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Electrospun LiFeTiO₄ 3D structured cathode material for lithium ion batteries

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Introduction

LiFeTiO₄ as well as $Li_2Fe_xMn_ySiO_4$ are promising cathode materials for lithium-ion-batteries (high voltage vs. Li and high theoretical capacity) [1,2]. However, they exhibit various handling difficulties when the electrodes are prepared by coating Al foils with a suspension of a powder mixture. Moreover it is assumed that the low electronic as well as low ionic conductivity of these materials keeps them from achieving their full theoretical capacity. One suggested strategy to allow the full ion insertion is the separation of active particles from each other [3]. Thus, the use of 3D fiber structured electrodes (made e.g. by electrospinning method) may improve their electrochemical performance. Electrospinning offers the following advantages: comparatively facile and fast electrode production, preparation of electrodes where the active particles are embedded into an electron conductive fiber matrix with no need for binder and current collectors. In the present investigation we make an effort to demonstrate the advantages of 3D-fiber structured over traditionally prepared cathodes.

Experimental

The traditonal powder electrode was prepared by grinding and mixing the cathode material with carbon black, graphite and PVdF binder (Polyvinylidene fluoride). An Al current collector foil was coated with a slurry of that powder mixture dissolved in NMP (N-Methyl-2-pyrrolidone). Afterwards, the electrodes were cut out from that foil and pressed at 7t.

The fiber mat electrodes were prepared by electrospinning a viscous dispersion consisting of either a powder or a precursor in a 10% polymer solution of PAN (Polyacrylonitrile) in DMF (Dimethylformamide). The obtained fiber mat was then thermally treated in argon gas atmosphere in order to carbonize the polymer.



Figure 1: Electrospinning apparatus, its working principle and an example of the electrode preparation process.

Results titanate





Figure 4: XRD patterns of the pure LiFeTiO4 powder (blue curve) and of the electrospun electrode (red curve).

Figure 2: SEM image (left) and STEM image (right) of the electrospun electrode, the active material is supported by fibers. The LiFeTiO₄ particles are well dispersed in the fibers, however, there are also larger agglomerates included in the fibers. Magnification: 10.000x for the left and 60.000x for the right image.







Results silicate



Figure 6: SEM images of the electrospun and of the powder electrode. Magnification: 50.000x for the left and for the right image.



Figure 7: Cycling stability of the electrospun and of the powder electrode

Figure 3: SEM images of the "classic" powder electrode. The small particles are the cathode powder/carbon black mixture, the large grains are graphite particles. The powder layer was not very homogeneous and it showed only weak adhesion to the Al foil. Magnification: 10.000x for the left and 50.000x for the right image

electrospun electrode	powder electrode
📕 Discharge capacity	🛑 Discharge capacity
electrospun electrode	powder electrode

Figure 5: Cycling efficiency of the electrospun and of the powder electrode measured at different currents.

measured at i = 0,3 [mA]. The electrodes have been cycled between 4,8 V and 1,5 V vs. Li. The capacity of the powder electrode decrease continuously while the electrospun one seems to be stable over the cycling number.

Discussion and Conclusion

Above results appear to be quite promising. It seems that the structuring of the cathode improves the cycling efficiency (ratio between discharge and charge capacity) and the cyclability. The better cycling stability may be the result of reduction of the cycling related strain by the fiber matrix. The improved efficiency may be due to the above mentioned active particle separation by the fibrous structure. However to study the correlation between the electrode structure and the battery performance in detail further investigations are planned.

References

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