In situ study of hydrothermal formation of spinel type $LiMn_2O_4$ nanocrystals

Steinar Birgisson, Bo Brummerstedt Iversen

Center for Materials Crystallography, Department of Chemistry and iNANO, Aarhus University, 8000 Aarhus C, Denmark

Solvothermal reactions have been shown to be a good way to synthesize nanocrystalline materials. Many properties of the product, such as phase composition, crystallite size, morphology and crystallinity, can be controlled by changing and controlling synthesis conditions, such as reaction temperature, heating rate, reaction time, precursor concentration and pH [1]. *Ex situ* investigation of the effect of every possible synthesis variable on the products can be a very time consuming and it also provides limited information on reaction mechanism. *In situ* investigations measure the properties of reactants and products in real time while the reaction is happening. This gives unique opportunity to study reaction mechanism and reaction kinetics. Following the product properties in real time maps the effect of reaction variables in one, or at least few measurements, and gives the possibility of controlling product properties.

Our group has developed and successfully implemented an experimental setup capable of *in situ* measurements of solvothermal reactions. The setup can use powder X-ray diffraction (PXRD) or total scattering (TS) as the measuring probe and measure data with 1-10 second time resolution. PXRD gives information about all crystalline material found in the reaction solution. The information, such as what crystalline phases are present and their weight fractions, structural parameters (e.g. unit cell parameters, site occupancies and bond lengths), crystallite sizes and morphology is extracted using sequential Rietveld refinements [2]. TS data can be used to calculate the pair distribution function (PDF) which gives information about all the materials in the reaction solution, from complexes to amorphous particles to crystalline particles. Information such as bond lengths, weight fractions of different species and particle sizes can be extracted via real space refinements of structural models [3].

Spinel type $LiMn_2O_4$ (LMO) is a well-known cathode material for Li-ion batteries. Nanosized LMO has been shown to have superior high discharge rate capability compared to microsized LMO [4]. In this study we do *in situ* PXRD measurements on hydrothermal formation of nanocrystalline LMO. The results show that LMO nanocrystals are instable towards formation of nanocrystalline Mn_3O_4. From the information we suggest the reaction route:

$$(1)\ 4LiOH_{(aq)} + 8KMnO_{4(aq)} + 7CH_3CH_2OH_{(l)} \xrightarrow{\Delta} 4LiMn_2O_{4(s)} + 8KOH_{(aq)} + 7CH_3COOH_{(l)} + 5H_2O_{(l)}$$

$$(2)\ 12LiMn_2O_{4(s)} + 5CH_3CH_2OH_{(l)} + H_2O_{(l)} \xrightarrow{\Delta} 8Mn_3O_{4(s)} + 12LiOH_{(aq)} + 5CH_3COOH_{(l)}$$

Rate constants for reaction (2) at different temperatures are extracted using Johnson-Mehl-Avrami model. Activation energy for reaction (2) is also evaluated using Arrhenius equation.

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