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Short communication

Performance improvement of $LiCoO_2$ by molten salt surface modification

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Abstract

The surface of commercial $LiCoO_2$ was modified by molten salt method. The structure and electrochemical and thermal performances of the $MgCl_2$-treated $LiCoO_2$ were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), X-ray photoelectron spectroscopy and galvanostatic cycling. It is found that surface modification improves the structural and thermal stability as well as the rate performance of $LiCoO_2$. These improvements were attributed to the formation of homogeneous solid solution on the surface of the $LiCoO_2$ particle.

Keywords: Surface modification; Molten salt; Performance improvement; Lithium ion batteries

1. Introduction

$LiCoO_2$ is the most commercialized cathode material for lithium ion batteries because of its favorable features such as high energy density, low self-discharge rate and excellent cycle life. However, its available specific capacity remains only *ca.* 140 mAh g^{-1} in a practical battery, only roughly half of its theoretical capacity (274 mAh g^{-1}). Higher capacity can be obtained by charging the material to higher potentials (>4.2 V *versus* Li^+/Li). Nevertheless, this will lead to severe structural deterioration due to irreversible phase transitions [1] and obvious electrolyte decomposition because of the formation of strong oxidizing oxygen at deep delithiation states [2].

Elemental substitution has proved an effective method to improve the structural stability of the cathode materials. However, the improvement of the structural stability was realized at the expense of specific capacity [3–8].

Surface chemistry is of great importance to the performance of the electrode [9]. Recent studies show that coating the $LiCoO_2$ particles with oxides such as Al_2O_3 [10,11], MgO [12], ZrO_2 [13], TiO_2 [13], SnO_2 [14], CeO_2 [15], ZnO [16], P_2O_5 [17] and SiO_2 [18] helps to suppress capacity fading at deep charge states (>4.2 V). Many researchers try every effort to coat the $LiCoO_2$ surface as compactly as possible because it was believed that the coating layer helps to avoid the direct contact between the electrolyte and the active cathode material and, therefore, the reaction between them. Our previous studies [19,20], on the other hand, indicated that even compact coating cannot prevent the corrosion of $LiCoO_2$ by the acidic electrolyte. Surface coating increases the acidity of the electrolyte by forming Lewis acids via interaction with the electrolyte rather than scavenges the acidic species in the electrolyte. Previous studies also indicated that the solid solution formed near the surface of $LiCoO_2$ during electrochemical cycling for MgO-coated $LiCoO_2$ and during $LiAlO_2$-coating on $LiMn_2O_4$ [21] improved the structural stability of the cathode materials.

Molten salt method is one of the simplest means to prepare pure and stoichiometric multi-component oxide powders. The molten salts, characteristic of low melting point but high decomposition temperature, work as solvent or reacting species or sometimes both [22,23]. This method has found applications in synthesis of electrode materials [24–27] at rather low temperatures and in a short time because the diffusion of the ions is much quicker in the molten salt than in the solid. We believe that this method can also be used to modify the surface chemistry of $LiCoO_2$ by controlling the temperature, time and other

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Table 1
Molar proportions of the chemicals in molten salt process

	$MgCl_2{\cdot}6H_2O$	$LiCoO_2$	$LiOH{\cdot}H_2O$
I	5	85	10
II	10	75	15
III	15	65	20
IV	20	55	25

conditions of the molten salt reaction. In this work, we improve the performances of commercial $LiCoO_2$ by bathing it in $MgCl_2$ molten salt to form a homogeneous modification layer.

2. Experimental

$MgCl_2{\cdot}6H_2O$ (99.0%, Beijing Shuanghuan Chemical Reagent Company), $LiOH{\cdot}H_2O$ (98.0%, Guangdong Longxi Chemicals) and commercial $LiCoO_2$ (Nippon Chemicals, battery grade; ~5 μm in diameter) were carefully mixed in a mortar at the required ratios (Table 1). $LiOH{\cdot}H_2O$ was used here to increase the Li content in the molten salt so as to compensate the lost lithium due to concentration difference in and out of the $LiCoO_2$ particles. The mixture was transferred to a muffler furnace when the temperature of the latter reached 750 °C. It was taken out after 2 h and cooled down outside the furnace to room temperature. The mixture was then washed with distilled water and filtered three times. Finally, the precipitates were heated at 100 °C for more than 12 h. Surface-modified $LiCoO_2$ was thus obtained. For comparison, the commercial $LiCoO_2$ was also annealed in the same way as the above samples.

X-ray diffraction (XRD) was carried out on a Holland X'Pert Pro MPD X-ray diffractometer equipped with a monochromatized Cu Kα radiation (λ = 1.5418 Å). The morphology of the samples was observed on a Hitachi S-4000 scanning electron microscope (SEM). Inductively coupled plasma (ICP) was conducted on ICP-8000 (Shimazu Co.) to determine the atomic ratio of the samples.

Descriptions of the electrode preparation and button-type test cell assembly can be found in Ref. [19]. The cells were charged and discharged on a LAND BT1-10 battery tester between 2.5 V *versus* Li^+/Li and various charge cut-off potentials. The ac impedance measurements were performed using an IM6e (Zahner Electric) impedance analyzer over a frequency range from 100 kHz to 5 mHz.

Differential scanning calorimetry (DSC) analysis was carried out on NETSCH STA 449 C in air by sealing the charged cathode sheet in an Al crucible in dry Ar and heated from 25 to 500 °C at a rate of 5 °C min^{-1}.

3. Results and discussion

Fig. 1 illustrates the morphologies of commercial and molten salt-treated $LiCoO_2$. It is seen that the surface of the 5% (not

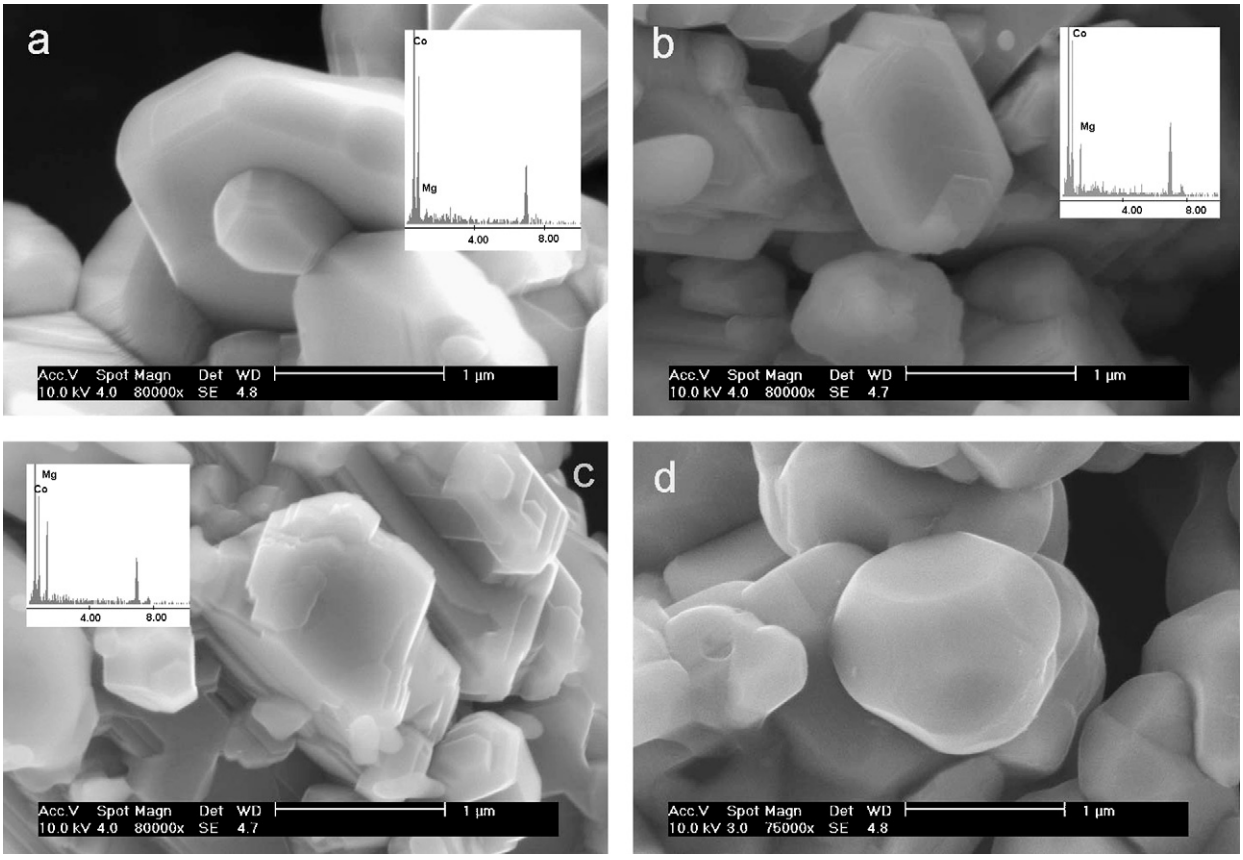

Fig. 1. Surface morphology of: (a) 10%, (b) 15%, (c) 20% $MgCl_2$ treated and (d) commercial $LiCoO_2$ (the insets are the corresponding EDAX patterns of the surface-modified $LiCoO_2$).