

MS13-04 *In situ* XRPD studies of Li intercalation in graphite in working Li-ion batteries. Rune E. Johnsen,^a Poul Norby,^a ^aDepartment of Energy Conversion and Storage, Technical University of Denmark, Frederiksborgvej 399, P.O. Box 49, DK-4000 Roskilde, Denmark. E-mail: runj@dtu.dk

Lithium batteries have a large potential for use e.g. in electrical vehicles, but several challenges must be tackled before large scale introduction of electrical vehicles is possible, including increasing the energy and power densities, improving safety and reducing the price. Improved materials and an increased fundamental understanding of the electrochemical reactions and microstructural changes taking place during operation are needed. Thus, we have investigated the possibility of obtaining real-time information about structural and microstructural changes during operation of large (10 Ah) and small (0.1 mAh) batteries by *in situ* synchrotron X-ray powder diffraction (XRPD).

We have performed *in situ* XRPD studies of large commercial batteries intended for electric vehicles during charge and discharge. The batteries are composed of stacks of more than 20 cells, giving a total thickness of ~8 mm. High-energy X-ray diffraction (at ESRF and PETRA III) was used to extract *in situ* information about the changes in the anode and cathode material during a charge-discharge-charge cycle. Here, we will focus on the graphite anode. The XRPD patterns showed the expansion of the basal spacing caused by the intercalation of lithium in graphite. Stoichiometric (LiC₆ and LiC₁₂) as well as non-stoichiometric phases (Li_xC) were observed. However, dominating diffraction from other phases present in a battery made a detailed study of the structural changes in the anode material impossible. In order to avoid diffraction from other crystalline phases present in the battery, we have developed a capillary-based micro-battery cell that enable us to obtain diffraction from one electrode phase at a time. We have recently performed the first *in situ* XRPD experiments using the newly developed micro-battery cell to study the initial intercalation of lithium into graphite (at MAX-lab); from graphite to LiC₁₈ via nonstoichiometric Li_xC. The experiments revealed interesting changes in the stacking sequence of the pure graphite (graphite 2H and graphite 3R) as well as of the lithiated graphite phases.

Keywords: *in situ* diffraction; battery materials; intercalation-deintercalation

MS13-05 Changing Properties of Hydrogen Storage Materials by Halide Substitution. Hilde Grove,^a Line H. Rude,^b Torben R. Jensen,^b Magnus H. Sřrby,^a Bjřrn C. Hauback.^a ^aInstitute for Energy Technology, P.O. Box 40 Kjeller, NO-2027, Norway. ^bDepartment of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Århus C, Danmark. E-mail: hilde.grove@ife.no

The search is ongoing to find clean and renewable energy systems. Hydrogen is an attractive energy carrier, since only water is formed when hydrogen is reacting with oxygen to release energy in a fuel cell or combustion engine. One of the main problems for hydrogen to become an effective energy carrier is to find effective ways to store hydrogen in vehicles or stationary storage units. Hydrogen fails to meet the demands to volumetric density set by e.g. US DoE even when stored under high pressure or condensed to a liquid at low temperature. A safer and more compact way is to store hydrogen in solid compounds, e.g. in metal hydrides such as MgH₂ and LaNi₅H₆. Bogdanovic discovered in 1997 that the complex metal hydrides, NaAlH₄, can store hydrogen reversibly by adding a dopant, TiCl₃[1]. A lot of focus has been given to alanate (M_n(AlH₄)_m), but lately more attention has been given to borohydrides (M_n(BH₄)_m) that contains more hydrogen per unit weight. The properties of both alanates and borohydrides can be changed by substituting part of the compound with different ions. Hydrogen in alanate can be substituted with fluorine [3], and the whole BH₄ group in borohydrides can be substituted with Cl, Br or I [4]. Substitution changes the hydrogen release properties, and can therefore be used to tune these properties. In this work, we have investigated possible substitution in Ca(BH₄)₂ with CaF₂, CaCl₂ and CaBr₂. Ca(BH₄)₂ has several polymorphs, α-Ca(BH₄)₂ is stable at room temperature. Above 200 °C the β-phase is more stable. α-Ca(BH₄)₂ crystallizes in the orthorhombic, space group *F2dd*, while β-Ca(BH₄)₂ crystallizes in the tetragonal space group *P42/m*. After ball milling α-Ca(BH₄)₂ with CaCl₂, no change is seen in the unit cell axes of α-Ca(BH₄)₂, indicating that no substitution takes place. The evolution with temperature was studied using *in-situ* synchrotron powder diffraction at SNBL, ESRF in Grenoble, France. At 150-200 °C, the α-phase is transformed into the β-Ca(BH₄)₂, then at about 250 °C the Bragg peaks of the β-phase are shifted to higher angles, indicating shrinkage of the unit cell volume, in agreement with substitution of smaller Cl. Substitution is seen with heat treatment of ball milled Ca(BH₄)₂ + CaCl₂ with ratio 1:0.5, 1:1, 1:2, giving Ca((BH₄)_{1-x}Cl_x)₂, where x varies with the ratio. No substitution was observed with CaF₂ and CaBr₂.

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