

MS19- Materials on energy saving and climate sustainability

Chairs: Dr. Klaudia Hradil, Dr. Claudia Weidenthaler

MS19-P01

Metal hydro-borates for Li- and Na-ion batteries

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Complex hydrides based on light hydro-borate anions such as borohydride BH_4^- or *closo*-borate anion $\text{B}_{12}\text{H}_{12}^{2-}$ find their place as solid stores for hydrogen, and since recently, also as solid electrolytes in Li- and Na-ion batteries. The mobility of the cations depends on the pathways available in the anion packing, chemical interaction of cations with anions and on the anion thermal motion such as tumbling or rotation. While the latter two require important experimental and theoretical effort, the first parameter can be easily analysed and quantified from the crystal structure data obtained by X-ray diffraction. A thorough crystal chemistry analysis of observed crystal structures, allows us to find the structural archetypes and to draw conclusions about the bonding and building principles in this important category of materials as it was done recently for the borohydrides (Figure 1).

Among others, the modification of $\text{Na}_2\text{B}_{12}\text{H}_{12}$, promising Na-ion solid electrolyte, by anion modification and anion mixing will be shown.¹⁻² Novel synthetic way completed by *ab initio* structural characterization using synchrotron X-ray powder diffraction and *ab initio* calculation allowed discovery of several 3d transition metal *closo*-borates - potentially battery electrodes (Figure 2).³

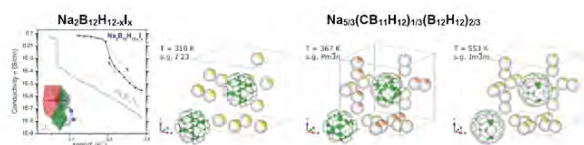


Figure 1: (left) Ionic conductivity of a sample containing 52 wt% $\text{Na}_2\text{B}_{12}\text{H}_{12}\cdot x$ and 48 wt% NaI. The conductivity of the precursor $\text{Na}_2\text{B}_{12}\text{H}_{12}$ is shown for comparison. Na-ion conduction channels in *hcp* sublattice with face-sharing T and O interstitial sites in *h*- $\text{Na}_2\text{B}_{12}\text{H}_{12}\cdot x$. In blue the static Na positions as optimized by DFT. (right) Evolution of anionic and cationic disorder in $\text{Na}_{50}(\text{CB}_{11}\text{H}_{12})_{10}(\text{B}_{12}\text{H}_{12})_{20}$. Green and yellow spheres represent boron and sodium atoms respectively. Orange spheres indicates a different Wyckoff site for Na (only in *Pm-3n*). The colour partial filling indicates the partial site occupation.

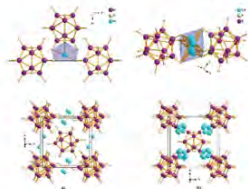


Figure 2: a) Disordered experimental structure of anhydrous *m*- $\text{M}(\text{B}_{12}\text{H}_{12})$ for bivalent M (Co, Ni). The metal is disordered on two neighbouring tetrahedral interstices. DFT optimized local structure is shown above. b) Disordered experimental structure of anhydrous *c*- $\text{Cu}_2(\text{B}_{12}\text{H}_{12})$. The metal is disordered around a position bridging two *closo*-borates. Local experimental coordination is shown above. Both compounds crystallize with *bcc* anion packing.

References:

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MS19-P02

Solvent-free synthesis of heterometallic metal-organic frameworks for the electrocatalytic reduction of carbon dioxide

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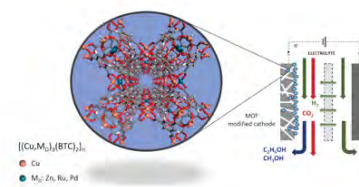
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Herein we report the solvent-free synthesis and doping of the benchmark HKUST-1(Cu) as a facile route to afford heterometallic MOFs and their proficient behaviour as electrocatalytic materials in the carbon dioxide reduction to alcohols. Precisely, Zn(II), Ru(III) and Pd(II) were selected as doping metals (M_D) with the aim of partially replacing the Cu(II) atoms of the pristine structure to afford HKUST-1($\text{Cu}, \text{M}_\text{D}$) type materials.

The introduction of a doping element implies a slight increase of the cell parameter with respect to the homometallic HKUST-1. This fact is attributable to the occurrence of longer $\text{M} \cdots \text{O}_{\text{carboxylate}}$ coordination bond distances that implies the presence of the dopant in the paddle-wheel shaped dinuclear $[\text{M}_2(\text{OOC})_4]$ secondary building unit. In the case of Ru(III) and Pd(II), which are elements of the second transition series, their greater ionic radii values are consistent with an increase in coordination bond distances and cell parameters. On the contrary, Zn(II) exhibits a rather similar ionic radius to that of Cu(II), but the Jahn-Teller effect of Cu(II) (d^9) implies shorter equatorial coordination distances than those found in analogous paddle-wheel shaped Zn(II) complexes.¹

Prepared samples were processed as gas diffusion electrodes (GDEs) and assembled in a continuous flow filter-press electrochemical cell with the aim of converting CO_2 into added-value chemicals.² The obtained products are mainly methanol and ethanol with Faradaic efficiencies that range from 6 to 60%, which are values comparable or greater than those provided by conventionally used elemental copper and copper oxides.



References:

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Keywords: Heterometallic MOFs, solvent-free synthesis, CO_2 reduction.