



Electrochemical properties of LiCoO₂ thin film surface modified by lithium tantalate and lithium niobate coatings



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ABSTRACT

Amorphous lithium tantalate (LTaO)- and lithium niobate (LNbO)-coated LiCoO₂ (LCO) thin film electrodes were fabricated by pulsed laser deposition (PLD). The LTaO- and LNbO-coated LCOs showed lower interfacial resistances and high-rate charge–discharge properties as compared with a bare LCO. The contribution of the LTaO and LNbO coatings to the electrochemical properties was considered using lithium diffusion and surface analysis. Tracer lithium diffusion coefficients (D_{Li^+}) of the LTaO and LNbO thin films were determined by secondary ion mass spectrometry (SIMS) using ⁶Li and ⁷Li isotopes. Surface analysis of the LTaO- and LNbO-coated LCOs before and after electrochemical measurement was performed using X-ray photoemission spectroscopy (XPS). The LTaO and LNbO thin films indicated fast lithium-ion diffusion; moreover, no degradation of the surface of the LNbO-coated LCO was observed during the electrochemical measurements. Therefore, LNbO is considered an excellent coating material for decreasing interfacial resistance.

1. Introduction

Recently, lithium ion batteries (LIBs) have become a promising energy storage technology solution for hybrid electric vehicles (HEVs) and electric vehicles (EVs) because of their advantages, e.g., high energy density, energy exchange efficiency, and long lifecycle. However, deterioration of LIBs at the interface between the positive electrode and electrolyte has been reported [1,2]. Positive active materials have been reported to be coated with metal oxides [3–8], metal fluorides [9,10], phosphates [11], and lithium-ion conductors such as lithium phosphorus oxynitride (Lipon) [12] and lithium tungsten oxide (LWO) [2,13–16] in order to improve their electrochemical properties. Positive active materials coated with LWO showed decreasing interfacial resistance in LIBs [2,13–16]. Our group has reported the mechanism for this decrease [2,15,16]: LWO-modification introduces a protective layer that suppresses the degradation of LiCoO₂ (LCO) during reaction with the electrode [2]. Moreover, the randomly oriented Li₂WO₄ structure with tetragonal symmetry displaying multiple lithium-ion diffusion paths enhances the diffusion of lithium ions at the interface [15]. By direct observation of the lithium-ion diffusion coefficients of the various structural LWO coatings using secondary ion mass spectrometry (SIMS) and electrochemical techniques, we have further revealed that

the high lithium-ion self-diffusion coefficients of an LWO-modified LCO contribute to enhancing the diffusion of lithium ions between the LWO and LCO layers, resulting in the decrease in the interfacial resistance [16]. Therefore, we have proposed that the lithium-ion diffusion coefficients of the coating materials are important in decreasing interfacial resistance.

Based on these previous studies, we aimed to fabricate new modified LCO electrodes coated with materials having high lithium-ion diffusion coefficients. For the coating materials, atmospheric stability is also an important feature. As such, lithium-ion-conducting materials, such as amorphous lithium tantalate (LTaO) [17–20] and amorphous lithium niobate (LNbO) [17,20], both of which are stable in the atmosphere, are assumed to be suitable candidates for coating materials. In the present study, we fabricated LTaO- and LNbO-coated LCO thin film electrodes using a pulsed laser deposition (PLD) method. Electrochemical measurements were conducted in order to confirm the effects of the LTaO and LNbO coatings.

To consider the contribution of the lithium-ion diffusion coefficients of the coating materials to electrochemical effects, the lithium diffusion coefficients of the LTaO and LNbO thin films were measured by a “step ion-exchange method” using SIMS analysis. Kuwata et al. determined the lithium diffusion coefficients in amorphous lithium phosphate (a-

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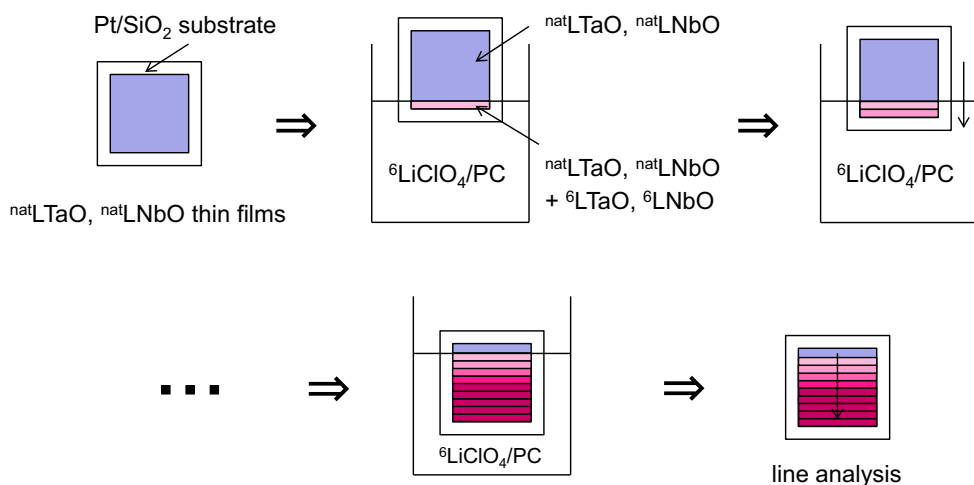


Fig. 1. Schematic of sample preparation for the step ion-exchange method.

Li₃PO₄) by an “ion-exchange method” using SIMS analysis [21].

In the present study, LTaO and LNB0 coating effects are comprehensively discussed based on electrochemical properties, lithium-ion diffusion coefficients of the coatings, and surface analysis of the LTaO- and LNB0-coated LCO electrodes before and after electrochemical measurement by X-ray photoemission spectroscopy (XPS).

2. Experimental

2.1. Fabrication of bare and coated LCOs

A bare LCO thin film was deposited onto a Pt substrate of 10 mm × 10 mm × 0.5 mm by the PLD method [16,21] using a LiCoO₂ target made by Toshiba Manufacturing Co. Ltd. The fourth harmonic of a Nd:YAG laser (Spectra-Physics GCR-150-10) operating at 266 nm was used at a laser energy fluence of 1.3 J/cm². The substrate temperature was kept at 500 °C under an O₂ atmosphere at 20 Pa. The substrate was placed parallel to the target at a distance of 40 mm and the repetition frequency was 10 Hz.

The LTaO and LNB0 thin films were deposited onto the bare LCO thin film electrodes and SiO₂ glass substrates by the PLD method using Li₃TaO₄ and Li₃NbO₄ targets from Toshiba Manufacturing Co. Ltd. An ArF excimer laser (Coherent COMPexPro 102) operating at 193 nm was used at a laser energy fluence of 1.5 J/cm². The substrate temperature was kept at room temperature under an O₂ atmosphere at 20 Pa. Again, the substrate was placed parallel to the target at a distance of 40 mm and the repetition frequency was 10 Hz.

2.2. SEM, XRD, and XPS measurements

The bare LCO thin film on the Pt substrate, together with the LTaO and LNB0 thin films on the SiO₂ glass substrates, were identified using an X-ray diffractometer (XRD, X'Pert PRO MPD, PANalytical) equipped with a Cu Kα source. Cross-sectional images of the LTaO- and LNB0-coated LCOs were observed using a field emission scanning electron microscope (FE-SEM, S-4700, Hitachi). Surface analysis of the LTaO- and LNB0-coated thin film electrodes was performed using an X-ray photoemission spectrometer (XPS, Versa Probe II, ULVAC-PHI) equipped with monochromated Al-Kα source.

2.3. Electrochemical techniques

In order to investigate the electrochemical properties of the bare LCO, and the LTaO- and LNB0-coated LCOs, coin cells were assembled. The negative electrodes were lithium metal. The electrolyte consisted of a 2:2:6 mixture of 1.2 M LiPF₆-ethylene carbonate, ethylmethyl carbonate, and dimethyl carbonate (v/v/v). Celgard® 2400 microporous

polypropylene membranes were used as the separators. These coin cells were assembled in an Ar-filled glove box.

Three types of electrochemical techniques, i.e., charge–discharge tests, electrochemical impedance spectroscopy (EIS), and rate–capacity measurements were performed. Charge–discharge tests were performed between 3.0 and 4.2 V at a rate of 0.2 C (2.1 μA/cm²). Subsequently, the coin cells were charged up to 4.0 V at a charging rate of 0.2 C and characterized by EIS from 25 °C to 50 °C. The amplitude voltage was 10 mV and the frequency range was from 0.01 to 100,000 Hz. Rate–capacity measurements were performed between 3.0 and 4.2 V at a charge–discharge rate of 0.3, 0.6, 3.0, 10, and 30 C for 5 cycles at each charge–discharge rate. Relative discharge capacities were calculated as the ratio of discharge capacity at each rate to the initial discharge capacity of 0.3 C.

2.4. SIMS measurements

Lithium diffusion coefficients (D_{Li}^*) of the LTaO and LNB0 thin films were measured using a “step ion-exchange method.” Kuwata et al. proposed the “ion-exchange method” and “mask method” using SIMS analysis by measuring D_{Li}^* in amorphous lithium phosphate (a-Li₃PO₄), the details of which were described in a previous paper [21]. In the present study, the LTaO and LNB0 thin films, which have a natural isotope composition with 92.4% ⁷Li and 7.6% ⁶Li (referred to as natLTaO and natLNB0 respectively), and a solution of 1 mol/L lithium perchlorate (⁶LiClO₄) in propylene carbonate (PC) were used for ion-exchange. The natLTaO and natLNB0 thin films were deposited onto Pt-coated (200 nm) SiO₂ glass substrates in the same way as described in Section 2.1. The deposition area was 11 × 11 mm² and the thickness of the thin films was 300 nm. In this method, to investigate the time dependence of ⁶Li and ⁷Li ion-exchange, the natLTaO and natLNB0 thin films were immersed in a solution of ⁶LiClO₄/PC at a rate of 0.5 mm per 6 min, as shown in Fig. 1.

After ion exchange, the samples were washed with dimethyl carbonate and dried in an Ar-filled glove box. The isotope profiles of ⁶Li and ⁷Li were measured by SIMS and the D_{Li}^* values were obtained by fitting the isotope profiles with the diffusion equation.

The diffusion profiles were analyzed using the double-focusing magnetic sector SIMS (IMS-7f, CAMECA) available at Tohoku University. Line profile analysis was conducted using a Cs⁺ primary ion beam operating at 15 keV and 1 nA. The spot size of the Cs⁺ ion beam was 1 μm. As ⁶Li and ⁷Li isotopes have the same chemical properties, ionization and detection efficiencies remain nearly constant. The quantitative isotope ratios were directly calculated from the counting rates of the ⁶Li and ⁷Li.

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