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$LiNi_{0.5}Mn_{1.5}O_4$ Thin-Film Cathodes on Gold-Coated Stainless Steel Substrates: Formation of Interlayers and Electrochemical Properties

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ABSTRACT

Thin films of $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) were prepared on gold-coated stainless steel substrates via a poly(vinylpyrrolidone)-based sol-gel process. Films with a thickness in the range of 1 μm were found to exhibit a capacity close to the theoretical one. The formation of interlayers (i) between the LNMO films and the LP30 electrolyte (mixture of dimethyl carbonate (DMC) and ethylene carbonate (EC) (1:1 v/v) containing 1 $mol{\cdot}l^{-1}LiPF_6$) and (ii) between the LNMO films and the gold-coated substrate was studied by means of electrochemical impedance spectroscopy (EIS), time-of-flight secondary-ion mass-spectrometry (ToF-SIMS), and scanning transmission electron microscopy together with energy dispersive X-ray spectroscopy (STEM/EDX). The combination of these methods turns out to be very powerful for understanding the chemical composition and properties of interlayers and for identifying the origin of semicircles in Nyquist impedance plots. At the LNMO/LP30 interface, we observe an interlayer (solid electrolyte interface, SEI) with a thickness of about 50 nm, while at the LNMO/gold interface, a mixed oxide layer with a thickness in the range of 250 nm is found. The mixed oxide layer is caused by diffusion of Cr and Ni from the stainless steel through the gold layer. While the LNMO/LP30 interlayer contributes significantly to the interfacial impedance, the impedance of the LNMO/gold interlayer seems to be negligible, despite its larger thickness.

1. Introduction

Nowadays, lithium-ion batteries are an integral part of our mobile life. They power not only laptops and mobile phones, but also electrical vehicles (EV) are equipped with this type of battery. For EV applications, battery cells with increased gravimetric and, in particular, volumetric energy density have to be developed. Here, all-solid-state batteries are promising [1,2], since compact multilayer battery structures can be prepared. In addition, the usage of non-flammable solid electrolytes improves safety issues.

The cathode materials used in such batteries should exhibit a high capacity and a high redox potential vs. Li^+/Li. A promising material is $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO), which crystallizes in a spinel structure allowing for three-dimensional Li^+ ion transport.[3] LNMO exhibits a redox potential of 4.7 V vs Li^+/Li and a capacity around 130 $mAhg^{-1}$ in composite cathodes and up to 148 $mAhg^{-1}$ as a thin-film material without additives.[4–6] While the mass production of composite battery electrodes with carbon additives and polymeric binders is well established, thin-film electrodes are mostly prepared via costly sputtering techniques. A cheaper alternative is sol-gel chemistry combined with spin or dip coating.[7] Here, liquid organic precursors are coated onto a substrate and are converted to oxides via a heating process. High temperatures of about 700 °C are needed to form crystalline oxides. However, many metallic substrates used as current collectors cannot withstand such high temperatures in air. In basic research, pure gold current collectors were used successfully.[8–10] As a cheaper alternative, we have deposited Au layers onto stainless steel substrates.

The electrochemical performance of cathode material can suffer from SEI formation at the cathode/electrolyte interface as well as from dissolution of metal ions in the liquid electrolyte. In various studies, these effects were investigated for composite LNMO electrodes containing graphite. The formation of metal fluorides on the LNMO surface and of polyethylene carbonate on the graphite surface [11–13] were observed. Caroll *et al.* [14] studied thin-film LNMO cathodes by means of X-ray photoelectron spectroscopy and

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did not detect any SEI formation. In contrast, Mohamedi *et al.* [5] carried out electrochemical impedance spectroscopy (EIS) measurements on thin-film LNMO samples in a three-electrode setup and found an impedance contribution, which they attributed to the impedance of the "solid-liquid interface". However from the EIS results alone, this interpretation is ambiguous. Alternatively, it is thinkable that an interlayer at the LNMO/current collector interface is responsible for the observed process. Recently, Norberg *et al.* [15] produced a binder-free electrode by simply pressing LNMO powder onto an aluminum foil. They investigated dissolution effects by means of fluorescence spectroscopy and found electrolyte decomposition and partial dissolution of the SEI.

All these studies do not yet provide a unique picture about interlayers at the LNMO/electrolyte and at the LNMO/current collector interface, respectively, and about the impact of such interlayers on the electrochemical performance. In this paper, we show that the combination of EIS with time-of-flight secondary-ion mass-spectrometry (ToF-SIMS) and scanning transmission electron microscopy/energy dispersive X-ray spectroscopy (STEM/EDX) provides valuable additional information about the formation and chemical composition of interlayers as well as about the impedance of the interlayers. Thin LNMO films prepared on gold-coated stainless steel substrates were first characterized in-situ in contact to a LP30 electrolyte by means of charge/discharge measurements and EIS. After completing the electrochemical measurements, the cells were disassembled, and the cathode multilayer structure was investigated by means of ToF-SIMS and STEM/EDX. Our results provide clear evidence that interlayers are formed at both interfaces, however with different contributions to the cell impedance.

2. Experimental

The Poly(vinylpyrrolidone) route (PVP route) was used for the preparation of a uniform solution. The starting materials were the following: PVP powder with an average molecular weight of 25,000 g/mol, $Li(CH_3COO)$ x 2 H_2O, $Ni(CH_3COO)_2 \times 4$ H_2O, $Mn(CH_3COO)_2 \times 4$ H_2O, CH_3COOH, *i*-C_3H_7OH, H_2O (molar ratio = 0.94: 0.69: 0.34: 0.94: 25.05: 28.19: 43.85). All starting materials, except the PVP powder (Roth), were obtained from Aldrich. The materials were mixed, heated to 50 °C and stirred for 6 hours to obtain a clear turquoise solution.

The metal substrate was prepared by electrochemical deposition of gold onto chromium-nickel steel (X5CrNi18-10, V2A). Before deposition, the steel surface was mechanically polished (0.25 μm diamond paste, MD-CHEM polishing pad). The electrolytes used for the gold deposition were "WILAPLAT Haftgoldbad AC3 SSF" (Wieland) for the adhesive layer and "WILAPLAT Goldplattierbad 750 SC" (Wieland) for obtaining a smooth surface. The overall thickness of the Au layer was about 2 μm.

Spin coating of the gel onto the substrates was carried out with a rotation speed of 3000 rpm. The gel film was converted to a ceramic oxide by heating to 600 °C in air for 4 minutes. The spin coating and heating steps were repeated 10 and 20 times, respectively. In the following, the samples are denoted by LNMO10L (10-layer film) and LNMO20L (20-layer film). Finally, the films were heated to 700 °C for 8 minutes in air in order to form crystalline LNMO. The films thicknesses were determined by means of cross-sectional STEM. The LNMO20L and LNMO10L films exhibited a thickness around 1 μm and 500 nm, respectively. Samples for powder X-ray diffraction (XRD) (Philipps X'PERT, Cu-Kα) were obtained by heating 1 ml of the sol to 700 °C for 1 h in air.

ToF-SIMS measurements on the LNMO films were carried out using a time-of-flight secondary ion mass spectrometer (IONTOF GmbH). As primary ion source, a Bi^+ ion gun was used in high-current bunched mode (pulsed target current: 0.5 pA). For sputtering, a dual source column sputter gun (DSC-S) with O_2^+ as sputter species was used to produce a sputter crater with a size of 300 μm· 300 μm (sputter current around 200 nA). For analysis, the Bi^+ ions rastered over a 100 μm · 100 μm area in the center of the crater. A low energy electron gun (20 eV) was used for charge compensation. After the ToF-SIMS analysis, the crater depth was determined with a surface profilometer (Sloan Dektak 3ST, Veeco Instruments).

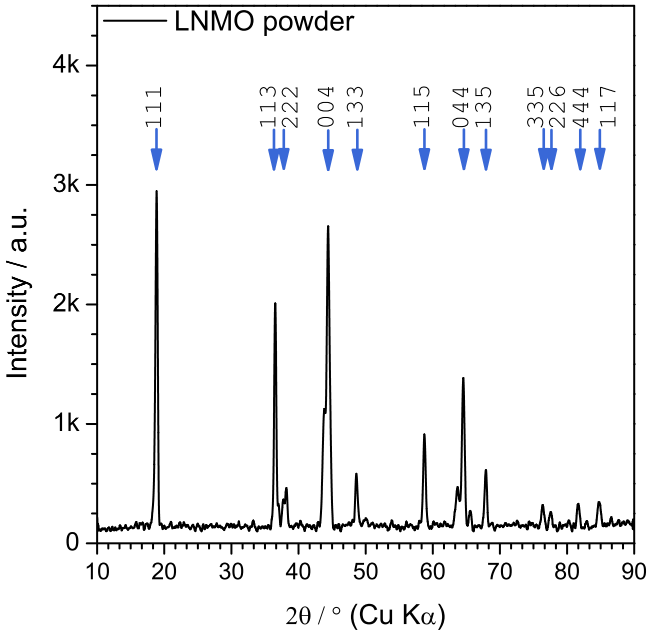

Fig. 1. Powder X-ray diffraction patterns of the $LiNi_{0.5}Mn_{1.5}O_4$ powders obtained via a sol-gel synthesis.

Surface morphology was analyzed by atomic force microscopy (AFM) (NT-MDT Solver P47) used in semi-contact mode.

STEM investigations have been performed on a double Cs corrected (scanning) transmission electron microscope (JEM 2200FS, JEOL) operating at 200 kV and equipped with an EDX detector (XFlash 5000, Bruker). To create cross-section samples thin enough for electron transparency, the lift-out method was used in a dual beam system (JIB 4601F, JEOL) which contains of a focused (gallium) ion beam (FIB) and a scanning electron microscope (SEM). As a protection layer for the FIB lamella a tungsten deposition was used.

Electrochemical measurements on the thin films were carried out at 25 °C in a two-electrode setup with lithium metal as counter electrode. To this end, a BioLogic SP-150 Potentiostat was used. LP30 (Merck) was chosen as electrolyte, and the electrodes were separated by 5 pieces of "Whatman GF/A" filters. Impedance measurements were performed at different dc voltages in a frequency range from 500 kHz to 100 mHz using an ac voltage of 10 mV_{rms}. In order to ensure an equilibrium state of the cell during each EIS measurement, the cell was potentiostatically polarized for 4 h before starting the EIS measurement. The obtained impedance data were analyzed using the home-made software suite "Relax Impedance Spectrum Analysis".

3. Results and Discussion

3.1. XRD and AFM

The XRD examination of the powders obtained from the sol proved the correct crystal structure (Fig. 1.). No significant impurities could be detected.