



Electrochemical properties of carbon-coated Si/B composite anode for lithium ion batteries

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ABSTRACT

Carbon-coated Si and Si/B composite powders prepared by hydrocarbon gas (argon + 10 mol% propylene) pyrolysis were investigated as the anodes for lithium-ion batteries. Carbon-coated silicon anode demonstrated the first discharge and charge capacity as 1568 mAh g^{-1} and 1242 mAh g^{-1} , respectively, with good capacity retention for 10 cycles. The capacity fading rate of carbon-coated Si/B composite anode decreased as the amounts of boron increased. In addition, the cycle life of carbon-coated Si/B/graphite composite anode has been significantly improved by using sodium carboxymethyl cellulose (NaCMC) and styrene butadiene rubber (SBR)/NaCMC mixture binders compared to the poly(vinylidene fluoride, PVdF) binder. A reversible capacity of about 550 mAh g^{-1} has been achieved at 0.05 mA cm^{-2} rate and its capacity could be maintained up to 450 mAh g^{-1} at high rate of 0.2 mA cm^{-2} even after 30 cycles. The improvement of the cycling performance is attributed to the lower interfacial resistance due to good electric contact between silicon particles and copper substrate.

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1. Introduction

Silicon is of special interest because the theoretical storage capacity for the $\text{Li}_{4.4}\text{Si}$ alloy is 4200 mAh g^{-1} (9200 mAh cm^{-3}). Although this value is 10 times greater than that of graphite, 372 mAh g^{-1} (830 mAh cm^{-3}), the large volume change accompanying lithium insertion results in the poor reversibility of the alloying and de-alloying process. Recently, this problem could be solved by preparing new silicon alloy powders and silicon-based composite powders [1–3]. These modified silicon anodes are found to exhibit a better cyclability with reversible capacity in comparison to the pristine silicon anode. It was reported that the alloying of silicon with inactive elements such as Co, Fe, Cu metals limited the reaction with lithium and also reduced the volume change of the anode during electrochemical cycling [4–6]. Nevertheless, the large irreversible capacity loss occurred during the first charge due to the electrolyte decomposition and the formation of solid electrolyte interphase (SEI) on the anode surface. This irreversible capacity could be reduced by surface modification such as carbon coating and metallic electroplating or electroless deposition method. A carbon layer with a thickness of 5–7 nm was easily formed on silicon powder by hydrocarbon gas pyrolysis under an inert atmosphere and it was observed that the initial irreversible

capacity of silicon anode could be reduced significantly by carbon coating [7]. Therefore, it is expected that these combined effects with silicon composites and carbon coating will lead to a promising cyclability with higher reversible capacity for silicon-based anode materials. Recently, the critical role of binder in the stabilization of the cycling performance of silicon-based anode was reported [8–10]. The cycle life of silicon anodes was improved using a binder containing the elastomeric styrene butadiene rubber (SBR) and sodium carboxymethyl cellulose (NaCMC). Although NaCMC is not an elastomeric binder, it was widely used to improve the cycling performances of silicon electrodes. The efficiency of NaCMC binder could be attributed to its extended conformation in solution that facilitates the formation of an efficient conductive material, binder and silicon components.

In this investigation, for the first time, the preparation and electrochemical performance of carbon-coated Si/B composite with silicon as the active matrix and boron as the inactive matrix is reported. We have also prepared carbon-coated Si/B/graphite composite anodes using various polymeric binders and investigated their electrochemical properties.

2. Experimental

Nanosized silicon (60-nm diameter, 98%, Alfa Aesar) and boron (below 600-nm diameter, 95%, Tangshan, China) powders were mixed at different portions. Then, the mixed powders were heat treated at 700°C under argon + 10 mol% propylene mixed gas flow

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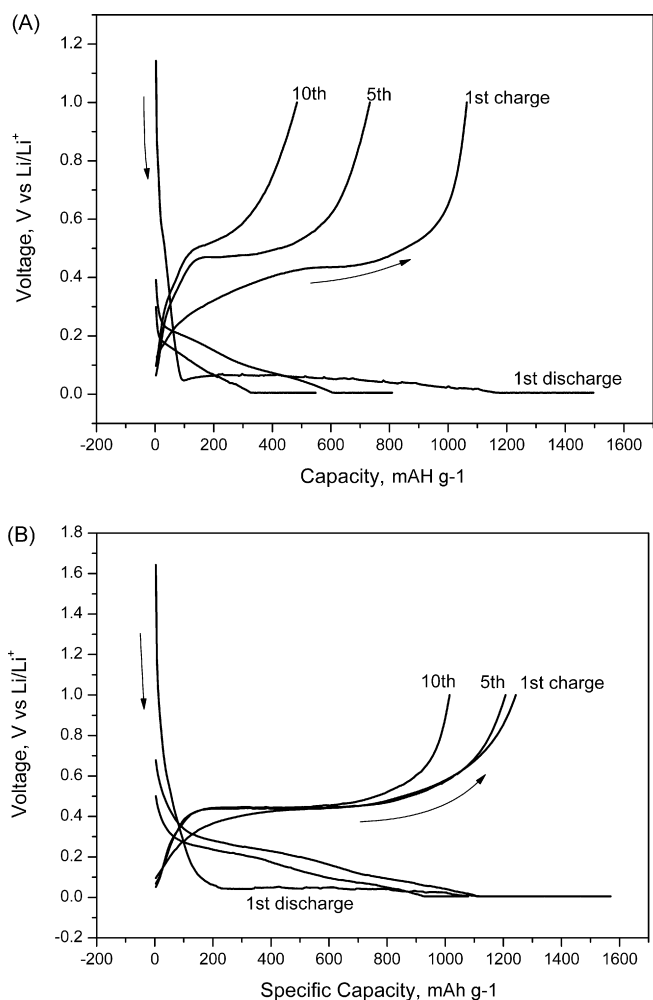


Fig. 1. Voltage curves of uncoated silicon (A) and carbon-coated silicon anode (B) (current density: 0.25 mA cm^{-2} , cut-off voltage range: $0.005\text{--}1.0 \text{ V vs Li/Li}^+$).

for 10 h. After this time, the carbon-coated powders were cooled down naturally to room temperature. The composite anodes used carbon-coated Si/B or Si/B/graphite as active materials and denka carbon black (Denki Kagaku K.K., Japan) as conductive materials. The average particle size and the surface area of carbon black material were 36 nm and $65 \text{ m}^2 \text{ g}^{-1}$, respectively.

In case of the carbon-coated Si/B/graphite active materials, the portion is 30 wt% of Si/B and 70 wt% of natural graphite (Sodiff Co. Ltd., South Korea). Three types of polymer binders were used: (1) poly(vinylidene fluoride, PVdF) binder (5 wt%, Kureha) in *N*-methyl pyrrolidone (NMP), (2) NaCMC (1 wt% in water, Sigma), (3) NaCMC (1 wt% in water) and SBR (40 wt% in water, Zeon) mixture. These materials were mixed at a rotation speed of 3000 rpm for 30 min in homogenizer. Then, the obtained viscous slurries were cast on to a copper foil current-collector by the doctor blade technique and dried at 80°C under vacuum for 24 h. The resulting electrode ($3 \text{ cm} \times 4 \text{ cm}$) was used as anode in a cell with a lithium metal electrode and LiCoO_2 cathode, respectively. The electrolyte was 1 M LiPF_6 (Hashimoto, Japan) in a mixture of ethylene carbonate (EC):dimethyl carbonate (DMC):ethyl methyl carbonate (EMC) (1:1:1 in vol%) with 2 vol% vinylene carbonate (VC) as an electrolyte additive. These organic solvents were obtained from Cheil Industries Inc. (South Korea). All chemicals were used as received. The separator was a Celgard 2400 microporous membrane. All cells were enveloped in aluminum plastic pouches and

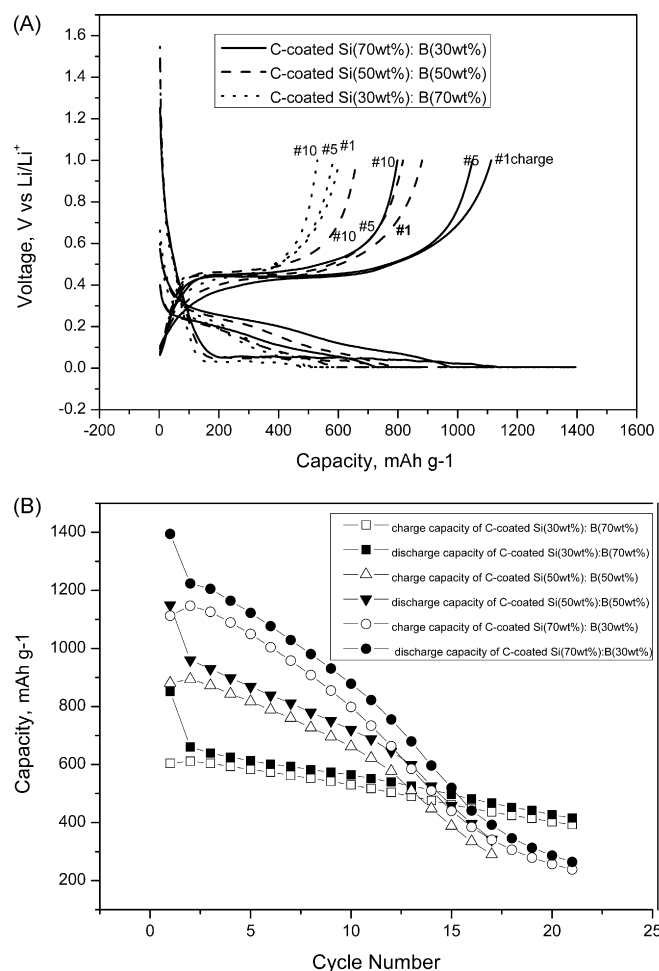


Fig. 2. Voltage curves (A) and cycling performances (B) of carbon-coated silicon/boron composite anode with boron amounts (current density: 0.25 mA m^{-2} , cut-off voltage range: $0.005\text{--}1.0 \text{ V vs Li/Li}^+$).

sealed under vacuum in a dry room (dew point; -50°C). Examination of the morphology of composite anodes was conducted by scanning electron microscope (SEM, Hitachi S-4200). Electrochemical impedance measurements were performed over the frequency 1 MHz to 0.1 Hz by a Solartron 1260 frequency response analyzer in combination with a Solartron 1286 electrochemical interface. The ac amplitude used during the measurements was 10 mV. The half cells and the full cells were galvanostatically charged and discharged in the voltage range of $0.005\text{--}1.0 \text{ V}$ and $3.0\text{--}4.2 \text{ V vs Li/Li}^+$ at various current densities using Maccor battery test cycler (S4200, USA), respectively.

3. Results and discussion

The electrochemical characterization of the uncoated silicon anode and the carbon-coated silicon anode using PVdF/NMP binder was investigated and compared in Fig. 1(A) and (B). There was an obvious shift in the charge potential plateau from the first cycle to the 10th cycle, which could be related to the irreversible phase transformation of silicon to amorphous state during the electrochemical alloying process [11]. However, the carbon-coated silicon anode shows that the plateau potential at around 0.45 V in the charge curve is more visible compared to the uncoated silicon anode even after 10 cycles. This result demonstrates that carbon coating treatment is effective for holding good morpho-

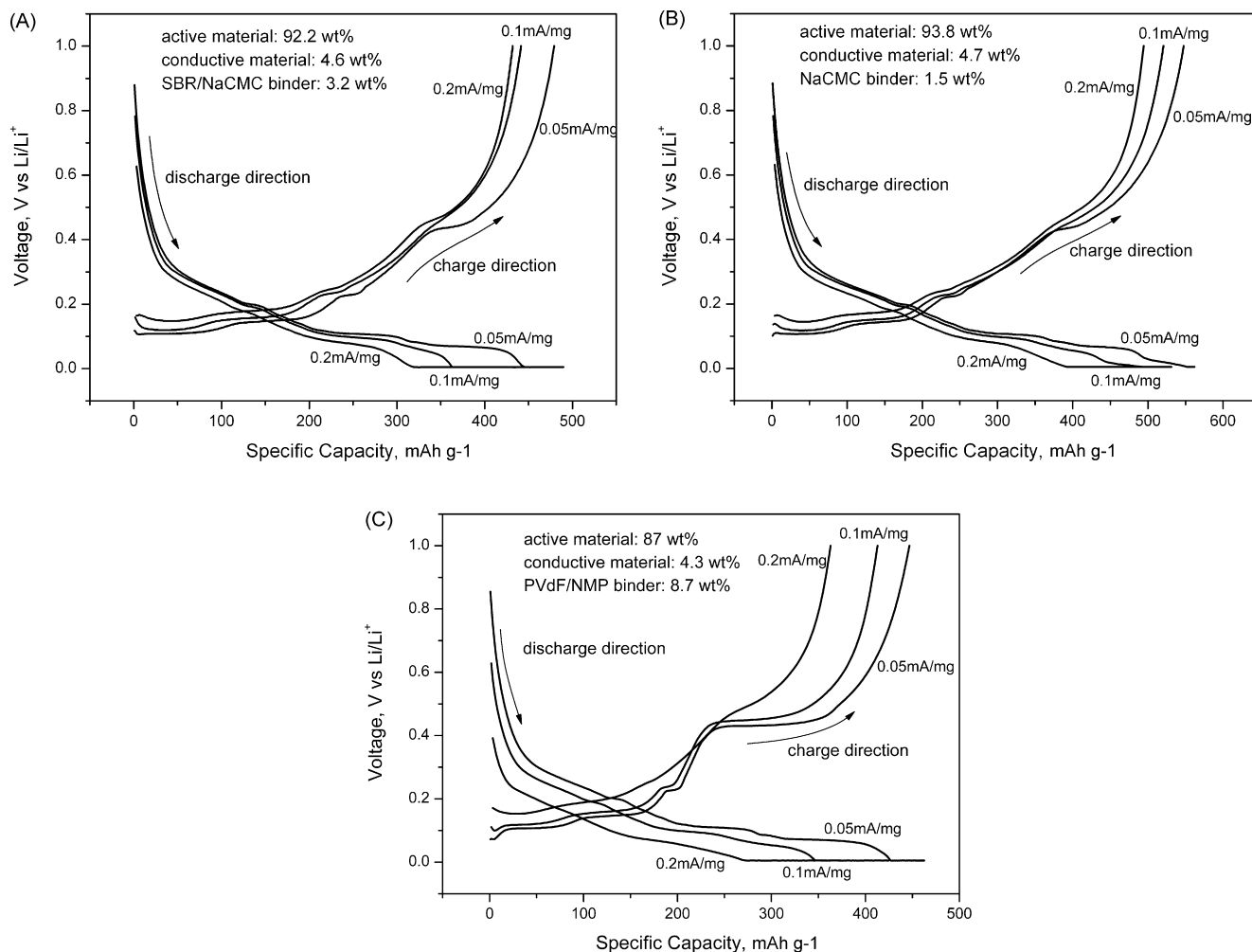


Fig. 3. Voltage curves of carbon-coated silicon/boron/graphite composite anodes at different cycling rates (A: SBR/NaCMC, B: NaCMC, C: PVdF/NMP, cut-off voltage range: 0.005–1.0 V vs Li/Li⁺).

logical stability of silicon anode during the cycling process. In addition, the initial coulombic efficiency for the carbon-coated silicon anode (79.2%) is higher than that of the uncoated silicon anode (71.1%). This indicates that carbon-coated silicon anode can reduce the first irreversible capacity and maintain the stable cyclability. The irreversible capacity can be also attributed to the loss of contacts between active particles, especially when active material undergoes large expansion changes during lithium insertion/removal. Fig. 2(A) shows the voltage curves of the carbon-coated silicon/boron composite anodes using PVdF/NMP binder with different weight ratios of silicon and boron for the first 10 cycles. Si(70 wt%)/B(30 wt%) and Si(50 wt%)/B(50 wt%) composite anodes do not show good cycling performances as expected. This is reasonable since the volume variation of silicon particles cannot be sufficiently protected by the above amounts of boron during cycling. In contrary, Si(30 wt%)/B(70 wt%) composite anode shows a remarkably good cycling performance. Although the initial coulombic efficiency is 71% and the reversible average capacity is about 500 mAh g⁻¹, the capacity fading rate is lower than that of other composite anodes even after 20 cycles as shown in Fig. 2(B). This result suggested that the anodic reaction mechanisms are due to the reactions of lithium with only silicon. Wherein, boron acted as an inactive matrix for the reactions and suppressed the volume change of silicon nano-particles. Fig. 3 shows the voltage curves of the carbon-coated silicon/boron/graphite composite anodes with

different polymer binders at various current densities. These composite anodes consisted of 30 wt% of carbon-coated silicon/boron and 70 wt% of natural graphite active materials. The capacity of graphite using 70 wt% corresponds to 260 mAh g⁻¹ based on the graphite weight. The rate capability of composite anode using SBR/NaCMC binder and NaCMC binder is similar and there is a small charge plateau potential as shown in Fig. 3(A) and (B). By contrast, the composite anode using PVdF/NMP binder produced small specific capacity and worse rate capability compared to that of the composite anode using SBR/NaCMC binder and NaCMC binder (Fig. 3(C)). It also shows a large charge plateau potential at lower current densities, while the cell which was cycled at high current density has no clear plateau due to the big morphological change in silicon. The great difference between the performances of nominally identical anodes using these binders proved that the choice of binder is a very important factor for composite anodes [12,13]. Fig. 4 shows the cycling performances of carbon-coated silicon/boron/graphite composite anodes using different polymer binders at various current densities. The specific capacity and the current density were calculated based on the weight of silicon/boron/graphite materials. For SBR/NaCMC anode, the specific capacity is about 500 mAh g⁻¹ at current density of 0.05 mA m g⁻¹. When the current density increased to 0.1 mA m g⁻¹ and 0.2 mA m g⁻¹, the specific capacity decreased slightly. This effect was due to the capacity decrease of natural graphite mate-

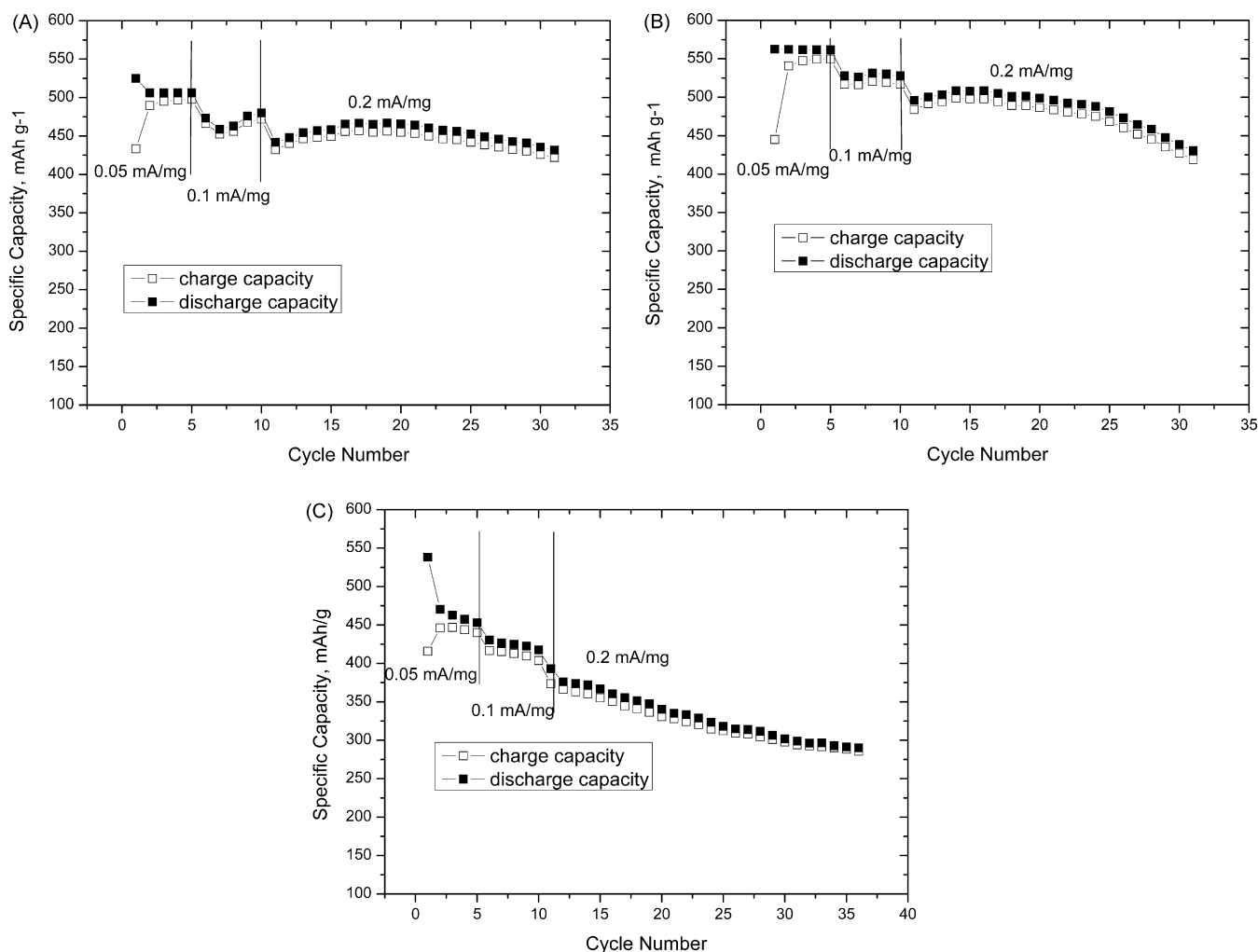


Fig. 4. Cycling performances of carbon-coated silicon/boron/graphite composite anodes at different cycling rates (A: SBR/NaCMC, B: NaCMC, C: PVdF/NMP, cut-off voltage range: 0.005–1.0 V vs Li/Li⁺).

rials as well as silicon-based materials. But the cycle life is stable until 30 cycles. In case of only NaCMC anode, the specific capacity increased to 550 mAh g⁻¹ at 0.05 mA m g⁻¹ rate and the behavior of cycle life is similar to that of SBR/NaCMC anode. With respect to PVdF anode, the specific capacity is about 450 mAh g⁻¹ at 0.05 mA m g⁻¹ rate and decreases significantly at high current densities. The enhancement in cycle stability of the silicon composite anode by replacing PVdF with SBR and SBR/NaCMC as the binder is clearly evident. In order to understand the influence of the binder of silicon-based anode, we performed electrochemical impedance studies on the anodes containing different binders after 30 cycles. As shown in Fig. 5, the Nyquist plots consisting of semicircle at high frequency and 45° straight line represented diffusion-controlled process in the solid electrode at low frequency. It has been reported that the diameter of semicircle in high frequency region is mainly related to the intrinsic electronic resistance and contact resistance of the electrode [14,15]. The semicircle at high frequency is also mainly induced from the contact resistance between active materials and current collector, which may be influenced by the geometric electrode and binder amount [16]. From this point of view, the difference in resistance of three electrodes may be caused by increased contact resistance between active material and copper substrate. This result may also be used to interpret the SEM images shown in Fig. 6. All the components tend to form agglomerates after 30 cycles, indicat-

ing that silicon could be highly dispersed and embedded within the graphite–boron matrix. Obviously, such a granular structure increases the interfacial affinity of silicon within the matrix and leads to an ensured electrical contact. Although silicon particles in

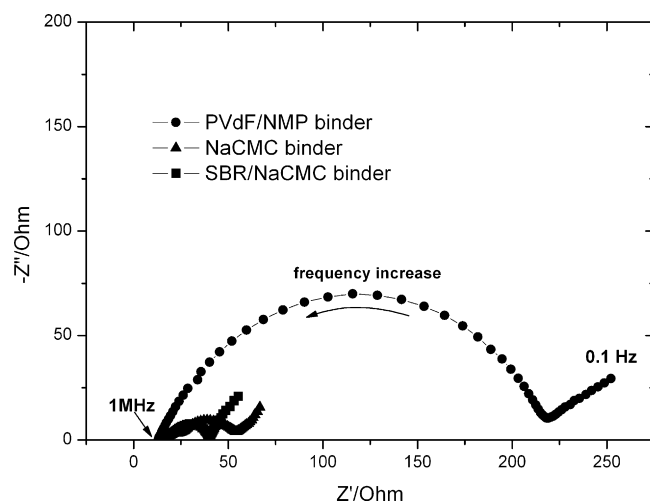


Fig. 5. AC impedance spectrum Li/silicon-based anodes with different binders after 30 cycles.

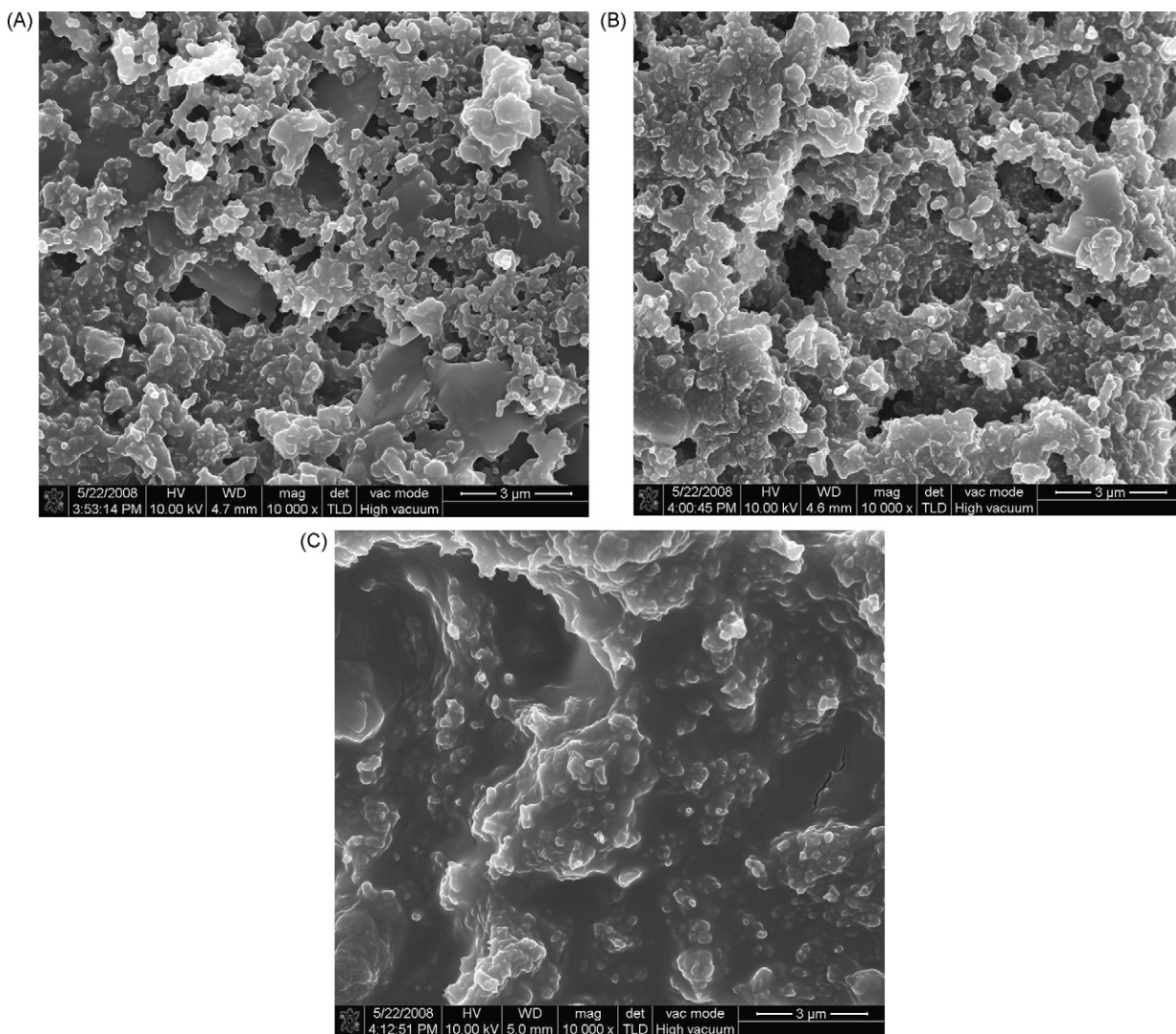


Fig. 6. SEM images of carbon-coated silicon/boron/graphite composite anodes after 30 cycles (A: SBR/NaCMC, B: NaCMC, C: PVdF/NMP).

all anodes are agglomerated, the agglomerates in silicon particles using PVdF/NMP binder are much dense. On the other hand, the low absolute volume effect of the composite silicon anode using SBR/NaCMC and NaCMC binder reduces the mechanical stress of

the dispersed silicon. Therefore, the anode containing PVdF/NMP binder easily loses the electrical contact with the current collector compared to the anode using SBR/NaCMC and NaCMC binders. These binders can stick to the particles and copper substrate

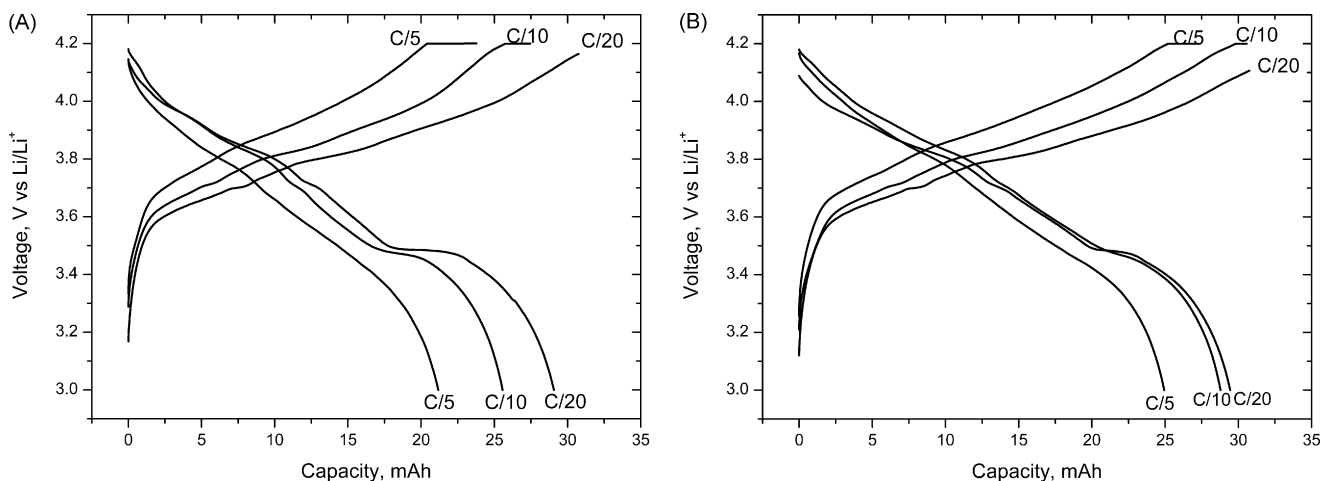


Fig. 7. Voltage curves of silicon-based composite anodes/LiCoO₂ full cell using different binders at various rates (A: SBR/NaCMC, B: NaCMC).

to withstand a greater extent of volume change with reversible capacity. A full cell using carbon-coated silicon/boron/graphite composite anodes with different binders and LiCoO₂ cathode was fabricated to study its rate capability at various current densities. The cathodic capacity of LiCoO₂ is sufficient enough to utilize completely the anodic capacity. The total capacity of cells is 30 mAh irrespective of types of binders at C/20 lower rate as shown in Fig. 7. However, the capacity of cell using NaCMC binder (Fig. 7(B)) is a little higher than that of the cell using SBR/NaCMC binder (Fig. 7(A)) at C/5 and C/10 rates, respectively. This effect may be originated from the formation of an efficient electrical-conducting network between conductive material and silicon active material. Another effect was also reported that NaCMC might have a positive role on the interfacial resistance as a polyelectrolyte [17]. NaCMC could play an additional role as a surface modifier in the silicon-based anodes. The surface modification of silicon particles may improve the formation of SEI passive layer, which increases the rate capability at high rates leading to better cycling performances.

4. Conclusions

The carbon-coated silicon anode exhibits good capacity retention, good coulombic efficiency, and low irreversible capacity compared to the uncoated silicon anode. The capacity fading rate of the carbon-coated silicon/boron composite anode also decreased as the amount of boron increased. This effect was due to the buffering effect that alleviates the volume expansion of silicon particle. The carbon-coated silicon/boron/graphite composite anodes using NaCMC and SBR/NaCMC binders also demonstrated stable cycling performances with high reversible capacity at high current densities. The improvement of cyclability of the composite anode could be attributed to good electrical contact between

active materials and copper substrate during electrochemical process.

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