Carbon-Coated $Li_4Ti_5O_{12}$ as Anode Material for Sodium-Ion Batteries

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The surface-coating of carbon was performed on the spinel $Li_4Ti_5O_{12}$ materials for the electrochemical sodium insertion in sodium ion battery application. The carbon-coated $Li_4Ti_5O_{12}$ was synthesized by using the citric acid sol–gel method. Carbon-coated $Li_4Ti_5O_{12}$ exhibits superior cycle performance as well as the rate capability in comparison to the pristine $Li_4Ti_5O_{12}$. Electrochemical impedance spectroscopy analyses also reveal that surface modification with carbon suppresses the increase in resistance concerning charge transfer reaction as well as solid electrolyte interface layer formation during cycle test.

Keywords: Lithium Titanate, Anode Material, Carbon Coating, Electrochemical Performance, Sodium-Ion Battery.

1. INTRODUCTION

Lithium ion batteries have been widely investigated for EVs and electric grid storage.[1,2] At the present time, owing to the exhaustion of lithium resource in the earth, the price of the lithium raw materials has been increased. Sodium, one of the alkali metals, is a promising alternative for large-scale storage batteries due to its abundant resources, low cost and similar charge–discharge mechanism with lithium.[3–5] For these reasons, the study and technology of sodium ion battery have been recently focused. The cathode materials of the sodium ion battery have been largely proposed, but only a very few anode materials of that have been introduced.[6,7] Among various carbonaceous materials, hard carbon demonstrates better suitability in sodium ion battery.[8,9]

Spinel-structured $Li_4Ti_5O_{12}$ is well known as a very promising anode material in lithium secondary batteries owing to the low cost, easy synthesis and the absence of solid electrolyte interphase (SEI) film.[10–22] Na-storage behavior in spinel lithium titanate has been recently introduced for sodium ion battery applications by Hu et al.[23] Average voltage for sodium reaction is about 0.9 V, and a reversible capacity around 145 mAh/g is achieved. Also,

Hu et al. proposed that the three-phase reaction has been found in the sodiation of $Li_4Ti_5O_{12}$ electrodes by using the density functional theory calculations for Li and Na ion batteries.[24] Generally, spinel $Li_4Ti_5O_{12}$ anode materials exhibit low electrical conductivity, which results in poor cyclability and rate capability of electrodes because of Ti^{4+} with electron configuration of $[Ar]3d^0$. In this study, we focus on surface modification of $Li_4Ti_5O_{12}$ materials with carbon coating technique to enhance the electrical conductivity and understand the important factors in sodium ion battery application.

2. EXPERIMENTAL DETAILS

For the parent cathode materials, $Li_4Ti_5O_{12}$ particles with an average size of 70 nm were obtained from the Sigma-Aldrich. Carbon-coated $Li_4Ti_5O_{12}$ powders were synthesized by using the citric acid ($C_6H_8O_7$) sol–gel method introduced by Yang et al.[25] The $Li_4Ti_5O_{12}$ in ethanol was stirred at room temperature to disperse the materials. Then the ethanol solution of the citric acid (citric acid to titanium molar ratio as 1:6) was added to $Li_4Ti_5O_{12}$ solution under continuous stirring. The mixture of the $Li_4Ti_5O_{12}$ and citric acid solution was stirred at room temperature for 1 day to form a white gel. The result products were aged in

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air for several hours and dried at 80 °C for about 12 hours. The powders were sintered at 800 °C for 15 hours in Ar atmosphere to gain the carbon-coated Li$_4$Ti$_5$O$_{12}$.

The carbon content was determined by elemental analysis using an organic elemental analyzer (Thermo Scientific company-Flash 2000). The structure of samples was characterized by X-ray powder diffraction (XRD, Rigaku X-ray diffractometer) using monochromatic Cu Kα (40 kV and 100 mA) between 10° and 80°. The unit-cell parameters were obtained with a least squares refinement to the diffraction peaks. To verify the effective surface-modification with carbon material, samples were examined by high-resolution transmission electron microscopy (HR-TEM, FEI company-TecnaiG2) and energy dispersive spectrometer analysis (EDS).

The electrochemical performances of the samples were evaluated with the CR2032 coin cell. The counter electrode was sodium metal and the electrolyte was 1 M NaClO$_4$ in ethylene carbonate, diethyl carbonate and propylene carbonate (1:1:1 in volume ratio). The glass fiber filter was employed as separator. Li$_4$Ti$_5$O$_{12}$ electrodes were fabricated by a slurry with a mixture of 87.5 wt% of Li$_4$Ti$_5$O$_{12}$ active material, 7.5 wt% of denka black and 5 wt% polyvinylidene fluoride (PVdF) in a solvent N-methyl-2-pyrrolidone (NMP) on an aluminum current collector. The galvanostatic measurements such as charge–discharge, rate capability and cyclability test were examined by using the battery test equipment (Maccor). The AC impedance measurements of the cells were carried out in the frequency range of 10^6 Hz to 10^{-3} Hz by a VSP-300, and the fittings of the data were carried out by Zview program.

3. RESULTS AND DISCUSSION

To confirm the effectiveness of sol–gel method for carbon coating using citric acid and determine the accurate carbon contents, the elemental analysis was performed. The carbon contents of the pristine and carbon-coated Li$_4$Ti$_5$O$_{12}$ powders were, respectively, 0.1 wt% and 1.1 wt%, as expected. Figure 1 exhibits the XRD patterns of the pristine and carbon-coated Li$_4$Ti$_5$O$_{12}$ powders after the heat treatment at 800 °C in Ar atmosphere. All the peaks of both samples can be indexed as cubic spinel structure with Fd$\bar{3}$m space group without any noticeable impurity-related peaks. Also, there is no significant difference between the pristine and carbon-coated Li$_4$Ti$_5$O$_{12}$, and the lattice parameter values obtained from the least square method are 8.365(4) Å and 8.351(6) Å, respectively, for the pristine and carbon-coated anodes, as demonstrated in Table I. This result confirms that the carbon-coating using citric acid does not affect the spinel structure of Li$_4$Ti$_5$O$_{12}$ during the heat treatment at argon atmosphere.

Figure 2 indicates the TEM images of the pristine Li$_4$Ti$_5$O$_{12}$ powders and carbon-coated Li$_4$Ti$_5$O$_{12}$ powders. The pristine Li$_4$Ti$_5$O$_{12}$ powders around 50–80 nm show well-defined edges in Figures 2(a) and (b) as well as

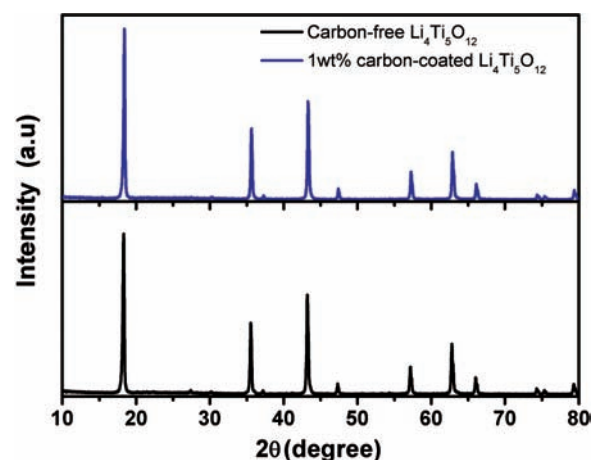**Figure 1.** X-ray diffraction patterns of pristine Li$_4$Ti$_5$O$_{12}$ and carbon-coated Li$_4$Ti$_5$O$_{12}$ powders.

smooth and crystalline planes from the view of the fringe patterns. The surface coating with carbon is confirmed, indicating that the porous and non-crystalline coating layer based on weak fringe patterns is formed on the crystalline Li$_4$Ti$_5$O$_{12}$ particle with a thickness of about 5–15 nm, as demonstrated in Figures 2(d) and (e). The EDS data in Figure 2(f) also certifies that the surface modification with carbon is successfully achieved whereas bare Li$_4$Ti$_5$O$_{12}$ exhibits the prominent peaks of oxygen and titanium in Figure 2(c).

Figure 3 presents the voltage profile and dQ/dV plot of the pristine Li$_4$Ti$_5$O$_{12}$ and carbon-coated Li$_4$Ti$_5$O$_{12}$ at first cycle and second cycle. The pristine Li$_4$Ti$_5$O$_{12}$ exhibits the electrochemical performance with a desodiated capacity around 104.4 mAh/g and coulombic efficiency of 79.3% in Figure 3(a) while the carbon-coated Li$_4$Ti$_5$O$_{12}$ exhibits a desodiated capacity of 107.1 mAh/g and coulombic efficiency of 71.1%. The low coulombic efficiency of Li$_4$Ti$_5$O$_{12}$ based electrodes for sodium insertion/deinsertion could be attributed to the formation of a SEI layer on the surface of Li$_4$Ti$_5$O$_{12}$, which explains the prominent irreversible capacity at first cycle for the both electrodes. Additionally, carbon-coated electrode shows larger irreversible capacity at first cycle compared to the pristine Li$_4$Ti$_5$O$_{12}$ electrode. As shown in Figure 3(a), voltage plateau around 1.4 V with the capacity values of 20 mAh/g is responsible for the increased irreversible capacity of carbon-modified electrode, which is possibly due to sodium insertion into the amorphous carbon. Although the surface modification with carbon

Table I. Comparison of the lattice parameters for the pristine and carbon-coated Li$_4$Ti$_5$O$_{12}$ powders.

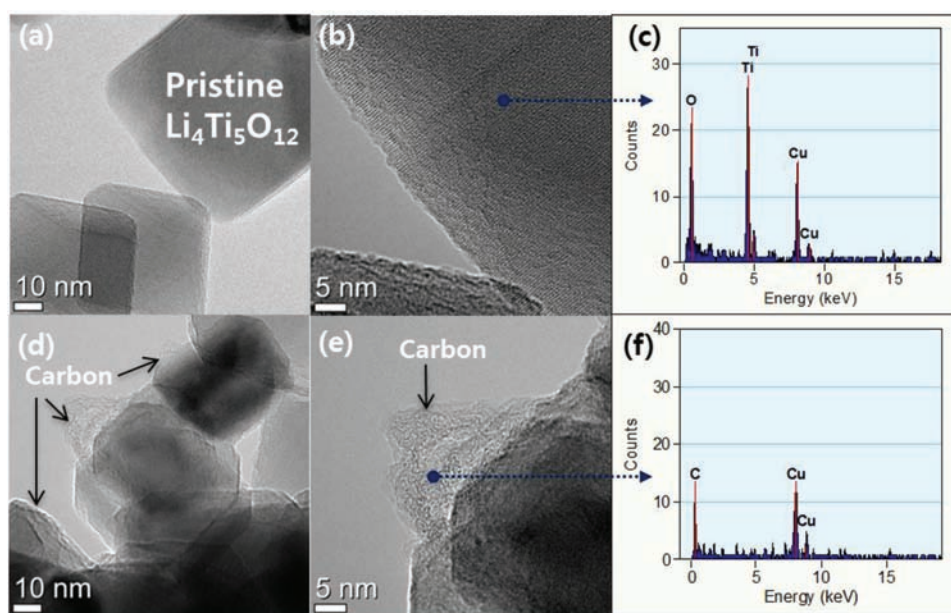| Sample	Lattice parameter (Å)
Pristine Li$_4$Ti$_5$O$_{12}$	8.365(4)
Carbon-coated Li$_4$Ti$_5$O$_{12}$	8.351(6)

Figure 2. HR-TEM images of (a), (b) pristine and (d), (e) carbon-coated $Li_4Ti_5O_{12}$ synthesized by using the citric acid sol–gel method. EDS results of spot in (c) pristine and (f) carbon-coated $Li_4Ti_5O_{12}$.
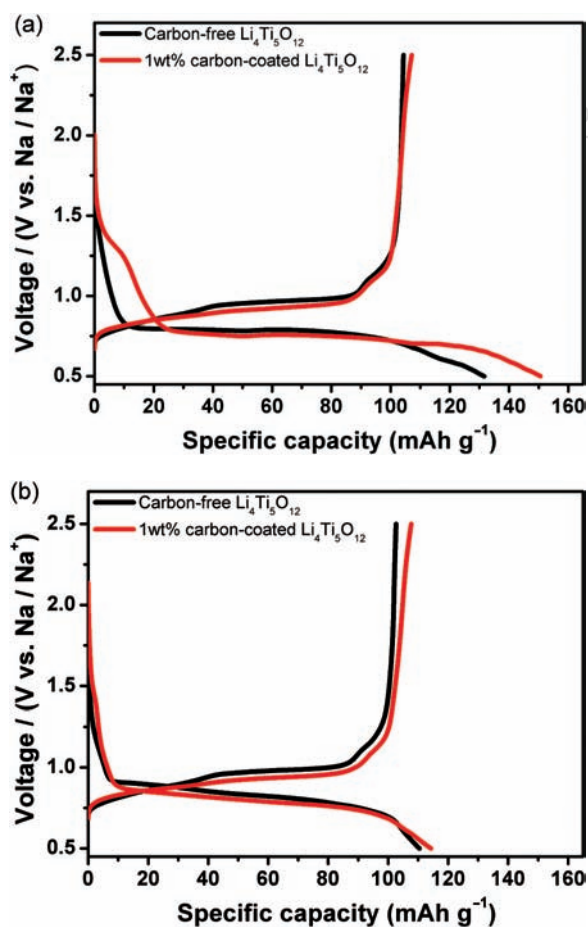

Figure 3. Comparison of the initial charge/discharge curves at (a) first cycle and (b) second cycle.

layer increases the irreversible capacity of electrode, carbon coating suppresses the overvoltage during the charge process, which corresponds to the amount around 40 mV, as demonstrated in Figures 3(a) and (b). The suppressed polarization during sodium deinsertion can be found for further cycles, implying that the carbon coating influences the cycle performances of $Li_4Ti_5O_{12}$ electrode.

The effect of carbon-coating on the cycle performances between 0.5 and 2.5 V at 0.05 C-rate for 50 cycles is demonstrated in Figure 4. Although the both samples suffer from capacity fading during 50 cycles, carbon-modified electrode maintains better electrochemical performance compared to the pristine $Li_4Ti_5O_{12}$ electrode. As presented in Figure 4, the carbon-coated $Li_4Ti_5O_{12}$ electrode exhibits the capacity retention of 75.9% whereas the bare electrode

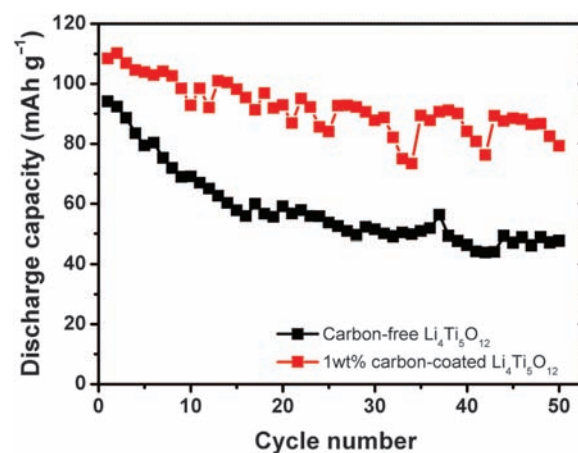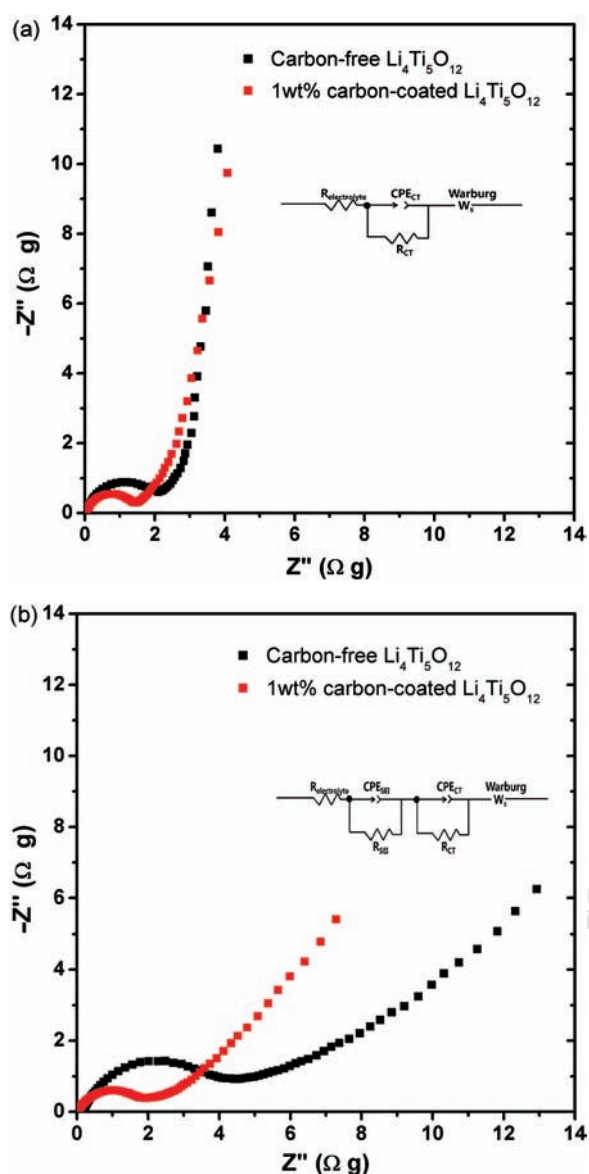**Figure 4.** Cyclic performances of the pristine and carbon-coated $Li_4Ti_5O_{12}$ electrode.

Figure 5. AC impedance plots of the pristine and carbon-coated $Li_4Ti_5O_{12}$ electrode (a) before and (b) after 50 cycles.

Figure 6. Desodiation voltage profiles illustrating the rate capabilities of (a) the pristine and (b) the carbon-coated $Li_4Ti_5O_{12}$.

retains 51.6% of initial capacity retention after 50 cycles at room temperature.

In order to elucidate the influence of surface modification on the electrochemical performances of electrode for sodium intercalation/deintercalation, electrochemical impedance spectroscopy (EIS) measurements before cycle and after 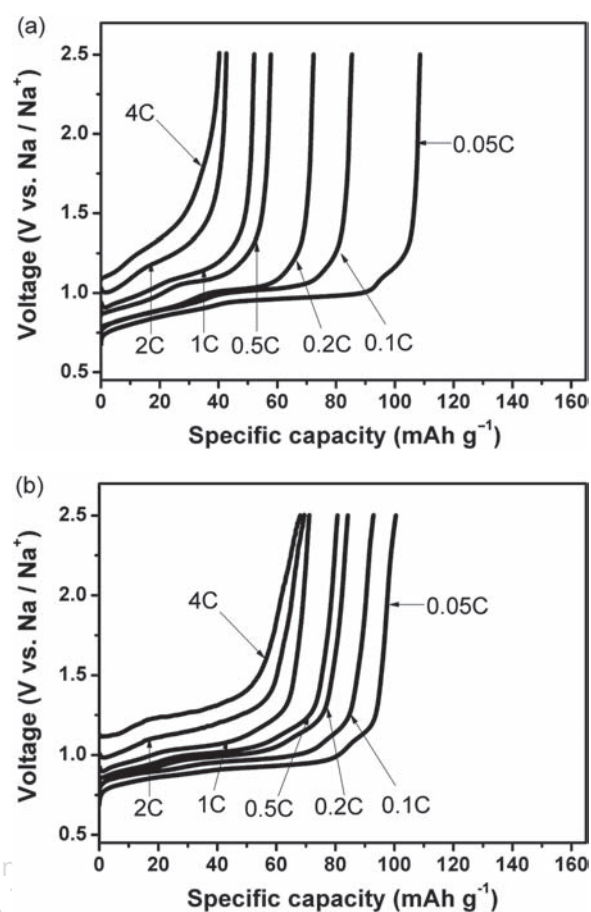50th cycle, respectively, for the pristine and carbon-coated $Li_4Ti_5O_{12}$ electrodes were performed and shown in Figure 5. The equivalent circuits to fit the data are also demonstrated, and the fitting results are shown in Table II. Generally, each of the spectra evaluated in EIS analysis consists of a semicircle in high frequency region and a linear line in low frequency region. The semicircle of the high frequency region corresponds to the charge reaction resistance (R_{CT}) and the diffusion resistance (R_{SEI}) of the surface layer including SEI layer while the linear line in the very low frequency region represents the diffusion of the sodium ions into the bulk of the anode material, which is called Warburg diffusion. The fitting results presented in Table II indicate that the surface-modified $Li_4Ti_5O_{12}$ electrode reduces the impedance values of R_{CT} and R_{SEI} before cycle and suppresses the increase of impedance after 50 cycles.

Table II. Measured EIS data of the pristine and carbon-coated $Li_4Ti_5O_{12}$ electrodes before and after 50 cycles.

	Before cycle		After 50 cycle		
	$R_{electrolyte}$ (Ωg)	R_{CT} (Ωg)	$R_{electrolyte}$ (Ωg)	R_{SEI} (Ωg)	R_{CT} (Ωg)
Pristine $Li_4Ti_5O_{12}$	0.05	2.45	0.17	1.83	2.83
Carbon-coated $Li_4Ti_5O_{12}$	0.02	1.50	0.03	0.73	1.55

Figure 6 compares the rate capability of the pristine and carbon-coated $Li_4Ti_5O_{12}$ electrodes evaluated at various C-rates from 0.05 C to 4 C-rate between 0.5 and 2.5 V. The cells were sodiated at a fixed current density of 0.05 C-rate before each desodiation test. The desodiation capacities of the pristine electrode in Figure 5(a) are rapidly decreased ongoing from low to high C-rate whereas the carbon-coated $Li_4Ti_5O_{12}$ in Figure 5(b) exhibits better electrochemical performances in rate characteristics. For example, the capacity retention of the pristine and surface-modified $Li_4Ti_5O_{12}$ is 37.1% and 67.2%, respectively, at 4 C-rate compared to 0.05 C-rate, implying that the carbon modification enhances the electrical conductivity of $Li_4Ti_5O_{12}$ anode electrodes.

4. CONCLUSION

Surface modification of $Li_4Ti_5O_{12}$ powders with carbon was prepared by employing a sol–gel method with citric acid. The charge curves in galvanostatic measurements reveal that the carbon coating suppresses the overvoltage during insertion of sodium and enhances the cyclability of electrode. The lower impedance characteristics and superior rate capability are also obtained via surface modification with carbon layer on the $Li_4Ti_5O_{12}$ anode materials, suggesting that the carbon coating improves electric conductivity of electrode in sodium ion battery applications.

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