

Altering the Properties of Fluorite Oxide Interfaces with Trivalent Impurity Cations

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e05-nandef-par

Fluorite structured oxides find use in a wide variety of applications, ranging from the use of Uranium Dioxide (UO_2) in nuclear fuel to Cerium Dioxide (CeO_2) used in catalysis, fuel cells and bio-medicine. In each application the efficiency is dependent on defect processes occurring at their interfaces. To date, most atomistic studies on interfaces in fluorite-structured materials have considered stoichiometric interfaces, In this project we use a combination DFT and potential based simulation techniques to explore the effect of trivalent dopants on interface processes of these two important fluorite oxides – UO_2 and CeO_2 . We will illustrate this effect by describing two examples.

The first example is an investigation of how the trivalent dopants modify the surface structures of several low index surfaces of CeO_2 and how the presence of these dopants affects the interaction with small molecules present in the environment, and hence illustrate how the dopants have the potential to modify the catalytic properties of the material.

In the second example, UO_2 , we are interested in whether trivalent dopants will segregate to grain boundaries, and when they do, evaluate the effect on oxygen migration. Thus enabling us to identify whether the presence of these dopants will modify the rate of the corrosion of the fuel, which ultimately will affect its mechanical properties. Our simulations, using potential based molecular dynamics show that the dopants modify the oxygen transport in grain boundaries.

Keywords: Cerium Oxide, Uranium Oxide, Grain Boundaries, Surfaces, Defects

Band Structures of Porphyrin Nanostructures: Linker Effects

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e05-nandef-cre

Recent progress in the synthesis of π -conjugated porphyrin arrays of different shapes and dimensionalities motivates us to examine the band structures of infinite (periodic) porphyrin nanostructures. We use screened hybrid density functional theory simulations and Wannier function interpolation to obtain accurate band structures of linear chains, 2D nanosheets and nanotubes made of zinc porphyrins. Porphyrin units are connected by butadiyne (C4) or ethyne (C2) linkers, or “fused” (C0), i.e. with no linker. The electronic properties exhibit strong variations with the number of linking carbon atoms (C0/C2/C4). For example, all C0 nanostructures exhibit gapless or metallic band structures, whereas band gaps open for the C2 or C4 structures. The reciprocal space point at which the gaps are observed also show fluctuations with the length of the linkers. We also discuss the evolution of the electronic structure of finite porphyrin tubes, made of a few stacked six-porphyrin rings, towards the behavior of the infinite nanotube. Our results suggest approaches for engineering porphyrin-based nanostructures to achieve target electronic properties.

Oxyanion Doping of Metal Oxide Materials

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e05-nandef-mol

Global demand for power is at an all-time high with a large emphasis on low carbon alternative to fossil fuel derived energy. Thermoelectric (TE) generators can convert heat directly to electricity and are of particular interest when used in conjunction with other devices that produce heat (*e.g.* car exhausts). Metal oxides offer a cheaper and less toxic alternative to conventional TE materials, however, they generally have a lower figure of merit (ZT), which is used to define a material TE performance. Oxyanion doping could offer a strategy to increase the performance of metal oxides and involves the doping of the structure with p-group elements.

Density functional theory (DFT) calculations have been utilized to investigate the bulk and defect chemistry of simple perovskite structures (ABO_3), focusing on $SrTiO_3$. Results show that the functionals PBE+U and PBE-sol+U are needed to reproduce the structural, electronic and vibrational properties of these structures. In doped structures, we have identified three different defect local environments that phosphorus can adopt, depending on oxygen stoichiometry. Electronic density of states calculations show the introduction of localized Ti^{3+} states when P and oxygen vacancies are introduced, which will play a role in modulating the electrical conductivity of the material. Analysis of the phonon spectra for these defective materials have shown complex modes related to the local environment of P, which will have implication on modulating the thermal conductivity.

Defect Formation in TCO

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e05-nandef-sok

We present a consistent interatomic forcefield for indium sesquioxide (In_2O_3) and tin dioxide (SnO_2) that has been derived to reproduce lattice energies and, consequently, the oxygen vacancy formation energies in the respective binary compounds. The new model predicts the dominance of Frenkel-type disorder in SnO_2 and In_2O_3 , in good agreement with ab initio defect calculations. The model is extended to include free electron and hole polarons, which compete with charged point defects to maintain charge neutrality in a defective crystal. The stability of electrons and instability of holes with respect to point defect formation rationalizes the efficacy of n-type doping in tin doped indium oxide (ITO), a widely employed transparent conducting oxide in optoelectronic applications. We investigate the clustering of Sn substitutional and oxygen interstitial sites in ITO, finding that the dopants substitute preferentially on the cation crystallographic d site in the bixbyite unit cell, in agreement with experiment. The forcefield described here provides a useful avenue for investigation of the defect properties of extended transparent conducting oxide systems.

Structural Diversity of Quasi 1D Zinc Oxide: A Global Optimisation Approach

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e05-nandef-smw

Bulk ZnO is a wide band gap semiconductor ($E_g = 3.37\text{eV}$, 298K), with a high excitonic binding energy (60 meV) making it a popular material in the photovoltaics industry. Carefully controlling impurity doping in ZnO can allow its properties to range from an insulator to an n-type semiconductor, with reports of p-type conductivity in ZnO crystals when doped with group V elements. ZnO, therefore, has many applications. While impurity doping is a well established method for band-gap tuning in ZnO, band-gap energetics has also been manipulated using quantum confinement effects (observed coupling between changes in atomic structure and electronic band-structure exhibited by nanoscale or low-dimensional materials). For quantum dots of ZnO, reports of band-gap values range from 3.64 eV to 4.72 eV for particles of radii 4.25nm and 2.17nm, respectively. Moreover, there are plenty of computational studies of even smaller particles of ZnO, so called nanoclusters, where the atomic structure does not resemble cuts from its bulk phase. Such studies also include the effect of doping; as in the bulk, Mg and Cd doped for Zn in these nanoclusters produces a red and blue shift, respectively.

There are fewer computational studies for quasi-1D systems: most of these focus on nanotubes (NT)/and nanorods (NR), assuming an atomic structure analogous to that of carbon NT and NR. Reports from experiment and theory are not as consistent; however, there are reports that include SEM images showing ZnO NT cross-sections that are either hexagonal or circular.

In this presentation I will show results from our exploration of the energy landscape for quasi-1D ZnO. Rather than constructing these structures, we have employed global optimisation techniques, and find not only the NT and NR, but other low energy minima. The energy landscape is too large for direct DFT exploration, so in this study we have developed suitable interatomic potentials that allowed us to filter out the suitable candidates. Materials software employed to evaluate each structure include GULP, Crystal, FHI-aims and Q-espresso. I will also describe the methodology developed (and implemented within G42+).

Intrinsic point defect study in bulk AlN and GaN using GULP

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e05-nandef-cat

Group-III (Al, In & Ga) nitrides and their doped alloys are engineered into various energy profiles and super-lattices for optimizing material's performance and improving efficiencies. Our work is based on QM/MM methodologies (developed at Daresbury in collaboration with UCL) to model the electronic structures of native defects and impurity centres in III-nitride materials and their interfaces. At this stage, two-body interatomic potentials are used and intrinsic point defect energies of AlN, as well as Schottky and Frenkel defect energies, are calculated for the system. Our results agree well with earlier work, upon which we will build by applying DFT and quantum mechanics calculations for further modelling on the system.

DFT+U Study of the Electronic, Magnetic and Mechanical Properties of Co, CoO, and Co₃O₄

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e05-surfin-lee

Cobalt nanoparticles play an important role as a catalyst in the Fischer-Tropsch synthesis (FTS). During the reaction process, cobalt nanoparticles can be oxidised leading to the formation of two phases: CoO and Co₃O₄. The nanoparticles oxidation has a negative impact on the FTS. Experimentally, it is possible to evaluate the phase change by measuring the magnetic moment as each material presents different magnetic structure. It is therefore important to describe at the atomic scale, using a common input, the three later materials.

Previous theoretical investigations described, separately, the metallic cobalt and oxide phases but a common protocol to describe all the three materials is missing: for instance, a common value for representing the electron correlation (U approach). This protocol should be able to explain also the electronic structure and magnetism.

We have used density functional theory with the Dudarev approach (DFT+U), for U ranging from 0 to 5 eV, to evaluate the mechanical properties and electronic structure of Co, CoO, and Co₃O₄. We have found that U = 3 eV is the common parameter that describes best the properties of the three materials at the same time.

We have also studied the adsorption of oxygen on top of Co(111) considering an oxygen coverage ranging from 1 to 9 oxygen atoms. We have determined the most stable adsorption sites: hollow-fcc and hollow-hcp. We have also compared the surface oxygen adsorption with the subsurface oxygen adsorption where we inserted one oxygen atom under the first atomic layer. We have observed that the surface oxidation is dominant for a number of oxygen atoms lower than 6 while the subsurface oxidation is dominant when the coverage is higher than 9 atoms. Between those two latter coverages, there is a competition between both surface and subsurface oxidations.

Adsorption of Actinyls (UO_2^{2+} , NpO_2^+ , PuO_2^+) on the Mackinawite {001} Surface

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e05-surfin-nik

Understanding the interaction between actinide elements and mineral surfaces is key to determining the fate of radionuclides should they escape into the environment. This knowledge can be used to develop strategies to prevent and control their migration by, for example, increasing the accuracy of predictive models or identifying materials that can be used for radionuclide containment. Data obtained using the synchrotron radiation based XAS technique EXAFS show actinides (U, Np and Pu) differ in their interaction with the surface of the iron sulfide mineral mackinawite.

We use computational chemistry (plane wave density functional theory within the periodic boundary condition framework) to model the adsorption of actinides on mackinawite, with the aim of understanding why these elements, neighbours in the periodic table, behave so differently. We present adsorption energies and geometries for the actinyls UO_2^{2+} , NpO_2^+ and PuO_2^+ in multiple binding configurations on the pristine mackinawite {100} surface. Whilst the geometries of all three actinyl complexes in equivalent binding configurations are essentially indistinguishable, our method predicts UO_2^{2+} and PuO_2^+ to have similar adsorption energies, whereas NpO_2^+ exhibits a greater affinity to the mineral surface, as observed experimentally.

We identify the most favourable binding configurations from our calculations and use the structural data to simulate the experimentally acquired EXAFS spectra, thus providing very direct links between theory and experiment. As such, we elucidate the nature of actinyl binding to mackinawite and evaluate the predictive capability of theory in this very understudied area.

Water Adsorption on the Surfaces of Minor Actinide Dioxides

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e05-surfin-nik

The minor actinides (MAs) Np, Am and Cm are of interest as they accumulate during the nuclear fuel cycle, ending up as high-level waste, with generally very long half-lives. They are commonly encountered in their oxide form, usually as the fluorite dioxides (MAO₂). Previous work on MAO₂ has mainly focused on their bulk properties,¹ but the properties of MAO₂ surfaces and their interactions with adsorbates are important both for potential applications in nuclear reactors and for various other processes in the nuclear fuel cycle. Here, the PBE + *U* method is applied to investigate water adsorption on stoichiometric and reduced {111}, {110}, and {100} MAO₂ surfaces. All calculations were performed using VASP 5.4.1

H₂O adsorption on MAO₂ surfaces are energetically favorable. On all stoichiometric NpO₂ and AmO₂ surfaces, as well as the stoichiometric CmO₂ {100} surface, dissociative H₂O adsorption is more stable than molecular adsorption, while on the stoichiometric CmO₂ {111} and {110} surfaces, molecular H₂O adsorption is more favourable. On all reduced MAO₂ surfaces, dissociative adsorption is more energetically favorable, and H₂O is dissociated upon adsorbing on some reduced surfaces. Additionally, the existence of oxygen defects on the reduced surfaces promotes H₂O adsorption, i.e. adsorption on reduced surfaces is more favourable than on the corresponding stoichiometric surfaces. Comparison with previous work within our group for H₂O adsorption on UO₂ and PuO₂ surfaces²⁻⁴ reveals clear trends in surface properties for actinides dioxides from U to Cm, and these will be presented and discussed.

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Cobalt as Promising Anti-Cancer Agent: Can vital oxygen be an issue?

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e05-surfin-lee

As development of nanotechnology expedites, nanomaterials have already found their roles in almost every aspect of human life. Unique properties of magnetic nanoparticles put them head to head with the most powerful medical technology, promising breakthroughs in many fields including cancer treatments. Nevertheless, certain difficulties when choosing the best material, such as high reactivity and desired heating power, are still to be resolved. Biocompatible iron oxides have been the best candidates and every effort has been given to improve their properties through changes in shape, size, and composition (doping). Unfortunately, with all these changes their heating performance seems to have reached its limit. High magnetisation of metallic cobalt could be a solution, if simple way of avoiding its reactivity with omnipresent molecules in human body, such as oxygen and water, can be found. Therefore, density functional theory with the Dudarev approach (DFT+U) has been used to model the adsorption of oxygen on low Miller index surfaces of hexagonal phase of cobalt. To test the influence this vital specie has on the properties of cobalt nanoparticles in the organism, body conditions, namely temperature and pressure of oxygen in the blood have been included. It has been shown that oxygen adsorbs spontaneously on all surfaces forming oxides, causing the lost in magnetisation, and disabling the direct use of promising magnetic properties of bare cobalt nanoparticles. In order to preserve favourable characteristics, modifications in form of organic and inorganic coatings are currently being tested, with gold offering additional advantages of optic and plasmonic activity. Resulting nanocomposite is expected to offer further improvement in cancer treatments and could bring cancer therapy one step closer to be side-effect free.

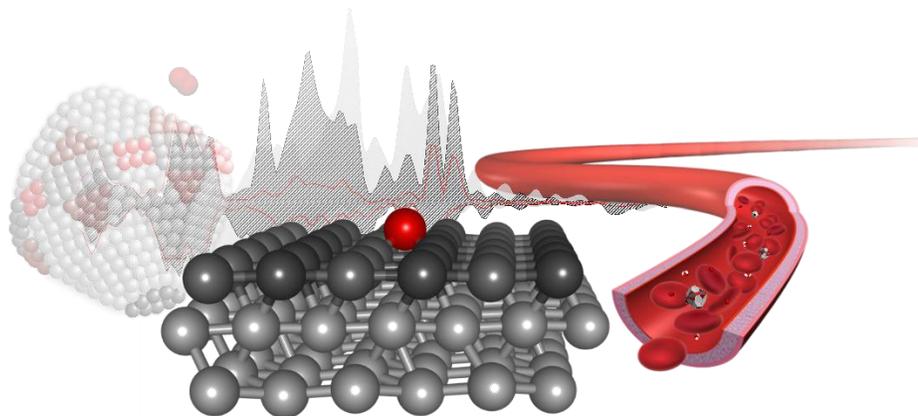


Figure 1. Influence of inhaled oxygen on cobalt nanoparticles.

Uranyl Minerals: Development of a Set of Interatomic Potentials for Use in Molecular Mechanical Simulations.

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e05-surfin-coo

Molecular mechanical (MM) models are able to model much larger systems than those modelled using density functional theory (DFT) techniques. Whilst MM calculations are quicker to execute than DFT ones, they require the derivation of a reliable and robust set of potentials that can model the atom-level interactions. This project seeks to develop a set of interatomic potentials for use in a wider system, modelling green rust (a layered double hydroxide) with interlayers populated by water and uranyl ions, along with various counterions; this system has the potential to reduce the uranyl ion and thus prevent it being mobile in the aqueous phase. This could have important implications in nuclear waste storage and pollution remediation.

Existing potential sets are used where possible as much work has already been done in their development. There is however a need to develop potentials where they do not already exist. Where mixing of Lennard-Jones potentials is required the Lorentz-Berthelot mixing rules have been used; where Buckingham potentials have been used we have used varied techniques for mixing, as described in the methodology.

Potentials are fitted to known mineral structures from the International Crystal Structural Database (ICSD) and compared to the results of DFT calculations. Results show that the set of potentials produced are capable of working successfully and that these potentials can be validated by reference to empirical data or DFT calculations.

Phosphate and Heavy Metal Co-adsorption on Goethite Surfaces for Water Remediation

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e05-surfin-par

Heavy metals are introduced into the environment through a wide variety of human activities (e.g. mining, electroplating, battery leaching, etc.). The potential for bioaccumulation through the food chain has caused global concerns. Research into effective, economical remediation methods will help to provide safer water-source for human consumption and help maintain a healthy biosphere.

We are particularly interested in using oxides and oxy(hydro)-oxides, as adsorbents to remove heavy-metal pollutants in contaminated water. Due to their low cost, environmental compatibility and inherent stability. Goethite (FeOOH) is one of the most common iron oxide minerals on Earth. Previous studies^{1,2,3} have shown its potential as a suitable sorbent for heavy metal cations such as Cu(II), Pb(II) and Zn(II).

We have applied atomistic simulation techniques based on density functional theory (DFT-PBEsol) to investigate if the adsorption of heavy cations on goethite surfaces is enhanced by co-adsorption with phosphate anions. Due to aqueous nature of the remediation, we have first determined the stability of various surface terminations of goethite which are hydroxylated. Then, the adsorption of phosphate groups in the form of H_2PO_4 and HPO_4 was considered, in order to explore the effect of varying pH. Finally, Zn(II) and Cd(II) were incorporated to the phosphorylated surfaces and the strength of adsorption compared to the non-phosphorylated surfaces.

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Adsorption of Small Organic Molecules onto the $\alpha\text{-Al}_2\text{O}_3$ (0001) Surface: A Computational Study

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e05-enviro-nat

More carbon is stored in soil than as atmospheric CO_2 , thus making soil the largest pool of organic carbon (OC) in the terrestrial biosphere.¹ Sorption of OC to mineral surfaces is a major process in the preservation of organic matter in soils: an estimated 20% of OC in soils is stored due to its interaction with reactive aluminium and iron oxides.² Sorption is considered a key process in the soil preservation due to its ability to protect OC from microbial degradation.² It is important to obtain quantitative description of the binding of organic molecules to soil minerals, in order to understand how OC is preserved in soils. In this work, we studied the binding of water and small organic molecules, typical building blocks of OC, on $\alpha\text{-Al}_2\text{O}_3$, a common soil mineral.

We used density functional theory (DFT) calculations, in particular the PBE functional with the Grimme D2 dispersion correction, as implemented in the CP2K software. The $\alpha\text{-Al}_2\text{O}_3$ (0001) surface was modelled using periodic slabs. The binding energies between this surface and small organic molecules were calculated to find out which organic functional groups bind most strongly to this mineral surface.

The calculated binding energy for molecularly adsorbed water was -1.32 eV and for dissociatively adsorbed water -1.62 eV. The amide, amine and carboxylic acid groups were found to bind more strongly to this surface compared to water. Methylamine was the strongest bound adsorbate, its calculated binding energies were -2.03 eV for molecular and -2.65 eV for dissociative adsorption. All the studied molecules bound more strongly to the $\alpha\text{-Al}_2\text{O}_3$ (0001) surface in the dissociated form than in the molecular form. Hydrogen bonding was a major contributor to the stability of adsorption. Overall, we found that organic molecules bind to $\alpha\text{-Al}_2\text{O}_3$ (0001) more strongly than water, and thus they are likely to displace adsorbed water from this mineral surface. This strong binding of organic molecules is likely to facilitate OC sorption in soils.

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Computational Investigation of Radiation Damage in Metals

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e05-enviro-mol

Due to the impact of fossil fuels on the environment, the need to find clean energy alternatives is becoming more and more apparent. Nuclear power could provide one possible solution due to reduced greenhouse gas emission. Within a nuclear reactor core, cladding materials are exposed to high energy neutron bombardment which can damage the material, reducing its performance and lifespan. Therefore, the design of radiation resistant materials is of paramount importance to the next generation of nuclear reactors. Tungsten and its alloys are promising candidates for use as cladding due to their high melting point and structural integrity at high temperature.

Quantum mechanical techniques have been used to simulate the structural, electronic and vibrational properties of tungsten and other metals, which are relevant for tungsten alloys. The PBE and PBEsol functionals have been compared, with particular emphasis paid to phonon properties. Furthermore, collision cascade simulations have been carried out using classical molecular dynamics to examine the structural changes of metals under irradiation. Common point defects and defect clusters are examined.

Atomistic Insights of Multiple Stacking Faults in CdTe Thin-film Photovoltaics

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e05-gener-pan

Cadmium telluride is the leading technology for thin-film solar cells. As deposited, CdTe films contain a very high concentration of stacking faults and exhibit poor photovoltaic efficiency. An extra annealing treatment with CdCl_2 is required to produce high efficiency cells. Although the precise mechanism for this performance increase is unknown, the concentration of stacking faults is greatly reduced in treated cells.

This work uses high accuracy density functional theory calculations to investigate the role of stacking faults in CdTe. All experimentally observed faults are found to be very low energy, correlating with their high concentrations. No fault clustering mechanism is found, suggesting a cause for the large observed quantities of small lone faults despite larger twin structures being more stable. While polytype faults are shown to significantly reduce CdTe's bandgap they are found to have high defect formation energies and are not observed experimentally, restructuring to bulk-like CdTe when multiple such faults are simulated. However, increased lone tetrahedral fault density may produce shallow carrier trap states, thereby reducing cell performance. The removal of these defects may therefore be a leading cause of CdTe's photovoltaic efficiency improvement through CdCl_2 treatment.

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La_xSr_{1-3x/2}TiO₃–Graphene Hybrid Interfaces

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e05-gener-par

Thermoelectric devices, which convert waste heat into electricity, represent a viable and under-utilized route for energy-harvesting. The current range of materials used in these devices are generally toxic, expensive and do not work at high temperatures. Oxides comprised of earth abundant and non-toxic elements show great promise and have the potential to be used in the recovery of waste heat from industrial processes and internal combustion engines. Important requirements include a low thermal conductivity and a high electrical conductivity. In the case of many of the prospective oxides, research is being carried out to reduce thermal conductivity by doping, nano-engineering and dimensionality reduction, but these often lead to difficulties in improving the electrical conductivity.

Recent experimental work has shown that synthesizing hybrid materials comprised of oxide and carbon may offer a good compromise. In this presentation we describe our preliminary work using density-functional theory (DFT) with dispersion corrections to understand and ultimately control the factors leading to enhanced thermoelectric properties. The work suggests that both p-type and n-type doping of SrTiO₃ can be achieved by coupling graphene to different surface terminations SrTiO₃. This results in desirable electronic properties. Currently, we are extending the work by evaluating the effect of doping SrTiO₃ with La, both on the electronic and the vibrational properties. Thus we will also present the results of our investigation of how the presence of La doping modifies the electronic and vibrational properties of the La_xSr_{1-3x/2}TiO₃-Graphene composites. These demonstrate that hybrid materials do indeed offer the potential for improving the thermoelectric properties, but that more work is needed.

High lithium ion diffusion in Al doped lithium phosphidosilicate Li_2SiP_2 : a solid Li electrolyte material

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e05-store-pan

The lithium phosphidosilicates are an interesting new class of potential solid Li electrolyte materials. These systems are made up of a complex framework comprised of $(\text{Si}_4\text{P}_{10}^{14-})$ corner-sharing “super-tetrahedra”. The high anionic charge on the super-tetrahedral framework allows for a large number of charge compensating lithium ions to be present in the interstitial space amongst the network. Experimentally, this results in very low energy barriers to lithium diffusion, within the region of 0.1 eV or below, with ionic conductivities of approximately 6×10^{-6} S/cm.^{1,2} Thus, the lithium phosphidosilicates are a promising new class of materials for solid state lithium ion batteries.

In this work, we have focused on the system Li_2SiP_2 (LSP)^{1,2} and studied both the doping and lithium diffusion properties using density functional theory (DFT). We find that trivalent cation dopants prefer to occupy the silicon site rather than the lithium site. The most favourable dopant is Al, showing similarities to oxide zeolite materials.⁴

Ab initio molecular dynamics (AIMD) calculations on both pure and 10% Al doped LSP imply increased lithium ion diffusion at 700 K and below in the doped LSP system. Nudged elastic band (NEB) calculations suggest an interstitial mechanism as the most favourable Li migration pathway.

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Atomistic Simulation of Oxide Interfaces in Energy Technologies

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e05-store-par

Materials used for energy storage and generation applications all have complex microstructures and the resulting interfaces may profoundly affect their properties. In this project we are investigating these interfaces at the atomic level. Our aim has been to develop a straightforward protocol for generating a range of grain boundary structures quickly and efficiently. Then investigate their properties using potential based molecular dynamics focusing on how their structure modifies atom transport. We have begun to apply this approach for materials used in both lithium ion batteries (LIBs) and in solid oxide fuel cells (SOFCs).

The focus of the work on LIBs has been to investigate two solid electrolytes; lithium lanthanum titanate (LLTO) and lithium lanthanum zirconate (LLZO). We show that there is an additional level complexity as the structures evolve with temperature. We then show how the presence of tilt grain boundaries modifies the Li transport. The results demonstrate that the distribution of lithium, lanthanum and oxygen vacancies in the lattice affects the dimensionality, magnitude and Li-ion diffusion mechanism. More recently, we have begun to explore heterointerfaces, *i.e.* boundaries between cathode and electrolyte materials, for example between lithium cobalt oxide (LCO) and LLTO.

This approach can be applied more widely, and we describe the application to interfaces in SOFC materials, in this case modelling oxygen diffusion. The initial focus was on an archetypal fluorite-perovskite system, $\text{CeO}_2 \parallel \text{SrTiO}_3$. Currently we have obtained a structural and energetically stable model for the (100) $\text{CeO}_2 \parallel \text{SrTiO}_3$ interface. In addition to considering the stoichiometric interfaces, we are also investigating the role of doping by modelling SrTiO_3 interfaces with gadolinium doped ceria (GDC). For each case considered we show that atom transport at these interfaces differs from that of the bulk.

NaVOPO₄ Polymorphs as Cathode Materials for Na-ion Batteries: Ion Diffusion and Cation Doping Behaviour

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e05-store-lee

Sodium-ion batteries (NIBs) have been attracting more attention in the last years due to the abundance of sodium in Earth. Among several different materials used as cathode materials for NIBs, the vanadium-based phosphates have drawn much attention in recent years. Recently, it has been demonstrated that the vanadyl phosphate VOPO₄ with a layered structure is a good candidate as cathode active material. There are several polymorphs of this compound with different structures, such as alpha, alpha-I, alpha-II beta, epsilon, delta, etc. So far only three sodiated products have been identified: alpha, alpha-I and beta.

In this work, we have performed density functional theory (DFT) calculations on the α , β and α_1 -NaVOPO₄ polymorphs. We have been able to reproduce the experimental structural and cell parameters. We have explored different diffusion paths to understand how the structure of the studied compounds affects the Na mobility by means of molecular dynamics (MD) calculations. We have performed cation doping studies on the three polymorphs by replacing some of the V atoms by other metal atoms (Al, Co, Fe, Mn, Ni and Ti). In conclusion, this computational study will help to unravel the electrochemical behavior of the different NaVOPO₄ polymorphs.