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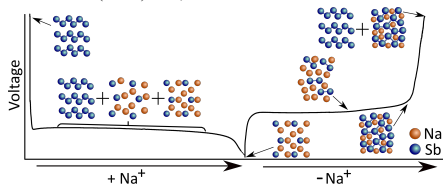


Figure 1. Schematic of the sodiation processes in antimony anodes

Keywords: pair distribution function analysis, batteries, in operando

MS19-O3 Quasi-Elastic Neutron Scattering Studies on Solid Electrolytes for all-solid-state Lithium Batteries

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The development of better batteries is paramount for market penetration of electrical vehicle and integration of renewable energy sources into the grid. For today's best technology, state-of-the-art lithium-ion battery, limited improvement in capacity and cost are expected because of the use of organic liquid or gel electrolytes limiting the choice of electrode materials and exposing to safety concerns. A choice alternative is to use solid electrolytes instead.

The high temperature phase of lithium borohydride (LiBH_4), hexagonal crystal structure at temperature above 383 K, is a fast Li^+ conductor ($\sigma \sim 10^{-3} \text{ W}^{-1} \cdot \text{cm}^{-1}$).^[1] This property is kept at room temperature by stabilizing the hexagonal phase with Li halides^[2] or confining LiBH_4 in nanoporous scaffolds.^[3]

We have studied the Li^+ diffusion in LiBH_4 with Density Functional Theory (DFT) coupled to Quasi-Elastic Neutron Scattering (QENS). DFT shows that lithium defects such as Frenkel pairs are easily formed at room temperature ($E_f = 0.44 \text{ eV}$) and low energy barriers (0.3 eV) are found between stable defect sites, giving rise to high defect mobility (Fig.1-a). The most favorable mechanism for the Li^+ conduction is calculated to occur in the hexagonal plane. The QENS results at 380 K show long range diffusion of Li^+ , with jump lengths of one unit cell in the hexagonal plane and rates in agreement with DFT. At 300 K, QENS reveals jumps of shorter length ($\sim 2 \text{ \AA}$), which could correspond to jump of Li^+ interstitials to intermediate lattice sites, in agreement with DFT.^[4]

QENS was also used to probe the dynamic of the BH_4^- anions in LiBH_4 confined in nanoporous SiO_2 . Four quasi-elastic components were found in two different temperature domains. At low temperature, $< 170 \text{ K}$, the components are an order of magnitude broader than those at high temperature, however still below the phase transition (Fig.1-b). The narrower components are associated with reorienting BH_4^- anions in crystalline LiBH_4 , while the broader components, with much more rapidly reorienting BH_4^- , can be associated with the fraction of LiBH_4 located at the SiO_2 surfaces, reflecting a disruption of the bulk crystal lattice. It suggests that the high Li^+ conductivity takes place at the interface between LiBH_4 and SiO_2 .

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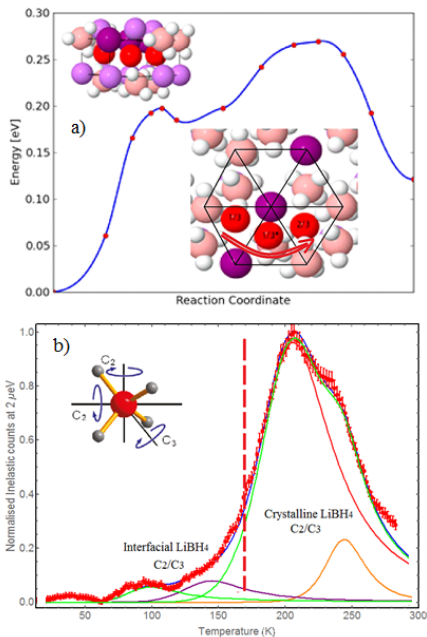


Figure 1. a) DFT energy path for interstitial Li diffusion. b) LIBH₄/SiO₂ neutron inelastic temperature scans. The four quasi-elastic components correspond to reorientational diffusion of the BH₄⁻ along the C₂ - C₃ axis for the interfacial LiBH₄ (low temp.) and crystalline LiBH₄ (high temp.).

Keywords: Battery, Quasi-elastic Neutron Scattering, Density Functional Theory, all-solid-state battery, solid electrolyte

MS19-O4 Characterization of cation ordering, oxygen vacancy distribution and proton sites in hexagonal and cubic BaTi_{1-x}Sc_xO_{3-δ}

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Proton conducting oxides find applications as electrolyte materials in fuel cells, steam electrolyzers and hydrogen and humidity sensors. Proton conducting fuel cells, which use H₂ as a fuel, stand out as a promising technology for future clean energy generation. However, its success relies on the discovery of novel electrolyte materials with high protonic conduction at intermediate temperatures (200 – 600 °C). Acceptor doped perovskites are actively studied in the search for improved proton conducting materials. We have synthesized and characterized the proton conducting properties of the series BaTi_{1-x}Sc_xO_{3-δ} (0.1 ≤ x ≤ 0.8). [1,2] The series shows a transition from a 6H perovskite structure at low scandium doping to a cubic phase for x ≥ 0.5. All the doped series show hydration behavior indicative of filling oxide ion vacancies within the structure and that protons are the dominant charge carriers below 600 °C. The conductivity of the materials with the 6H structure is significantly lower than those with the cubic structure. X-ray data suggest different oxygen vacancy ordering within the 6H perovskite structure at low doping levels, whereas the vacancies are distributed randomly in the cubic structure with no evidence of long range ordering of the Ti and Sc ions on the B-site. However, due to the weak scattering from oxygen *cf.* the transition metals and barium, coupled with the similar scattering power of the Ti and Sc, the presence of cation and/or oxygen ion order and the driving force for the phase transition to the cubic structure are unknown. Moreover, the origin of the poorer conductivity of the 6H *cf.* the cubic structure upon hydration is also unknown and is likely related to the proton sites and the exchange pathways within the material. Neutron powder diffraction (NPD) and recent *in situ* studies using combined NPD/thermogravimetric analysis resolving these key questions will be presented and coupled to DFT calculations.

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Keywords: neutron, powder diffraction, structure