

## Sol-gel synthesis of nanosized phosphoolivine composites LiCoPO<sub>4</sub>/CNFs as cathode materials for lithium ion batteries

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The phosphoolivine LiCoPO<sub>4</sub> has been synthesized as a component for a composite cathode material in Li-ion batteries by a sol-gel ethanol-based method, similar to the technique previously applied for the synthesis of apatite [1]. The chosen method is found to be advantageous in producing nanocrystalline LiCoPO<sub>4</sub>/carbon nanofibres (CNFs) with preferred physical and electrochemical properties as required for rechargeable lithium-ion batteries.

The starting reactants used were LiNO<sub>3</sub> (99.99%, Aldrich), Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (ACS, 98.0-102.0%, Alfa Aesar) and P(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (98%, Alfa Aesar). An as-prepared ethanol precursor solution (0.1M) was hydrolyzed and a stoichiometric amount of it was brought into contact with nanofibres (CNFs) for 24-72 h. After the solvents were driven off at 60°C, the obtained gel was annealed at different calcination temperatures from 400 to 800°C in Ar flow for 12h. X-ray powder diffraction (STOE STADI P) shows that the highest purity of the olivine phase is obtained in the 650°C-750°C temperature interval.

The particle size of the precursor particles during the sol-gel process depends on the concentration of the precursor solution and duration of the sol ageing period. Dynamic light scattering (DLS) was performed on the sols immediately after the reactants have been mixed. The observed general trend is that particle size of precursor increases only initially with time for about 6 hours and remains constant after that. The four times increase in concentration from 0.1M to 0.4M results in approximately twice as large particle sizes. The full-profile Rietveld analyses of the X-ray patterns of sample obtained from 0.1M precursor solution reveal after final annealing at 650°C LiCoPO<sub>4</sub> as the main phase with volume-weighted average crystallite diameter of 60 nm, while at 700°C LiCoPO<sub>4</sub> is obtained with crystallites of 400 nm.

Different concentrations of CNFs/LiCoPO<sub>4</sub> composites containing 30, 50 or 70% of active material were obtained from 0.05-0.1M precursor solutions (700°C) and used for the electrochemical characterization. The best result was obtained with a discharge capacity of 68 mAh/g for the composite with 30% of active material, this is ca. 40% of the theoretical capacity of 167 mAh/g for LiCoPO<sub>4</sub> [2]. The discharge capacity decreases with increasing amount of active material (50, 70%), probably due to the accompanied increase of particle sizes. In conclusion, the presence of CNFs in combination with their coating by electrochemically active LiCoPO<sub>4</sub> nanoparticles can result in enhanced electrochemical properties of this hybrid material, but the specific sizes and amounts must be further optimized.

### References

1. D.-M.Liu et. al. *Biomaterials* 22 (2001) 1721.
2. K. Amine, H. Yasuda, and M. Yamachi *Electrochem. Solid-State Letters* 3 (2000) 178