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Characterization of MgO-coated-$LiCoO_2$ particles by analytical transmission electron microscopy

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HIGHLIGHTS

- Sub-micron sized particles for TEM analysis synthesized by sol-gel method.
- MgO-$LiCoO_2$ exhibited a much more homogeneous distribution of Li after the cycling tests.
- A coherent orientation relationship was observed at the MgO//$LiCoO_2$ interface.

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ABSTRACT

The surfaces of $LiCoO_2$ particles were modified to improve the charge-discharge cycling properties of Li-ion batteries containing $LiCoO_2$ cathodes. The sol-gel technique was used to modify the surface of $LiCoO_2$ particles with magnesium oxide. Capacity retention during cycling of the magnesium oxide-coated $LiCoO_2$ cathode was superior to that of a cathode comprising pristine $LiCoO_2$. Moreover, results obtained from TEM measurements indicate that the Li concentration was relatively homogeneous in the magnesium oxide-coated $LiCoO_2$ particles after cycling tests. The crystallographic planes of the coating were found to be coherently oriented with those of the substrate, MgO(111)[1−10]//$LiCoO_2$(003)[100]. Therefore, we believe that a thin cover of Mg on the surface of $LiCoO_2$ stabilizes the surface, contributing to the homogeneity of charge and discharge reactions.

1. Introduction

Lithium-ion batteries are used in electric vehicles and various electronic devices such as mobile phones. Because of their wide usage, the demand for improved Li-ion battery performance is increasing.

To extend battery capacity, it is necessary to increase the operating voltage range of the cell while maintaining the working life of the battery. Although these two properties are in a trade-off relationship, improving both at the same time has been attempted through surface modification and the doping of the bulk cathode materials. Surface modification, in particular, can reduce capacity fading. Modification of a $LiCoO_2$ sample using elemental Mg for the purpose of both surface modification and modifying the bulk properties has been reported, and MgO has been reported as a candidate coating material [1–6]. Reports of the coating or doping of cathode materials by Mg have mainly focused on a discussion of the crystal structure and composition, analyzed using X-ray diffraction and techniques such as X-ray photoelectron spectroscopy (XPS) [7–10]. In particular, to understand the effect of surface modification, the fine structure of the surface region in the modified samples must be studied at high spatial resolution.

The high spatial resolution of transmission electron microscopy (TEM) makes it the ideal technique for the analysis of localized sample areas. Furthermore, an analytical TEM measurement that integrates chemical analysis techniques such as energy dispersive X-ray spectroscopy (EDS) and electron energy-loss spectroscopy (EELS) with scanning TEM (STEM) observation is a powerful tool to investigate the local structure of samples. EELS analysis, in particular, can be used to obtain chemical information about a sample because the energy loss near edge structure (ELNES) is sensitive to the chemical state of a sample. To obtain individual pure EELS spectra from a series of spectra without a reference spectrum, the application of a self-modeling curve resolution technique to the series of spectra to

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perform the spectral decomposition has become popular [1–15].

TEM observations require thin samples because the electron beam must pass through the sample. The focused ion beam (FIB) technique is one of the most common methods of sample preparation. However, care must be taken during sample preparation because FIB irradiation can damage the structure of the surface region, introducing artifacts. In the present study, we used small $LiCoO_2$ particles that can be observed directly by analytical TEM without the use of a thinning process. Using the optimized samples, we studied the electrochemical properties of the samples and the effect of the coating and surface state in detail using analytical TEM measurements.

2. Experimental

2.1. Sample preparation and electrochemical testing

$LiCoO_2$ particles were prepared by Pechini's method [18]. $Co(CH_3COO)_2 \cdot 4H_2O$, $LiCH_3COO \cdot H_2O$, and citric acid were mixed at 165 °C in an ethylene glycol solution (Co:Li = 1:1 atom ratio). The obtained gel was pre-calcined at 400 °C in air to decompose the precursor. The precursors were calcined at 800 °C for a few hours under a flow of air.

The Mg-oxide coating was carried out by a sol-gel method. $Mg(EtO)_2$ (1 wt% of MgO) and synthesized $LiCoO_2$ powder were mixed in methanol solvent. Dipropyleneglycol (DPG) was used as a chelating agent. The molar ratio of DPG/Mg was about 32. Ammonia was used as a catalyst. The reaction time and temperature were 180 min and 50 °C, respectively. The hydrolysis reaction was carried out in a dry environment to maintain hydrolyzing conditions. The gel sample was dried under vacuum at 250 °C for 1 h. Finally, the sample was calcined at 500 °C for 2 h under a flow of air, yielding the product, MgO-$LiCoO_2$.

A mixture containing 90 wt% $LiCoO_2$, 5 wt% acetylene black, and 5 wt% polyvinylidene fluoride (PVDF) was used as the positive electrode. Two-electrode electrochemical cells were assembled using Li metal as the counter electrode. A two-electrode cell with 2 cm × 2 cm working electrodes sealed in an Al laminated film was assembled. A mixture of $LiPF_6$ (1.0 mol dm^{-3}), EC (ethylene carbonate), DMC (dimethyl carbonate), and EMC (ethyl methyl carbonate) (1:1:1 in volume) was used as the electrolyte. Cells were cycled in the voltage range between 3.0 V and either 4.2 or 4.5 V at a 1 C charge-discharge rate (1C = 150 mAg^{-1}). The temperature around the cell in the charge-discharge tests was set to 20 °C.

2.2. Analytical TEM procedure

The MgO-$LiCoO_2$ powder was directly dispersed on a holey carbon film supported on a Cu mesh for TEM analysis. A vacuum transfer holder (GATAN 610) was used for TEM observation. The samples were transferred to the electron microscope from a dry air environment without exposure to the ambient atmosphere using the transfer holder. A $TITAN^3$ G2 60-300 electron microscope (FEI Company) was used for analytical TEM measurements. The accelerating voltage was 300 kV. The energy dispersive X-ray spectroscopy (EDS) and electron energy-loss spectroscopy (EELS) measurements were carried out using Super-X (Bruker) and GIF-Quantum ERS (Gatan Inc.) in the spectrum-imaging based on STEM observations. Spectrum-imaging is a method to acquire a data cube of two spatial axes and an energy axis [19,20]. For EELS measurements, the energy dispersion of each spectrum was set to 0.05 eV per channel (ch). A monochromator was used to achieve a higher energy resolution to collect fine Li K-edge signals (less than 0.3 eV with 0.05 $eVch^{-1}$ dispersion) [16].

To obtain pure individual spectra for a series of EELS spectra without a reference spectrum, we applied the self-modeling curve resolution technique, i.e., the alternating least-squares (ALS) method [21]. We applied the ALS method to a series of measured EELS spectra for spectral decomposition [21–24]. As an initial estimation for ALS, the orthogonal projection approach (OPA) was used [25,26].

3. Results and discussion

3.1. Electrochemical measurements

Capacity-voltage profiles (charge-discharge curves) of the first 3.0–4.2 V cycle for the bare $LiCoO_2$ and MgO-$LiCoO_2$ cathodes are shown in Fig. 1. For the MgO-$LiCoO_2$ sample investigated in this study, the charge-discharge curve was very similar to that of the bare $LiCoO_2$, which was used as a reference. Interestingly, compared with those of bare $LiCoO_2$, the specific discharge capacity and coulomb efficiency of Mg-$LiCoO_2$ were improved.

The specific discharge capacity during the cycling tests was improved by surface modification, as shown in Fig. 2. In the case of the bare $LiCoO_2$, capacity fading occurs much more rapidly than that of the MgO-$LiCoO_2$ sample. This capacity fade can be related to the change in both the surface and bulk of the positive electrode material. As a result of the magnesium oxide coating, capacity fade was reduced. From this result, we concluded that the surface structure and chemical states govern the cycling performance.

3.2. TEM observation of bulk region in $LiCoO_2$

3.2.1. EELS analysis at the Li K-edge

Measurement of the spatial distribution of Li ions is a direct way to study the degradation of Li-ion battery materials. A method to map the Li distribution in $LiCoO_2$ by EELS analysis at the Li K-edge has been previously reported [16]. Using this technique, we constructed a Li intensity map of the cathode materials after the 100th discharge, and both bare $LiCoO_2$ and MgO-$LiCoO_2$ were examined in this way. The Li intensity was calculated from the signal intensity ratio of the Li-K and Co-M edges [16]. In the present study, we constructed Li/Co intensity maps using the electron energy loss ranges of60–62 eV (Li K) and 64–65 eV (Co M_2,3). The resultant Li maps are shown in Fig. S1.

Fig. 3 shows the Li concentration mapping obtained using the

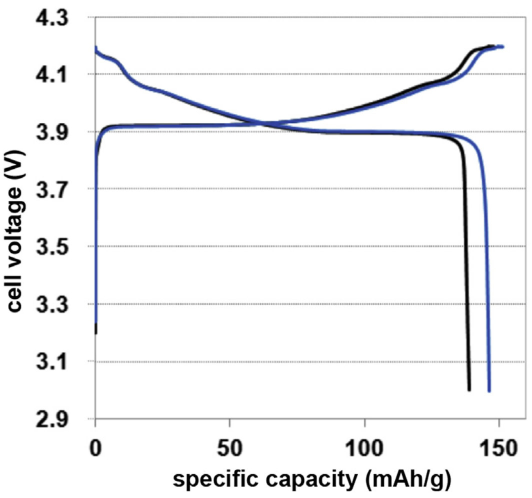

Fig. 1. Charge-discharge curve for small-sized $LiCoO_2$ particles obtained by the Pechini method. Blue and black lines correspond to MgO-$LiCoO_2$ and bare $LiCoO_2$ [16], respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)