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Synergistic effects of coating and doping for lithium ion battery cathode materials: synthesis and characterization of lithium titanate-coated $LiCoO_2$ with Mg doping

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ABSTRACT

Lithium titanates are introduced as coating materials on the surface of Mg-doped $LiCoO_2$ in which the residual Li_2CO_3 after synthesis of the active materials is used as a lithium source. It is revealed that two completely different lithium titanate phases (monoclinic Li_2TiO_3 and spinel $Li_4Ti_5O_{12}$) can be obtained as the coating materials depending on the concentration of a titanium source. Characterization of the coating materials is performed with various experimental techniques including XRD, nano SIMS, TEM, EELS and current measurement using nano probe. The $Li_4Ti_5O_{12}$ coating layer from the high concentration of titanium source secures better electrochemical performances than the Li_2TiO_3 one from the low concentration of titanium source due to its "zero-strain" characteristic. In addition, it is shown that the doped ions (Mg^{2+}) from the active materials move to the coating layer and strongly enhance the conductivity of $Li_4Ti_5O_{12}$. Consequently, synergistic effects on the cell performances of cyclability and rate capability from coating and doping for the $LiCoO_2$ cathode materials are rigorously investigated.

1. Introduction

Since the first commercialization of lithium ion battery (LIB), the layered lithium transition metal oxides ($LiMO_2$, M: Co, Ni, Mn, and so forth) have been one of the most predominant cathode materials in LIBs, particularly, for portable electronics. However, as the usage of LIBs has increased in other area, such as, transport applications (electric vehicles and hybrid electric vehicles) and massive energy storage facilities, demands for better electrochemical performances of LIBs are drastically increasing. From various experimental evidences, several degradation mechanisms of the layered cathode materials have been proposed [1–4]. One is the dissolution of transition metal ions into the electrolytes when the electrode is delithiated. Another mechanism is that the MO_2 layer at the delithiated state shears from the electrode surface, which results in the capacity fade. In addition, the mechanically vulnerable charged form of the materials with the expanded lattice suffers from oxygen loss and side reaction with electrolytes at the highly oxidized surfaces. None of these mechanisms are mutually exclusive, and conceivably multiple mechanisms are concurrently involved in a cathode degradation.

Coating is one of the simplest as well as most effective methods to be considered for minimization of the degradation and consequent capacity fade during cycling. The primary role of the coating layer is physical protection from chemical reaction with the electrolytes. The common feature of successful coating materials, such as, ZrO_2, SiO_2, ZnO, Al_2O_3, $Al(OH)_3$, $AlPO_4$, and AlF_3, is that the metal ion in the coating layer has only one stable valence state at ambient condition [5], therefore, the active materials can obtain much enhanced stability. However, because the coating materials generally exhibit poor lithium ion conduction, recently, inorganic materials containing lithium ions have been proposed. For example, Lu et al. suggested that monoclinic Li_2TiO_3, a Li-rich layered material similar to Li_2MnO_3, would be a good candidate [6]. They showed that the Li_2TiO_3-coated $LiMO_2$ nanobelts strongly improved rate capability and cycling ability as cathode materials. The effect of Li_2TiO_3 is not limited only to the layered materials. Deng et al. reported that this material worked well for the $LiNi_{0.5}Mn_{1.5}O_4$ spinel cathode [7]. They showed that the Li_2TiO_3-coated samples delivered excellent discharge capacities even at a very high charging/discharging rate of 5C. Meanwhile, $Li_4Ti_5O_{12}$ is another example of lithium ion conductor

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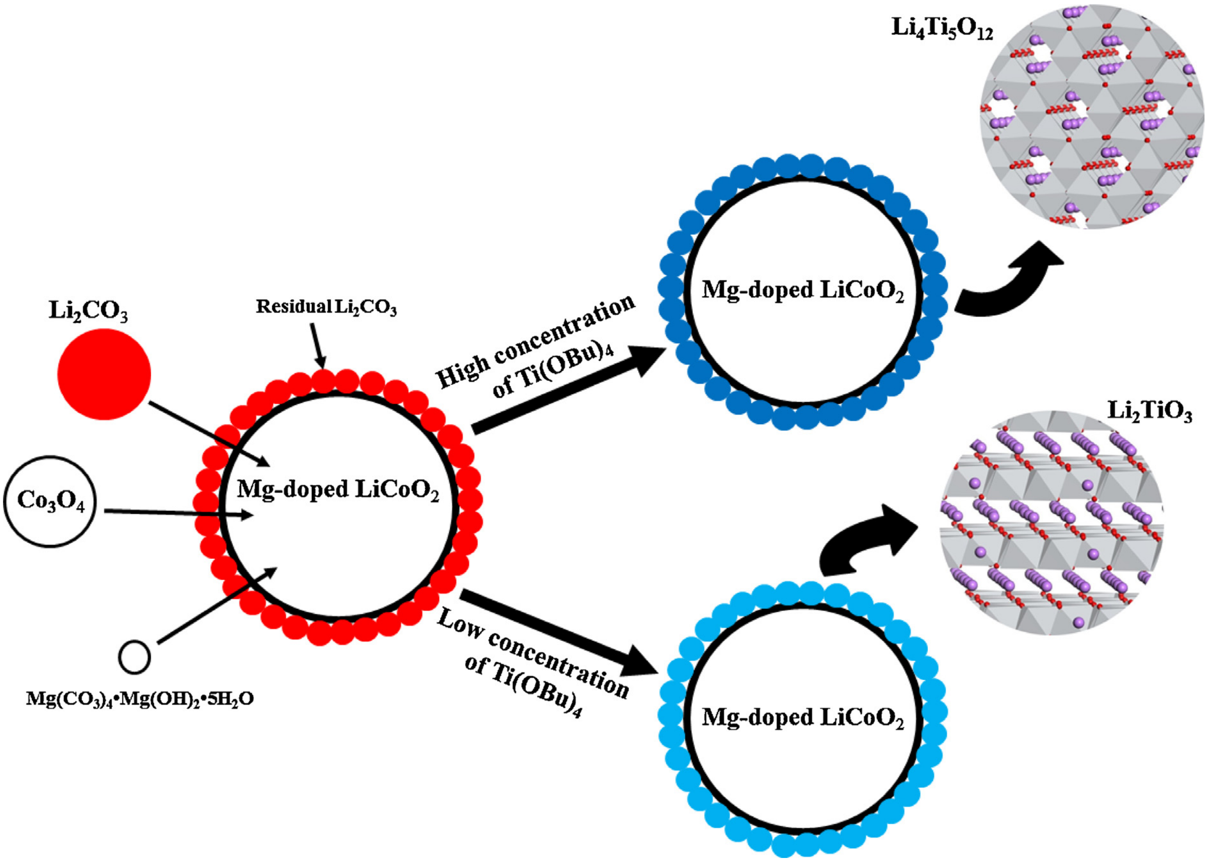
being used as a coating material. In fact, it has been extensively used as an anode material for a long time because it rarely suffers from volume change, which is so called a "zero-strain" material, during ion insertion and extraction [8–10]. However, because $Li_4Ti_5O_{12}$ shares the same structure of spinel ($Fd\overline{3}m$) with $LiMn_2O_4$ and the crystallographic mismatch between them (lattice parameter a of $Li_4Ti_5O_{12}$: 8.248 Å and that of $LiMn_2O_4$: 8.357 Å) is not significant, $Li_4Ti_5O_{12}$ or its similar derivatives have been suggested as a coating material on the spinel cathodes [11–14]. Meanwhile, even though a few studies reported that $Li_4Ti_5O_{12}$ can be applied to the layered materials, for example, $LiCoO_2$ [15–18], it has not been so successful in industry, probably because it does not produce acceptable electrochemical performances, such as, cycling lifetime and high rate capability. This disqualification is mainly ascribed to its low electrical conductivity ($\sigma < 10^{-13}$ S cm^{-1}) [19].

By modifying electronic structure of original active materials, doping is a simple method to efficiently improve cell performances. For example, because Mg has a valence state of 2^+ rather than Co (3^+) or Li (1^+), the Mg-doped $LiCoO_2$ exhibits strong electrical conductivity compared to the bare $LiCoO_2$ and, therefore, it shows excellent cell performances [20–24]. Besides Mg, various dopants for $LiCoO_2$, such as, Al [25], Zr [26], Sn [27], B [28], and so forth [29], have also been explored. In this study, with combination of the above-mentioned coating of lithium titanate and doping of Mg, we investigate their synergistic effects on the $LiCoO_2$ cathode materials. From various experimental works including X-ray diffraction (XRD), nano secondary ion mass spectrometry (nano SIMS), transmission electron microscopy (TEM), electron energy-loss spectroscopy (EELS), current measurement by nano probe, and electrochemical characterization, it is revealed that the doped ions (Mg^{2+}) have an effect not only on the active materials themselves but also on the coating layer. In addition, utilizing limited amounts of residual lithium ions, it is shown that the phase of lithium titanate is varied with the contents of Ti source. Because the phases are very different in several respects, the electrochemical performances of the cells employing them are also consequently different.

2. Experimental Section

2.1. Synthesis of materials

The Mg-doped $LiCoO_2$ ($LiMg_{0.01}Co_{0.99}O_2$) was prepared by solid-state reaction. Starting materials of Li_2CO_3, Co_3O_4 and $Mg(CO_3)_4{\bullet}Mg(OH)_2{\bullet}5H_2O$ were mixed by a mechanical mixer with a rotating speed of 80 rpm for 1 h. The ratio of Li: Co: Mg was adjusted to 1.04: 0.99: 0.01 considering that unreacted Li_2CO_3 remains on the surface of Mg-doped $LiCoO_2$ particles after synthesis. Then, the powder mixtures were heated at 1000 °C for 5 h in air to produce the Mg-doped $LiCoO_2$. The sol-gel technique was employed for the lithium titanate coating. For this purpose, various amounts of $Ti(OBu)_4$ (0.457 g, 1.372 g, and 2.286 g) were, respectively, dissolved in 100 g of ethanol with 3 h stirring at room temperature. Then, 50 g of the synthesized active materials was added into each of the solutions with 4 h stirring at 80 °C. The residual Li_2CO_3 on the surface of the active materials was used as a lithium source for the coating. Utilization of the residual Li_2CO_3 has a benefit because impurities such as LiOH or Li_2CO_3 usually impede the Li ion diffusion and charge transfer reactions at the interfaces and promote the formation of HF [30]. Moreover, Li_2CO_3 has been considered as a main source of CO_2 gas at high temperatures. Then, each of the solutions was heated at 950 °C for 6 h and then naturally cooled down to room temperature. As described in Scheme 1, the structure of lithium titnate coating layer is



Scheme 1. Synthesis and Coating Process of Lithium Titanate-Coated $LiCoO_2$.