	69.3	1968	1.12 (2–30)
CPE	39.5	50 nm	5/95	28	66.5	1441	0.54 (2–40)
CPE	39.5	50 nm	10/90	13	68.3	1740	0.92 (2–30)
CPE	39.5	50 nm	20/80	5	67.4	1146	0.90 (2–30)
PVC	56.8	50 nm	10/90	48	69.2	973	0.25 (2–40)
PVC	56.8	50 nm	20/80	31	56.3	951	0.6 (2–30)
PVC	56.8	50 nm	30/70	20	59	1072	0.10 (2–30)
PVC	56.8	50 nm	50/50	7	59	1193	0.83 (2–30)
PVC	56.8	0.7 μm	10/90	58	72.6	898	0.72 (2–30)
PVC	56.8	4 μm	10/90	51	78.6	1457	1.8 (2–30)
PVC	56.8	10 μm	10/90	51	73.5	1248	2.4 (2–30)
CPE	70.0	50 nm	10/90	62	27	324	0.63 (2–30)
CPE	70.0	50 nm	20/80	53	49.4	671	0.2 (2–30)
CPE	70.0	50 nm	30/70	30	56.4	1011	0.16(2–50)

Fig. 6. Cycling performance of carbon–Si composite prepared by pyrolysis of Si (50 nm)–PVC with different compositions. Cut-off voltage: 20–1500 mV. (♦) Si–PVC 10:90 in weight (Carbon: 48 wt.%), (●) Si–PVC 20:80 in weight (Carbon: 31 wt.%), (▲) Si–PVC 30:70 in weight (Carbon: 20 wt.%), and (▼) Si–PVC 50:50 in weight ratio (Carbon: 7 wt.%).

efficiency of 69.2% in the first cycle, and a low capacity degradation rate of 0.24% per cycle. These electrochemical performances of the electrode are compared with those of the carbon-free nano-Si (mean diameter: 12 nm) reported by Grattz et al. [11], where the first cycle discharge capacity and the coulombic efficiency were 1000 mAh g⁻¹ and 41%, respectively, and the capacity degradation rate was 1.0% per cycle. Li et al. [5] also reported the electrochemical performance of nano-size Si (mean size: 78 nm). The first cycle discharge capacity was as high as 2000 mAh g⁻¹, but the capacity degradation rate was as high as 1.8% per cycle. It means that the carbon–nano-Si composite is quite effective to improve the cycling performance as well as the charge–discharge coulombic efficiency in the first cycle.

The effect of carbon content in the carbon–Si composite on the electrochemical performance has been examined for the nano-Si powders. The nano-Si (50 nm) and PVC mixtures with different ratios were heated in 2% H₂–Ar at 900 °C for 2 h. The carbon content in the composite electrode decreases with decreasing PVC content in the precursors (see Table 2); a carbon content of 48 wt.% decreases to 20 wt.% by decreasing the PVC content from 90 to 70 wt.% in the Si–PVC precursors. Fig. 6 shows the cycling performance of the carbon–nano-Si composite anode as a function of the carbon content in the composite at room temperature. The carbon–Si composite electrode with a low carbon content of 7 wt.% shows a high discharge capacity of 1800 mAh g⁻¹ and a low coulombic efficiency of 58.8% in the first cycle. The capacity fade upon cycling is larger than those with high carbon content. The high carbon content composite gives a high coulombic efficiency in the first cycle and a good cycling performance. The reversible capacity is slightly lower than that of the sample with low carbon content.

Gao et al. [12,13] reported the electrochemical performance of the Si–C composite anode, where carbon was coated on nano-Si (average particle size: 80 nm) by pyrolysis of polyvinyl alcohol (PVA). The initial reversible capacities were found to be 1100 mAh g⁻¹ for the composite with 29.6 wt.% carbon and 950 mAh g⁻¹ for that with 19.5 wt.% carbon. The degradation rate of 0.9% per cycle upon cycling was higher than that of our result of 0.24% per cycle. The polymer of PVA used by Gao had no chlorine. In this study, we have examined the effect of chlorine in the precursor. It is known that PVC eliminated HCl from 200 to 350 °C, PVC pitch formed at 400–450 °C, and the pitch is carbonized from 350 to 550 °C. Adhesive carbonaceous layer was prepared on metal oxides by pyrolysis of PVC [14]. This process depends on the starting polymer materials. We have examined the effect of the chlorine content in the precursor. PVC (chlorine 56.8 wt.%)
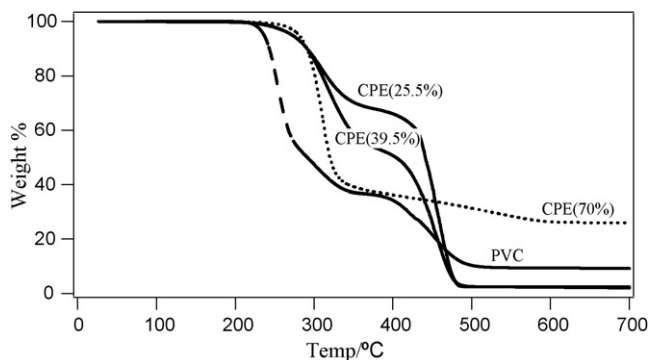
Fig. 7. Thermogravimetric analysis of PVC and CPE.

and CPE with different chlorine contents (70, 39.5 and 25.5 wt.%) were used for the carbonized materials on nano-Si (50 nm). Fig. 7 shows thermal gravimetric results of PVC and CPE with different chlorine contents. PVC shows two-step decompositions; the first one is between 200 and 350 °C, and second one between 400 and 500 °C. The carbonized temperature and the residual carbon content depend on the chlorine content in the polymers. CPE with high chlorine content shows a high carbonizing temperature and a high residual carbon. The carbonizing temperature may affect the character of the decomposed carbon. However, Raman results show no clear difference for the carbon prepared from the different content of chlorine in the polymers. Fig. 8 shows the cycling performance of the carbon–nano-Si composite prepared from the polymers with different chlorine contents, along with pure Si (50 nm) and the carbon prepared by pyrolysis of PVC at 900 °C. The carbon anode without Si shows the coulombic efficiency in the first cycle was 73.8% and the reversible capacity after second cycles was about 280 mAh g^{-1}. The nano-Si–C composite prepared from CPE with low chlorine content shows a high reversible capacity and a high coulombic efficiency in the first cycle, but the capacity fade upon cycling is slightly higher than those for the Si–C composites prepared from CPE and PVC with high chlorine content. The Si–C composites prepared from CPE with a low chlorine content show low carbon content (see Table 2). The carbon–nano-Si composite prepared by pyrolysis of Si–CPE (CPE:with 39.5 wt.% chlorine; Si:CPE = 5:95 in weight) shows a carbon content of 28 wt.% and a low capacity fade of 0.27% per cycle between 2 and 20 cycles. However, the capacity fade increases upon further cycling. The carbon–nano-Si composite prepared by pyrolysis of CPE with 70 wt.% chlorine gives
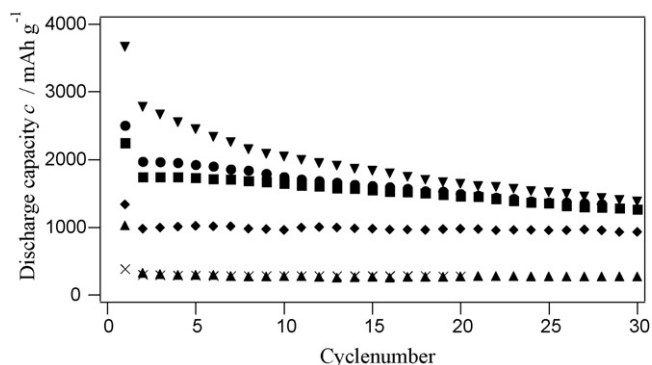
a low coulombic efficiency at the first cycle and low reversible capacity of 324 mAh g^{-1}, where the carbon content in the composite was about 62 wt.%. The composite with 53 wt.% carbon prepared by pyrolysis of CPE with 70 wt.% chlorine also gives low reversible capacity of 671 mAh g^{-1}. These results suggest that CPE with high chlorine content and low chlorine content as the carbon source for the C–Si composite electrode is not suitable to obtain a high-performance anode and PVC is the best candidate for the electrode.

The electrode performances of the carbon–Si composite are summarized in Table 2. The anode performance of the carbon–Si electrode depends strongly on the size of Si particles as well as the carbon content in C–Si composite. The large size Si shows a high initial charge–discharge capacity, but the degradation rate is high. The carbon content in the composite plays an important role. The optimum content is observed. The low carbon content sample shows a low first cycle coulombic efficiency as well as a high carbon content one. The low carbon content sample shows a high reversible capacity, but the capacity fade upon cycling is faster than that of sample with optimized carbon content. The optimum carbon content in nano-size Si is about 50 wt.%.

4. Conclusion

The charge and discharge performances of the carbon–Si composite prepared by pryolysis of PVC and CPE were examined as a function of the particle size of Si powder, carbon content on Si, and the chlorine content in the precursor. The carbon–nano-sized Si composite shows a high coulombic efficiency in the first cycle. A low carbon content nano-Si composite gives a high reversible capacity, but the capacity fade upon cycling is higher than that of high carbon content. The best result in this study is found in the carbon–50 nm Si by pyrolysis of the mixture of 10 wt.% Si–90 wt.% PVC (chlorine content: 56.8 wt.%) at 900 °C for 2 h, where the carbon content is 48 wt.%. The first cycle charge–discharge coulombic efficiency is 69.2%, the reversible capacity 970 mAh g^{-1}, and the capacity fade upon cycling 0.24% per cycle.

Fig. 8. Cycling performance of carbon–Si composite prepared by pyrolysis of Si–PVC and Si–CPE (10:90 in weight). Cut-off voltage: 20-1500 mV. (▲) CPE (chlorine: 70%), carbon 62 wt.%, (◆) PVC (chlorine: 56.8%), carbon 48 wt.%. (■) CPE (chlorine: 39.5%), carbon 13wt.% (●) CPE (chlorine: 25.5%), carbon 3 wt.% (▼) Pure Si × Pure carbon (Pyrolysis of PVC).

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