Project Report 2029

Synthesis of new hybrid hydrides by combination of anionic borohydride and imidazolate ligands: the first member, Li(BH4)Im

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Objectives: short, medium and long term

The family of borohydrides, also named tetrahydroborates has been studied extensively during the past few years. Being seen as a pseudo-chloride anion in the beginning, the tetrahedral BH4 group is now regarded as a directional bridging ligand, coordinating metals preferably via its edges. This behavior was put into light by the recent discovery of porous gamma phase of Mg(BH4)2. The long-term objective of this project is to extend the family of these porous hydrides by combining borohydrides with another directional bridging ligand: imidazolate ([C3N2H3]-), aiming for compounds with improved selectivity for gas adsorption, increased reactivity towards CO2 etc. The short and medium-term objectives are to characterize the first borohydride-imidazolate, having the composition Li2(BH4)Im.

Brief summary of work carried out

Lithium, sodium and potassium imidazolates have been prepared for the first time in our laboratory and characterized by single crystal and powder diffraction. The coordination of imidazolate is highly unusual and the compounds, especially in LiIm. They are highly hygroscopic, that can be consiered as a proof of their eagerness to complete the coordination sphere of the metal atoms. Ball milling LiIm and LiBH4 leads to the formation of a new compound of which the structure was partially solved from synchrotron radiation powder diffraction data. The compound has an orthorhombic unit cell and space group Imma. The cell parameters are: a = 6.051476, b = 15.099486 and c = 6.537907 A. All atom positions were refined by the Rietveld method except the hydrogen atoms belonging to the borohydride group. The orientation of the BH4 group and, therefore, its coordination mode still has to be determined. This information is crucial for further understanding of the coordination behavior of BH4 group and for the synthesis of other mixed BH4/Im compounds. A sample of the same compound was prepared using Li11BD4 for neutron powder diffraction study and measured at PUS instrument at JEEP II. The sample will contains only 3 hydrogen atoms per formula unit of Li2[C3N2H3][11BD4], i.e. 20 mole % of H-atoms. Long data acquisition allowed to suppress the noise coming from the incoherent scattering of hydrogen.

Main achievements intended for publication

Neutron data suggests lower symmetry for Li2(BH4)Im structure, as well as a disorder for the BH4 group. We are completing the analysis of the data, but are inspired by the BH4 disorder. This probably will lead to the Li-ion conductivity. Thus, we are planning to do ionic conductivity measurements. The foreseen publication will describe synthesis, crystal structure of Li2(BH4)Im, its stability and Li ionic conductivity, setting the start to the new series of Hybrid Hydrides.

Difficulties encountered

No special difficulties encountered.

Further comments

None.