

# Impedance spectroscopic study of the charge transfer resistance at the interface between a $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ high-voltage cathode film and a $\text{LiNbO}_3$ coating film



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## ARTICLE INFO

### Article history:

Received 9 September 2015

Received in revised form 12 January 2016

Accepted 19 January 2016

Available online 10 February 2016

### Keywords:

Lithium ion batteries

Planar film structures

Electrochemical impedance spectroscopy

## ABSTRACT

We have carried out a basic study on the charge transfer across the interface between  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  (LNMO) high-voltage cathode films and amorphous  $\text{LiNbO}_3$  solid electrolyte films of variable thickness. Planar film structures were prepared on top of Au substrates by means of sol-gel chemistry and spin coating. The film structures were characterized by combining electrochemical impedance spectroscopy (EIS), cross-sectional scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). SEM imaging revealed that the films are dense and contain no detectable pinholes. Nb 3d XPS spectra of the  $\text{LiNbO}_3$  films indicate that Nb is present in a single oxidation state and are in perfect agreement with literature spectra of  $\text{LiNbO}_3$ . Three-electrode EIS was carried out in a half-cell configuration of Au substrate/LNMO/ $\text{LiNbO}_3$ /liquid electrolyte with a reference electrode being placed in the liquid electrolyte. The analysis of the impedance spectra for different  $\text{LiNbO}_3$  film thicknesses enables us to differentiate between (i) the overall charge transfer resistances of both interfaces LNMO/ $\text{LiNbO}_3$  and  $\text{LiNbO}_3$ /liquid electrolyte and (ii) the bulk resistance of the  $\text{LiNbO}_3$  films. We obtain interfacial charge transfer resistances  $< 50 \Omega \text{ cm}^2$ , which is a very promising result in view of the application of such coatings in high-power solid-state batteries.

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## 1. Introduction

The development of all-solid-state lithium ion batteries opens up new opportunities for enhancing the energy density and the safety of battery systems for electromotive applications as well as for the stationary storage of renewable energies [1–5]. In conventional lithium-ion batteries, safety risks are closely related to the usage of volatile and thus flammable liquid electrolytes. In contrast, solid electrolytes are in general non-flammable and exhibit a high thermal stability. For high-power applications, solid electrolytes with high lithium ion conductivity are required. Here, sulfide-based lithium superionic conductors seem to be promising candidates [6,7]. Besides their high lithium ion conductivity, these materials are rather soft, which is beneficial for bringing all-solid state batteries into the desired shape. However, a drawback of sulfide-based electrolytes is their limited oxidation stability, which manifests in reactions with common cathode materials, such as  $\text{LiCoO}_2$  or  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  (LNMO) [1,8,9]. These reactions lead to the formation of highly resistive interfacial layers.

In order to prevent this, cathode materials have been coated with thin layers of stable solid ion conductors. Examples are  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$  and  $\text{LiNbO}_3$  layers [1,4,8,10–13]. While  $\text{Li}^+$  ion transport across such layers is possible, the layers prevent electron transport from the cathode to the battery electrolyte and thus a decomposition of the electrolyte. In particular, amorphous  $\text{LiNbO}_3$  was identified as a promising coating material for cathodes, since it exhibits high oxidation stability and a rather high ionic conductivity (about  $10^{-6} \text{ S/cm}$ ). For instance, a  $\text{LiNbO}_3$ -coated  $\text{LiCoO}_2$  cathode and a highly conductive  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  electrolyte were used in a prototype high-power solid-state lithium ion battery [14].

For further enhancing the energy density of such batteries, it would be desirable to replace  $\text{LiCoO}_2$  by the high-voltage spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ , which intercalates/deintercalates Li at about 4.7 V vs.  $\text{Li}^+/\text{Li}$  [15–17]. For the power density of such batteries, not only the coating layer resistance is relevant, but also the charge transfer resistance at the cathode/coating interface. In principle, electrochemical impedance spectroscopy (EIS) is suitable for differentiating between these resistances. However, if the thickness of the coating layers is in the nanometer range, then this differentiation is very difficult, since coating layer capacitance and cathode/coating interfacial capacitance are similar. Consequently, we prepared LNMO cathode films coated with a 550 nm thick  $\text{LiNbO}_3$  film and carried out EIS measurements on this planar film structure [18].

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Remarkably, we observed only one major semicircle in the impedance spectra. An impedance semicircle originating exclusively from the LiNbO<sub>3</sub> layer could not be identified. This indicates that the interfacial charge transfer impedance and the LiNbO<sub>3</sub> layer impedance do not lead to well-separated semicircles in the Nyquist plot.

In order to study this phenomenon in more detail, we now carried out additional EIS measurements on planar film structure with different thickness of the LiNbO<sub>3</sub> layer ranging from 550 nm to 1.5 μm. The thickness and morphology of the film structure was investigated by means of cross-sectional scanning electron microscopy (SEM) subsequent to a focused ion beam (FIB) cut into the layer structure. In addition, the oxidation state of Nb in the LiNbO<sub>3</sub> layers was characterized by means of X-ray photoelectron spectroscopy (XPS). For the EIS measurements, we used a half-cell configuration Au substrate/LNMO /LiNbO<sub>3</sub>/liquid electrolyte with a reference electrode being placed in the liquid electrolyte. Thus, the resistance of the LiNbO<sub>3</sub> layer as well as the charge transfer resistance of the interfaces LNMO/LiNbO<sub>3</sub> and LiNbO<sub>3</sub>/liquid electrolyte should contribute to the impedance spectra. Remarkably, we again observe only a single major semicircle, even for the film structure with the thickest LiNbO<sub>3</sub> layer. However, an important new finding is that the resistance of the semicircle increases in a linear fashion with increasing thickness of the LiNbO<sub>3</sub> layer and that the conductivity extracted from this linear relation is exactly in line with the well-known ionic conductivity of amorphous LiNbO<sub>3</sub>. This allows us to determine the sum of the charge transfer resistances of the two interfaces by extrapolating the layer thickness to zero. We obtain a value of only 48 Ω cm<sup>2</sup> for the area-specific charge transfer resistance of both interfaces. This result demonstrates that the charge transfer resistance between an LNMO cathode and well-prepared coating layers is sufficiently low for high-power solid-state batteries.

## 2. Experimental

Polished planar gold electrodes were chosen as substrates for the preparation of the planar film structures. The polishing was done by means of 0.25 μm diamond paste and a MD-CHEM polishing pad.

The poly(vinylpyrrolidone) route (PVP route) was applied for the preparation of uniform LNMO precursor solutions. [19] The starting materials for the LNMO precursor solution were PVP powder with an average molecular weight of 25,000 g/mol, Li(CH<sub>3</sub>COO) × 2 H<sub>2</sub>O, Ni(CH<sub>3</sub>COO)<sub>2</sub> × 4 H<sub>2</sub>O, Mn(CH<sub>3</sub>COO)<sub>2</sub> × 4 H<sub>2</sub>O, CH<sub>3</sub>COOH, i-C<sub>3</sub>H<sub>7</sub>OH, H<sub>2</sub>O (molar ratio = 0.94:0.69:0.34:0.94:25.05:28.19:43.85). All starting materials, except for the PVP powder (Roth), were obtained from Aldrich. The powdered starting materials were dissolved in the solvent mixture CH<sub>3</sub>COOH + i-C<sub>3</sub>H<sub>7</sub>OH + H<sub>2</sub>O, heated to 50 °C, and stirred for 6 h to obtain a clear turquoise solution. The sol was then spin coated at a rotational speed of 3000 rpm for 30 s onto the gold substrate to form a gel. Subsequently, the gel film was converted to ceramic oxide by heating to 700 °C for 10 min. The spin coating and heating steps were repeated 12 times. Finally, the films were heated to 800 °C for 60 min in air in order to form crystalline LNMO.

The starting materials for LiNbO<sub>3</sub> were: lithium (Rockwood Lithium, Germany), Nb(C<sub>2</sub>H<sub>5</sub>O)<sub>5</sub> (Alfa Aesar, USA), C<sub>2</sub>H<sub>5</sub>OH (Aldrich), H<sub>2</sub>O (molar ratio = 5.5:5.0:85.0:1.6). Lithium was dissolved in dry ethanol, before Nb(C<sub>2</sub>H<sub>5</sub>O)<sub>5</sub> was added. The solution was stirred for 30 min, then H<sub>2</sub>O was added. Spin coating of the sol onto the LNMO-coated substrates was carried out with a rotation speed of 1800 rpm for 40 s. The formed gel film was then dried at 150 °C for 10 min. The spin coating and heating steps were repeated several times. Finally, the films were heated to 450 °C for 60 min in air in order to form an amorphous LiNbO<sub>3</sub> (LNO) layer. Three different layer structures with three, six and nine LNO layers, respectively, were fabricated.

For the electrochemical measurements, we used a battery-type cell setup (Microcell HC &TSC battery cell, RHD Instruments, Germany) in combination with a Zahner Zennium electrochemical workstation. The measurements were carried out at 293 K in a half-cell configuration

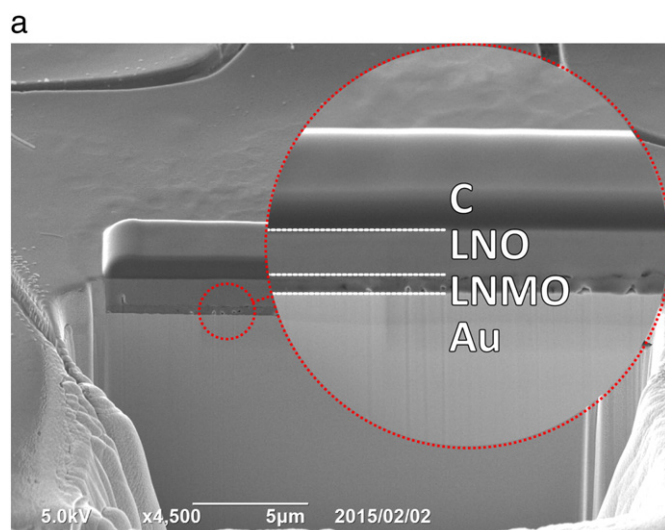


Fig. 1a. Representative cross-sectional SEM image of the Au/LNMO/LNO\_9L structure (covered by a protective carbon layer) after a FIB cut at a viewing angle of 53°.

Au/LNMO/LiNbO<sub>3</sub>/(liquid electrolyte in a separator), with a silver wire pseudo reference electrode being placed in the middle of 10 pieces of Whatman GF/A separators. The liquid electrolyte (LP30, Merck, Germany) consisted of a mixture of dimethyl carbonate (DMC) and ethylene carbonate (EC) (1:1 v/v) containing 1 mol l<sup>-1</sup> LiPF<sub>6</sub>. The cells were subjected to three voltammetric cycles in a voltage range between 3.5 V and 4.9 V with a scanning speed of 1 mV/s, before any other measurements were done. Then EIS measurements were performed at different electrode dc potentials in a frequency range from 500 kHz to 10 mHz using an AC voltage of 10 mV<sub>rms</sub>. Before starting an impedance measurement at a specific DC potential, the cell was first held at this potential for 1 h. The collected impedance data were analyzed using the software suite RelaxIS (RHD Instruments, Germany). After finalizing the electrochemical measurements, the cells were discharged to 3.5 V vs. Li<sup>+</sup>/Li, disassembled and the cathode was rinsed with dimethyl carbonate.

To determine the thickness of the films, cross sections of the samples were prepared and investigated by using a focused (gallium) ion beam (FIB) and a scanning electron microscope (SEM) (dual beam system, JIB 4601F, JEOL, Japan). Ion beam damage in the sample was reduced by depositing a protective carbon layer on the sample surface before carrying

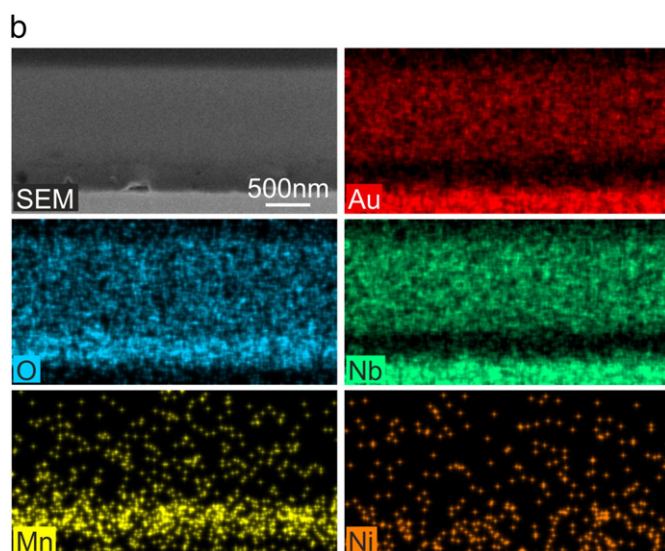


Fig. 1b. EDX elemental distribution maps of the Au/LNMO/LNO\_9L layer structure.

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