

MS19 Solid state oxygen fuel cell, hydrogen storage & battery materials

Chairs: Bernhard Frick, Kristina Edstrom

MS19-O1 Structure and dehydration mechanism of the proton conducting brownmillerite $\text{Ba}_2\text{In}_2\text{O}_5$

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Proton conducting oxides are currently accumulating considerable attention due to their potential as efficient electrolytes in various electrochemical technologies, including intermediate temperature solid oxide fuel cells [1]. An important material is the brownmillerite structured oxide $\text{Ba}_2\text{In}_2\text{O}_5$, which may be described as an oxygen deficient variant of the perovskite structure, with alternating layers of InO_6 octahedra and InO_4 tetrahedra. Like many other oxygen-deficient oxides, $\text{Ba}_2\text{In}_2\text{O}_5$ transforms upon hydration into a hydrogen-containing material, $\text{Ba}_2\text{In}_2\text{O}_5(\text{H}_2\text{O})_x$, which show proton conducting properties. In this contribution, I will report on detailed investigations of the local structure and dehydration mechanism of $\text{Ba}_2\text{In}_2\text{O}_5(\text{H}_2\text{O})_x$, using a combination of variable temperature Raman spectroscopy together with inelastic neutron scattering and computer simulations [2,3]. The results suggest that $\text{Ba}_2\text{In}_2\text{O}_5(\text{H}_2\text{O})_x$ evolves upon heating from a perovskite-like structure for the fully hydrated material ($x = 1$) at room temperature, through a partially hydrated intermediate phase, appearing at ca. 370 °C, to an essentially fully dehydrated ($x \approx 0$) brownmillerite material at 600 °C. The dehydration process appears to be a two-stage mechanism characterized by a homogenous release of protons below the hydrated-to-intermediate phase transition, whereas at higher temperatures a preferential desorption of protons originating in the nominally tetrahedral layers is observed.

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Keywords: Proton, conducting, oxide, fuel cells, SOFC, neutron scattering, Raman spectroscopy

MS19-O2 *In operando* pair distribution function analysis and solid-state NMR studies of antimony anodes for sodium-ion batteries

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Sodium-ion batteries have attracted attention recently because of the high natural abundance of sodium compared to lithium, making them particularly attractive in applications such as large-scale grid storage where low cost and sustainability, rather than light weight is the key issue. Several materials have been suggested as cathodes but far fewer studies have been done on anode materials and, because of the reluctance of sodium to intercalate into graphite, the anode material of choice in commercial lithium-ion batteries, the anode represents a significant challenge to this technology. Materials which form alloys with sodium, particularly tin and antimony, have been suggested as anode materials; their ability to react with multiple sodiums per metal-atom give potential for high gravimetric capacities. However, relatively little is known about the reaction mechanism of these materials in the battery, primarily due to drastic reduction in crystallinity during (dis)charging conditions, but also because the structures formed on electrochemical cycling may not be alloys known to exist under ambient conditions.

We present a study of antimony-based anodes for sodium-ion batteries, using *in situ* pair distribution function (PDF) analysis combined with *ex situ* solid-state nuclear magnetic resonance studies¹. Inclusion of diffuse scattering in analysis is able to circumvent some of the issues of crystallinity loss, and gain information about the local structure in all regions, independent of the presence of long-range order in the material. As a result, we separate the crystalline and amorphous phases present in the Na-Sb system and probe the nature of previously unknown amorphous intermediate phases. This analysis has been linked with *ex situ* ²³Na solid-state NMR experiments to examine the local environment of the sodium; these show evidence of known Na₂Sb phases but indicate additional metastable phases are present at partial discharge. The electrochemical signatures are linked with structural processes taking place in the battery to show that the different electrochemical profile observed on the second sodiation is a result of complex multiphase electrode formed after the first desodiation as the amorphous and crystalline phases take different sodiation pathways.

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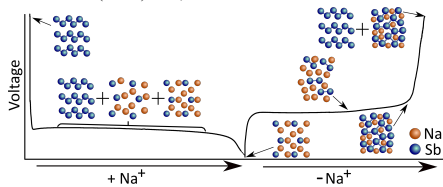


Figure 1. Schematic of the sodiation processes in antimony anodes

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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