Carbon nanotubes (CNTs) with a 1D host lattice have received much attention as a Li insertion host material in higher energy density Li-ion rechargeable batteries. It is well reported that the reversible Li storage capacity (C_{rev}) of two types of CNTs, multi-wall carbon nanotubes (MWN Ts) and single-wall carbon nanotubes (SWNTs) is greatly enhanced by various processing methods such as thermal and chemical treatments. However, the large irreversible capacity (C_{irr}) and the large hysteresis of CNTs was a limiting factor as the Li insertion host material. It is also well known that Si can alloy with Li up to 4.4 Li per Si at high temperature, which is equal to a Li storage capacity of 4000 mAh/g. But the reversibility of normal Si powder at room temperature is poor.

The CNTs and silicon composites were produced using the purified CNTs and silicon powder with maximum particle size of 45 μm by the high energy ball-milling process with different weight ratios. The C_{rev} of the ball-milled CNTs/Si composites for 60 min increased to 1770 mAh/g for the ball-milled MWN Ts/Si_{0.5} composites and 1845 mAh/g for the ball-milled SWNTs/Si_{0.5} composites. In contrast, the C_{irr} of the ball-milled CNTs/Si composites for 60 min decreased to 469 mAh/g for the ball-milled MWN Ts/Si_{0.5} composites and 474 mAh/g for the ball-milled SWNTs/Si_{0.5} composites. The change of C_{rev} and C_{irr} in the ball-milled CNTs/Si composites resulted in the increase of the coulombic efficiency from 50 % for the ball-milled CNTs to 80 %. The charge/discharge curves of the ball-milled CNTs/Si composites presented a different curve shape from those for the ball-milled CNTs and Si powder, demonstrating that the small voltage hysteresis and the large voltage plateau were observed in the charge/discharge curves for the ball-milled CNTs/Si composites.

Most of Li ions were inserted into the ball-milled CNTs/Si composites by alloying with Si particles and extracted from the ball-milled CNTs/Si composites by dealloying with Si particles well covered by CNTs which offered electron conductivity to the alloying and dealloying process of Li ions with Si particles. The CNTs around Si particles in the ball-milled CNTs/Si composites prevented Si particles from electrical insulating by crumbling of Si particles, and more soft CNTs absorbed a volume expansion of LiSi compound formed during the charge/discharge process.

The ball-milling process contributed to decrease in the particle size of CNTs and Si particles, and increase in the electrical contact between CNTs and Si particles in the CNTs/Si composites. These factors enhanced a cycle capacity for the ball-milled CNTs/Si composites during the charge/discharge process.