Spinel LTO (Li4Ti5O12) has an excellent reversibility of Li-ion intercalation/de-intercalation and exhibits zero-strain volume change during cycling with excellent safety performance. Moreover, LTO has a high voltage plateau at 1.55 V vs. Li/Li+, which can avoid the formation of metallic lithium. Therefore, LTO has been investigated to use as the anode material of lithium ion batteries for energy storage, electric vehicles, and hybrid electric vehicles. However, unfortunately LTO has a low electronic conductivity with a low theoretical capacity of 175 mAh g−1. These drawbacks restrict its applications in high-power storage devices. Many efforts have been investigated for improving its low capacity, including composites with metal oxides such as TiO2, SiO2, SnO2, and ZnO. These metal oxides have a high theoretical capacity, however, they have a high irreversible capacity caused by volume expansion and particle aggregation, resulting in poor cycling performance. Among them, Co3O4 has the same spinel crystal structure as LTO and it can accommodate up to 8 Li+ ions per formula unit according to the redox reaction Co3O4 + 8Li+ → 4Li2O + 3Co0. The theoretical capacity of Co3O4 can be calculated as 890 mAh g−1 from this proposed reaction.

In this work, we attempted to overcome the low theoretical capacity of LTO and the poor cycling performance of Co3O4 by synthesizing the LTO/Co3O4 composites. Firstly, pristine LTO was synthesized by a two-step solution-combustion method and then LTO/Co3O4 composites were synthesized by a solution precipitation method.

**Experimental**

**Materials synthesis.**—LTO was synthesized using a solution-combustion reaction. Titanium (IV) isopropoxide [Ti(OCH(CH3)2)4] was slowly dropped into distilled water under 10°C. After white precipitates (Ti(OH)4) were observed, nitric acid was added and the mixture was constantly stirred until the appearance turned to transparent. Then, lithium nitrate was dissolved in distilled water and glycine was added as a fuel. After stirring at 80°C for 5 h to form a viscous gel, the precursor was dropped into an alumina crucible preheated to 500°C. This crucible was placed in a muffle furnace and heated at 750°C for 12 h. LTO/Co3O4 composites were synthesized by using precipitation reaction of Co2+ ion. The as-prepared LTO was uniformly dispersed in distilled water under stirring for 30 min, after that a certain quantity of Co(NO3)6·6H2O was dropped into the solution with mass ratios of 20 and 40, respectively. Then, NH4·H2O was slowly added into the above suspension and stirred for several hours. The precursor powders were filtered and washed three times with distilled water and dried under vacuum at 80°C for 12 h. The dried powders were calcined at 450°C for 1 h to obtain LTO/Co3O4 composites. In addition, Co3O4 was synthesized using the same process without the addition of LTO.

**Characterization.**—The crystalline phases of LTO-pristine, Co3O4, LTO/Co3O4-20, and LTO/Co3O4-40 were identified by powder X-ray diffraction (XRD) using a D/Max 2500-VPC diffractometer (Rigaku, Japan) with Cu Kα radiation (λ = 1.54056 Å) in the 2θ range of 10–90° with a step size of 0.02° sec−1. The morphology of the samples was observed by field emission scanning electron microscope (FE-SEM) using a JSM-6500F (JEOL, Japan) with an accelerating voltage of 10 kV. The Co3O4 amounts in LTO/Co3O4 composites were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a 720-ES (Varian, USA).

In situ X-ray absorption spectroscopy (XAS) measurements were carried out on the BL10C beamline at the Pohang Light Source. To control the X-ray photon energy, a Si (111) double crystal monochromator was used.

**Electrochemical measurement.**—The working electrodes were made by mixing active materials, conducting agent (carbon black), and binder (PVDF) with a weight ratio of 80:10:10. The CR 2032 coin-type cells were assembled in an argon-filled glove-box using lithium metal foil as the counter electrode. 1.0 M LiPF6/EC+DMC (1:2 in volume) electrolyte and Celgard polypropylene separator were used. Cyclic voltammetry was performed using a WBCS3000 battery tester (WonAtech, Korea) with a scan rate of 0.1 mV s−1 in the voltage range of 0.01–3.0 V. Galvanostatic charge-discharge measurements were conducted with current densities ranging from 16 mA g−1 to 1600 mA g−1 at room temperature. The galvanostatic intermittent titration technique (GITT) was conducted using a SP-300 (Biologic, France) with a current density of 10 mA g−1 in the voltage range of 0.01–3.0 V.

**Results and Discussion**

Fig. 1 shows a schematic diagram of the synthesis process of LTO/Co3O4 composite via a precipitation method. After the Co2+ ions adsorbed on LTO, the Co(OH)2 precipitates settled on the surface of LTO when NH4OH solution was added. Finally, the LTO/Co(OH)2 precursor was subsequently converted into the LTO/Co3O4 composite by calcination at 450°C under air atmosphere.

The crystal phase and structural information of the samples have been obtained by XRD. The XRD patterns of LTO, Co3O4, LTO/Co3O4-20, and LTO/Co3O4-40 are presented in Fig. 2a. The
diffraction patterns of LTO and Co$_3$O$_4$ are well-indexed as the cubic spinel structure (JCPDS card No. 49-0207) with a Fd-3m space group and no impurity phase. This confirms the successful synthesis of LTO and Co$_3$O$_4$. All main peaks of the composites are indexed as the mixture of LTO and Co$_3$O$_4$ phase with no impurity phase. The intensity of Co$_3$O$_4$ increases as the Co$_3$O$_4$ content increases.

The average crystalline size of Co$_3$O$_4$ can be calculated by the Debye-Scherrer formula, as follows:

$$D = \frac{k \lambda}{\beta(1/2 \cos \theta)}$$

where $\lambda$ is the wavelength of the X-ray radiation taken 0.15406 nm for Cu K$_\alpha$, $\theta$ is the Bragg angle, $D$ the crystallite size, $k$ the Scherer constant as 0.89, and $\beta$ the full width at half maximum (FWHM) of the diffraction peak (311) measured at 2$\theta$ in radians. The calculated average crystalline size of Co$_3$O$_4$ is 44.6 nm.

Rietveld refinement results using Fullprof program are shown in Fig 2b and Table I, respectively. The obtained cell parameter $a$ for composites are not significantly changed compared to the pristine LTO, indicating that Co$_3$O$_4$ did not affect original structure of LTO during the synthesis process.

ICP-OES results indicate that the Co$_3$O$_4$ content in LTO/Co$_3$O$_4$-20 and LTO/Co$_3$O$_4$-40 are approximately 12.5 and 25.2 wt%, respectively. The calculated weight loss of Co$_3$O$_4$ during synthesis is 37.5 and 37%, respectively. These results may be attributed by the washing process.

Fig. 3 shows the SEM images of the samples. Nano-sized LTO particles have many pores, which are produced by vigorous gas evolution during the combustion reaction. Co$_3$O$_4$ particles are composed of the aggregated primary particles with a particle size ranging from 30 to 100 nm. This result corresponds to the calculated value by the Debye-Scherrer formula. For the LTO/Co$_3$O$_4$-20 composite, LTO particles are covered with the Co$_3$O$_4$ particles. This result means that the precipitation occurred after the Co$^{2+}$ ions reached the surface of LTO. For the LTO/Co$_3$O$_4$-40 composite, slightly aggregated Co$_3$O$_4$ particles cover on the LTO.

Table I. The lattice constants obtained from rietveld results.

| Sample           | Cell parameter $a$ (Å) | $R_p$ (%) | $R_{wp}$ (%) |
|------------------|------------------------|-----------|--------------|
| LTO              | 8.3584(2)              | 9.84      | 11.4         |
| LTO/Co$_3$O$_4$-20| 8.3583(8)              | 12.8      | 14.2         |
| LTO/Co$_3$O$_4$-40| 8.3584(5)              | 11.4      | 13.6         |
Figure 3. SEM images of (a, b) LTO, (c, d) Co$_3$O$_4$, (e, f) LTO/Co$_3$O$_4$-20 and (g, h) LTO/Co$_3$O$_4$-40.

with the first cycle due to the irreversible electrode reaction.\textsuperscript{17} In contrast, the cathodic peak negatively shifts and the anodic peak positively shifts due to the hysteresis.\textsuperscript{18} LTO/Co$_3$O$_4$-20 exhibits two pairs of redox peaks corresponding to the LTO and Co$_3$O$_4$ peaks and the intensity of the LTO peak is greater than that of Co$_3$O$_4$. In the second cycle, the cathodic peak for Co$_3$O$_4$ is increased to 1.31 V, and it leads to decrease the gap between cathodic and anodic peak, indicating that the polarization is reduced. The peak intensity of LTO and Co$_3$O$_4$ is changed, but integral areas are remained during cycling. However, LTO/Co$_3$O$_4$-40 has a higher Co$_3$O$_4$ peak and a lower LTO peak, and the two peaks overlap at around 1.0 V.

The discharge-charge curves of LTO, Co$_3$O$_4$, LTO/Co$_3$O$_4$-20, and LTO/Co$_3$O$_4$-40 at a current density of 10 mA g$^{-1}$ are shown in Fig. 5. The voltage range is expanded from 1.0–2.6 V to 0.01–3.0 V to observe the influence of Co$_3$O$_4$. LTO delivers the initial and second discharge capacity of 281.9 and 243.9 mAh g$^{-1}$, respectively. The irreversible capacity is attributed by the formation of an SEI layer. The voltage profile of LTO has three plateaus at around 1.5, 0.7, and 0.5 V. These plateaus correspond to the intercalation of 3 moles of lithium ions per mole of LTO. Especially, the voltage plateau at 1.5 V is related to the insertion of lithium ion into the octahedral (16c) site according to the general mechanism. At the same time, 3 mol of lithium ions located at the 8a site is transported to the octahedral (16c) site. The SEI layer is formed at around 0.7 V. It has been reported that the extra capacity can be delivered by intercalating another 2 mol of lithium ions into the vacant tetrahedral (8a) sites below 0.6 V. This mechanism is formulated as follows.\textsuperscript{19}

\begin{equation}
\text{Li}_3[\text{LiTi}_5\text{O}_{12}]+6\text{Li}^+\rightarrow 3\text{Li}_2\text{Ti}_6\text{O}_{12}+5\text{e}^-+5\text{Li}^+
\end{equation}

Also, they suggested that the extra capacity caused by the steep voltage region below 0.6 V may negatively affect its practical utilization. LTO/Co$_3$O$_4$-20 and LTO/Co$_3$O$_4$-40 deliver initial discharge...
Discharge and charge curves of (a) LTO, (b) Co$_3$O$_4$ (c) LTO/Co$_3$O$_4$-20 and (d) LTO/Co$_3$O$_4$-40 for the first and second cycles at a current density of 10 mA g$^{-1}$.

The quasi-open circuit voltage (QOCV) curves of the samples obtained by GITT measurement are shown in Fig. 6. The electrochemical cells were charged and discharged at a constant current density of 10 mA g$^{-1}$ for 1 h with a relaxation time of 2 h. As shown, the profiles can be divided into two regions based on the characteristics of the curves. The up and down-side of the colored blocks indicate the charge and discharge processes, respectively. Relatively small polarization is observed in Region I, indicating that Region I is related to the LTO. In contrast, Region II with large polarization is related to the Co$_3$O$_4$. This suggestion is associated with the volume expansion of Co$_3$O$_4$ particles during cycling and they can lead to weakness of electrical contact between Co$_3$O$_4$ and the conducting agent particles. We can suggest that, therefore, the charge-discharge profile of LTO/Co$_3$O$_4$-20 is more affected by LTO than Co$_3$O$_4$. In contrast, the characteristic of LTO/Co$_3$O$_4$-40 is more related to Co$_3$O$_4$.

The cycling performances up to 50 cycles at a current density of 160 mA g$^{-1}$ are shown in the Fig. 7. The discharge capacity of LTO is constantly maintained over 200 mAh g$^{-1}$ with no significant decrease. The initial discharge capacity of Co$_3$O$_4$ is 1000 mAh g$^{-1}$ with rapid decrease during cycling. This capacity fade is mainly attributable to the volume expansion and particle aggregation. LTO/Co$_3$O$_4$-20 delivers an initial discharge capacity of 319.8 mAh g$^{-1}$ with excellent cycling performance. This result may be caused by the synergistic effect of LTO and Co$_3$O$_4$. Meanwhile, LTO/Co$_3$O$_4$-40 shows an initial discharge capacity of 580.4 mAh g$^{-1}$, which is higher than that of LTO/Co$_3$O$_4$-20. However, it has a large irreversible capacity and poor cycling performance, indicating that LTO could not act as a buffer due to the excess Co$_3$O$_4$ particles on the LTO surface.

Fig. 9 indicates the rate capabilities at various current densities ranging from 160 mA g$^{-1}$ to 1600 mA g$^{-1}$. LTO delivers a discharge capacity of 230.9 mAh g$^{-1}$ and 200.4 mAh g$^{-1}$ at a current density of 160 mA g$^{-1}$ and 1600 mA g$^{-1}$, respectively. Co$_3$O$_4$ delivers an initial discharge capacity of 1000 mAh g$^{-1}$ at a current density of 160 mA g$^{-1}$. However, the capacity dramatically decreases to 50 mAh g$^{-1}$ at a current density of 1600 mA g$^{-1}$. LTO/Co$_3$O$_4$-20 delivers a discharge capacity of 307.3 mAh g$^{-1}$, which is slightly higher than that of LTO, at a current density of 160 mA g$^{-1}$ and maintains the capacity as...
Figure 6. QOCV curves of (a) LTO, (b) Co$_3$O$_4$, (c) LTO/Co$_3$O$_4$-20, and (d) LTO/Co$_3$O$_4$-40 electrodes. The solid lines are the GITT results and the dashed lines are the open circuit voltages.

Figure 7. Discharge capacity retention of the (a) LTO, (b) Co$_3$O$_4$, (c) LTO/Co$_3$O$_4$-20, and (d) LTO/Co$_3$O$_4$-40 at a current density of 160 mA g$^{-1}$.

Fig. 10a shows the initial charge-discharge curve of LTO/Co$_3$O$_4$-20 during in-situ XAFS measurement. X-ray absorption near-edge structure (XANES) spectroscopy was conducted at each red point in the voltage range of 0.01–3.0 V. The normalized XANES spectra of Ti K-edge for LTO/Co$_3$O$_4$-20 during the discharge and charge process are presented in Fig. 9b. The K-edge XANES spectra are formed by transitions of the 1s electron at the inner shell to unoccupied states with appropriate symmetry. The weak triplet pre-edge (peak A) at around 4971 eV corresponds to the transition of 1s$\rightarrow$3d unoccupied states, which is the electric dipole-forbidden and quadruple-allowed transition due to the hybridization of 3d and 4p orbitals. The shoulder peaks (peak B) at higher energy represent a shakedown process transition of 1s$\rightarrow$4p caused by ligand-to-metal charge transfer (LMCT). The strongest absorption main edge (peak C) is the pure
dipole-allowed 1s→4p transition without the shakedown process. 21 These pre-edge peaks decrease due to the decrease in distortion of the octahedral during the discharge process. The main Ti K-edge at approximately 4990 eV gradually shifts to the lower energy region during the lithium ion insertion process, indicating that the oxidation state of titanium is reduced. These changes, especially, are most visible at points 3–7 and 16–21. On the other hand, the peaks have no visible change at the points 8–11 and 22–24. These results correspond to Fig. 6, indicating that Ti contributes only to the region of LTO. Therefore, the extended plateau of capacity is introduced by the addition of Co$_3$O$_4$.

Conclusions

We attempted to overcome the low theoretical capacity of LTO and the poor cycling performance of metal oxides by synthesizing LTO/Co$_3$O$_4$ composites. LTO particles can trap Co$_3$O$_4$ particles and they can prevent the volume expansion and particle aggregation of Co$_3$O$_4$. As expected, LTO/Co$_3$O$_4$ composites have higher capacity than that of LTO. QOVC curves show that LTO/Co$_3$O$_4$-20 is more dominated by LTO, whereas LTO/Co$_3$O$_4$-40 has similar characteristics with Co$_3$O$_4$. The XANES results show that the Ti K-edge changes at certain region, which is specified as Region I in GITT results.

Acknowledgments

This work was supported by the Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2009-0093818) and by the Ministry of Knowledge Economy (MKE), Korea Institute for Advancement of Technology (KIAT) through the Inter-ER Cooperation projects.

References

1. E. Ferg, R. J. Gummow, A. d. Kock, and M. M. Thackeray, J. Electrochem. Soc., 141, L147 (1994).
2. T. Ohzuku, A. Ueda, and N. Yamamoto, J. Electrochem. Soc., 142, 1431 (1995).
3. L. Aldén, P. Kubiak, M. Womes, J. C. Jumas, J. Olivier-Fourcade, J. L. Tirado, J. J. Corredor, and C. Perez Vicente, Chem. Mater., 16, 5721 (2004).
4. Y. B. He, B. Li, M. Liu, C. Zhang, W. Lv, C. Yang, J. Li, H. Du, B. Zhang, Q. H. Yang, J. K. Kim, and F. Y. Kang, Sci. Rep., 2, 913 (2012).
5. A. Guerfi, S. Seviüny, M. Lagace, P. Hovington, K. Kinoshita, and K. Zaghib, J. Power Sources, 119, 88 (2003).
6. J. Wang, H. Zhao, Q. Yang, C. Wang, P. Lv, and Q. Xia, J. Power Sources, 222, 196 (2013).
7. S. Jiang, B. Zhao, Y. Chen, R. Cai, and Z. Shao, J. Power Sources, 238, 356 (2013).
8. K. M. Yang, Y. J. Hong, S. H. Choi, B. K. Park, and Y. C. Kang, Int. J. Electrochem. Sci., 8, 1026 (2013).
9. T. Zhou, Y. Lin, G. Zhao, Y. Huang, H. Lai, J. Li, Z. Huang, and S. Wu, Int. J. Electrochem. Sci., 8, 1316 (2013).
10. Z. S. Wu, W. Ren, L. Wen, L. Gao, J. Zhao, Z. Chen, G. Zhou, F. Li, and H. Cheng, ACS Nano, 4, 3187 (2010).
11. B. Guo, C. Li, and Z. Y. Yuan, J. Phys. Chem. C, 114, 12805 (2010).
12. G. Binotto, D. Larcher, A. S. Prakash, R. H. Urbina, M. S. Hedge, and J. M. Tarascon, Chem. mater., 19, 3012 (2007).
13. N. Yan, L. Hu, Y. Li, Y. Wang, H. Zhong, X. Hu, X. Kong, and Q. Chen, J. Phys. Chem. C, 116, 7227 (2012).
14. A. S. Prakash, P. Manikandan, K. Ramesha, M. Sathiya, J-M. Tarascon, and A. K. Shukla, Chem. Mater., 22, 2857 (2010).
15. X. Zheng, C. Dong, B. Huang, and M. Lu, Int. J. Electrochem. Sci., 7, 9869 (2012).
16. X. Yang, K. Fan, Y. Zhu, J. Shen, X. Jiang, P. Zhao, S. Luan, and C. Li, ACS Appl. Mater. Interfaces, 5, 997 (2013).
17. W. Mei, J. Huang, L. Zhu, Z. Ye, Y. Mai, and J. Tu, J. Mater. Chem. B, 22, 9315 (2012).
18. P. Lian, X. Zhu, H. Xiang, Z. Li, W. Yang, and H. Wang, Electrochim. Acta, 56, 834 (2010).
19. H. Ge, N. Li, D. Li, C. Dai, and D. Wang, J. Phys. Chem. C, 113, 6324 (2009).
20. Y. S. Jung, K. T. Lee, J. H. Ryu, D. M. Im, and S. M. Oh, J. Electrochem. Soc., 152, 1452 (2005).
21. W. S. Yoon, P. Clare Grey, M. Balasubramanian, X. Q. Yang, and J. McBreen, Chem. Mater., 15, 3161 (2003).
22. M. Venkateswarlu, C. H. Chen, J. S. Do, C. W. Lin, T. C. Chou, and B. J. Hwang, J. Power Sources, 146, 204 (2005).
23. P. E. Lippens, M. Womes, P. Kubiak, J. C. Jumas, and J. Olivier-Fourcade, J. Solid State Sci., 6, 161 (2004).