



Magnesium-based additives for the cathode slurry to enable high voltage application of lithium-ion batteries



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ABSTRACT

The kinetic stabilization of the cathode/electrolyte interface is essential to enhance cycle life and safety of lithium-ion batteries at high voltage application. The addition of only 2 wt.% Mg powder to the cathode slurry were found to significantly increase the cycle life of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂/Li half cells upon cycling to 4.6 V vs. Li/Li⁺, in terms of higher capacity retention, less parasitic reactions and less self-discharge. The presence of dissolved Mg²⁺ cations in the electrolyte during formation of the cell lead to an increased hydrolysis of the conducting salt LiPF₆ and the formation of stable and effective LiPF_xO_y/Mg(PF_xO_y)₂ species on the charged cathode surface.

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1. Introduction

The development of the next generation lithium-ion batteries (LIBs) for implementation in large-scale high power systems operating at higher operation voltages, requires the kinetic stabilization of the cathode/electrolyte interface (CEI) [1]. Compared to research efforts invested on the graphite/electrolyte interface, the understanding of the CEI, in particular at high voltage application, is still rather limited [2–5]. In order to kinetically stabilize the electrolyte as well as the cathode against degradation at high voltages, various approaches have been intensively followed in literature, including the addition of film-forming electrolyte additives, [6–8] surface coatings, [9–14] and host structure doping with heteroatoms [15].

Nowadays, LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ (NMC111) can be regarded as one of the most established cathode materials [1,16,17]. With increasing the charge cut-off potential, an almost linear increase in specific charge and specific energy is obtained [7,18]. However, the increase in charge cut-off potential inevitably results in a more

severe capacity fade [7,16,18] and lower Coulombic efficiency (CE) [19].

We have recently reported that the metal cation Mg²⁺ has a beneficial effect on the cycling performance of NMC111-based cathodes at the elevated upper cut-off potentials of 4.6 V vs. Li/Li⁺ when used as electrolyte additive. Based on the example of Mg (TFSI)₂ we could demonstrate, that the addition of already 1 wt.% (21.4 mmol L⁻¹) to conventional LiPF₆/organic carbonate-based electrolyte leads to the *in situ* formation of an effective CEI layer. The formed CEI layer suppresses further oxidative decomposition of the electrolyte, reduces the overall internal cell impedance and prevents the degradation of the active cathode material during ongoing cycling. Moreover, the use of 1 wt.% Mg(TFSI)₂ as electrolyte additive did not show any adverse effect on the cycling performance of graphite anode. With regard to the mechanistic elucidation, Mg²⁺ cations were found to have a significant impact on the hydrolysis of the conducting salt LiPF₆ and furthermore on the composition of the formed CEI layer [20].

Surface coating of various cathode materials for stabilization of the electrolyte against oxidation at high voltage application and simultaneous suppression of acidic dissolution of transition metals from the cathode material are well known in the literature [2,12]. However, metallic coatings have not been applied to cathode surfaces, in particular taking into account the usually low oxidation potential of non-noble metals [2].

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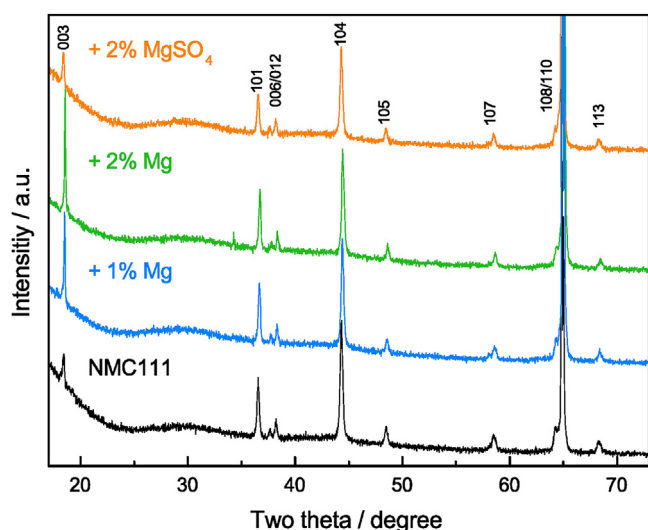


Fig. 1. XRD patterns of pristine NMC111 electrodes without additive, as well as with 1 wt.% Mg powder, 2 wt.% Mg powder and 2 wt.% MgSO₄.

Within the scope of this paper, we report the use of Mg-based species, including Mg powder, MgO and MgSO₄, as additives for the cathode slurry to enable the use of NMC111-based cathodes at the elevated upper cut-off potential of 4.6 V vs. Li/Li⁺. Based on the results obtained with the Mg(TFSI)₂ electrolyte additive in our previous work, the main motivation of this research was to localize the active Mg²⁺ cations directly on the cathode surface [20]. In particular, Mg powder used as cathode slurry additive leads to an increased decomposition of the electrolyte salt LiPF₆ and an associated formation of a kinetically stable CEI layer on the NMC111 surface.

2. Experimental Section

2.1. Electrolyte preparation

Battery grade electrolyte 1 M LiPF₆ in EC:EMC (1:1, by wt.) (LP50 Selectilyte™, BASF) was used as received. The water content was detected to be less than 20 ppm by coulometric Karl-Fischer titration (Mitsubishi CA 200).

2.2. Electrode preparation

The composition of NMC111 electrodes was 85 wt.% NMC111 (BASF), 7 wt.% PVdF (Kynar® 761, Arkema), and 8 wt.% SuperC65

(Imerys). The preparation procedure has been described in detail elsewhere [21]. For the investigation of the Mg-based cathode additives 1–2 wt.% of Mg powder (Riedel-de Haën, 99%), MgO (Carl Roth, 98%) and MgSO₄ (Alfa Aesar, 99.5%) were added to the cathode slurry in place of the active material NMC111. The additives were found to be hardly soluble in the processing solvent. All the investigated electrodes (Ø12 mm) had an active mass loading between 2 and 3 mg cm⁻². The water content of all electrodes was less than 150 ppm as determined by means of Karl-Fischer titration (Coulometer 851 Titrand and furnace 860 KF Thermoprep, both from Metrohm). The exact stoichiometry of the pristine NMC111 electrode was Li_{1.00}(Ni_{1/3}Mn_{1/3}Co_{1/3})_{1.00}O₂ as determined by means of inductively coupled plasma-mass spectrometry (ICP-MS) after dissolving the electrode by microwave assisted acid digestion [22]. X-ray diffraction (XRD) patterns (Fig. 1) were collected from the pristine electrodes on a D8 Advance (Bruker) using Ni filtered Cu K_α (1.54 Å, generator: 40 kV, 40 mA) radiation, equipped with a Lynx-eye detector. XRD studies were carried out in a 2θ range from 17°–90° in continuous mode (step size: ca. 0.02°). The clear splitting of the (006)/(012) pair of reflection in all electrode patterns indicates a well-layered structure of the NMC111. The (108)/(110) doublet is superimposed with the aluminum peak arising from the current collector.”

2.3. Electrochemical investigations and cell setup

Electrochemical investigations were carried out at 20 °C in a climate chamber (Binder) using three-electrode T-type Swagelok® cells. The reference electrode (Ø5 mm) and counter electrode (Ø12 mm) were made of lithium metal (Rockwood Lithium). Glass microfiber filters (GF/D Whatman, Ø13 mm) were used as separator in all experiments. All cells were assembled in an argon-filled glove box (H₂O and O₂ content < 0.1 ppm, MBRAUN). The constant current experiments were performed on a battery tester Series 4000 from MACCOR.

NMC111/Li half cells were cycled according to the following procedure. After three formation cycles with a charge and discharge rate of 30 mA g⁻¹ (corresponding to C/5, when considering a practical specific capacity of 150 mAh g⁻¹), 50 cycles with a charge and discharge rate of 150 mA g⁻¹ (1C) in the potential range from 3.0 V to 4.6 V vs. Li/Li⁺ were performed. In case of the upper cut-off potential of 4.3 V vs. Li/Li⁺, a practical specific capacity of 135 mAh g⁻¹ was considered.

Self-discharge tests were performed at 20 °C according to the following testing protocol. After three formation cycles at C/5, the cells were charged to the upper cut-off potential of 4.6 V vs. Li/Li⁺ with an applied rate of C/5. Subsequently, the cells were stored under open circuit potential (OCP) conditions for 500 h and the potential of the working electrode was recorded.

Table 1
Electrochemical performance summary of the investigated additive-containing electrodes compared to the bare NMC111 electrode in half cells with 1 M LiPF₆ in EC:EMC (1:1, by wt.) electrolyte. Depicted is their electrochemical performance as measured by the specific discharge capacities in the 5th and 50th cycle as well as the capacity retentions at the upper cut-off potentials 4.3 V and 4.6 V vs. Li/Li⁺.

Investigated slurry additives	Upper cut-off potential vs. Li/Li ⁺ /V	5th cycle specific discharge cap. /mAh g ⁻¹	50th cycle specific discharge cap. /mAh g ⁻¹	Cap. retention [50th/5th] /%
No additive	4.3	131.6	129.4	98.3
No additive	4.6	167.9	146.4	87.2
1 wt.% Mg powder	4.6	156.5	152.0	97.1
2 wt.% Mg powder	4.6	147.8	152.5	103.2
2 wt.% MgO	4.6	160.6	147.4	91.8
2 wt.% MgSO ₄	4.6	153.3	154.0	100.5

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