



Water-based LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂-cathodes with good electrochemical performance by use of additives



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ABSTRACT

The manufacture of lithium nickel manganese cobalt oxides (NMC) suspensions for cathodes is typically performed with organic solvents like N-methyl-pyrrolidone (NMP) or N-ethyl-2-pyrrolidone (NEP). It is widely known that these substances are caustic and toxic to reproduction. The utilization of water for the preparation of a cathode suspension is less hazardous and saves costs. Unfortunately NMC alkalizes the water to a very pH value, which leads to a pit corrosion of the aluminum substrate. The development and optimization of water-based NMC suspensions therefore must include investigations on lowering the pH value without deteriorating the electrochemical performance of the material. One option is the addition of amphoteric oxidic additives. This work focusses on Al₂O₃ and SiO₂ as additives and explores their effects on the pH of the suspension and on the substrate corrosion as well as on the electrochemical performance of the NMC-cathode prepared therefrom. Furthermore the impact of the particle sizes of the additives was studied.

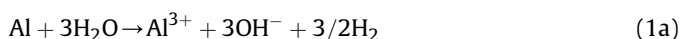
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1. Introduction

Lithium ion batteries (LIBs) are the most widely used energy storage systems in mobile electronic devices. In the course of an increasing need for environmental protection measures and regarding the forecast of a possible worldwide depletion of non-renewable resources in a few decades, the application of LIBs as power units for electro traction in electric vehicles or plug-in hybrids gains more and more attention in the field of battery research and development [1]. However, the manufacturing process of LIBs for automotive applications includes several safety issues. The standard solvent applied for the fabrication of the state-of-the-art cathode Li[Ni_xMn_yCo_{1-x-y}]O₂ (NMC) is N-methyl pyrrolidone (NMP), which is a toxic and teratogenic liquid. One approach to improve the safety and the environmental sustainability of the manufacturing process is therefore to substitute this suspension medium by water. The usage of water instead of NMP would also notably lower the production costs, since the price for 1 L of NMP is hundred times as high as the price of commercially available demineralized water.

Within the last few years a number of publications report the application of water soluble binders for water-based cathode suspensions [1–10]. In fact, water-based processing of NMC implicates obstacles, which are unusual in the field of the preparation of cathode suspensions. NMCs are oxides of non-noble metals, which in contact with water strongly alkalize the solvent with unfavorable consequences for the aluminum substrate.

When metallic aluminum is exposed to ambient oxygen or water, a passivation layer composed of Al₂O₃ is generated on the surface. This layer is stable towards moisture or water, provided that the pH value of the medium resides in a range between 4.0 and 8.5 [12]. At a high pH value, dissolution of the passivation layer sets in, stripping it and converting it into hardly soluble Al(OH)₃ [12], which at even higher pH is transformed into soluble tetrahydroxaluminate [Al(OH)₄]⁻. The metallic aluminum is exposed to water and reduces the protons of H₂O to hydrogen according to Equation (1a)



The corrosion is mainly superficial, affecting the entire area of exposure. However, the collector foil applied in the electrode manufacture usually contains intermetallic impurities like Si, Fe, Cu, Zn, Ga, Mn, Mg, V [8]. They create very small local galvanic elements with the surrounding aluminum after contact with the

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alkaline solution [8,13,14]. These impurities are randomly distributed within the aluminum bulk and work as the cathode of the galvanic microelement. After pitting corrosion occurred, they are the center of small cavities with a diameter in the range of several micrometers [8,13].

Corrosion of the aluminum substrate can affect the cell performance, since it affects the interface between the current collector and the coating, e.g. by creating a passivation layer between them [9].

Current literature mainly suggests two approaches to overcome this obstacle, which are (1) to decrease the pH of the suspension to a suitable value by the use of acidic additives [10,11] and (2) to interpose a mechanical barrier hindering contact of OH⁻ with the surface [9,10].

For the first approach, formic acid and phosphoric acid were added to the NMC suspension as a pH regulating agent [10,11]. An ICP analysis of a formic acid-water solution, which was in contact with NMC, revealed pronounced leaching of transition metals out of the NMC structure, whereas the amount of leached metal increases with increasing acid concentration [10,11]. However, the addition of the same concentration of phosphoric acid did not lead to significant transition metal dissolution in the aqueous medium. The authors assume that the dissolved metals form hardly soluble phosphates and hydrogen phosphates which precipitate on the particle surface and form a protective layer [11]. The authors could not detect any corrosion products at the inner coating layer after applying formic or phosphoric acid.

As a second approach, a 2–5 μm thin water-based carbon film was cast onto the aluminum substrate, which successfully protected the current collector from being corroded. With this method the reversible discharge capacity of an NMC electrode at 1C rate is increased from 80 mAh g⁻¹ to 110 mAh g⁻¹ [9,10].

The application of a water-based carbon layer as a barrier is a suitable solution for small lab scale electrodes. However, application of water-based carbon coatings with the thickness of a few μm and a homogeneously distributed mass loading in large scale dimensions creates an additional challenge in terms of feasibility. Moreover, it increases the electrode thickness without providing additional capacity and therefore with lowers the energy density of a multilayer custom cell.

Besides the use of an acidic additive and a carbonaceous protection layer, a third option, the addition of amphoteric non-transition metal oxides to the water-based suspension was reported [15]. According to the authors' theory, the oxides serve as H₂O scavengers and therefore avoid the formation of OH⁻ as given in equation (1b):



Besides MgO, also SiO₂, Al₂O₃, In₂O₃, and SnO₂ are assumed to scavenge H₂O [15]. However, no electrochemical data has been reported so far, which would provide insight into the influence of the use of oxidic additives in cathode coatings.

In this work, Al₂O₃ and SiO₂ with different particle sizes are applied as additives. Their effects on the electrochemical performance of water-based NMC (111) cathodes as well as on the applied substrate are studied depending on their content in the electrode suspension. Electrodes with mass loadings of 12 mg cm⁻² to 20 mg cm⁻² were prepared. This allows a comparison to industrial electrodes relevant for high energy cells. To the best of our knowledge, electrochemical data of water-based NMC electrodes with such high mass loadings have not been reported so far.

2. Experimental part

To examine the extent of Li leaching and transition metal dissolution, 50 g of fresh NMC powder are mixed with 50 g of water to yield a 50 wt% aqueous suspension. The suspension is stirred for 2 h at room temperature, before filtering and subjecting the supernatant to ICP-OES analysis. Analog investigations are performed with additive containing suspensions. In the case of γ-Al₂O₃, 2.3 g of the oxide is added to 47.7 g of NMC, corresponding to 4.6 wt% related to the NMC. In the case of SiO₂, 1 g of oxide is added to 49 g NMC, corresponding to 2 wt%.

The chemical analysis of the solutions and the powders is conducted via inductively coupled plasma optical emission spectrometry (ICP-OES) using a spectrometer from SPECTRO.

For the suspension preparation a DISPERMAT[®] LC 30 dissolver from VMA-Getzmann with 250 ml double-walled vessel and a 45 mm dissolver disk is used. The water-based suspensions contain the active material (NMC (111), Toda Kogyo Europe), carbon black as conductive agent (SuperP, Imerys Graphite & Carbon) and water soluble binder (Na-Carboxymethyl cellulose (Na-CMC), Dow Wolff Cellulosics GmbH and a 50 wt% emulsion of styrene butadiene rubber (SBR) in water, Styron Europe GmbH). The applied additives were Al₂O₃ (d₅₀ ≤ 15 μm, Merck KGaA and d₉₀ ≤ 5 μm, Sasol Germany GmbH) and SiO₂ (particle size distribution of 35–70 μm, Amicon Corporation). The SiO₂ is ball-milled and sieved to obtain a value of d₅₀ ≤ 12 μm for the purpose of comparison. Furthermore SiO₂ d₉₀ ≤ 5 μm (Sigma Aldrich) is used.

A Mastersizer Micro from Malvern Instruments Ltd is used for measuring the particle size distribution of the additive ball milled in-house.

The basic formulation of the suspension free of additives related to the dry mass is 94 wt% NMC(111), 3 wt% Na-CMC, 2 wt% of SuperP and 1 wt% of SBR. Every percent of additive substituted one percent of active material, whereas carbon black and binder ratios were kept constant.

The powders are mixed thoroughly by stirring with a spatula. Afterwards water is added in 20 ml steps. After every step, the obtained paste is homogenized with the dissolver to obtain a smooth suspension free of agglomerates. After reaching a solid matter content of around 60%, the suspension is stirred for 1.5 h at 2000 r.p.m. Before the addition of SBR in form of a 40 wt% aqueous emulsion of the polymerized rubber, the rotational speed is decreased to 400 r.p.m. because SBR is sensitive to too high shearing forces, thus the final mixing process is conducted with reduced energy application. After the homogenization of the suspension containing all ingredients, it is diluted to a solid matter content of 50% to obtain a fluent suspension which can be well coated onto the substrate. The pH values of the final slurries are recorded with a pH meter.

For the preparation with organic solvent a binder solution of 5 wt% polyvinylidene fluoride (PVdF, Solef) in N-Methyl-2-pyrrolidone (NMP, Honeywell) was prepared, to which the carbon black and the active material are added stepwise and are homogenized intensely to obtain a smooth and shiny paste free of agglomerates. The paste is finally diluted with NMP to obtain a solid matter content of around 70 wt% and a viscosity appropriate for good process ability in the coating procedure. The formulation of the final dry coating is 93 wt% active material, 2 wt% carbon black, 2 wt% graphite (SFG6L, Imerys) and 3 wt% PVdF.

Each suspension is cast onto aluminum foil (alloy 1085, 20 μm thickness, Korff) and coated with a doctor blade using a tabletop coater from Erichsen with a vacuum suction plate. Afterwards the tapes are dried on a hotplate at 60 °C for 2 h followed by 80 °C overnight. The tapes are roll-pressed with a tabletop calender (Sumet Messtechnik) applying a linear load of 23 N mm⁻¹ and a

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