Article

Ageing and Water-Based Processing of LiFeMnPO_4 Secondary Agglomerates and Its Effects on Electrochemical Characteristics

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Abstract: LiFeMnPO_4 secondary agglomerates have been aged under different temperature and moisture conditions. The aged and pristine powder samples were then processed to water- and solvent-based cathodes. Structural studies by means of neutron and X-ray diffraction revealed that neither ageing nor water-based processing significantly modified the crystal structure of LiFeMnPO_4 secondary agglomerates. Electrochemical characterization was carried out with full-cells. It was found that long-term cycling is similar independent of the solvent used for slurry preparation. Full-cells assembled with water-based cathodes show a better C-rate capability due to a more homogeneous distribution of cathode constituents compared to solvent-based ones. In no case was any negative effect of initial active material ageing on the electrochemical performance found. During ageing and processing, LiFeMnPO_4 is effectively protected by carbon coating and water can be completely removed by drying since it is only reversibly bound. This contribution shows that LiFeMnPO_4 secondary agglomerates allow simplified active material handling and have a high potential for sustainable water-based electrode manufacturing.

Keywords: lithium ion battery; LiFeMnPO_4 ; ageing; water-based processing; sustainable battery production

1. Introduction

Since the phospho-olivine LiFePO_4 has been considered to be an excellent active material for lithium ion batteries in 1997, it has been studied intensively [1]. In comparison to spinel-type oxides like lithium cobalt oxide (LCO) it features very good safety characteristics in terms of thermal runaway [2]. Besides operational safety it provides very good long-term cycling, cost efficiency and is environmentally friendly due to the absence of metals like cobalt [3,4].

By partial substitution of Fe by Mn atoms, the isostructural $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$ is obtained. In addition to the above mentioned advantages of LiFePO_4 , it provides a higher cell voltage due to the presence of Mn. The influence of Mn in $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$ is visible in the typical charge and discharge curve of $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$. In contrast to LiFePO_4 , two voltage plateaus can be observed which correspond to the redox couples $\text{Fe}^{2+}/\text{Fe}^{3+}$ at approximately 3.6 V vs. Li/Li^+ and $\text{Mn}^{2+}/\text{Mn}^{3+}$ at approximately 4.1 V vs. Li/Li^+ . High reversible capacities of up to $164 \text{ mAh}\cdot\text{g}^{-1}$ are reachable over a wide range of Mn content [5–9].

Despite all of the advantages, LiFePO_4 and $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$ have been reported to be sensitive to moisture and water. Direct contact to water causes a loss of active lithium from the olivine structure under formation of Li_3PO_4 on the particle surface and thus reduces the material's energy density [10].

Exposure to air and moisture causes similar effects and a disordered crystal structure as it was investigated for LiFePO_4 [11,12] and it is expected to be similar for $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$. In addition, $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$ is known for the problem of manganese dissolution like other Mn-containing cathode materials (e.g., LMNO) as well [13]. For $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$, a relation between the presence of traces of water in the battery and manganese dissolution has been found [14].

These facts indicate that $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$ has to be treated with care in the production process of batteries and that an environmentally friendly water-based cathode production tends to result in poor electrochemical characteristics.

However, water-based cathodes could significantly improve a battery's ecobalance by avoiding solvents such as *N*-methyl-2-pyrrolidone (NMP), which are hazardous to the environment and health [15,16]. During cathode drying, NMP has to be removed from the exhaust by downstream VOC-combustors or recovered by condensation. These exhaust treatment technologies cause high costs of equipment acquisition and operation. The flammability of NMP vapor furthermore requires several safety measures to protect employees inside the facilities [17]. These characteristics of organic solvents such as NMP and the related necessary safety measures to protect the environment and humans underline the economic and ecological significance of good working water-based processes in battery production.

Motivated by the promising effects of simplified material handling and water-based cathode manufacturing, we have designed a parameter setup to evaluate these effects. In this experiment we have studied how $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$ is affected by different unfavorable storage conditions and water-based slurry processing and quantified its effects by comparison with pristine $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$ powder samples and solvent-based cathode production.

2. Experimental

2.1. Sample Ageing and Cell Preparation

For this experiment a development-grade carbon coated $\text{LiFe}_{0.33}\text{Mn}_{0.67}\text{PO}_4$ secondary agglomerates (referred to as LFMP) have been used. Samples of the active material had been stored under two different conditions. The first represents ambient conditions at 23 °C and 35% relative humidity (rh) and the second a warm and moist environment at 40 °C and 100% rh to represent harsh ageing conditions or use in very humid, tropical environments. All samples were stored dust protected for 21 days. Ageing at 40 °C and 100% rh was realized by using a water-filled desiccator stored in an oven (Binder, Tuttlingen, Germany). During ageing the samples were stirred several times to provide equal contact to the surrounding atmosphere.

The aged powder samples and a pristine sample have then been processed as water-based and solvent-based slurries resulting in a total of 6 different slurries with a solid fraction of 50.5%.

Water-based slurries were prepared by dissolving carboxymethyl cellulose (CMC MAC 200 HC, Sunrose) in water. The obtained CMC-solution was then mixed with LFMP, carbon black (Super C65, TIMCAL, Bironico, Switzerland) and SBR (BM-400B, ZEON, Tokyo, Japan). All components were dispersed in a dissolver (DISPERMAT, VMA Getzmann GmbH, Reichshof, Germany) for 20 min at 3000 rpm. The final solid content fractions were 88.6 wt % LFMP, 6.0 wt % carbon black, 3.6 wt % SBR and 1.8 wt % CMC.

For solvent-based slurries PVDF (Solef 5130, Solvay, Brussels, Belgium) was dissolved in *N*-methyl-2-pyrrolidone (NMP, Roth, Karlsruhe, Germany). The PVDF-Solution was then mixed with LFMP and carbon black. The components were dispersed analogously as the water-based slurries in the dissolver. The final solid content fractions were 88.0 wt % LFMP, 6.0 wt % PVDF and 6.0 wt % carbon black.

All slurries were degassed in a planetary centrifugal mixer (THINKY, Tokyo, Japan) for 4 min at 2200 rpm. Electrodes were produced by using a doctor blade in fixed position. The current collector foil to be coated was moved under the blade at constant speed of approx. $2\text{ cm}\cdot\text{s}^{-1}$ in a roll-to-roll

process. The coated current collector foil passed a drying line prior to rolling up. For cathodes and anodes, a carbon-coated aluminum foil and uncoated copper foil was used, respectively. Solvent- and water-based slurries showed good coatability and adhesion to the collector foil. After the coating step, electrodes were placed into an oven under vacuum for 12 h at 110 °C. The obtained electrodes had an areal capacity of $1.17 \pm 0.07 \text{ mAh}\cdot\text{cm}^{-2}$. The dried electrodes were stored under argon until assembling of full-cells.

Full-cells were assembled with an inorganic-filled PVDF separator and anodes composed of synthetic graphite (MAG-D, Hitachi Chemical Co., Ltd., Tokyo, Japan) (91.4 wt %), conductive carbon (Super C65, TIMCAL) (4.0 wt %), SBR (BM-400B, ZEON) (2.8 wt %) and CMC (MAC 200 HC, Sunrose) (1.8 wt %). For comparing the anodic influence on fading during long-term cycling, additional cells were assembled with anodes containing natural graphite (SGB 10 MOZ V12, Graphit Kropfmühl, Hauzenberg, Germany) instead of synthetic graphite. The ratio of constituents was equal for these anodes. As electrolyte 1500 μL of RD1001 (1 mol/L LiPF_6 in EC:DMC (1:1) + 2 wt % VC (BASF, Ludwigshafen, Germany)) was used. The areal capacity balancing of anode and cathode in $\text{mAh}\cdot\text{cm}^{-2}$ of the full-cells was 1:1. During the first cycle, the solid electrolyte interface (SEI) on the anode surface is formed under consumption of active lithium, which is mainly provided by the cathode active material. This shifts the capacity balancing of anode to cathode towards values >1 with respect to the reversible capacity. A capacity ratio of anode/cathode >1 allows a complete (de-)lithiation of the cathode and avoids safety-critical dendrite formation and lithium plating [18–21].

2.2. Electrochemical Characterization

For electrochemical characterization of the cells a battery test system (BaSyTec GmbH, Asselfingen, Germany) was used. Full-cells were formed at room temperature with a charge rate of C/10 up to 4.3 V with a potential hold until the current dropped below C/20 and a discharge rate of C/10 to 2.0 V. An upper cut-off potential of 4.3 V has been chosen in order to ensure complete de-lithiation.

The C-rate test was carried out with a charge rate of C/10, C/5, C/2, 1 C, 2 C and 5 C up to 4.3 V with a potential hold until the current dropped below C/20 and discharged with the corresponding C-rate to 2.0 V. Each C-rate charging and discharging was repeated three times. The long-term cycling and capacity fading of full-cells has been examined by charging at 1 C to 4.3 V with a potential hold until the current dropped below C/20 and discharging to 2.0 V at 1 C for 200 cycles.

2.3. Analytical Methods

The sample moisture uptake during ageing has been measured by using coulometric Karl-Fischer titration (TitroLine 7500 KF trace, SI Analytics GmbH, Weilheim, Germany) combined with an oven (AG-B-585, Büchi Labortechnik, Flawil, Switzerland) heating the sample to 150 °C under the flow of dry air. Further analysis of the aged samples was carried out by means of inductively coupled plasma optical emission spectrometry (ICP-OES) and energy-dispersive X-ray spectroscopy (EDX).

A field emission scanning electron microscope (FE-SEM) (Merlin Compact, Zeiss, Oberkochen, Germany) was used to take micrographs of pristine and aged powder samples and prepared cathodes. The working distance was 4 mm and a voltage of 2 kV has been applied.

The crystal structure of pristine and aged LFMP samples was studied based on neutron powder diffraction analysis. Elastic coherent neutron scattering experiments were performed on the high-resolution powder diffractometer SPODI at the neutron source FRM II at the Heinz Maier Leibnitz Zentrum (MLZ) in Garching, Germany [22–24]. Monochromatic neutrons ($\lambda = 1.5482 \text{ \AA}$) were obtained at a 155° take-off angle using the (551) reflection of a vertically-focused composite Ge monochromator. A vertical position-sensitive multidetector (300 mm effective height) consisting of 80 ^3He tubes and covering a 2θ angular range of 160° was used for data collection. Measurements were performed in Debye-Scherrer geometry. The powder sample (ca. 2 cm^3) was filled into a vanadium can of 13 mm in diameter with a wall as thin as 0.15 mm. For minimization of the preferred orientation effect on diffraction pattern, the sample was constantly rotated during data collection.

The structural properties of LFMP in prepared water- and solvent-based cathodes were additionally investigated with an X-ray diffractometer (Empyrean, PANalytical, Almelo, The Netherlands) of the Materials Science laboratory of MLZ which is running in collaboration with TU Muenchen and Helmholtz Zentrum Geesthacht.

The X-ray diffraction patterns were obtained in Debye-Scherrer geometry using Mo-K $_{\alpha 1/\alpha 2}$ radiation ($\lambda = 0.70932$ Å, $U = 55$ kV, $I = 40$ mA). The diffraction patterns were measured in repetition mode in a 2θ -range between 5.0 and 55.0° with a step size of 0.008° and a step time of 18 s. Data acquisition time of the solvent-based sample was 3 h and of the water-based sample was 18 h. The electrodes were enclosed inside a polymer bag to avoid exposure to the ambient atmosphere. Data analysis was performed by RIETVELD refinements using the Highscore software package [25]. RIETVELD refinements were carried out using THOMPSON-COX-HASTINGS pseudo-Voigt function [26] and FINGER-COX-JEPHCOAT [27] profile asymmetry treatment to fit the data. The aluminum current collector phase was treated with a PAWLEY-Fit [28]. More details on the refinement can be found in the supplement to this article.

3. Results

3.1. Powder and Cathode Characterization

The initial moisture of LFMP measured via Karl-Fischer titration was 229 ppm H $_2$ O. After one day of exposure, the sample stored at 23°C and 35% rh contained 3790 ppm H $_2$ O. The water content reached a value of 4844 ppm after 14 days and 4867 ppm after 21 days. The powder sample stored at 40°C and 100% rh contained 5819 ppm H $_2$ O after one day, rising to 7485 ppm and 7757 ppm after 14 and 21 days, respectively.

SEM micrographs of the aged powder samples are shown in Figure 1. The sample aged at $23^\circ\text{C}/35\%$ rh (Figure 1a) is optically identical to the pristine sample. After ageing at $40^\circ\text{C}/100\%$ rh (Figure 1b), acicular crystals evenly spread on the surface of the secondary agglomerates can be found. They have a length of approximately $2\text{--}10$ μm and tend to arrange parallel and in clusters. Figure 1c shows the observed crystals in detail at $10,000\times$ magnification. In order to separate the acicular crystals from the LFMP, the powder sample was stirred with a glass rod. The crystals adhere to the glass rod and can be stripped off. The harvested crystals (Figure 1d) arrange parallel as in the powder sample. The acicular crystals show a poor conductivity which causes electric charging on the sample surface and disturbs image recording. Some smaller LFMP spheres incorporated in the acicular crystals can be observed.

Analysis of the acicular crystals has been carried out via ICP-OES and EDX measurements and results are shown in Table 1.

Table 1. Element ratios of acicular crystal sample obtained by ICP-OES and EDX measurements. No values are given if the applied method is not suitable for the detection of the respective element. For each measurement method the element ratio values are normalized to Phosphorus (P).

Method	Element Ratio					
	P	Li	Fe	Mn	O	C
ICP-OES	1.00	2.65	0.11	0.22	-	-
EDX	1.00	-	0.09	0.19	3.88	0.37

The combined results of ICP-OES and EDX indicate the acicular crystals to be a phosphate compound with high lithium content. Thus, we assume them to be Li $_3$ PO $_4$.

Figure 1. SEM micrographs of aged powder samples: (a) Sample aged at 23 °C/35% rh (scale bar: 5 μ m); (b) Sample aged at 40 °C/100% rh (scale bar: 5 μ m); (c) Detail of acicular crystals growing at 40 °C/100% rh (scale bar: 1 μ m); (d) Isolated acicular crystals with small incorporated LFMP spheres (scale bar: 10 μ m).

Neutron diffraction has been conducted for the pristine and aged samples. Neutron diffraction has the advantage that the Mn/Fe ratio and Li occupancy can be determined. The measurement time was 7 h for each sample. XRD has been applied to study the structure of LFMP in the prepared cathodes and the influence of water- and solvent-based slurry preparation on the active material. The measured cathodes had been prepared with pristine LFMP. A variation of time (3 h and 18 h) proofed that sufficient data quality is already obtained after 3 h and the 18 h data set shows that no additional reflections have been overlooked. Neutron diffraction could not be applied for the prepared cathodes since they do not contain a sufficient amount of LFMP. For better comparison of the neutron and X-ray diffraction, the data in Figure 2 are plotted vs. d-spacing.

As shown in Table 2, lattice parameters of pristine and aged LFMP powder samples are almost similar.

Table 2. Structural data determined using the RIETVELD refinement for pristine and aged powder samples obtained by neutron diffraction (SPODI at MLZ); The standard 1 σ -deviations of the refinement for the last digits are given in parentheses.

Parameter	Pristine	23 °C/35% rh	40 °C/100% rh
<i>a</i> in (Å)	10.4113(1)	10.4125(1)	10.4126(1)
<i>b</i> in (Å)	6.0707(1)	6.0711(1)	6.0709(1)
<i>c</i> in (Å)	4.7298(1)	4.7306(1)	4.7311(1)
<i>V</i> in (Å ³)	298.940(2)	299.050(2)	299.072(3)

There is a very small trend towards larger values for *a* and *c* in the aged active material, but in all cases, differences are smaller than 0.0013 Å. Although the uncertainties from the refinement program

are lower than this value, these values usually underestimate the real uncertainties of the measurements, and interpretation of differences in this range of magnitude should be handled with care [29–32]. Changes of lattice parameters of the sample aged at 23 °C/35% rh show the same tendencies as observed for the sample aged at 40 °C/100% rh.

Figure 2. Comparison of the neutron and X-ray diffraction patterns of studied LFP samples. (a) Neutron diffraction data of pristine and aged LFMP-powders ($\lambda = 1.5482$ Å); (b) X-ray diffraction patterns of prepared cathodes ($\lambda = 0.70932$ Å). Data are plotted versus d-spacing for better comparison of the different wavelength data. For better visualization only raw data are presented. Thus the visible shifts of the XRD patterns are due to different sample offset values. Sample offset was refined as a parameter in the RIETVELD refinements and thus had no impact on the lattice parameter estimation. Diffraction patterns are arbitrarily offset in y-axis for better visibility.

From the data given in Table 3 it can be deduced that the solvent used for slurry preparation has no significant influence on the structural properties of LFMP. In our search for any structural changes, we tried to refine the site occupancy factors of Li and Fe/Mn freely as well as the O and P occupancy factors. However, none of them gave results shifted discernibly from the idealized values, so we decided to keep only the refined Fe/Mn ratio in our published final data. Although we have hints on Li_3PO_4 from ICP-OES we could not find any hints of the relevant peaks in our diffraction

patterns, probably because the absolute phase fraction of Li_3PO_4 is far below the resolution of the diffraction method.

Table 3. Structural data of LFMP determined using the RIETVELD refinement of X-ray diffraction data for water- and NMP-based cathodes. The standard 1σ -deviations of the refinement for the last digits are given in parentheses.

Parameter	Solvent	
	NMP	H ₂ O
a in (Å)	10.4119(3)	10.4092(3)
b in (Å)	6.0705(1)	6.0689(1)
c in (Å)	4.7306(1)	4.7293(1)
V in (Å ³)	299.00(1)	298.76(1)

In comparison to the lattice parameters of the pristine powder sample, RIETVELD refinement of XRD data reveals a very slight increase for a and c when the material is processed as NMP-based slurry, water-based processing causes a slight decrease of a but b and c remain unaffected in the range of measurement inaccuracy. As it was also advised for the neutron diffraction data, differences in this range should be handled with care. SEM micrographs of the prepared cathodes are shown in Figure 3.

Figure 3. SEM micrographs of prepared cathodes: (a) Water-based cathode (scale bar: 20 μm); (b) NMP-based cathode (scale bar: 20 μm).

As it can be seen in Figure 3a, a homogeneous distribution of all constituents and a complete coverage of LFMP with conductive carbon is achieved. In comparison to the water-based cathodes, the NMP-based cathode (Figure 3b) also shows a homogeneous distribution of constituents, but at least some of the LFMP spheres on the cathodes surface are only partially covered with conductive carbon.

3.2. Electrochemical Characterization

The charge and discharge capacity during the forming step has been measured. The difference between charge and discharge capacity represents the irreversible capacity loss (ICL) which is mainly caused by the formation of the solid electrolyte interface (SEI). Table 4 gives an overview of the relative charge and discharge capacities and the ICL observed during the full-cell forming step. All charge and discharge capacities in Table 4 are set into relative relation to the highest observed specific charge capacity (full-cells assembled with NMP-based cathode produced with LFMP aged at 40 °C and 100% rh).

Table 4. Relative charge and discharge capacities and irreversible capacity loss (ICL) observed during the full-cell forming step. Table shows all combinations of sample ageing conditions and subsequently used solvent for slurry preparation. The highest observed charge capacity ($147.2 \text{ mAh}\cdot\text{g}^{-1}$) was set to 100% and all other charge and discharge capacities set in relative relation to this value. ICL was calculated within each parameter set. Errors are estimated from a minimum of three full-cells for each parameter set.

Solvent	Storage Condition	Relative Capacity and ICL/%		
		Charging	Discharging	ICL
NMP	Pristine	99.3 ± 0.3	81.3 ± 1.8	18.1 ± 1.4
	23 °C/35% rh	98.0 ± 0.6	81.9 ± 1.1	16.4 ± 0.9
	40 °C/100% rh	100.0 ± 1.1	81.2 ± 2.7	18.8 ± 1.6
	Average of all cells	99.1 ± 1.2	81.4 ± 1.5	17.7 ± 1.8
H ₂ O	Pristine	97.6 ± 1.3	80.6 ± 2.8	17.4 ± 1.1
	23 °C/35% rh	98.5 ± 3.1	81.3 ± 2.6	17.5 ± 3.0
	40 °C/100% rh	98.2 ± 1.1	82.7 ± 1.5	15.7 ± 0.3
	Average of all cells	98.1 ± 1.9	81.5 ± 2.1	16.6 ± 1.8

The data vary only in a narrow range for any initial ageing condition and solvent used for slurry preparation and no systematic relation between ageing, solvent and measured capacities can be observed. The average over all NMP-based full-cells results in a relative charge capacity of $99.1 \pm 1.2\%$ and a relative discharge capacity of $81.4 \pm 1.5\%$. The average over all full-cells assembled with water-based cathodes gives a relative charge capacity of $98.1 \pm 1.9\%$ and relative discharge capacity of $81.5 \pm 2.1\%$. The specific charge and discharge capacities of full-cells assembled with NMP- and water-based cathodes can be regarded to be identical in the range of error as well as the ICL of NMP- and water-based full-cells which are $17.7 \pm 1.8\%$ and $16.6 \pm 1.8\%$, respectively.

After the forming step, the C-rate test has been conducted for full-cells assembled with cathodes representing all combinations of ageing conditions and solvents. The different C-rate currents were calculated in consideration of the discharge capacity observed after the second cycle. Since no significant difference in C-rate performance was observed, Figure 4 only illustrates the results for a water-based and NMP-based full-cell assembled with pristine LFMP. For each full-cell the highest observed discharge capacity ($116.9 \text{ mAh}\cdot\text{g}^{-1}$ for NMP-based and $118.7 \text{ mAh}\cdot\text{g}^{-1}$ for water-based full-cell at C/10) was set to 100% and all other discharge capacities at higher C-rates into relative relation to this value.

Figure 4. Relative discharge capacities of a water- and NMP-based full-cell prepared with pristine LFMP at different C-rates: (a) full-cell assembled with water-based cathode; (b) full-cell assembled with NMP-based cathode.

As can be seen in Figure 4a, the relative discharge capacity of full-cell assembled with the water-based cathode drops only slightly with increasing C-rate and at a 5 C-rate still 84.5% are reached. Figure 4b shows the C-rate behavior of the full-cell assembled with the NMP-based cathode. For C-rates up to 1 C, no significant decrease in discharge capacity can be observed since 95.6% are reached at 1 C. At a 2 C-rate, the relative discharge capacity is lower in comparison to the full-cell assembled with the water-based cathode and this difference becomes more pronounced at a 5 C-rate by reaching 79.6%. There is also a major difference in initial IR-drop at a 5 C-rate. While the voltage of the full-cell assembled with a water-based cathode drops down to 3.6 V, the full-cell assembled with NMP-based cathodes drops down to approximately 3.2 V.

After the C-rate performance test, all cells were cycled 200 times at a 1 C-rate. The results of the long-term cycling are illustrated in Figure 5.

Figure 5. Relative discharge capacities at a 1 C-rate of full-cells assembled with cathodes representing all combinations of ageing conditions and solvents used for slurry preparation. The highest specific discharge capacity ($120.6 \text{ mAh}\cdot\text{g}^{-1}$, observed for full-cells assembled with water-based cathodes produced with LFMP aged at 40°C and 100% rh) was set to 100% and all other discharge capacity into relative relation to this value. Legend indicates the solvent used for slurry preparation and the initial powder sample storage conditions are in brackets.

The left side of the graph shows the C-rate test before the long-term cycling. Prior to the C-rate test the discharge capacities are mainly equal, but after the C-rate test water-based full-cells tend to have a better capacity recovery. Their fading rate is slightly higher during the first 80 cycles but then converges with the one of NMP-based full-cells leading to a parallel curves and similar long-term discharge behavior.

In order to further study the long-term capacity fading, full-cells with different anodes were assembled and cycled 200 times at a 1 C-rate. For these full-cells pristine LFMP was used. Figure 6 shows that full-cells assembled with an anode containing natural graphite (SGB 10 MOZ V12) have a lower discharge capacity fading and still reach 92.1% while those full-cells assembled with anodes containing synthetic graphite (MAG-D) reach 87.2% relative discharge capacity after 200 cycles.

Figure 6. Comparison of long-term discharge capacity fading of full-cells assembled with anodes containing different types of graphite. MAG-D is a synthetic and SGB 10 MOZ V12 is natural graphite. For better comparability, the measured initial discharge capacities are set to 100%.

Thus the difference in discharge capacity fading after 200 cycles is 4.9%. The selection of anodic graphite has a stronger influence on the full-cell capacity fading than different ageing conditions and slurry processing.

Additionally, the coulomb efficiency ($Q_{\text{Discharge}}/Q_{\text{Charge}}$) of the full-cells used for the long-term cycling has been analyzed and is shown in Figure 7.

Figure 7. Coulomb efficiency of full-cells used for the long-term cycling at a 1 C-rate. Inset shows the coulomb efficiency observed during the first 3 cycles and illustrates the correlation between initial capacity loss caused by the formation of the SEI layer and reduced coulomb efficiency.

As can be seen in the inset of Figure 7, the coulomb efficiency during the first cycle is reduced due to the formation of the SEI layer. The average coulomb efficiency of all full-cells observed after

the first cycle varies in the range of $82.7 \pm 1.1\%$ and correlates to the observed initial capacity losses of $17.3 \pm 1.1\%$. Due to ongoing formation of SEI layer, the coulomb efficiency is still reduced in the second cycle and varies in the range of $97.4 \pm 0.5\%$. After the first two cycles, the SEI formation is largely completed and the coulomb efficiency reaches values above 99%. Overall, the coulomb efficiency does not reveal any differences possibly caused by different ageing conditions and solvents used for the slurry preparation since all curves are more or less overlapped. A slight, constant increase of the coulomb efficiency during the long-term cycling is caused by stabilization of the SEI layer in terms of growth rate per cycle.

4. Discussion

The moisture uptake of aged samples had been measured via coulometric Karl-Fischer titration and revealed that water adsorption mainly takes place in the beginning of atmospheric exposition. The powder sample aged at $23\text{ }^{\circ}\text{C}/35\%\text{ rh}$ reached 4844 ppm H_2O after 14 days and remained more or less constant, while the sample aged at $40\text{ }^{\circ}\text{C}/100\%\text{ rh}$ took up 7485 ppm H_2O within 14 days of exposure and still increased slightly. Thus it can be said that the relative humidity is correlated with the moisture uptake of the active material and the sample aged at ambient conditions had reached saturation.

SEM micrographs have shown that ageing at ambient conditions ($23\text{ }^{\circ}\text{C}/35\%\text{ rh}$) does not cause any optical changes of the secondary agglomerates, but storage at $40\text{ }^{\circ}\text{C}/100\%\text{ rh}$ causes the formation of acicular crystals and based on EDX and ICP-OES analyses we assumed them to be Li_3PO_4 . It is possible that the present LFMP contained some residual Li_3PO_4 which was used in excess during the active material synthesis. Warm and moist atmosphere caused the recrystallization in the form of acicular crystals. It is unlikely that active lithium was involved in the formation of the crystals since we observed the highest initial charge capacity for full-cells assembled with LFMP aged at $40\text{ }^{\circ}\text{C}$ and $100\%\text{ rh}$ (see Table 4).

Neutron diffraction of the powder samples revealed a slight increase of the lattice parameters a and c . The effect was barely more distinct after storage at $40\text{ }^{\circ}\text{C}/100\%\text{ rh}$. However, the change of lattice parameters was insignificant and essentially within the error of measurement. Thus even if a negligible dissolution would take place, this effect cannot be seen in the electrochemical characteristics of the material.

During the slurry preparation no influence of the powder sample ageing on the processibility or quality of the slurry was found, and the adhesion and homogeneity of the coated electrodes was also equal.

XRD measurements have been conducted to investigate the influence of slurry preparation on the crystal structure of LFMP. This measurement is relevant because water-based slurry processing represents the contact to water under the influence of high mechanical stress and application of energy, whereas moist storage of powder samples represents a static exposition to H_2O . Pristine LFMP had been used for the measured cathodes. As an insignificant influence of moist atmosphere was found by neutron diffraction, we also stated a minor decrease of the lattice parameters a and b and in contrast to neutron diffraction also a decrease of c when LFMP is handled in a water-based process. However, the observed changes are so small and within the range of measurement inaccuracy that no statement on differences can be made and therefore water-based processing is assumed to be uninfluential, especially since no negative effect can be found in the electrochemical characteristics of full-cells assembled with water-based electrodes.

Microscopic investigation of the prepared water- and NMP-based cathodes via SEM has shown partially incomplete coverage of secondary agglomerates with binder/conductive carbon of cathodes prepared with NMP-based slurries. Water-based cathodes had an optimum distribution and coverage. The reasons therefor might be found in the longer period of cathode drying when NMP-based slurry is used. As long as the coated cathodes contain a high NMP fraction, the solid constituents can move

and separate resulting in an inhomogeneous distribution. On the contrary water evaporates much faster and leads to an optimum distribution of constituents.

The fact of partially incomplete coverage with binder/conductive carbon has shown its effect in the C-rate test. While no difference in specific discharge capacity between water- and NMP-based cathodes was found at C/10, C/5, C/2 and 1 C, a difference was observed at 2 C becoming more distinct at a 5 C-rate. The better distribution of constituents and homogeneity of water-based cathodes is regarded to be the reason for a higher discharge capacity at elevated C-rates. The uniformity of distribution of conductive carbon particles significantly influences the charge and discharge kinetics. Differences in the homogeneity of conductive carbon distribution show negligible effects at low C-rates but become significant at elevated C-rates [33]. A similar correlation between distribution of carbon black, discharge kinetics and accessible capacity has been found in this study.

Thus, we conclude that in addition to their environmental friendliness, water-based cathodes are in particular suitable for high power applications.

The long-term cycling did not reveal any difference in discharge capacity fading and for this reason we conclude that neither ageing of LFMP nor water-based processing or a combination of both have any negative effect on the full-cell performance and life-time.

Cycling full-cells prepared with different anodes has shown that a lower capacity fading can be realized if natural graphite is used. In case of our experiment it is proven that after 200 cycles a capacity loss of 4.9% of the initial discharge capacity was definitely caused by anodic processes consuming active lithium and not by degradation mechanisms of LFMP. Reasons for the difference might be explained by the different morphology of the graphites. Synthetic MAG-D is mainly flake-shaped and the natural graphite SGB 10 MOZ V12 is potato-shaped as it can be seen in Figure 8a,b.

Figure 8. SEM micrographs of graphites: (a) flake-shaped MAG-D (scale bar: 20 μm); (b) potato-shaped SGB 10 MOZ V12 (scale bar: 20 μm).

The influence of the graphite morphology on battery ageing has been studied [21]. Different graphite morphologies influence the initial SEI formation as well as the long-term fading characteristics. The morphology of each graphite has its own specific particle surface, degree of crystallinity, pore size and basal-to-edge-plane ratio. These properties have been found to be key factors for battery performance. In the case of potato-shaped graphite, the sum of those properties appears to be favorable for the battery characteristics.

An explanation for the insensibility of the characterized LFMP towards water-based processing might be the morphology of the material. For the isostructural LFP, it has been found that carbon coating plays an effective protective role in terms of active material corrosion [34]. However, this protective carbon coating is not fully stable upon contact with water [35]. As we have shown in a previous study on LFP, the agglomeration of single active material particles to spheres leads to a protection of the inner

particles from mechanical stress and shearing force and thus the carbon coating of nearly all particles is well-preserved [36]. The influence of morphology appears to apply also in the case of LFMP.

Additionally, other studies had found that even traces of water can significantly lower the performance of LFMP-based batteries [14]. In our experiment we have shown that either absorbed water during sample ageing and after water-based slurry preparation is most probably only reversibly bound to LFMP and can be completely removed by drying LFMP powder or cathodes. Otherwise we would have found a poorer performance of full-cells assembled with water-based cathodes and/or aged active material. Chemical bonding is unlikely because it would result in the formation of new or modified chemical species detectable via structural analysis. However, the results of neutron and X-ray diffraction did not reveal any structural changes upon moist ageing condition and water-based processing.

5. Conclusions

In this work, the influence of different atmospheric ageing conditions of LFMP have been studied. The material was aged under moderate (23 °C/35% rh) and moist, warm (40 °C/100% rh) conditions. Neutron diffraction of the pristine and aged LFMP samples has shown that no negative influence on the crystal structure is caused by ageing. Subsequently, all powder samples of LFMP were processed to water- and solvent-based slurries. The combination of pristine and aged powder samples and solvents resulted in six different cathodes. XRD measurements stated that water does not affect LFMP during the slurry preparation. Based on the results of neutron and X-ray diffraction, we derive that LFMP is stable in moist conditions and water. Electrochemical characteristics were studied in full-cells and no negative influence of ageing and water-based processing on battery performance was found. In comparison to NMP-based cathodes, water-based ones even provided a better C-rate capability. Referring to our data, this leads to the conclusion that the characterized LFMP has the full potential for environmentally friendly battery production. The results are important since they provide access to many beneficial aspects of water-based processing. Compared with NMP, water-based production requires no special protection of employees and equipment for explosions prevention and complex exhaust treatment, which allows simplified and cheaper manufacturing. Furthermore, water as a solvent is significantly cheaper and less toxic in comparison to NMP. For the water-based system, CMC and SBR are used as binder, which are both non-toxic hydrocarbons and even approved as food additives [37,38]. In contrast, the solvent NMP is most commonly used with the binder PVDF, a highly fluorinated compound, which releases hazardous di-/trifluorobenzenes and highly toxic hydrofluoric acid (HF) in the case of a battery fire [39]. Numerous advantages reaching from processing to environmental friendliness and operational safety emphasize the importance of progress towards the future of a cleaner and cheaper battery production without organic solvents.

Supplementary Materials: The following are available online at www.mdpi.com/1996-1073/10/12/2135/s1, Table S1: Al Phase starting parameters, Table S2: LFMP Phase literature parameters, Li occupancy was set to 1 prior to starting the refinements. *Structure originally published in space group $P\bar{6}3/m$. The structure was transformed to the standard setting $Pnma$. Transformed data set as presented here was used as starting model for the refinements, Table S3: Instrumental setup. $K\alpha_2/K\alpha_1$ ratios were determined by refinement using a Si-powder standard (NIST 640d), Table S4: R -values of the refinements and not phase-specific (general) parameters, Table S5: refined Al phase parameters, Table S6: Refined LFMP phase parameters. Standard uncertainty values are given in parentheses as refined by Highscore without multiplying the values with the R_{wp} -value of the fit.

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analyzed XRD measurements, analyzed the data of neutron diffraction and helped to draft the manuscript. Oleksandr Dolotko carried out the neutron diffraction measurements and helped to draft the manuscript. Ralph Gilles helped to analyze X-ray and neutron diffraction data and to draft the manuscript. Karl-Heinz Pettinger helped to analyze electrochemical data and to draft the manuscript.

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