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Activation and degradation of electrospun $LiFePO_4$ battery cathodes

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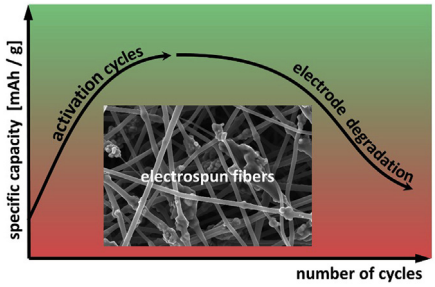
HIGHLIGHTS

- Composites of $LiFePO_4$ and carbon nanofibers have been prepared via electrospinning.
- Samples show activation during first 100 cycles of galvanostatic cycling.
- Degradation of the samples can be observed after 500 cycles.
- Activation and degradation mechanisms have been elucidated by SEM, TEM, and XPS.

GRAPHICAL ABSTRACT



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ABSTRACT

Electrodes prepared by electrospinning often exhibit an activation behavior, i. e. they are reaching their full capacity only after numerous charge and discharge cycles. The activation mechanism can be explained by the improvement of the accessibility of Li^+ ions to the active particles of the cathode, which increases with the number of cycles. It is assumed that, as an effect of cycling, the dense, impermeable carbon layer which covers the active material due to the carbonization step during processing cracks and delaminates, allowing this way the Li^+ ions to access the active material and to intercalate into it. This has been confirmed by scanning and transmission electron microscopy performed in correlation with the electrochemical performance of electrospun electrodes. However, with even further cycling a decrease in capacity is observed. The microscopic results suggest that this is partly caused by cracks at the carbon-$LiFePO_4$ interfaces. Thus, the cracking responsible for the activation of the electrospun electrodes at the beginning of cycling seems also to cause a part of their degradation at the end of their life. Another slow degradation mechanism confirmed by scanning electron microscopy and by X-ray photoelectron spectroscopy is the ongoing formation of a cathode electrolyte interphase.

1. Introduction

Lithium-ion batteries technology is well established, however, alternative ways of their manufacturing are being currently developed in order to improve their performance, reduce their production costs and/or to enhance their environmental compatibility [1–3]. Electrospinning is one of the suggested methods for production of structured electrodes for lithium-ion batteries, in which carbon fibers, spun into a fibrous mesh, serve as conductive medium connecting the active material particles. Such three-dimensionally (3D) interconnected battery

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architectures are expected to improve the battery performance significantly [4–6]. In electrospun electrodes, the active particles are embedded into a carbon fiber matrix, where the direct contact between active Li-intercalating material and conducting network should increase the amount of material being electrochemically accessed, even at high charge and discharge rates.

Electrospinning, a method to obtain fibers of nanometer and submicrometer diameters out of polymer melts or solutions, is based on the interaction between the electrically chargeable, viscous polymer solution and the electric field. The resulting polymer fiber covers the surface of the collecting electrode and forms a nonwoven felt. In such electrospun structures, the polymer fibers are highly interconnected and build up a 3D structure with open porosity. The obtained polymer nonwoven can be turned into an electron-conductive carbon felt, provided that the used polymer is suitable for carbonization or graphitization. By adding active material powders or their precursors into the polymer solution for electrospinning, it is possible to obtain composite fibers with the active material directly integrated into the fibers [7–9]. However, not much is known about the durability of these electrodes and possible degradation mechanisms, while the ageing mechanisms of the active materials and of the lithium-ion battery as a whole are well studied [10–13].

In this work, electrospun electrodes were prepared with $LiFePO_4$ as the active material and then electrochemically cycled. Lithium iron phosphate $LiFePO_4$ (LFP) was chosen to be the model material for this study, because it has been often referred to as a “green battery material”, which is non-toxic, cheap and has good chemical and temperature stability [14,15]. It has very poor electronic conductivity [16] and is, therefore, a suitable model system to elucidate the specific role of conductive additives in the functionality and specific fatigue mechanisms of such composite electrodes.

By combining the electrochemical measurements with the characterization through scanning and transmission electron microscopy (SEM and (S)-TEM) the activation and degradation mechanisms of the electrospun electrodes was revealed.

2. Experimental section

Electrodes were prepared using the electrospinning technique with the nanoparticulate active material integrated into conductive carbon fibers. The as-spun electrode-precursors were post-treated in order to convert the polymer into conductive carbon [17,18]. Electrochemical cycling of the obtained electrodes was combined with additional characterization methods (scanning electron microscopy, transmission electron microscopy and X-ray photoelectron spectroscopy) at various intermediate stages during the electrodes' life. Electron microscopy (SEM and TEM) was used to trace the activation and degradation mechanisms in the structure of those electrospun electrodes, performed at different cycling stages: as prepared, during the activation and after degradation.

2.1. Sample preparation

The nonwoven felt electrodes were prepared by electrospinning the viscous dispersion consisting of an 8% polymer solution of PAN (Polyacrylonitrile) in DMF (Dimethylformamide) and the LFP powder („EQ-Lib-LFPO“, MTI Corporation). The Climate-Controlled Electrospinning Apparatus (EC-CLI from IME Technologies) allows the variation of different parameters, while the climate parameters can be kept constant. The variable parameters of the electrospinning process are the temperature (T = 27 °C), relative air humidity (12% H_2O), distance (L = 17 cm) and applied voltage between electrodes (U = 12 … 15 kV), pumping velocity of the polymer solution or suspension (0.2–0.7 mL/h) and the diameter of the needle (0.8 mm). The obtained fiber mat was thermally stabilized at 250 °C for 6 h in air and then heated in argon gas atmosphere at 750 °C for 3 h in order to carbonize the polymer with a heating rate of 5 K/min in both cases.

During the thermal treatments the pieces of nonwoven material were fixed between ceramic plates in order to avoid bending of the fibrous structure. From such obtained sheets circular samples of 12 mm diameter were cut out. Samples cut out from the sheet before carbonization (after stabilization) shrunk to a diameter of 10 mm. The electrospun electrodes are freestanding and do not necessarily need a binder or aluminum foil as a support. The relative amount of active material in the obtained electrodes was estimated via elementary analysis and EDX and is indicated in the text describing results obtained on the particular sample. The rest of the sample consisted of carbon and nitrogen (2%) coming from the PAN polymer. The loading of the active material for the samples used here was about 1 mg/cm^2. This is lower than the 4–10 mg/cm^2 of standard $LiFePO_4$ electrodes [19] and the 3–6 mg/cm^2 of those for high power applications [20]. However, by using several electrospinning layers, we could also fabricate samples with loadings of ca. 10 mg/cm^2.

2.2. Electrochemical tests

The electrochemical characterization was performed with a VMP3 potentiostat (BioLogic, France). In addition to cyclic voltammetry (CV), galvanostatic cycling was performed at different C rates, electrochemical cycling in a voltage window between 2.3 and 4.5 V. Two electrodes were measured in parallel for reproducibility check and in order to exclude occasional errors. The electrodes were measured in dismountable half-cells made from Swagelok® parts. Li foil (Sigma-Aldrich, 0.5 mm thickness) served as the anode and glass fiber separators (GF/D Whatman®) were used. The electrolyte was a 1:1 solution of ethylene carbonate and dimethyl carbonate (EC:DMC) with lithium hexafluorophosphate ($LiPF_6$) as the conductive salt. C rates were related to the mass of the active material $LiFePO_4$ and to its theoretical capacity of 170 mAh/g calculated from the molar mass of $LiFePO_4$, 157.75 g/mol, assuming that all of the Li can be extracted.

2.3. Visual/structural characterization

The electrospun electrodes were characterized by SEM and TEM. The SEM (Zeiss Merlin) images were taken before electrochemical cycling and at different stages during the cycling (after 100, 300 and 700 cycles). For SEM the electrode was dismounted from the cell in argon atmosphere and then washed with DMC in order to remove electrolyte residuals. After drying, the electrode was transferred into the vacuum chamber of the SEM by using an inert-gas transfer system. For the topography imaging the secondary-electron (SE) detector was used. However, to display the material contrast between active material, supporting carbon fiber and the appearing cathode electrolyte interphase (CEI) layer the EsB-detector (energy selected backscattered electron detector) was applied [21]. The automated scanning software (Mosaic ATLAS) enabled the imaging of the whole surface of the electrode, which helped to find the same place for the subsequent imaging. In such a way all changes of the electrode (same spot on the electrode) could be easily traced. After SEM measurements the electrode was transferred again under vacuum to the glovebox and mounted into the half-cell for further cycling.

The sample for TEM was prepared by dropping a suspension droplet containing the sample on the TEM grid. The suspension was prepared by dispersing the sample in absolute ethanol and sonicating it for 2 min (S)-TEM characterization was performed on samples before cycling (as carbonized), after about 100 cycles and after about 500 cycles. The (S)-TEM measurements were performed using an aberration-corrected (image) FEI Titan 80–300 operated at 300 kV acceleration voltage, equipped with a Gatan US1000 CCD camera.

Complementary X-ray photoelectron spectroscopy (K-Alpha XPS-Spectrometer, ThermoFisher Scientific, East Grinstead, UK) was conducted on pristine and cycled samples before and after washing out the