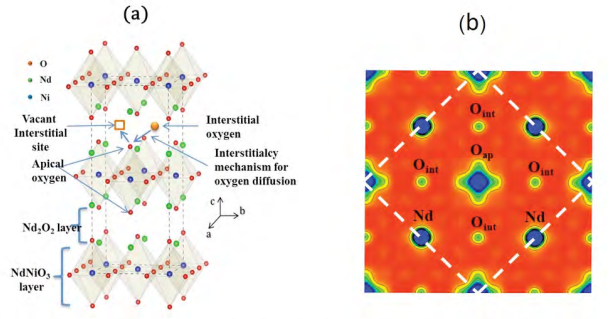

Fig. 1. (a) Crystal structure of $Nd_2NiO_{4.25}$ in F*mmm* space group (b)Anharmonic displacements of apical oxygen atoms at room temperature for $Nd_2NiO_{4.25}$ obtained with MEM. White lines represent F-cell.

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Keywords: Interstitialcy mechanism, Arrhenius-type diffusion, Anharmonic apical oxygen displacement.

MS19-O4

The aluminium-ion battery

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The expansion of renewable energies and the growing number of electric vehicles and mobile devices demand for improved and low-price electrochemical energy storage. In order to meet the future needs for energy storages novel material systems with highest energy densities, readily available raw materials, and safety are required. Currently, especially lithium and lead dominate the battery market, but beside cobalt and phosphorous, in particular lithium may show substantial supply challenges in the future. Therefore, the search for new chemistries will become increasingly important in the future in order to diversify battery technologies.

Due to its high abundance and triple charge, aluminium is a highly interesting candidate for high-valent, *post*-lithium batteries, since for stationary application large quantities of active mass are necessary.

Within the crystalline structure of potential solid aluminium-ion conductors, the high charge of the trivalent aluminium ion poses the challenge of high attraction towards anions and high repulsion from cations. In this context, an optimised crystal structure is of paramount importance. By analysing the necessities for good ionic transport and applying this knowledge to large crystallographic databases by means of high-throughput crystal-chemical analyses, we address the identification of promising materials candidates for a future all-solid-state aluminium-ion battery technology.

Traditionally, the search for Al-conductors was started with oxygen-containing materials. We opened up the chemical space of potential aluminium-ion conductor materials by first analysing bonding differences in aluminium and oxygen, sulphur, or selenium-containing materials. Due to the decreasing electronegativity and increasing size, we found an increasing polarisation of the chalcogenides and a better shielding of charge from the aluminium-ions. We have studied varying ternary spinel-like structures by means of density functional theory (DFT) calculations to quantitatively evaluate the chemical bonding in aluminium-chalcogenides.

Eventually, this knowledge was applied to the ICSD to filter out promising materials for the conduction of aluminium-ions. We applied Voronoi-Dirichlet partitioning to first geometrically filter for materials with interconnected interstitial voids that are large enough to host aluminium-ions. Secondly, bond-valence site-energies were calculated to estimate respective activation energies for the percolation of aluminium-ion conduction paths. As a last step, DFT will is be used to simulate a full, dynamic diffusion process for the most interesting candidates *ab initio*.

We will present the current state of the aluminium-ion battery, including theoretical and first experimental results. This work is funded by the German BMBF (R2RBattery: 03SF0542A), the Russian Megagrant (14.B25.31.0005), and the RSF (16-13-10158).

Keywords: Battery, post-lithium, ion conductor

MS19-O5

Investigating CO_2 uptake in Sc_2BDC_3 using XRD, *ab initio* DFT and GCMC methods

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Despite the large number of MOFs that have been synthesised and are present in the Cambridge Structural Database, 84,185 as of Nov. 2017, very few have been studied for both their gas adsorption and mechanical properties.[1] Most investigations concerning the former are based upon adsorption isotherms and hence there is a lack of understanding concerning the location of adsorbed guest molecules within the pores and the nature of specific interactions between the guest molecules and the framework. Up to 2014, 120 crystallographic studies on frameworks containing adsorbed gas molecules had been reported, with only 47 frameworks investigated in all.[2] A more detailed understanding of these interactions will help us develop more insightful structure-property relationships, thereby aiding chemists in designing MOFs with enhanced or specific guest uptake.

The small-pore MOF Sc_2BDC_3 (where BDC = benzenedicarboxylate) was initially observed to undergo an orthorhombic-to-monoclinic phase transition, via rotation of one pair of BDC linkers, under CO_2 uptake at p = 1 bar and 235 K.[3] Here, we have used a combination of capillary gas cell XRD experimental and *ab initio* DFT and GCMC computational methods to show that the framework also undergoes the same phase transition, gradually, at 298 K at higher CO_2 pressures (complete at 3 bar). Additionally, a third adsorption site, which was not seen in the original investigation at 235 K, was observed; this discovery verified the expected maximum uptake of CO_2.

Ab initio DFT calculations determined that the monoclinic form of Sc_2BDC_3 is the lower energy geometry-optimised structure (by 13.3 kJ mol^{-1}); the orthorhombic phase however is present at 298 K due to the entropic term having greater weighting at this temperature. Therefore, the formation of the monoclinic phase at room temperature upon CO_2 uptake is a result of CO_2-framework interactions exceeding the energy barrier to linker rotation. This was shown using GCMC to model CO_2 uptake in the experimental framework structures, with stronger CO_2-framework interactions in the monoclinic phase. Additionally, there was good agreement between the binding site hierarchies observed by the three different methods, with a clear switching of the site hierarchy between the two phases. When a CO_2/CH_4 gas mixture was applied to this material, the XRD and computational methods showed that Sc_2BDC_3 has selectivity for CO_2 over CH_4; this was a result of weaker CH_4-framework interactions and specific CH_4 adsorption site locations which allowed CO_2 to occupy its strongest adsorption site unhindered.