In situ XRPD studies of Li intercalation in graphite in working Li-ion batteries. Rune E. Johnsen, a Poul Norby, a “Department of Energy Conversion and Storage, Technical University of Denmark, Frederiksbergvej 399, P.O. Box 49, DK-4000 Roskilde, Denmark.
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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 cycle. Here, we will focus on the graphite anode. The XRPD experiments using the newly developed micro-battery/diffraction from other crystalline phases present in the anode to study the initial intercalation of lithium into graphite (at Acta Cryst. (2012). A 68, s43

Changing Properties of Hydrogen Storage Materials by Halide Substitution. Hilde Grove, a Line H. Rude, b Torben R. Jensen, b Magnus H. Siiby, a Bjørn C. Hauback. a a Institute for Energy Technology, P.O. Box 40 Kjeller, NO-2027, Norway. b Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Århus C, Denmark.
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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, TiCl4. A lot of focus has been given to alanate (Mn(AlH4)0x), but lately more attention has been given to borohydrides (Mn(BH4)0x) 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-xClx)2, where x varies with the ratio. No substitution was observed with CaF2 and CaBr2.


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