Advanced Multiphase Silicon-Based Anodes for High-Energy-Density Li-Ion Batteries

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We report on the formation of composite silicon-based multiphase nanopowders as promising active-anode materials for high-energy-density, high-capacity-retention lithium-ion batteries. Simple synthetic routes have been developed for the preparation of core-shell Si and p-doped SiNi composite particles attached to carbon nanotubes. The particles were characterized by a variety of analytical and electrochemical methods. Environmental scanning-electron-microscopy and transmission-electron-microscopy images and electron-energy-loss-spectroscopy maps indicated formation of nanoparticles wrapped by carbon nanotubes and coated by nanometer-thick amorphous carbon. It was found that nickel diffuses to the bulk of silicon and forms either nickel-rich or nickel-depleted composite entities. The presence of boron in the synthesized composite powder has been detected by time-of-flight secondary-ion mass spectroscopy (TOFSIMS). Li/LiPf6 EC:DEC/Si-C-MWCNT cells with anodes composed of about 80% core-shell Si-C composite (36% Si in the anode) ran for more than 1000 cycles with a degradation rate of 0.07%/cycle (beginning from cycle 25). The SiNi/MWCNT composite anode revealed a remarkably higher capacity-retention rate at initial cycles and higher C-rate capability. Li/SiNi/MWCNT cells ran for about 250 cycles demonstrating a reversible capacity of about 620 mAh/gSi at 120 μA/cm2 and cycle 210, and 800 mAh/gSi at 50 μA/cm2 at cycle 240.

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Given that lithium-ion batteries will be the preferred choice for EVs and plug-in applications for the next 10–15 years, the focus of research is on improving their safety and performance. New, high-capacity materials are required in order to address the need for greater energy density, longer cycle life and safer high-power operation. Silicon offers the highest gravimetric and volumetric capacity as an anode material (e.g. Li22Si5 with nearly 4,200 mAh/g, 9,800 mAh/ml). 1 The lithium-rich silicon compounds have high melting points. Their higher working potentials (vs. Li) eliminate the possibility of metallic-lithium deposition due to overcharge. Silicon is the second-most abundant element in the earth’s crust, and it is environmentally benign.

Unfortunately, silicon-based electrodes typically suffer from poor capacity retention. The capacity fade and large initial irreversible capacity of silicon anodes are caused by the extreme volume changes in silicon during lithiation/de-lithiation. The silicon is the second-most abundant element in the earth’s crust, and it is environmentally benign.

The lithiation-induced stress cracking was followed by electrode–electrolyte reaction kinetics because the pathways of lithium-ion diffusion are shorter than those of large particles. Depending on the method of preparation, significant improvement in performance and cycle life can be achieved. 7 For example, double-walled Si-C nanotubes and yolk—shell Si-C nanoparticles have been proposed as the most successful designs for diminishing the negative effects of silicon expansion/contraction on charge/discharge. 3,5 However, the synthesis of nanomaterials and nanowires in particular, typically requires complex methods and expensive instruments, like CVD and plasma spray PVD. For example, in Ref. 6, silicon-nickel-alloy and graphite composites were synthesized by arc-melting followed by high-energy mechanical milling. The reversible capacity of 780 mAh/g at 50 cycles was achieved for a silicon-nickel alloy-graphite composite (6:4 by weight ratio). Son et al. 7 synthesized the ternary silicon alloy by melt-spinning to embed silicon nanoparticles in a matrix of Ti3Ni5Si2. A lithium/silicon composite cell provided about 800 mAh/g at the 50th discharge-charge cycle.

Our strategy for reducing the deterioration of silicon involves attaching composite silicon and silicon-nickel nanoparticles to multi-wall carbon nanotubes (MWCNT) in order to create a silicon-based active anode material supported by a strong, rigid and high-electrically-conducting network. The method is based on the pyrolysis of the mixture of nanoparticles and nanotubes with carbon precursor. Alloying of silicon is achieved by electrowless coating of the nanoparticles by the monolayer of metal followed by pyrolysis. Nickel has been chosen since, when alloyed with silicon, this metal is expected to stabilize the structure of lithiated silicon nanoparticles, increase electron conductivity and possibly induce graphitization of the carbon shell. In the ideal case, we aim at the formation of silicon nanoparticles encapsulated in either hard or soft carbon shells and tailored to MWCNT. The current research is focused on the tuning of the structure-composition relationship of silicon-based active anode materials for better electrochemical performance in EC:DEC and Pyr14LiTFSI-based ionic-liquid (IL) electrolytes for lithium-ion-battery applications.

Experimental

Silicon powders were prepared under different conditions of pyrolysis, including flow rate of argon-hydrogen mixture, dwell time and grinding conditions. Prolonged grinding of the pyrolyzed Si/MWCNT

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MWCNTs are described elsewhere.8 1.2 g (30% w/w) SBR or SCR sucrose (SCR) in water. The details of the activation process of the butadiene rubber (SBR) precursor was dissolved in toluene and the was mixed for 2 hours. In the next step, NH4OH was added to the HCl. Then, 1 g of silicon nanoparticles was added and the solution under an argon/hydrogen mixture (96%/4%) at 1000 ◦C for 30 minutes. The solvents were then evaporated at 100 ◦C and this was followed by additional mechanical stirring of the suspensions and stirred by a high-power ultrasonic homogenizer for 30 minutes and this was followed by additional mechanical stirring to form homogeneous suspensions. Following this, 2.4 g (60% w/w) silicon nanoparticles (30–100 nm, Umicore, Belgium) was added to the suspensions and stirred by a high-power ultrasonic homogenizer for 30 minutes. The solvents were then evaporated at 100 ◦C in order to obtain a solid blend. The blends were subjected to pyrolysis for an hour under an argon/hydrogen mixture (96%/4%) at 1000 ◦C in a carbolite TZF 12/65/550 oven. The heating rate was 5.5 ◦C/min and the gas flow rate was 50 cm3/min. The products obtained were ground by mortar and pestle into smaller particles and labeled as Si/MWCNT/SBR and Si/MWCNT/SCR for styrene butadiene rubber and sucrose (SCR) respectively. In order to synthesize a nanostructured multiphase Si/MWCNT active powder, the process of electrosless coating of the silicon nanoparticles by a nickel monolayer was carried out before pyrolysis. 0.6 g of NiCl2·6H2O was dissolved in 300 ml of 0.3 M HCl. Then, 1 g of silicon nanoparticles was added and the solution was mixed for 2 hours. In the next step, NH4OH was added to the solution in order to reach a pH of 11. Then, a solution of 0.4 g NaBH4 reducing agent in 10 ml of water was added and the solution was stirred for 2 hours.

The final SiNi powder was obtained after the solution was filtered (Whatman No. 42 filter paper) and rinsed with DI water in order to remove residual chloride. The SiNi powder was pyrolyzed together with MWCNT and SCR as described above, to produce multiphase alloyed active powder, labeled SiNi/MWCNT/SCR.

The morphology of the powders was measured with an FEI Quanta 200 FEG Environmental Scanning Electron Microscope (ESEM-EDS) system. The ultrahigh-resolution analytical JEM-2100F, a Field Emission Gun Transmission Electron Microscope (TEM) coupled with Electron-Energy-Loss Spectroscopy (EELS) was used to provide atomic imaging and microstructure analysis of material samples. X-ray-photoelectron-spectroscopy (XPS) measurements were performed under ultra-high vacuum (2.5 × 10−10 Torr base pressure) with the use of a 5600 Multi-Technique System (Physical Electronics Inc., USA). Depth profiles were obtained by argon-ion sputtering, at a sputtering rate of 0.5 nm/min, on the basis of an SiO2/Si reference. X-ray diffraction (XRD) data were obtained with the use of an X-ray diffractometer equipped with a 1D LynxEye detector.

For the electrochemistry tests, the electrodes were prepared as follows: 0.02–0.04 g of (6–10% w/w) sodium carboxymethyl cellulose (NaCMC) binder was dissolved in 2.5 ml deionized water for 30 minutes. After solution was complete, 0.1 L–0.2 L of TRX was added and this was mixed for 10 minutes. 0.09 g of (20% w/w) Shawinigan Black (SB) carbon was added and the slurry was mixed. Finally, 0.32–0.4 g (70–80% w/w) active powder was added and the electrode slurries were thoroughly mixed for 24 hours. The slurry was spread on 20 μm copper foil (Schenk, Germany) by a doctor-blade technique and was heated under vacuum at 100 ◦C for 2–3 hours. The coin-type 2032 cells were assembled, with Li-foil (Rockwood Lithium) as the counter electrode, a composite silicon anode and LiPF6 EC:DEC or LiTFSI- Pyr14TFSI electrolytes. Table I presents the list of the tested cells, with different values of silicon content in the anode, mass loading, ink composition and electrolyte. Galvanostatic cycling was performed with a BioLogic VMP3 system or a Maccor series 2000 battery-test system or Arbin cycler (at 0.05 – 0.4 mA). The galvanostatic voltage cutoffs were 0.03 and 1 V vs Li/Li+.

### Results and Discussion

In order to simulate the pyrolysis process, TGA tests of SCR, SBR, MWCNT and their mixtures with Si and SiNi were undertaken. By the TGA-IR tests (not shown here) it was found that in argon flow, the SBR burns completely and generates gases of ethane, methane, propylene and CO2. Theoretically, the pyrolysis of 100 g of sucrose should produce 42 g of carbon. However it was found that only half of the pristine SCR is converted to carbon. Both Si and MWCNT catalyze the formation of carbon from SCR. Nanoparticles of SiNi alloy catalyze this process even more with a carbon yield three times that of the pyrolysis of pristine sucrose (Fig. 1a). However, when the pyrolyzed composite powders were tested by TGA under a flow of dry air (Fig. 1b), it appeared that the weight loss related to the burning of MWCNT and carbon is lower than calculated. This observation may serve as indirect evidence of the formation of highly thermally stable carbon-containing compounds, like silicon carbide, which are not decomposed at 750 ◦C. Instead of this, a gradual increase in weight is observed at about 800 ◦C, and this is assigned to the oxidation of bare silicon and silicon-nickel alloy.

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**Table I. Cell characteristics: Cell label, active powder, anode loading, silicon percent in the anode, electrolyte and ink formulation.**

| Cell Label | Active powder | Mass loading [mg/cm²] | Si content in the anode [%] | Electrolyte | Ink formulation | Remark |
|------------|---------------|-----------------------|----------------------------|-------------|----------------|--------|
| Si/MWCNT/SBR | Si/MWCNT/SBR | 0.7 | 56 | EC:DEC,2%VC +15%FEC (Solway) | 1 M LiPF6 | 70% powder 10% NaCMC 20% SB | Cycling under capacity limited mode |
| Si/MWCNT/SCR1 | Si/MWCNT/SCR | 0.35 | 36 | EC:DEC,2%VC 1 M LiPF6 | 80% powder 10% NaCMC 10% SB | |
| Si/MWCNT/SCR2 | -/- | 1.4 | 42 | -/- | 70% powder 10% NaCMC 20% SB | |
| Si/MWCNT/SCR3 | -/- | 1.1 | 42 | EC:DEC,2%VC +15%FEC | 1 M LiPF6 | 74% powder 6% NaCMC 20% SB | |
| Si/MWCNT/SCR4 | -/- | 1.5 | 42 | PYR14 TFSI/0.3 MLiTFSI | -/- | |
| SiNi/MWCNT/SCR1 | SiNi/MWCNT/SCR | 1.0 | 33 | EC:DEC,2%VC +3%FEC | 1 M LiPF6 | -/- | |
| SiNi/MWCNT/SCR2 | -/- | 1.0 | 33 | PYR14 TFSI/0.3 MLiTFSI | -/- | |

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Figure 1. (a) TGA runs in dry N2 of SCR (dash black) Si/SCR (solid black) and SiNi/SCR (solid gray); (b) TGA runs in air of pyrolyzed Si/MWCNT/SCR (black) and SiNi/MWCNT/SCR (gray).

Figure 2 shows ESEM images of pristine Si, Si/MWCNT/C and SiNi/MWCNT/C nanopowders after pyrolysis. The nanotubes are uniformly distributed between the nanoparticles. The irregular appearance of the surface of the crystalline silicon nanoparticles suggests that they are covered by an amorphous shell.

TEM with analysis by EELS was applied in order to assess the composition of single nanoparticles. From TEM images of Si/MWCNT/SCR (Fig. 3a, 3b) and Si/MWCNT/SBR (Fig. 3c, 3d) it is seen that silicon nanoparticles are wrapped by, or attached to the carbon nanotubes. The enlarged TEM view of a single nanoparticle supports our suggestion that crystalline Si particles are covered by a layer of amorphous carbon, the thickness of which varies from 5 to more than 20 nm. The bi-layer structure shell on top of silicon, seen in TEM micrographs, is composed of SiO2 and carbon. When the SBR is used as a precursor, the bi-layer coating is more conformal than in the case of SCR and the carbon layer is thinner. This is confirmed by EELS maps and histograms (Fig. 4).

Synthesis of SiNi alloy nanoparticles grafted to MWCNT has been carried out with the aim of stabilization of the structure of the silicon active-anode material, inducing graphitization of the carbon shell and increasing the electron conductivity. EELS elemental mapping for nickel (Fig. 5d) shows that nickel diffuses into the bulk of silicon and forms either nickel-rich or nickel-depleted composite entities. The line scan of nickel acquired across the single nickel-rich particles goes through a maximum in the bulk (right bottom), while for the nickel-depleted particles the intensity of the nickel signal is lower than that of silicon (left bottom). The silicon-nickel nanoparticles were found to be covered by a 15–25 nm-thick silicon oxide layer. Contrary to our expectations, nickel does not facilitate graphitization of the carbon shell forming silicon carbide after pyrolysis.

Figure 3. TEM images of Si/MWCNT/SCR (a,b) and Si/MWCNT/SBR (c,d) composite powders.

Figure 2. (a,b,c) ESEM images of pristine Si nanoparticles, Si/MWCNT/SCR and SiNi/MWCNT/SCR, respectively.
Figure 4. Silicon, oxygen and carbon elemental EELS mapping for Si/MWCNT/SCR (top images), Si/MWCNT/SBR (bottom images); histograms of silicon, oxygen and carbon for Si/MWCNT/SBR powders. The lighter is the EELS map – the higher is the concentration of the element.

Figure 5. EELS elemental mapping for silicon, carbon, oxygen and nickel for SiNi/MWCNT/SCR; Bottom) histograms of SiNi/MWCNT/SCR for (left) nickel-depleted particle and (right) nickel-rich particle. The lighter is the EELS map – the higher is the concentration of the element.
Figure 6. (a) X-ray diffraction patterns of a Si/MWCNT/SCR before pyrolysis (black), Si/MWCNT/SCR after pyrolysis (green), MWCNT (blue) and sucrose after pyrolysis (red). (b) SiNi/MWCNT/SCR after pyrolysis (blue), SiNi/MWCNT/SCR after pyrolysis and after 200 cycles (red).

Figure 7. (a) High-resolution C1s surface XPS spectra of Si/MWCNT/SCR powder before (solid line) and after pyrolysis (dash line). (b) High-resolution C1s bulk XPS spectra of Si/MWCNT/SCR powder. (c) Si2p surface XPS spectra of Si/MWCNT/SBR powder after pyrolysis. (d) Si2p bulk XPS spectra of Si/MWCNT/SBR powder after pyrolysis.
Table II. Surface and bulk composition of Si/MWCNT/SBR, Si/MWCNT/SCR and SiNi/MWCNT/SCR powders, determined by XPS measurement.

| Active powder/component | Si* | Si-O | Si-C |
|-------------------------|-----|------|------|
| Si/MWCNT/SBR 0 min sputtering (surface) | 31.41 | 68.59 | - |
| Si/MWCNT/SBR 10 min sputtering (bulk) | 68.35 | 31.64 | - |
| Si/MWCNT/SCR 0 min sputtering (surface) | 4.35 | 92.18 | 3.47 |
| Si/MWCNT/SCR 20 min sputtering (bulk) | 24.52 | 54.81 | 20.66 |
| NiSi/MWCNT/SCR 0 min sputtering (surface) | - | 100 | - |
| NiSi/MWCNT/SCR 10 min sputtering (bulk) | (Si and Si-Ni) 28.14 | 65.16 | 6.70 |

The Ni2p spectrum (not shown here) of the SiNi/MWCNT composite, is the strong overlapped band of nickel silicide (NiSi and Ni2Si) compounds at 853.0 and 853.5 eV, respectively. In addition to the signals of silicon, nickel silicide and silicon carbide, the presence of boron in the synthesized powder has been detected by TOFSIMS tests (the spectra are not shown here). Boron may appear as an inclusion in the nickel deposit when sodium borohydride is used as a reducing agent.

Electrochemical characterization of the cells containing MWCNT-supported Si and SiNi anodes was carried out in the typical coin-cell setup with LiPF6 EC:DEC and LiTFSI-Pyr14 electrolytes. Ionic-liquid-based electrolytes were chosen for the electrochemical tests, since they are safer, have greater thermal stability, a wider potential window, and lower vapor pressure than the typical electrolytes of carbonate-based lithium-ion batteries.

We have found that the Li/Si cells containing an anode of just-mixed silicon nanoparticles and MWCNT show very poor electrochemical performance with the dramatic capacity fade over 20 cycles. Pyrolysis of the mixed active-anode-material components improves the cycleability of the cells. Figure 8a shows the charge (deintercalation) and discharge (intercalation) capacity curves of the Si/MWCNT/SCR composite anode in LiPF6 EC:DEC electrolyte at current densities of from 0.02 to 0.08 mA/cm2. The anode composed of 80% core-shell silicon-carbon composite (36% Si in the anode) exhibits a deintercalation capacity of 1717 mAh/gSi after 123 cycles and 624 mAh/gSi after 900 cycles. The increase of capacity detected over the first 20 cycles may be caused by partial utilization of the active material.11 The faradaic efficiency (FE) increases with cycling up to 99.5% at the 40th cycle. The cell tested in the capacity-limited mode of 1000 mA/gSi shows stable electrochemical behavior for 140 cycles (Fig. 8b). However, the gradual increase in cell...
impedance under these operating conditions shortens the life of the cell.

It is well known that the most severe structural changes in electrode materials followed by a strong capacity drop occur in the initial charge/discharge cycles of silicon anodes. Figure 8c shows comparative longeviy plots of lithium cells containing Si/MWCNT/SBR, Si/MWCNT/SCR and SiNi/MWCNT/SCR anodes. Intercalation and deintercalation capacities of the Si/MWCNT/SCR anode over the first cycle were 3285 and 2160 mA/g, and 34% irreversible capacity. Capacity retention after 50 cycles, at a rate of 0.04 mA/cm², was only 25%. First intercalation and deintercalation capacities of the Si/MWCNT/SCR anode were 3567 and 2314 mA/g, respectively, with 35% irreversible capacity. The capacity retention after 50 cycles was higher (40%) at the same current density. As can be seen from the plots, while the SiNi alloy composite anode exhibits lower capacity than do Si-based anodes, it shows an exceptionally high capacity-retention rate (no capacity loss was detected after 50 cycles). After 200 cycles, the capacity of the cell with an alloyed anode was 809 mA/g, almost twice that of the Si/MWCNT/SCR anode. After 200 cycles, the capacity of the cell with an alloyed anode was 809 mA/g, almost twice that of the Si/MWCNT/SCR anode.

In most of the experiments carried out by our group and in several publications, it was found that the electrochemical performance of silicon-based anodes is much poorer in IL electrolytes. However, this was not observed on cycling of the cells with SiNi/MWCNT/SCR composite (Fig. 9). The electrochemical tests of the anodes conducted in LiTFSI-Pyr14 electrolytes show that, as with the EC:DEC electrolyte, the alloyed SiNi/MWCNT/SCR composite anode exhibits lower capacity (1600 mA/hg) than does the Si/MWCNT/SCR anode during the first 20 cycles (see Fig. 9a), but an exceptionally high capacity-retention rate (0.5%/cycle vs. 3%/cycle capacity loss of Si-C/MWCNT). The lower values of reversible capacity can be ascribed to the reduced amount of neat-silicon nanoparticles as a result of the formation of inactive SiC phase and active Ni2Si phase with lower theoretical capacity (562 mA/hg). The irreversible capacity is about 1200 mA/hg for both anodes. On prolonged 100% DOD cycling, the capacity loss of the alloyed anode decreases from 0.5 to 0.27%/cycle. Increase of the current density by a factor of 5 (for example, at cycle 86, Figure 9b) is followed by a decrease in capacity of about 32% only, which indicates high-power capability of the anodes. The faradic efficiency of the cells with composite SiNi anodes is close to 99.5%. One-minute-long pulse-polarization tests of fully lithiated SiNi/MWCNT/SCR composite anode in IL electrolyte (not shown here), confirm that at C/2-rate the delithiation overvoltage is one third that of bare Si/MWCNT of the same capacity. Whilst the Si/MWCNT/SCR anodes could not withstand the 2C pulse rate, the cells with SiNi/MWCNT/SCR anodes delivered 44 mA/hg for the one-minute-long test. The Li/SiNi/MWCNT/SCR cells with LiTFSI-Pyr14 electrolyte displayed stable cycleability for about 200 cycles.

Figure 10 shows normalized dQ/dV plots for Si/MWCNT/SBR, Si/MWCNT/SCR and SiNi/MWCNT/SCR anodes for the 10th, 20th, 31st, 41st and 51st cycles. It is well established that on the first lithiation, crystalline silicon becomes amorphous at about 90 mV (completely or partially, depending on the current density and voltage range). During delithiation, on the second and subsequent cycles at 100% DOD, typically two dQ/dV peaks are observed. The dQ/dV peak at about 450 mV corresponds to the transformation of the lithium-rich c-Li3.75Si phase and partially delithiated/more disordered (defective) c-Li3.75Si crystalline phase, to amorphous lithium silicide (a-Li1.1Si). The dQ/dV peak at about 270 mV is assigned to the delithiation of a-Li1.1Si. Two lithiation peaks, at about 100 and 250 mV, clearly visualized in the dQ/dV plots on cycling, are ascribed to the lithiation of large clusters of silicon, and to the conversion of amorphous lithium silicide to crystalline phases such as L13-Si, assisted by the formation of small clusters of silicon. These clusters may act as nuclei for the transformation of c-Li3.75Si/c-Li1.1Si into a-Li1.1Si on further cycling. The different overpotentials associated with the amorphous–crystalline lithium silicide conversions on discharge and charge are ascribed to the hysteresis of the charge/discharge reaction paths, caused by different kinetics. Ogata et al. found that it is much easier to add additional Li to c-Li3.75Si/c-Li1.1Si than to remove Li from the structure. The defective structure formed on adding 1 Li atom to a supercell formed with two Li3Si unit cells, that is, L10Si57Si, has a lower formation energy than the structure formed by removal of Li, L10Si52Si. The differential-capacity plots (Fig. 10) show, that for the Si/MWCNT/SCR anode (Fig. 10a), the contribution of the 270 mV peak increases at the expense of the 450 mV peak. This is accompanied by the similar lithiation tendency with increased charge/discharge overpotential. For the SiNi/MWCNT/SCR anode the relative intensities of the dQ/dV delithiation/lithiation peaks remained almost the same on prolonged cycling, which results in the enhancement of the cycling stability of the silicon-nickel alloy anode.

In agreement with the literature, the XRD analysis of an SiNi/MWCNT/SCR cell disassembled after 200 cycles (see Fig. 6b), shows that the Bragg lines of crystalline silicon disappear, but it is still possible to distinguish the XRD lines associated with crystalline nickel silicide and MWCNT. On the basis of the above, we believe that silicon nanoparticles, enriched by nickel silicide and attached to MWCNT, produce a synergetic effect, which results in increased electronic conductivity, stable structure and electrochemical behavior of the silicon-nickel-based composite anode. The effect of p-doping by boron seems to be positive as well, since poorer electrochemical characteristics were measured when the Ni-P electroless coating leading to n-doping of silicon nanoparticles was applied.
rubber (SBR) or sucrose (SCR). SiNi-MWCNT powder was synthesized by an electroless method and then pyrolyzed under the same conditions, in order to improve the electronic conductivity of the anode. We have found that SCR shows promise as a carbon precursor in the pyrolysis of multiphase silicon nanoparticles with MWCNT. ESEM, TEM, EELS and XPS tests indicated the formation of silicon nanoparticles wrapped by MWCNT and coated by amorphous carbon when pyrolyzed with the SCR precursor. For the SiNi/MWCNT/SCR composite, it was found that nickel completely diffuses into the bulk of silicon and forms either nickel-rich or nickel-depleted composite entities. The anode composed of 80% Si/MWCNT/SCR (36% Si in the anode) exhibits deintercalation capacities of 1717 mAh/gSi at cycle 123 and 624 mAh/gSi after 900 cycles. The SiNi/MWCNT/SCR composite anode displays a remarkably higher capacity-retention rate (0.27%/cycle) and high C-rate capability, as compared to silicon-based active anode material. Similar electrochemical performance of the alloyed composite anode in LiPF6 EC:DEC:VC:FEC and LiTFSI-Pyr14 ionic-liquid electrolytes shows promise for application in high-energy, safe, Li-ion batteries.

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References

1. T. D. Hatchard and J. R. Dahn, J. Electrochem. Soc., 151(6), A838 (2004).
2. F. Tariq, V. Yufti, D. S. Eastwood, Yu Merla, M. Biton, B. Wu, Z. Chen, K. Freedman, G. Offer, E. Peled, P. D. Lee, D. Golodnitsky, and N. Brandon, Electrochem. Lett., 3(7), A76 (2014).
3. M. L. Terranova, S. Orlanducci, E. Tamburri, V. Guglielmiotti, and M. Rossi, J. of Power Sources, 246, 167 (2014).
4. H. Wu, G. Chan, J. W. Choi, I. Ryu, Y. Yao, M. T. McDowell, S. W. Lee, A. Jackson, Y. Yang, L. Hu, and Y. Cui, Nat. Nanotechnol., 7, 310 (2012).
5. N. Liu, H. Wu, M. T. McDowell, Y. Yao, C. Wang, and Y. Cui, Nano Lett., 12(6), 3315 (2012).
6. M. S. Park, Y. J. Lee, S. Rajendran, M. S. Song, H. S. Kim, and J. Y. Lee, Electrochim. Acta, 50, 5561 (2005).
7. S. B. Son, S. C. Kim, C. S. Kang, T. A. Versak, Y. C. Kim, C. G. Lee, S. H. Moon, J. S. Cho, J. T. Moon, K. H. Oh, and S. H. Lee, Adv. Energy Mater., 2, 1226 (2012).
8. S. Menkin, Z. Barkay, D. Golodnitsky, and E. Peled, J. Power Sources, 245, 345 (2014).
9. M. S. Wang, L. Z. Fan, M. Huang, and X. Xu, J. Power Sources, 219, 29 (2012).
10. M. Klasson, A. Berndtsson, J. Hedman, R. Nilsson, R. Nyholm, and C. Nordling, J. Electron Spectroscopy. Relat. Phenom., 3, 427 (1974).
11. M. Si, Z. Wang, H. Gao, X. Li, S. Huang, and L. Gan, Adv. Power Technology, 24, 921 (2013).
12. C. Erk, T. Brezesinski, H. Sommer, R. Schneider, and J. Janek, ACS Appl. Mater. Interfaces, 5, 7299 (2013).
13. J. E. Trevey, K. W. Rason, C. R. Stoldt, and S. H. Lee, Electrochem. Solid State Lett., 13(11), A154 (2010).
14. H. Kim and J. Cho, Nano Lett., 8(11), 3688 (2008).
15. X. H. Liu, L. Q. Zhang, L. Zhong, Y. Liu, H. Zheng, J. W. Wang, J. H. Cho, S. A. Deyeh, S. T. Pirzrau, J. P. Sullivan, S. X. Mao, Z. Z. Ye, and J. Y. Huang, Nano Lett., 11, 2251 (2011).
16. A. Magasinski, P. Dixon, B. Hertzberg, A. Kvit, J. Ayala, and G. Yushin, Nat. Mater., 9, 353 (2010).
17. H. Jung, Y. U. Kim, M. S. Song, Y. Hwa, G. Jeong, B. G. Kim, and H. J. Sohn, J. Mater. Chem., 21, 11213 (2011).
18. H. T. Nguyen, F. Yao, M. R. Zamfir, C. Biswas, K. P. So, Y. H. Lee, M. S. Kim, S. N. Cha, J. M. Kim, and D. Pribat, Adv. Energy Mater., 1, 1154 (2011).
19. B. S. Lee, S. B. Son, K. M. Park, W. R. Yu, K. H. Oh, and S. H. Lee, J. Power Sources, 199, 53 (2012).
20. M. T. McDowell, S. W. Lee, W. D. Nix, and Y. Cui, Adv. Mater., 25, 4966 (2013).
21. K. Kierzek, J. Machnikowski, and F. Beguin, J. Appl. Electrochem., 45, 1 (2015).
22. B. Liang, Y. Liu, and Y. Xu, J. Power Sources, 267, 469 (2014).
23. J. W. Song, C. C. Nguyen, and S. W. Song, RSC Adv., 2, 2003 (2012).
24. J. N. Lund, J. H. Lee, E. Efthastious, P. Haldar, and R. E. Geer, J. Power Sources, 246, 177 (2014).
25. K. Ogata, E. Salager, C. J. -Kerr, A. E. Fraser, C. Ducati, A. J. Morris, S. Hofmann, and C. P. Grey, Nat. Commun., 5, 3217 (2014).

Conclusions

The novelty of the research resides in the creation of core/shell silicon and silicon alloy/carbon hetero structures by combining electrochemical synthesis with pyrolysis. Encapsulation of silicon nanoparticles by hard carbon attached to MWCNTs has been achieved by the pyrolysis of styrene-butadiene rubber (SBR) or sucrose (SCR).