Journal of Power Sources 321 (2016) 241–247

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Time-of-flight secondary ion mass spectrometry study of lithium intercalation process in $LiCoO_2$ thin film

C. Dellen [a, b, *], H.-G. Gehrke [a, b], S. Möller [a], C.-L. Tsai [a, b], U. Breuer [c], S. Uhlenbruck [a, b], O. Guillon [a, b], M. Finsterbusch [a, b], M. Bram [a, b]

[a] Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research (IEK), 52425 Jülich, Germany
[b] Jülich Aachen Research Alliance: JARA-Energy, Germany
[c] Forschungszentrum Jülich GmbH, Central Institute for Engineering, Electronics and Analytics – Analytics, 52425 Jülich, Germany

HIGHLIGHTS

- Magnetron sputtering of crystalline $LiCoO_2$ on CrN thin film current collector.
- Systematic study of the Li de-/intercalation in $LiCoO_2$ thin films by TOF-SIMS.
- Stepwise Li profiles in charged state indicate a lithium extraction below $Li_{0.5}CoO_2$.
- Thin film pinning is identified as possible cause for delithiation under $Li_{0.5}CoO_2$.

ARTICLE INFO

Article history:
Received 15 December 2015
Received in revised form
8 March 2016
Accepted 18 April 2016
Available online 7 May 2016

Keywords:
ToF-SIMS
GDOES
Radio frequency magnetron sputtering
$LiCoO_2$
Thin film cathode

ABSTRACT

A detailed time-of-flight secondary ion mass spectrometry (ToF-SIMS) analysis of the lithium de-/intercalation in thin films of the insertion cathode material lithium cobalt oxide is presented. The $LiCoO_2$ (LCO) thin films are deposited by radio frequency magnetron sputtering at 600 °C, having a (003) preferred orientation after the deposition. The thin electrode films are cycled with liquid electrolyte against lithium metal, showing 80–86% extractable capacities. After disassembling the cells, the depth resolved elemental distribution in the LCO is investigated by ToF-SIMS and glow discharge optical emission spectroscopy. Both techniques show a stepwise lithium distribution in charged state, leading to a lithium depleted layer close to the surface. In combination with the electrochemical results, the qualitative comparison of the different lithium depth profiles yields a reversible lithium extraction in the depleted area below the stability limit for bulk materials of LCO. For bulk LCO, a phase change normally occurs when the lithium concentration in Li_xCoO_2 is lower than $x = 0.5$. As a possible cause for the inhibition of the phase change, the preferred orientation and thus pinning of the crystal structure of the film by the substrate is proposed.

1. Introduction

To optimisze material properties and processing conditions of functional battery layers, knowledge about the lateral and vertical distribution of lithium is crucial. By analyzing the lithium depth distribution of electrode or electrolyte layers, one can, for example, investigate the impact of different processing parameters on the elemental composition of battery components [1,2] or visualize the interdiffusion of lithium between active layers and inactive components of batteries [3,4]. An even more fundamental field of application is the analysis of cycled battery cells in different states of charge, to get a deeper understanding of Li transport and de-/intercalation process inside the functional layers of a battery [5,6]. Currently, inductively coupled plasma spectroscopy or spectrometry techniques (ICP-OES, ICP-MS) are typically used for the compositional analysis of bulk batteries or powders for battery production. However, when applied to thin film batteries with typical layer thicknesses of ~1 μm, these techniques are not feasible, especially if spatial and depth resolved elemental profiles are of interest, since it can only yield elemental concentrations averaged over all functional layers. Conventional thin film analytical

* Corresponding author. Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, Wilhelm-Johnen-Str., 52425 Jülich, Germany.
E-mail address: c.dellen@fz-juelich.de (C. Dellen).

http://dx.doi.org/10.1016/j.jpowsour.2016.04.084
0378-7753/

techniques using X-rays for the analysis, like X-ray Photoelectron Spectroscopy (XPS) or in a wider sense energy/wavelength dispersive X-ray spectroscopy (E/WDX), are also not capable to detect lithium with a sufficient sensitivity. Driven by these difficulties in detection and quantification of lithium, an innovative combined approach is introduced, where time-of-flight secondary ion mass spectrometry (ToF-SIMS) and glow discharge optical emission spectroscopy (GDOES) are used to characterize the depth profile of Li distribution in $LiCoO_2$ (LCO) thin films prepared by unbalanced radio frequency magnetron sputtering. The capability of ToF-SIMS to detect the spatial lithium distribution with high sensitivity makes this technique an ideal candidate for the investigation of thin functional layers in batteries [4–8]. As a reference, GDOES is used as independent comparative analytical technique for the lithium depth profile analysis, and to evaluate potential measurement artefacts of the ToF-SIMS analysis (e.g. SIMS matrix effects [9]). In addition, nuclear reaction analysis (NRA) is used as a reference method, which is able to quantify lithium concentration in thin films.

For the presented investigations, LCO is chosen as a model system for layered intercalation cathodes because it has a high relevance for commercial applications and is a well-studied electrode material [10–13]. While the theoretical capacity for complete delithiation of Li_xCoO_2 where $x = 0$ is 138 μAh cm^{-2} μm^{-1} or 275 mAh g^{-1}, the useful capacity in conventional bulk LCO batteries is only half the value, because the reversible lithium extraction is limited to Li_xCoO_2 where $x = 0.5$. In the case of LCO bulk materials, a delithiation of $x < 0.5$ is reported to cause a rapid capacity fading, due to a phase change of the material which is connected to a large variation in the c lattice parameter [11,14,15]. In contrast, for LCO thin films, a reversible cycling below the limit of $Li_{0.5}CoO_2$ was already reported in literature [16,17].

2. Experimental

2.1. Thin film deposition process

The investigated thin film half-cells consist of a CrN current collector which has a thickness of around 300 nm and a submicron LCO cathode layer. The substrates for the thin film deposition process were quartz glass sheets with an area of 25 × 25 mm^2 and a thickness of 1.25 mm. After cleaning in acetone and isopropanol, chromium nitride (CrN) current collector and LCO cathode layer were grown onto the glass substrate by physical vapor deposition (PVD) one after the other. Firstly, the CrN was deposited by a reactive radio frequency sputter process using a CS 400 ES PVD cluster system (Von Ardenne GmbH). Prior to the deposition, the substrates were sputter etched and then transferred to the process chamber while the vacuum was maintained. The deposition was done at 500 °C and a pressure of 6×10^{-3} mbar with a nitrogen flow of 50 sccm. For the subsequent deposition steps, samples were transferred to a CS 800 ES PVD cluster system (Von Ardenne GmbH). The surface of the CrN layer was again cleaned by sputter etching. After the etching process, samples were transferred to an electron beam (e-beam) evaporation chamber without breaking the vacuum. In the e-beam deposition process, an additional 10 nm chromium metal layer was deposited as adhesion layer. Afterwards, samples were transferred under vacuum to a sputtering chamber equipped with a commercial ceramic LCO target of 250 mm in diameter (Evochem Advanced Materials GmbH). The composition of the LCO target was determined by inductively coupled plasma – optical emission spectroscopy (ICP-OES), which gives the Li:Co ratio of 1.1:1.0. The successive deposition of the LCO was performed in a pure argon atmosphere with an Ar flow of 20 sccm and a processing pressure of 5×10^{-3} mbar. The sputter power was 500 W, which is equivalent to 1 W cm^{-2}, and the substrate temperature was set to 600 °C during the 1 h deposition. At first, the heating rate was 10 K min^{-1} up to a temperature of 550 °C and then switched to 5 K min^{-1} to avoid overshooting the targeted substrate temperature of 600 °C. After the sputtering, samples were cooled down with a controlled cooling rate of 5 K min^{-1}. The crystal structure of LCO thin films was analyzed by X-ray diffraction (XRD), using a Bruker D4 Endeavour X-ray diffractometer. The XRD analysis (not shown here) revealed that the as deposited LCO thin films were already in crystalline phase with a preferred (003) orientation. Therefore, no additional annealing step was needed prior to the electrochemical tests.

2.2. Electrochemical tests

The electrochemical activity of LCO thin films was tested by cyclic voltammetry (CV) experiments. For cell assembly, LCO thin films were transferred from the PVD system into a glove box with a protective Ar atmosphere without any contact to ambient atmosphere. As a standard liquid electrolyte, 1 M $LiPF_6$ (Alfa Aesar) dissolved in ethylene carbonate (EC) (Sigma-Aldrich) and dimethyl carbonate (DMC) (Sigma-Aldrich) mixed in a 1:1 M ratio was used. The electrolyte was pipetted onto two stacked round pieces of a commercially available glass fiber separator (Whatman) with a diameter of 12.7 mm limiting the active area of the LCO thin film. Metallic lithium foil (Alfa Aesar) was pressed on a nickel current collector disk and used as anode. The cells were sealed under a protective Ar atmosphere in a pouch bag with an aluminum lead for cathode contact and a nickel lead for anode contact. CV measurements were performed outside the glove box by using a Biologic VMP-300 multipotentiostat (BioLogic Science Instruments). The scan rate was set to 0.04 mV s^{-1} and the cells were cycled between 3.0 V and 4.1 V vs. Li^+/Li. The relatively slow scan speed was chosen to ensure the maximum utilization of the whole film during the cycling. The voltage range was chosen to cycle the thin films well within the reversible limits of Li_xCoO_2 with $0.5 < x < 1$ and to prevent a fast degradation of the material at a higher potential [14,15,18].

2.3. Analysis of elemental composition

ToF-SIMS analysis were performed by using a TOF-SIMS IV system (ION-TOF GmbH). The measurements were done with a dual beam setting [19] in non-interlaced mode. For the material erosion, a 2 keV Cs^+ ion beam was rasterized over an area of 300 × 300 μm^2. For the generation of analyzed secondary ions, a focused 25 keV Bi_3^+ ion beam was used and the Bi ion gun was operated in the high current bunched mode. The analyzed area was 82 × 82 μm^2 and centered within the sputter crater to avoid crater edge effects. Between the sputtering and analysis pulses, a low energy (20 eV) electron flood gun was used to compensate for sample charging during the sputter processes. The data analysis was carried out by using Software package SurfaceLab 6 (ION-TOF GmbH).

The depth calibration of the SIMS profiles was conducted by measuring each sputter crater depth by using a confocal scanning laser microscope VK-9700 (Keyence Corp.) and converting the sputter time into a depth scale.

For complementary depth profiling results on the lithium ion distribution, GDOES measurements were done using a glow discharge analyzer (GDA) 750 HR (Spectruma Analytik GmbH). The GDA is equipped with a set of photomultipliers which cover the spectral range from 200 to 1200 nm. An additional charge-coupled device (CCD) optic, covering the spectral range between 200 and 800 nm, increases the number of parallel detectable elements. For the GDOES analysis of the LCO thin films, a radio frequency