

Processing of water-based $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ pastes for manufacturing lithium ion battery cathodes

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Abstract. In order to meet the demand for more ecological and economic fabrication of lithium ion (Li-ion) batteries, water is considered as an alternative solvent for electrode paste preparation. In this study, we report on the feasibility of water-based processing of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ -based pastes for manufacturing cathode electrodes. The influence of the total solid content, the amount of conductive agent and binder materials on paste rheology and the final electrode properties was investigated. Suitable paste formulations which enable favourable paste flow behaviour, appropriate electrode properties and good electrochemical performance have been found. Results show that a substitution of the conventional organic solvent-based manufacturing route for $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ cathodes by water-based processing exhibits a promising way to realise Li-ion batteries with comparable electrochemical behaviour, while avoiding toxic processing aids and reducing overall manufacturing costs.

Keywords. Lithium ion battery; processing; coating; paste; rheology; electrochemical properties.

1. Introduction

N-Methyl-2-pyrrolidone (NMP) represents the solvent of choice for homogeneous and stable pastes applied for the manufacturing of lithium ion (Li-ion) battery electrodes (Li and Daniel *et al* 2011a). It is known for its good solubility for polyvinylidene fluoride (PVDF), which usually acts as a standard binder due to its good dispersion quality and high adhesion strength of the electrodes to the current collector foil. However, NMP is also known for its toxicity and high costs. In recent times, water has gained attention as an alternative solvent for electrode paste preparation due to its significantly lower material costs (Orlenius *et al* 2012; Li and Wang 2013; Xu *et al* 2013). Considering environmental issues such as work protection, recycling and waste gas treatment, the economic difference between NMP-based and aqueous processing has been rising dramatically (Muthu and Battaglini 2009). By rule of thumb, water-based pastes are 10–20 times cheaper than NMP-based ones (Li *et al* 2013). For fabrication of anodes, the performance and suitability of water-based pastes were already successfully evaluated (Lee *et al* 2006; Hochgatterer *et al* 2008) and established for large-scale manufacturing. In contrast, water-based processing of cathode pastes involves some concerns about its feasibility for use in industrial-scale battery manufacturing (Li *et al* 2011b; Orlenius *et al* 2012). There are still many open issues and drawbacks of water-based cathode pastes such as agglomeration effects and poor paste homogeneity as well as ageing of active materials upon exposure to water

(Kim *et al* 2006; Zhang *et al* 2011). Thus, up to now only a limited number of studies about water-based pastes for Li-ion cathode production have been reported, wherein primarily lithium iron phosphate (LiFePO_4 , LFP) and lithium cobalt oxide (LiCoO_2 , LCO) as active materials were investigated (Li *et al* 2005; Li *et al* 2006; Guerfi *et al* 2007; Li *et al* 2007; Lee *et al* 2007; Lee *et al* 2008; Cai *et al* 2009; Porcher *et al* 2009; Lux *et al* 2010; Böckenfeld *et al* 2011; Li *et al* 2011a; Jabbour *et al* 2012; Li and Lin 2012; Li *et al* 2012; Orlenius *et al* 2012; Zheng *et al* 2012; Li and Wang 2013; Li *et al* 2013; Xu *et al* 2013). There is a considerable lack of knowledge and experience regarding the usability of water-based lithium nickel manganese cobalt oxide ($\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$, NMC) pastes for cathode fabrication (Li *et al* 2007). Besides lithium nickel cobalt aluminium oxide ($\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$, NCA), NMC is widely used in automotive battery production (Fergus 2010), as the latter shows good capacity, improved rate capability and pulse powder density (Mulder *et al* 2013). Therefore, aqueous processing of cathode pastes based on NMC exhibits a promising prospect for economic as well as ecological manufacturing of Li-ion batteries for electromobility and stationary applications.

In this study, we investigated the applicability of NMC for preparation of aqueous cathode pastes. Material- and process-related parameters such as total solid content (TSC) and inactive materials were varied and the influence on paste rheology, coating quality and cell performance was measured, respectively. Finally, the performance of the cells based on aqueous processed cathodes was compared with conventional NMP-based electrodes.

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2. Experimental

Aqueous pastes were prepared using a laboratory vacuum dissolver (Dispermat, VMA-Getzmann, Germany). NMC powder with a mean particle size of $9.6 \mu\text{m}$ (NM-3100, Toda, Japan) was used as cathode material. Slurry formulations were prepared by blending the NMC powder with 3 wt%[#] (carbon black CB; Super C65, Timcal, Switzerland) as a conductive aid, 2 wt%[#] sodium carboxymethyl cellulose (CMC) with a degree of substitution (DS) 0.91 (Walocel CRT 2000 PA, Dow Wolff Cellulosics, Germany) as a thickening agent and 3 wt%[#] water-based fluor-acrylic copolymer (ACP) binder (TRD202A, JSR Corporation, Japan). The reference TSC of the pastes was set as 21 vol%. The rheological properties of the pastes were analysed with a rotational rheometer (MCR 300, Anton-Paar, Austria). The technique of electroacoustic spectroscopy (DT-1200, Dispersion Technology, USA) was used to measure the zeta-potential of the dispersions. For this, aqueous CB and NMC dispersions with a solids loading of 1 wt% and 10 wt%, respectively, were prepared and measured. A continuous doctor blade coating device (KTF-S, Mathis, Switzerland) with two heating zones, each with 1 m length, was used for coating of the pastes on the aluminium foil. The active mass loading of the cathodes was about 11 mg/cm^2 . The coating quality was evaluated by measuring the averaged surface roughness height R_z (DIN 4768 1990) of the electrodes using a non-contact metrological surface measuring system (MicroProf, Fries Research & Technology, Germany). The coating porosity was calculated by determining the coating weight per unit area and the coating height. Compaction of the coated electrodes was performed by calendaring at $60 \text{ }^\circ\text{C}$ (GKL 200, Saueressig, Germany). Before assembling was performed in a dry room (dew point $-50 \text{ }^\circ\text{C}$), the electrode sheets were dried under vacuum for 12 h at $130 \text{ }^\circ\text{C}$. Pouch cells were prepared with $50 \times 50 \text{ mm}^2$ cathode sizes, graphite anode, ceramic coated separator and a standard electrolyte (LP30, Merck, Germany). The rate capability of the pouch cells was tested in the voltage range of 3.0–4.2 V at a constant temperature ($20 \text{ }^\circ\text{C}$). After two formation cycles with C/20, the cycling tests were performed with charge and discharge rates in constant current CC-mode with C/2, C, 2C and 3C, respectively (nominal capacity: 183 mAh/g) using a custom-made battery cyclers.

3. Results and discussion

3.1 Rheological properties of water-based NMC pastes

The processability of paste formulations is mainly determined and characterised by their flow behaviour. For a given active material, it can be altered by varying the type and amount of inactive materials as well as by the TSC of the

pastes. A viscosity range of 1–10 Pa·s (relating to a shear rate of 40s) was defined as an appropriate process window for processable pastes. This process window was determined empirically for doctor blade technique. It mainly depends on the applied coating process and has to be addressed specifically, when the coating technique changes (e.g., from doctor blade to the slot-die coating technique that is typically used for industrial-scale manufacturing of electrodes). It was found that the paste rheology is significantly affected by the variation in the amounts of CMC and CB. An increasing amount of the thickening agent CMC is accompanied by a distinct viscosity increase and pronounced shear thinning behaviour (figure 1). For low CMC amounts (0.5 wt%), it was possible to prepare pastes with solid contents up to 50 vol% within the processing range of 1–10 Pa·s, whereas for increasing amounts of CMC up to 2 wt% processable pastes could be prepared only for lower TSCs at 20–30 vol% (figure 2). A similar effect on the flow behaviour was observed for increasing amount of CB that also results in an increase of viscosity. However, the formation of a pronounced yield point becomes obvious after adding CB (figure 3). Considering the paste process window (1–10 Pa·s)

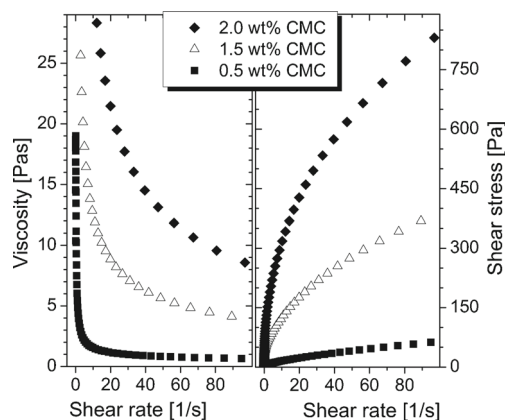


Figure 1. Exemplary viscosity and flow curves of aqueous NMC pastes with 32 vol% total solid content and varying CMC amounts.

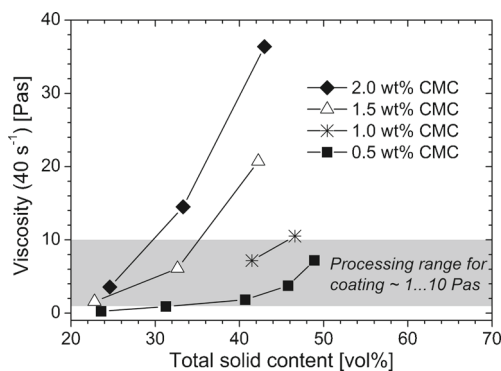


Figure 2. Viscosity of aqueous NMC pastes with varying CMC amounts in dependency on the total solid content of the paste formulations.

[#]Based on NMC weight.

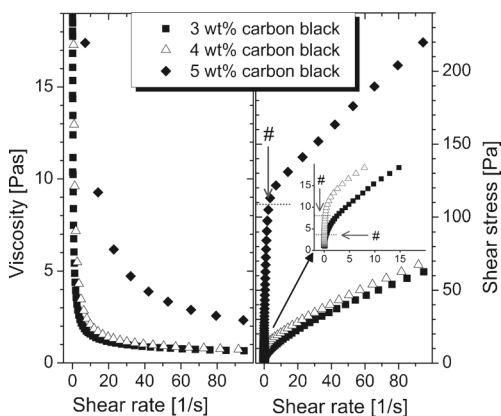


Figure 3. Exemplary viscosity and flow curves of aqueous NMC pastes with 32 vol% total solid content and varying CB amounts (yield points are marked as #).

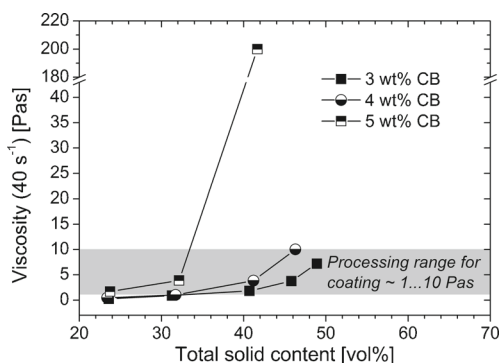


Figure 4. Viscosity of aqueous NMC pastes with varying CB amounts in dependency on the total solid content of paste formulations.

processable formulations could be prepared only with CB amounts upto 4 wt% (figure 4).

As a thickening agent, CMC has the function to adjust the viscosity of the paste. However, CMC also acts as a binder that glues the particles together and increases the adhesion of the dried electrode on the current collector foil. Finally, CMC has stabilising potential as it suppresses the reagglomeration of the dispersed CB particles. Unfortunately, due to the very distinct effect on the viscosity of the paste, the acceptable amount of CMC is limited. Low CMC amounts cause insufficient adhesion of the coating on the current collector foil (Drofenik *et al* 2003), while the amount that would be required for sufficient adhesion might cause high viscosity beyond the processing range (figure 2). To compensate this problem, different binders can be added, e.g., styrene butadiene rubber (SBR) or acrylic copolymer ACP dispersions, which allow improvement of the adhesion and mechanical strength of the coating without strongly affecting the paste viscosity (Buqa *et al* 2006; Guerfi *et al* 2007; Lee *et al* 2007; Li and Wang 2013).

The large particle size of the NMC powder promotes undesired sedimentation. In order to prevent segregation of

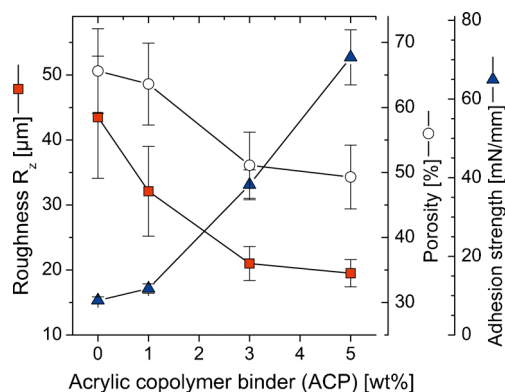


Figure 5. Surface roughness, porosity and adhesion strength of electrodes in dependency on the amount of ACP (paste receipt for 21 vol% TSC, 3 wt% CB and 2 wt% CMC based on 100 g NMC).

the particles, a weakly coagulated state of the slurry is favourable. This state is characterised by a gel-like behaviour with a distinctive yield point and extensive shear thinning behaviour at relatively low solids loading (volume fraction $\ll 60\%$) (Lewis 2000). Suitable systems provide sufficient attraction between the particles to stabilise the dispersion against the influence of gravity, but are able to become fluidised at sufficiently low-shear rates during the coating process. Using only CMC or SBR or ACP, it is not possible to induce a yield point in the NMC dispersion (figure 1). For the formation of a gel network the CB particles play a major role, which are primarily added for increasing the electrical conductivity of the electrodes, as the formation of a particulate based gel can take place even if no binder is added to the slurry (Bauer and Nötzel 2013).

3.2 Electrode properties

It is known that the type of CMC (Lee *et al* 2005b) as well as the mixing ratio of SBR to CMC might affect the dispersion stability (Lee *et al* 2005a; Li and Wang 2013). According to this, for CMC types with a DS < 1 and increasing amounts of SBR or ACP an improvement in dispersion stability is expected. These findings could be confirmed in our study with pastes exhibiting a comparably low TSC of 21 vol% and containing a fluoric ACP binder. By measuring the averaged surface roughness height R_z of the dried electrodes a gradual improvement of the surface quality with an increasing amount of ACP was observed (figure 5). This correlates well with the evolution of coating porosity, which decreases in a similar way for increasing amounts of ACP. This is seen as a result of an improved stabilisation of the powder particles, which leads to better particle packaging after drying and could be verified by measuring the zeta-potential of aqueous CB as well as NMC dispersions. In case of addition of CMC to the particle suspensions, the negative charge density and the magnitude of the zeta-potential of CB (figure 6) as well as NMC (figure 7) increased by the specific adsorption of the CMC on the particle surface, as CMC

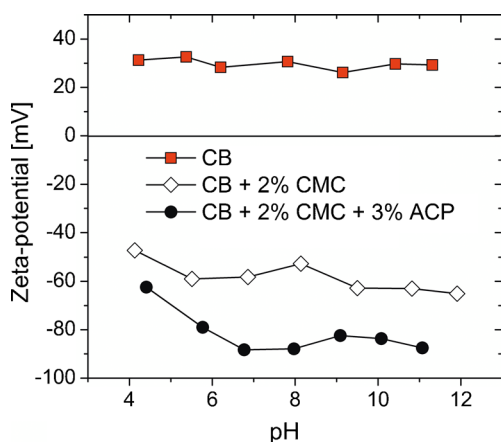


Figure 6. pH-dependent zeta-potentials of 1 wt% aqueous CB dispersions in the presence of 2% CMC and 3% ACP.

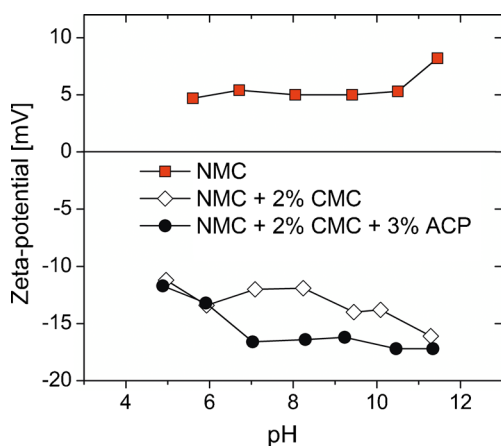


Figure 7. pH-dependent zeta-potentials of 10 wt% aqueous NMC dispersions in the presence of 2% CMC and 3% ACP.

dissociates in water and, thus, is able to carry anionic charges (Li and Lin 2012) originating from the carboxymethyl side-groups of the CMC molecules (Lee *et al* 2005a). Admixing ACP to the CB–CMC and NMC–CMC systems, respectively, causes a further increase of the zeta-potential magnitude (figures 6 and 7). This might be explained by the repulsive force between the carboxymethyl side-groups of the CMC and the carboxylic surface groups in the ACP resulting in an increased near-surface fraction of carboxylate sites of the CMC that is adsorbed on the CB and NMC particles, respectively (Lee *et al* 2005a). As seen in the literature (Liu *et al* 2005; Buqa *et al* 2006), the adhesion strength of the electrodes also significantly improved by the addition of the ACP binder (figure 5).

In the case of pastes with a high TSC of 42 vol%, an unfavourable time-dependent change of flow behaviour was observed. A gradual increase in viscosity and shear stress occurred a few minutes after adding ACP to the premixed paste (figure 8). This behaviour affected the coating quality of the electrode sheets detrimentally and could also be confirmed with surface roughness measurements. During the

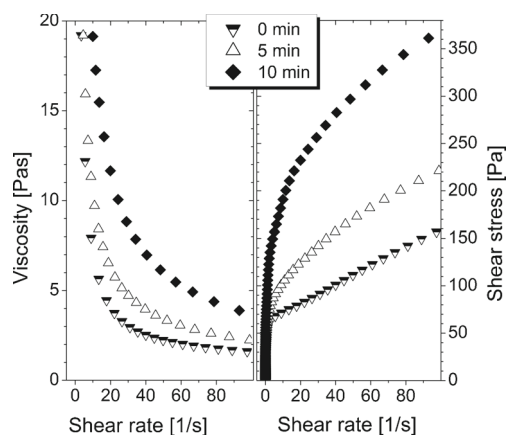


Figure 8. Flow curves of instable NMC pastes with high TSC exhibiting a pronounced time-dependent increase of viscosity and shear stress.

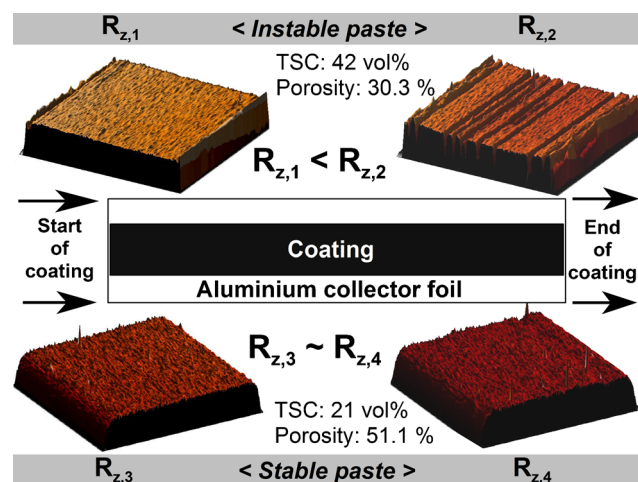


Figure 9. Surface roughness of cathodes fabricated with instable (time-dependent flow behaviour at high TSC) and stable NMC pastes (no time-dependent flow behaviour at low TSC).

coating process the averaged roughness height of the electrodes prepared from the basic paste formulation with a TSC of 42 vol% increased upto 20% (figure 9). Also, remarkable groove lines appeared with the ongoing coating process as a result of the formation of large agglomerates, which got caught in the gap of the coating device (gap height 150 μm). By contrast, electrodes prepared with the identical formulation but a lower TSC of 21 vol% showed no time-dependent increase of viscosity and shear stress and also no grooves. Compared to the electrodes with TSC of 42 vol% the roughness values of the electrodes with TSC of 21 vol% remain constant during the entire coating process (figure 9). From this, it is obvious that, in the case of high TSC, the addition of the ACP binder resulted in instability in the paste. This leads to the assumption that in the case of high TSC, particle–particle interactions are affected by admixing the ACP dispersion, which exhibits a polymer particle size at around 200 nm. It is very likely that the latex particles interact with

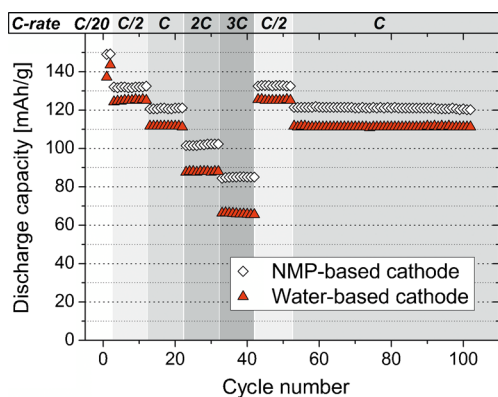


Figure 10. Cycling performance of NMP-based cathodes compared to water-based cathodes.

the CB primary particles and aggregates, as the applied CB exhibits a median primary particle size of 32 nm and an average aggregate size of 150 nm (Spahr *et al* 2011). There are probably further additives within the ACP latex dispersion, which are likely to interact with CMC, CB, as well as with NMC and might have caused the observed time-dependent thickening behaviour. It seems to be easily induced, when high powder packing densities are available. However, in the case of low TSC the effect of the admixed ACP binder on paste thickening seems to be not relevant. Practically, pastes with high TSC are desired in order to reduce the energy input and the probability of crack occurrence during the drying step. However, our results show that there are limitations, as the formulation of a stable and homogeneous paste represents the main prerequisite for manufacturing of reliable and precise cathodes for Li-ion batteries.

3.3 Cycling performance

The cycling performance of the water-based NMC cathodes investigated in this study is comparable to conventionally fabricated NMP-based cathodes with similar paste formulations (figure 10). However, the absolute value of the discharge capacity slightly suffers, which is ascribed to the exposure of NMC to water during paste preparation. In a comprehensive study (Zhang *et al* 2011) the evidence is provided that the surface of NMC particles is subjected to delithiation, when exposed to water even for a short time (e.g., some minutes). A surface layer of lithium carbonate (Li_2CO_3) with a thickness of upto 10 nm is formed rapidly. As a result of this, the capacity is reduced by the amount of lithium in the NMC particles that has become inactivated in the Li_2CO_3 surface layer. Comparing the cycling performance of cells made of pristine (no exposure to water) and aged NMC powder, respectively, the capacity loss of cells fabricated with aged powder was reported to be about 10 mAh/g at a C-rate of 1C. Also, a significant capacity fading was reported after ageing already within the first 30 cycles. A similar capacity fading of aqueous processed NMC cathodes is reported elsewhere (Li *et al* 2007). A capacity

loss of about 10 mAh/g is consistent with our results, when the cycling performance of NMP-based cathodes is compared with aqueous processed ones (figure 10). By contrast, capacity fading could not be observed in our study even after 100 cycles, which is likely to be ascribed to (i) a good compatibility of the active and inactive materials, (ii) a stable manufacturing process from raw materials to final pouch cells and (iii) the use of graphite counter electrodes, which are practically used in large-scale Li-ion battery production.

4. Conclusions

Aqueous $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC)-based cathode pastes were prepared and studied regarding their rheological properties and coating quality. By adjusting the TSC of the pastes as well as the amount of conductive agent and binder materials, appropriate formulations could be defined in order to obtain stable and homogeneous pastes, which are suitable for coating. Using 3 wt% CB, 2 wt% sodium CMC and 3 wt% fluor-ACP binder (percentages based on NMC) with a TSC of 21 vol% yielded in processable pastes with proper flow behaviour and final electrode properties. Higher amounts of CMC and CB usually result in increased viscosity, and, in the case of CB, also result in the formation of a distinctive yield point. Both, an increase in viscosity and the formation of a distinctive yield point, limit the achievable TSC of the pastes. By increasing the amount of the ACP binder favourable electrode properties were obtained, such as an improvement of the adhesion strength of the coating on the current collector foil and an enhanced coating surface quality as well as compaction behaviour. However, the ACP binder was found to have a detrimental effect on paste stability in case of higher TSCs, as a time-dependent thickening behaviour could be observed. The electrochemical properties of the NMC cathodes investigated in this study are comparable to conventionally fabricated cathodes, which were fabricated by applying similar paste formulations and using the organic and toxic solvent NMP. However, the magnitude of the discharge capacity slightly suffers, when comparing water-based with NMP-based cathodes (ca. 10 mAh/g at a discharge rate of 1C). This is ascribed to the hydrolysis and ageing of NMC, when exposed to water during paste preparation. In order to prevent this capacity loss due to the interaction of NMC with water, it is proposed to introduce a protection layer against water on NMC particles.

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