

energy density limit. Further, for application in electric vehicles there is increasing focus on producing a low cost, highly stable battery with high capacity. In line with this has been the re-emergence of aqueous electrolyte based cells [1]. Defect perovskite structures such as $\text{Li}_{3x}\text{La}_{0.67-x}\text{TiO}_3$ and $\text{Li}_{3x}\text{La}_{0.33-x}\text{NbO}_3$ present a possible choice of cathode for these cells due to their ideal voltage range, high ionic conductivity, structural flexibility and high intercalation limits [2-3]. However, in order to further develop the properties of defect perovskites a thorough understanding of the structural changes which occur during lithium intercalation and how these affect the electrochemical properties is essential.

We have previously synthesised the defect perovskite compounds $\text{Sr}_{0.8}\text{Ti}_{0.6}\text{Nb}_{0.4}\text{O}_3$ (STN) and $\text{Li}_{0.18}\text{Sr}_{0.66}\text{Ti}_{0.5}\text{Nb}_{0.5}\text{O}_3$ (LSTN). While STN intercalated only a small amount of lithium via chemical means, LSTN readily intercalated lithium. A combination of neutron diffraction studies and bond valence calculations has provided significant insight into the early stages of structural changes during intercalation as well the diffusion properties of the material.

Both STN and LSTN have been able to intercalate lithium electrochemically exhibiting a sloping discharge profile between 1 – 2 V (Fig. 1). This type of voltage profile would normally be associated with solid solution type intercalation behaviour. However, both in-situ neutron and ex-situ synchrotron diffraction experiments have revealed multiphase intercalation behaviour.

This contribution will address the structural changes which occur in STN and LSTN during chemical and electrochemical intercalation and the connection of these structural changes to the observed properties.

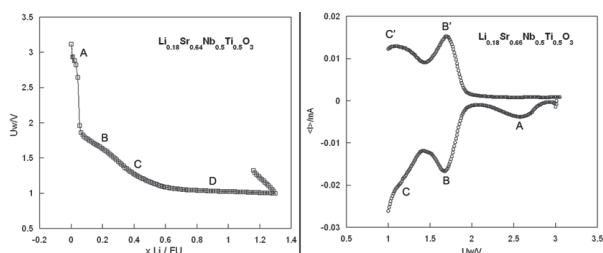


Figure 1: Cyclic voltammogram showing the voltage output during intercalation into LSTN and the location of several electrochemical processes.

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Structure and dehydrogenation properties on ammine borohydride system as hydrogen storage materials

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Complex metal hydride materials have received a great deal of attention owing to their high gravimetric hydrogen contents [1, 2]. Recently several novel ammine borohydride complex materials, which contain high wt % hydrogen, have been synthesized. The use of ammonia complex of metal borohydrides $\text{Me}(\text{BH}_4)_x \cdot n\text{NH}_3$ (Me = Li, Mg, Al, Zn, Ca) has shown to be a considerable strategy for achieving improved

dehydrogenation mechanism by the interaction between NH_3 and BH_4 molecules. Several compounds release most of hydrogen at a relatively low temperature with no undesirable gas emission. The structures have subsequently been solved by synchrotron powder diffraction method. First principles calculations were performed using density functional theory (DFT), with the projected augmented wave method, to evaluate the electronic properties. The ground state structures are subjected to full structural optimization. The chemical bonding of the material has been analyzed by means of electron localization function (ELF). The development of materials which allow the low temperature release of a large volume of hydrogen is significant, thereby demonstrating the potential of to be used as solid hydrogen storage.

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Altering the properties of metal borohydrides by substitution

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Effective hydrogen storage is one of the bottlenecks for widespread use of hydrogen as a clean energy carrier. Hydrogen storage in solids, most notably metal hydrides, is the only option which can potentially meet the requirements for volumetric hydrogen density. To achieve high gravimetric hydrogen densities, the research focuses on light element such as aluminum and boron. However, no complex hydride with suitable stability and high hydrogen content has yet been found.

The heavy intermetallic hydrides have highly tunable properties by metal substitution over wide compositional ranges, but this possibility is lacking for complex metal hydrides which take stoichiometric metal compositions. However, the use of anion substitution has turned out to be a viable method to change the stability of metal hydrides, e.g. by partly substituting H^- by F^- in Na_3AlH_6 [1].

The system $\text{NaBH}_4 - \text{NaCl}$ has been investigated by powder (lab and synchrotron) X-ray diffraction (PXD), powder neutron diffraction (PND) and various thermal methods. A continuous range of chlorine substitution in NaBH_4 , $\text{Na}(\text{BH}_4)_{1-x}\text{Cl}_x$ ($0 < x < 1$) has been obtained by ball-milling mixtures of NaBH_4 and NaCl up to 24 hours. The $\text{Na}(\text{BH}_4)_{1-x}\text{Cl}_x$ phases take NaCl-type structures and show almost ideal Vegard's law behavior. In-situ SR-PXD shows a gradual depletion in BH_4^- upon thermal decomposition and hydrogen release and NaCl is the only crystalline final decomposition product. The changes in thermal stability upon chlorine substitution are small, with only a slight stabilization with increasing chlorine content. On the other hand, a drastic change in the order-disorder temperature is observed. Hydrogen ordering in NaBH_4 induces a phase transition from cubic to tetragonal symmetry around 190 K, however, no phase transformation was observed in $\text{Na}(\text{BH}_4)_{0.75}\text{Cl}_{0.25}$ down to 9 K by PND. Phase transformations in more dilute systems are under investigation.

Halide substitution in $\text{Ca}(\text{BH}_4)_2$ mixed with calcium halides has been investigated by in-situ SR-PXD. No substitution of BH_4^- by Cl^- is observed in the low-temperature modification $\alpha\text{-Ca}(\text{BH}_4)_2$, but an appreciable chlorine substitution is observed into the high-temperature phase $\beta\text{-Ca}(\text{BH}_4)_2$. No substitution with bromide or iodide was achieved.