Effect of surface fluorination and conductive additives on the electrochemical behavior of lithium titanate (Li$_{4/3}$Ti$_{5/3}$O$_4$) for lithium ion battery

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ABSTRACT

Effect of surface fluorination and conductive additives on the charge/discharge behavior of lithium titanate (Li$_{4/3}$Ti$_{5/3}$O$_4$) has been investigated using F$_2$ gas and vapor grown carbon fiber (VGCF). Surface fluorination of Li$_{4/3}$Ti$_{5/3}$O$_4$ was made using F$_2$ gas (3×10^4 Pa) at 25–150 °C for 2 min. Charge capacities of Li$_{4/3}$Ti$_{5/3}$O$_4$ samples fluorinated at 70 °C and 100 °C were larger than those for original sample at high current densities of 300 and 600 mA/g. Optimum fluorination temperatures of Li$_{4/3}$Ti$_{5/3}$O$_4$ were 70 °C and 100 °C. Fibrous VGCF with a large surface area (17.7 m^2/g) increased the utilization of available capacity of Li$_{4/3}$Ti$_{5/3}$O$_4$ probably because it provided the better electrical contact than acetylene black (AB) between Li$_{4/3}$Ti$_{5/3}$O$_4$ particles and nickel current collector.

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1. Introduction

Lithium ion batteries have been mainly used as electric sources for electronic devices such as computers, mobile phones, watches and so on. However, recent interest for lithium ion batteries is the application to electric sources for hybrid cars and electric vehicles. For this purpose, new electrode materials showing high rate charge/discharge are urgently requested. It was reported that electrochemical intercalation and deintercalation of lithium is quite reversible in lithium titanate (Li$_{4/3}$Ti$_{5/3}$O$_4$ + Li$^+$ + e$^-$ ↔ Li$_{7/3}$Ti$_{5/3}$O$_4$) though the electrode potential is ca. 1.5 V relative to Li/Li$^+$ higher than that of lithium-intercalated graphite [1]. It is recently known that Li$_{4/3}$Ti$_{5/3}$O$_4$ is a new candidate as anode with high rate charge/discharge. Many attempts for preparing Li$_{4/3}$Ti$_{5/3}$O$_4$ showing excellent charge/discharge properties have been reported [2–26]. Nano-sized Li$_{4/3}$Ti$_{5/3}$O$_4$ powders with large surface areas were synthesized and characterized [2–10]. They showed high capacities and good cycleability even at high current densities. Preparation of fine Li$_{4/3}$Ti$_{5/3}$O$_4$ particles with large surface area is important because Li$_{4/3}$Ti$_{5/3}$O$_4$ is an electric insulator. High density spherical Li$_{4/3}$Ti$_{5/3}$O$_4$ powders were synthesized, showing high reversible capacities and good cycleability [11,12]. Syntheses of porous Li$_{4/3}$Ti$_{5/3}$O$_4$ [13], Li$_{4/3}$Ti$_{5/3}$O$_4$ nanotube/nanowire [14], Li$_{4/3}$Ti$_{5/3}$O$_4$ with hollow-sphere structure [15] and flower-like

Li$_{4/3}$Ti$_{5/3}$O$_4$ [16] showing good electrochemical characteristics were also reported. Synthesis using microwave yielded Li$_{4/3}$Ti$_{5/3}$O$_4$ powders with uniform particle size [17]. Composite electrodes were prepared to improve electric contact of insulating Li$_{4/3}$Ti$_{5/3}$O$_4$ particles [18–20]. Titanium nitride coating [18], Li$_{4/3}$Ti$_{5/3}$O$_4$/carbon nanotube composite [19] and Li$_{4/3}$Ti$_{5/3}$O$_4$/polyacene composite [20] well improved the cycle performance of Li$_{4/3}$Ti$_{5/3}$O$_4$ at high current densities. The Li$_{4/3}$Ti$_{5/3}$O$_4$ synthesized via a composite molten salt method showed high capacity and good rate performance [21]. A lithium ion cell composed of Li$_{4/3}$Ti$_{5/3}$O$_4$ and LiVPO$_4$F was also examined, showing good cycling stability [22]. Substitution of a metal such as Mg, Al, Ga or Co for Ti in Li$_{4/3}$Ti$_{5/3}$O$_4$ was reported to be a good method increasing reversible capacity and improving cycling stability [23,24]. Li-doping in Li$_{4/3}$Ti$_{5/3}$O$_4$ increased the capacity and improved cycling performance [25,26]. Thermal properties of Li$_{4/3}$Ti$_{5/3}$O$_4$ were also investigated by calorimetry, which indicated its good thermal stability [27,28]. Safety of Li$_{4/3}$Ti$_{5/3}$O$_4$/LiMn$_2$O$_4$ cell was studied by differential scanning calorimetry (DSC) and accelerated rate calorimetry (ARC). The cell showed no thermal runaway, explosion or fire [29]. Safety performance of Li$_{4/3}$Ti$_{5/3}$O$_4$ and graphite was also compared using ARC [30]. These results show that Li$_{4/3}$Ti$_{5/3}$O$_4$ is an important candidate as anode having good electrode characteristics at high current densities.

Since electrochemical redox reactions usually occur at the surface of a solid electrode, surface area, surface pore size distribution and surface chemical species are important structural factors for influencing electrode characteristics. Surface of oxide

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powder is often hydrated, which may interfere smooth redox reactions. Therefore oxide materials are normally dehydrated before use by pumping at an elevated temperature. It was found that mild fluorination is a quite effective method for drying hydrated materials [31–33]. Graphite oxide containing a large number of carboxyl and hydroxyl groups is well dehydrated by fluorination using F_2 gas at about 100 °C. Another possible surface structure change obtained by surface fluorination is decrease in surface roughness because the possible products such as O_2, OF_2 and TiF_4 may be lost as gases. In the present study, surface fluorination of $Li_{4/3}Ti_{5/3}O_4$ was performed after pumping at 120 °C and its charge/discharge behavior was investigated in organic solvent for lithium ion battery. Since $Li_{4/3}Ti_{5/3}O_4$ is an electric insulator, a conductive additive should be used to keep good electrical contact between $Li_{4/3}Ti_{5/3}O_4$ particles and current collector. Acetylene black (AB) is usually used for such purpose in electrode preparation. In the present study, vapor grown carbon fiber (VGCF) with fibrous structure (Fig. 1) was examined to improve the electrical contact between $Li_{4/3}Ti_{5/3}O_4$ and nickel current collector. Thus the present paper deals with the effect of surface fluorination and conductive additives on the charge/discharge properties of $Li_{4/3}Ti_{5/3}O_4$ by using F_2 gas and VGCF.

2. Results and discussion

2.1. Surface structure and composition of fluorinated $Li_{4/3}Ti_{5/3}O_4$ samples

Surface fluorination of $Li_{4/3}Ti_{5/3}O_4$ powder was conducted using low pressure F_2 (3×10^4 Pa) at 25–150 °C for a short time, 2 min. Fig. 2 shows X-ray diffraction patterns of original and surface-fluorinated $Li_{4/3}Ti_{5/3}O_4$ samples. The samples fluorinated between 25 °C and 100 °C exhibited the same diffraction peaks as those for original $Li_{4/3}Ti_{5/3}O_4$ though the peak intensity slightly weakened with increasing fluorination temperature, which suggests the slight increase in the disorder of $Li_{4/3}Ti_{5/3}O_4$ lattice in surface region. On the other hand, the sample fluorinated at 150 °C gave other weak peaks indicating Li_2TiF_6, anatase TiO_2, rutile TiO_2, LiF and $TiOF_2$ as shown in Fig. 2. Formation of these compounds in surface region may increase the surface resistance, interfering the electrochemical redox reactions. The optimum fluorination temperature would be below ca. 100 °C. BET surface areas and meso-pore volumes of $Li_{4/3}Ti_{5/3}O_4$ samples are given in Table 1, in which average data are listed for fluorinated samples because the data were
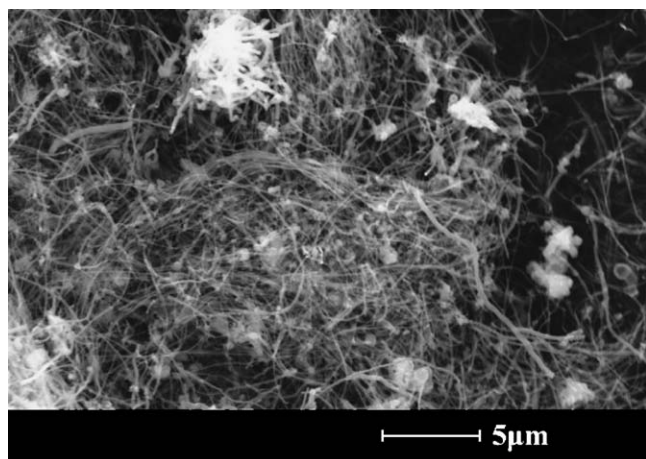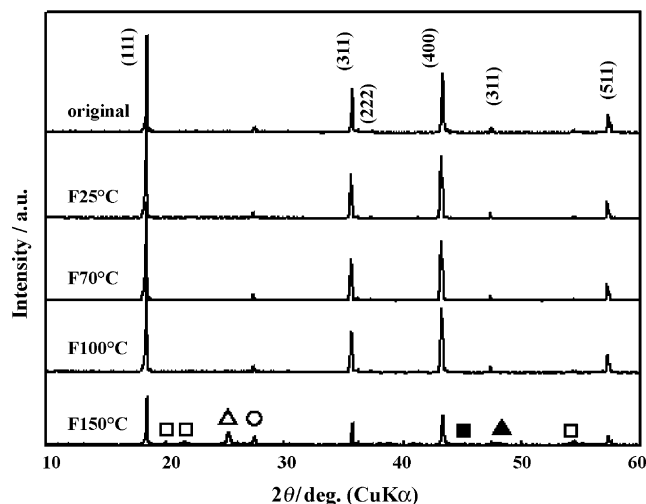

Fig. 2. X-ray diffraction patterns of original and surface-fluorinated $Li_{4/3}Ti_{5/3}O_4$ samples. original: non-fluorinated $Li_{4/3}Ti_{5/3}O_4$; F25, F70, F100 and F150: $Li_{4/3}Ti_{5/3}O_4$ samples fluorinated at 25 °C, 70 °C, 100 °C and 150 °C, respectively; (□) Li_2TiF_6, (△) anatase TiO_2, (○) rutile TiO_2, (■) LiF, (▲) $TiOF_2$.

scattered within ± 0.3 m^2/g. The surface area was slightly decreased with increasing fluorination temperature from 25 °C to 150 °C. The meso-pore volume had the same trend with temperature. The slight decrease in the surface area by the fluorination at 70–150 °C suggests the decrease in surface roughness probably by the loss of gaseous products, TiF_4 and oxygen species such as O_2 and OF_2. Fig. 3 and Table 2 show XPS spectra and surface composition calculated from peak areas of XPS spectra, respectively. Binding energies were shifted to the larger values by the fluorination. Particularly the peak shift was the largest for $Li_{4/3}Ti_{5/3}O_4$ fluorinated at 150 °C. Peak intensity for Li1s and F1s electrons increased with increasing fluorination temperature while that for Ti2p and O1s electrons decreased. Table 2 clearly shows the same trend in surface composition with fluorination temperature. Surface concentrations of Li and F increased with increasing temperature. However, those for Ti and O were significantly reduced. The result suggests that LiF film was formed at the surface of $Li_{4/3}Ti_{5/3}O_4$ and trace amounts of gaseous products such as O_2, OF_2 and TiF_4 were lost.

2.2. Electrochemical properties of surface-fluorinated $Li_{4/3}Ti_{5/3}O_4$ samples

The $Li_{4/3}Ti_{5/3}O_4$ is expected as a new anode material for lithium ion battery since its electrode potential is low, i.e. ca. 1.5 V vs Li/Li$^+$. However, $Li_{4/3}Ti_{5/3}O_4$ electrode is cathode in the electrochemical cell used in the present study because the potential of Li counter electrode is lower than that of $Li_{4/3}Ti_{5/3}O_4$, i.e. 0 V. Therefore Li release from $Li_{7/3}Ti_{5/3}O_4$ ($Li_{7/3}Ti_{5/3}O_4 \rightarrow Li_{4/3}Ti_{5/3}O_4 + Li^+ + e^-$) is charge reaction, which corresponds to discharge reaction in a usual lithium ion battery with transition metal oxide

Fig. 1. SEM image of VGCF heat-treated at 2800 °C.

Table 1
Surface areas and meso-pore volumes of original and surface-fluorinated $Li_{4/3}Ti_{5/3}O_4$ samples.

Fluorination temperature (°C)	Surface area (m^2/g)	Meso-pore volume (cm^3/g)
Original	2.8	0.0052
25	3.1	0.0068
70	2.7	0.0045
100	2.7	0.0049
150	2.1	0.0035
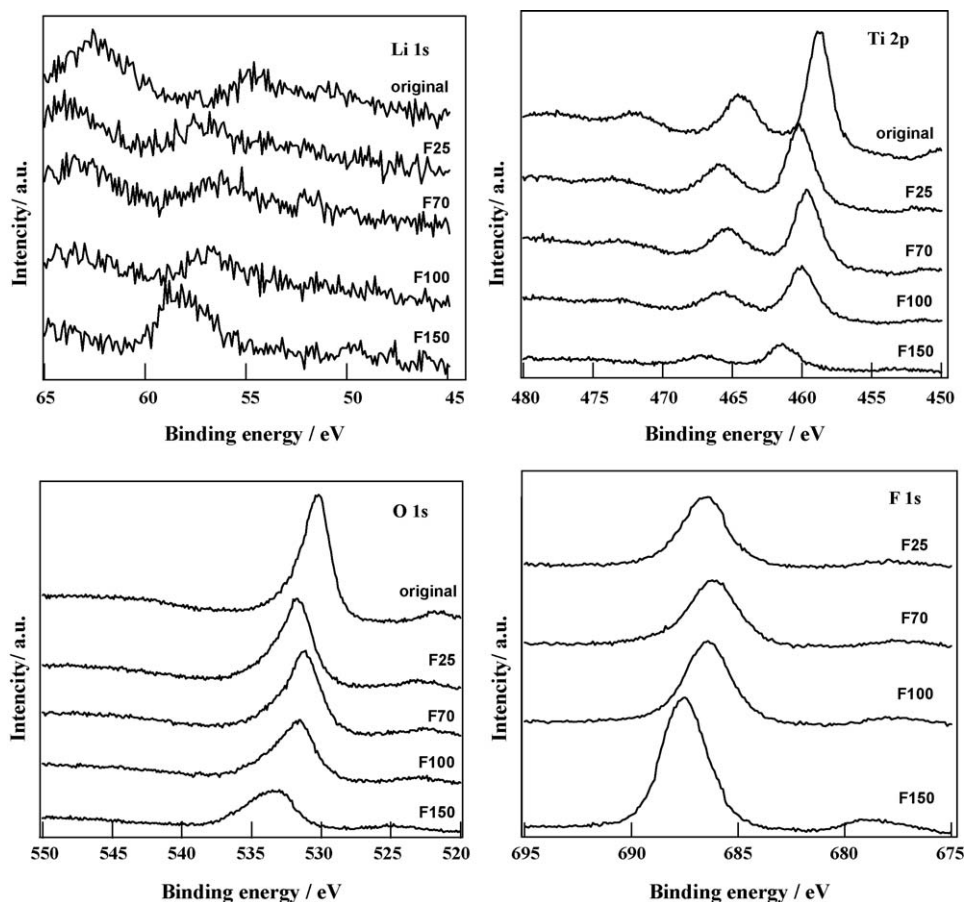
Fig. 3. XPS spectra of original and surface-fluorinated $Li_{4/3}Ti_{5/3}O_4$ samples. original: non-fluorinated $Li_{4/3}Ti_{5/3}O_4$; F25, F70, F100 and F150: $Li_{4/3}Ti_{5/3}O_4$ samples fluorinated at 25 °C, 70 °C, 100 °C and 150 °C, respectively.

cathode having a potential of about 4 V vs Li/Li$^+$. Effect of conductive additives and mixing ratios among $Li_{4/3}Ti_{5/3}O_4$, conductive additive and PVdF on first charge capacities is given in Table 3, in which the charge capacity increased with increasing

Table 2
Surface composition of original and surface-fluorinated $Li_{4/3}Ti_{5/3}O_4$ samples, obtained from XPS spectra.

Fluorination temperature (°C)	Li	Ti	O	F (at%)
Original	24.7	16.2	59.1	–
25	24.6	10.1	37.2	28.1
70	26.8	9.3	35.2	28.7
100	36.9	6.0	25.7	31.4
150	48.6	2.2	13.9	35.3

Table 3
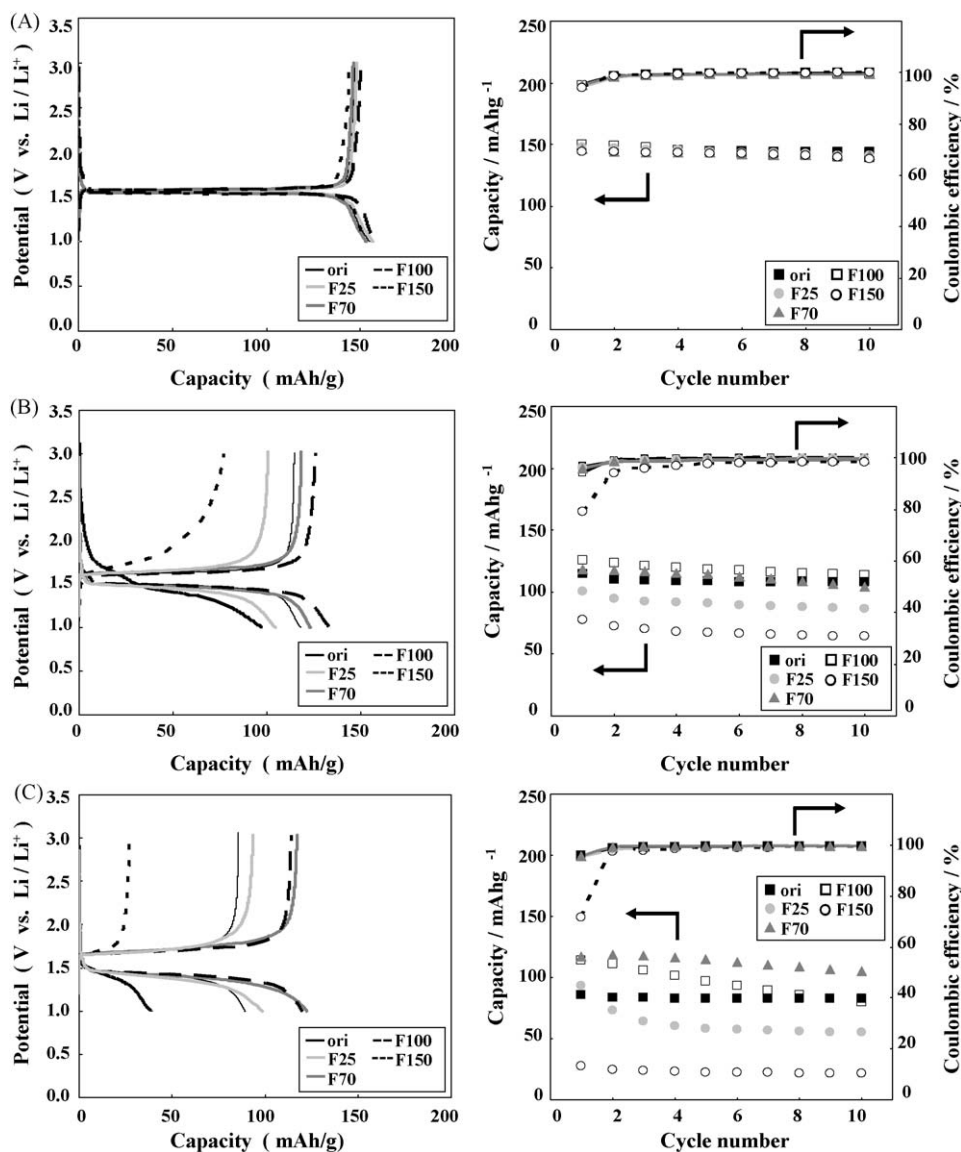First charge capacities for $Li_{4/3}Ti_{5/3}O_4$ in different mixing ratios with conductive additives (CA) and PVdF, obtained at 60, 300 and 600 mA/g in 1 mol/ℓ LiClO$_4$ – EC/DEC.

Conductive additive (CA)	Mixing ratio (wt.) $Li_{4/3}Ti_{5/3}O_4$: CA:PVdF	First charge capacity (mAh/g)		
		60 mA/g	300 mA/g	600 mA/g
	6:1:2	142	110	75
AB	6:2:2	147	115	86
	6:3:2	148	120	90
	6:0.5:2	143	111	89
VGCF	6:1:2	149	113	93
	6:2:2	150	119	93

First charge capacity: first discharge capacity in a lithium ion cell with transition metal oxide cathode.

conductive additive at three current densities. In the same mixing ratios, first charge capacities were higher in VGCF-mixed electrodes than in AB-mixed ones, which may be because VGCF consisting of thin fibers with diameters of 40–100 nm gives better electrical contact between $Li_{4/3}Ti_{5/3}O_4$ particles and nickel current collector, increasing the utilization of available capacity of $Li_{4/3}Ti_{5/3}O_4$. Lithium intercalation into graphite occurs below 1 V vs Li/Li$^+$. Since charge/discharge cycling was made between 1.0 and 3.0 V, lithium intercalation into conductive additives is negligible. The difference in the charge capacities would therefore be caused by the conductive additives which change the electrical contact between $Li_{4/3}Ti_{5/3}O_4$ and current collector.
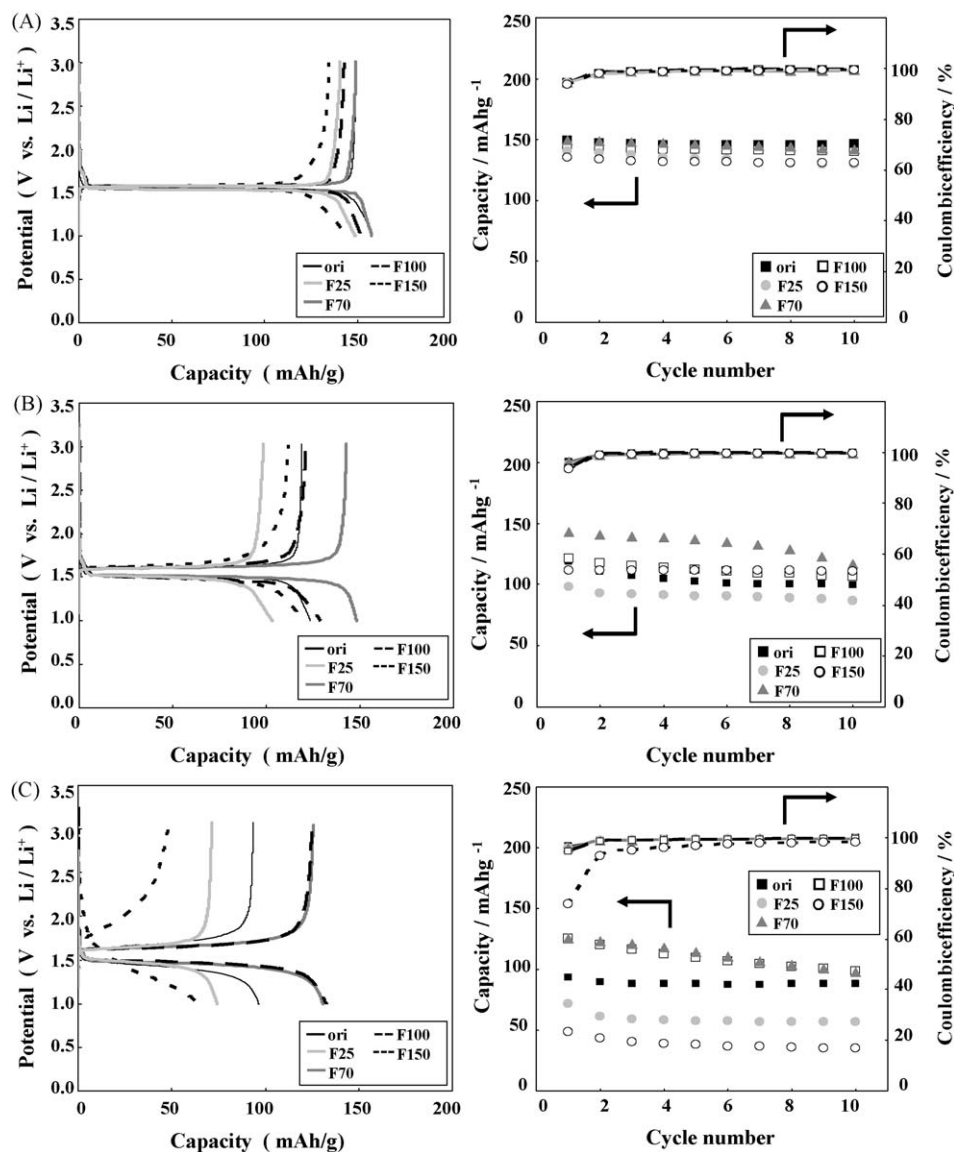
Figs. 4 and 5 show first charge/discharge curves and charge capacities and coulombic efficiencies as a function of cycle number for original and surface-fluorinated $Li_{4/3}Ti_{5/3}O_4$ samples at current densities of 60, 300 and 600 mA/g. The average data are shown in Figs. 4 and 5 and Tables 3 and 4. The error of charge capacities of $Li_{4/3}Ti_{5/3}O_4$ was 3–4%. There was no large difference in the data obtained at a current density of 60 mA/g, particularly when AB was used as a conductive additive. However, a large difference in the profiles of charge/discharge curves, charge capacities and coulombic efficiencies was found at the higher current densities of 300 and 600 mA/g. The larger capacities than those for non-fluorinated sample were observed for $Li_{4/3}Ti_{5/3}O_4$ samples fluorinated at 70 °C and 100 °C in both conductive additives ((B) and (C) in Figs. 4 and 5). Peak intensity of X-ray diffraction lines was slightly weakened by surface fluorination, which suggests the slight increase in lattice disorder of $Li_{4/3}Ti_{5/3}O_4$ in the surface region. The increase in lattice disorder may facilitate Li diffusion in $Li_{4/3}Ti_{5/3}O_4$,

Fig. 4. First charge/discharge curves and charge capacities and coulombic efficiencies for original and surface-fluorinated $Li_{4/3}Ti_{5/3}O_4$ samples with AB, obtained at (A) 60 mA/g, (B) 300 mA/g and (C) 600 mA/g. ori: original $Li_{4/3}Ti_{5/3}O_4$; F25, F70, F100 and F150: $Li_{4/3}Ti_{5/3}O_4$ samples fluorinated at 25 °C, 70 °C, 100 °C and 150 °C, respectively.

increasing the utilization of available capacity. On the other hand, the low charge/discharge capacities were obtained for $Li_{4/3}Ti_{5/3}O_4$ fluorinated at 150 °C. The phases such as Li_2TiF_6, TiO_2, LiF and $TiOF_2$ detected by X-ray diffraction (Fig. 2) may have formed insulating layers in the surface region. Coulombic efficiencies were high for original and surface-fluorinated samples at three current densities except $Li_{4/3}Ti_{5/3}O_4$ fluorinated at 150 °C. The charge/discharge capacities were stabilized after 10 cycles. Slight decrease in the charge capacities with cycle was observed for the fluorinated samples, enhancing with increasing current density from 60 mA/g to 600 mA/g as shown in Figs. 4 and 5, which may be due to slight decrease in the electrical contact of fluorinated samples with current collector. Table 4 summarizes first charge capacities for original and surface-fluorinated $Li_{4/3}Ti_{5/3}O_4$ samples. The $Li_{4/3}Ti_{5/3}O_4$ sample fluorinated at 25 °C gave nearly the same first charge capacities as those of non-fluorinated sample or slightly smaller values. Hydrolysis of fluorinated surface may have partly occurred by the reaction with moisture. First charge capacities for original and surface-fluorinated $Li_{4/3}Ti_{5/3}O_4$ samples were nearly the

same at a current density of 60 mA/g in both AB-mixed and VGCF-mixed electrodes. However, a large difference in first charge capacities was observed at the higher current densities of 300 and particularly 600 mA/g. First charge capacities of $Li_{4/3}Ti_{5/3}O_4$ samples fluorinated at 70 °C and 100 °C were larger than those for non-fluorinated sample as already seen in Figs. 4 and 5. The increase in first charge capacities for $Li_{4/3}Ti_{5/3}O_4$ samples fluorinated at 70 °C and 100 °C was ~13% at 300 mA/g and 33–36% at 600 mA/g for AB-mixed electrode, and ~20% at 300 mA/g and 34–35% at 600 mA/g for VGCF-mixed electrode. Comparison between two conductive additives indicates that VGCF gave the larger first charge capacities than AB at the higher current densities of 300 and 600 mA/g. The sample fluorinated at 150 °C showed very small first charge capacities at 600 mA/g irrespectively of conductive additives. It was found from these results that the optimum fluorination temperatures of $Li_{4/3}Ti_{5/3}O_4$ were 70 °C and 100 °C. Surface dehydration and slight increase in lattice disorder of $Li_{4/3}Ti_{5/3}O_4$ in surface region may be attained by light fluorination using F_2 gas, improving the charge/discharge behavior of $Li_{4/3}Ti_{5/3}O_4$ electrode.

Fig. 5. First charge/discharge curves and charge capacities and coulombic efficiencies for original and surface-fluorinated $Li_{4/3}Ti_{5/3}O_4$ samples with VGCF, obtained at (A) 60 mA/g, (B) 300 mA/g and (C) 600 mA/g. ori: original $Li_{4/3}Ti_{5/3}O_4$; F25, F70, F100 and F150: $Li_{4/3}Ti_{5/3}O_4$ samples fluorinated at 25 °C, 70 °C, 100 °C and 150 °C, respectively.

Table 4
First charge capacities of original and surface-fluorinated $Li_{4/3}Ti_{5/3}O_4$ samples with (a) AB and (b) VGCF, obtained at 60, 300 and 600 mA/g in 1 mol/ℓ $LiClO_4$ – EC/DEC ($Li_{4/3}Ti_{5/3}O_4$/AB or VGCF/PVdF = 6:2:2 in weight).

Fluorination temperature (°C)	First charge capacity (mAh/g)		
	60 mA/g	300 mA/g	600 mA/g
(a) AB			
Original	147	115	86
25	148	101	94
70	146	118	117
100	150	126	114
150	145	77	28
(b) VGCF			
Original	150	119	93
25	141	98	71
70	149	143	126
100	143	121	125
150	153	112	48

First charge capacity: first discharge capacity in a lithium ion cell with transition metal oxide cathode.

3. Conclusion

Effect of surface fluorination and conductive additives on the charge/discharge behavior of lithium titanate ($Li_{4/3}Ti_{5/3}O_4$) has been investigated using F_2 gas and VGCF. Light fluorination of $Li_{4/3}Ti_{5/3}O_4$ at 70–150 °C slightly decreased the peak intensity of X-ray diffraction lines, which suggests slight increase in the disorder of $Li_{4/3}Ti_{5/3}O_4$ lattice in surface region. BET surface areas and mesopore volumes were reduced with increasing fluorination temperature from 70 °C to 150 °C, which suggests slight decrease in the surface roughness. XPS analysis indicated that concentrations of Li and F increased with increasing fluorination temperature while those for Ti and O were reduced probably because trace amounts of O_2, OF_2 and TiF_4 were gasified. The $Li_{4/3}Ti_{5/3}O_4$ samples fluorinated at 70 °C and 100 °C provided the higher charge capacities than non-fluorinated sample at high current densities of 300 and 600 mA/g while those fluorinated at 25 °C and 150 °C gave the lower capacities than original sample, particularly $Li_{4/3}Ti_{5/3}O_4$ fluorinated at 150 °C showed very low capacities at 600 mA/g. The results indicated that the optimum fluorination temperatures were

70 °C and 100 °C. Since $Li_{4/3}Ti_{5/3}O_4$ is an electric insulator, a conductive additive plays an important role for utilization of available capacity of $Li_{4/3}Ti_{5/3}O_4$. The result showed that VGCF with fibrous structure gave the higher capacities than normally used AB.

4. Experimental

Lithium titanate, $Li_{4/3}Ti_{5/3}O_4$ (purity: >99.98%, average particle size: 4.6 μm) supplied by KCM Corporation was used for the electrochemical measurements. Surface fluorination of $Li_{4/3}Ti_{5/3}O_4$ was performed by F_2 gas (3×10^4 Pa) at 25 °C, 70 °C, 100 °C and 150 °C for 2 min. Surface structure and composition were analysed by X-ray diffractometry (Shimadzu, XRD-610), X-ray photoelectron spectroscopy (XPS) (Kratos, ESCA-3400) and BET surface area measurement using nitrogen gas (Shimadzu, Tristar 3000).

Electrode was prepared as follows. The $Li_{4/3}Ti_{5/3}O_4$ and AB (BET surface area: 63.4 m^2/g) or VGCF heat-treated at 2800 °C (BET surface area: 17.7 m^2/g) were well dispersed in N-methyl-2-pyrrolidone (NMP) containing 12 wt% polyvinylidenefluoride (PVdF). The slurry was pasted on a foamed nickel sheet. The prepared electrode was dried at 120 °C for 12 h in vacuum oven and then pressed before use. The appearance of the electrodes was the same for both AB- and VGCF-mixed ones. The mixing ratios of $Li_{4/3}Ti_{5/3}O_4$/AB or VGCF/PVdF were 6:0.5:2, 6:1:2, 6:2:2 or 6:3:2 in weight. When surface-fluorinated $Li_{4/3}Ti_{5/3}O_4$ samples were examined, the mixing ratio for $Li_{4/3}Ti_{5/3}O_4$/AB or VGCF/PVdF was 6:2:2. A three-electrode cell with $Li_{4/3}Ti_{5/3}O_4$ working electrode and Li counter and reference electrodes was used for galvanostatic charge/discharge experiments. The electrolyte solution was 1 mol/ℓ $LiClO_4$ – ethylene carbonate (EC)/diethyl carbonate (DEC). Charge/discharge cycling was made at 60, 300 and 600 mA/g between 1.0 and 3.0 V vs Li/Li$^+$ in a glove box filled with Ar at 25 °C.

Acknowledgements

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