MM 22: Materials for Energy Storage and Conversion

Sessions: Computational I and II

Time: Wednesday 10:15–13:15 Location: H43

MM 22.1 Wed 10:15 H43

First-Principles Calculations of Charge States in Defective SOFC/SOEC Perovskite Materials — •Daniel Mutter[1], Daniel F. Urban[1], and Christian Elsässer[1,2] — [1]Fraunhofer IWM, Wöhlerstraße 11, 79108 Freiburg — [2]Freiburger Materialforschungszentrum FMF, Stefan-Meier-Str. 21, 79104 Freiburg

Solid oxide fuel cells (SOFC) and solid oxide electrolyzer cells (SOEC), which transform chemical into electrical energy and vice versa, have the potential to make a significant contribution to the efforts of overcoming future problems of the energy economy. An optimal functionality of these devices requires a high catalytic activity at the electrodes. This strongly depends on point defect concentrations and on the capability of the material to allow for fast charge transfer reactions. Promising anode materials regarding these requirements are perovskite compounds (ABO_3), where the transition-metal ion on the B site can adopt different oxidation states by accepting and releasing electrons during the oxygen reactions at the SOEC/SOFC surfaces. We present results of density functional theory GGA+U calculations for the changes in oxidation states of the transition metal ions Fe and Mn in $LaFeO_3$ and $La_xCa_{1-x}MnO_3$ ($0 \le x \le 1$), respectively, when point defects such as anionic and cationic vacancies are present near the metal ions. After identifying the dominant defect species, a Bader charge analysis was performed and partial electronic densities of states were derived. The latter are compared to electron energy-loss near-edge spectra (ELNES), which are sensitive to changes of the bonding environment and hence of the oxidation states of individual atoms.

MM 22.2 Wed 10:30 H43

Interaction of the H_2 molecule with carbon nanostructures: A DFT study — •Dominik Nöger and David Holec — Department of Materials Science, Montanuniversität Leoben, Franz-Josef-Strasse 18, A-8700 Leoben, Austria

On a long path of finding appropriate materials to store hydrogen, graphene and carbon nanotubes have drawn a lot of attention as potential storage materials. Their advantages lie at hand since those materials provide a large surface area (which can be used for physisorption), are cheap compared to metal hydrides, are abundant nearly everywhere, and most importantly, can increase safety to existing storage solutions. The present Density Functional Theory (DFT) study employs Tkatchenko-Schäffler (TS) van-der-Waals correction. The preferred adsorption site for an H_2 molecule is the hollow (centre of hexagon) site of planar graphene, with the molecule orientated parallel to graphene. Next, the influence of vacancy and Stone-Wales defects in graphene was studied. Neither of them provides increased adsorption energies for H_2. Interestingly, vacancy shows a capability to capture H_2 inside the defect in a metastable state; this configuration is unstable both for pure graphene as well as for the Stone-Wales defect. Finally, the impact of different carbon nanotube diameters and geometries (zigzag & armchair configuration) on physisorption energetics and behaviour is presented.

MM 22.3 Wed 10:45 H43

6Mg(NH2)/9LiH/LiBH4: Molecular Dynamics and Hydrogen Diffusion — •Neslihan Aslan[1,2], Wiebke Lohstroh[2], Sebastian Busch[1], Claudio Pistidda[1], Klaus Pranzas[1], and Martin Müller[1] — [1]Helmholtz-Zentrum Geesthacht, Germany — [2]Heinz Maier-Leibnitz Zentrum, TUM, Garching, Germany

Methods to store hydrogen are e.g. physical technologies (compression) or chemical bonding in metal hydrides. Within the complex hydrides, the metal amides Mg(NH2)2-LiH have recently gained in importance. They have good hydrogen storage properties with high capacity (ca. 4 wt%) and good reversibility. The drawback of these materials is the high kinetic barrier for hydrogenation, which results in a long loading time. This can be overcome with the addition of LiBH4. So far Mg(NH2)2-LiH-LiBH4 is an outstanding candidate for hydrogen storage. Interestingly, some compositions can even reach operation temperatures below 100 °C and the desorbed products contain amongst others liquid phases. The hydrogen uptake and release properties of this system are well characterized in terms of capacity, kinetics and phase composition, but the basic mechanism how the reaction takes place and why it has these excellent storage facilities is still unknown. With 6Mg(NH2)/9LiH/LiBH4 we want to understand the system and the reaction mechanism. We will present first data of neutron scattering experiment using quasielastic scattering at TOFTOF to study hydrogen diffusion of the desorbed and absorbed state, as well as small angle neutron scattering to study particle sizes to gain further insight on the hydrogenation/dehydrogenation mechanism.

MM 22.4 Wed 11:00 H43

Applicability of MAX phases as diffusion barrier for hydrogen and chromium in SOFC — •Daniel F. Urban[1,2], Dimitrios Satkas[1], and Christian Elsässer[1,2] — [1]Fraunhofer IWM, Freiburg, Germany — [2]University of Freiburg, FMF, Germany

Promising candidates in the search for corrosion protection coatings for high temperature energy-conversion devices such as solid oxide fuel cells (SOFC) are MAX phases which are ternary metal carbides and nitrides with multi-layered crystal structures. To assess the capability of MAX phases as diffusion barriers for hydrogen and chromium, we investigate the absorption and migration of H and Cr atoms in a variety of MAX-phase carbides and nitrides by means of first-principles calculations based on density functional theory. Based on the calculated formation and migration energies we discuss how MAX-phase coatings can act as efficient protective diffusion barriers for both hydrogen and chromium and explain the underlying migration mechanisms. While Cr atoms are found to diffuse via a vacancy mediated mechanism and substitute M- and A-atoms, H diffusion occurs on essentially decoupled bilayer dice-lattices of tetrahedrally and octahedrally coordinated interstitial sites. [1]. We discuss the possibility to tailor specific material properties like lattice constants or thermal expansion coefficients for a given required diffusion barrier impact by making use of the flexibility of the MAX-crystal structure which allows for mixed $(M_1,M_2)(A_1A_2)X$ phases.

[1] F. Colonna, C. Elsässer, RSC Advances 7, 37852 (2017).

MM 22.5 Wed 11:15 H43

Description of bulk and surface polarons in oxide materials using DFT+U — •Matthias Kick, Cristina Grosu, Christoph Scheurer, Karsten Reuter, and Harald Oberhofer — Technische Universität München

Lithium titanium oxide $Li_4Ti_5O_{12}$ (LTO) is an intriguing anode material promising particularly long lived batteries, due to its remarkable phase stability during (dis)charging of the cell. Moreover, its high intercalation potential also prevents the formation of Li dendrites. Unfortunately, the low intrinsic electronic conductivity of LTO still severely limits its use. An elegant way to improve on this drawback, is to introduce oxygen vacancies resulting in formation of Ti^{3+} centers. In our study we use *Hubbard corrected density-functional theory* (DFT+U) to show that this leads to the formation of polaronic states, which can again hamper electron conduction. In order to gauge the polaronic charge mobility we compare the relative stabilities of different polaron location patterns in bulk and surface LTO for a number of oxygen defects.

15 min. break

MM 22.6 Wed 11:45 H43

Solid-State Li_2S-P_2S_5 Electrolytes: A DFT based Force-Field Parameterization — •Carsten Staacke[1], Simon Rittmeyer[1], Hendrik Heenen[1], Johannes Voss[2], Christoph Scheurer[1], Alan Luntz[2], and Karsten Reuter[1] — [1]Theoretische Chemie, TU München — [2]SLAC National Accelerator Laboratory, USA

All-solid-state Li-ion batteries promise gains in safety and durability by replacing the liquid by a solid-state electrolyte (SSE). In this context, the xLi_2S-$(100\text{-}x)P_2S_5$ (LPS) SSE group, especially $Li_7P_3S_{11}$, has gained much attention. While $Li_7P_3S_{11}$ glass has a rather limited conductivity, a meta stable glass-ceramic state shows impressive conductivity [1]. Understanding the reasons for this large change of conductivity, requires a detailed atomistic description not directly accessible from experiment. On the other hand, the material complexity and timescales involved in realistic glass-ceramic SSE simulations are beyond current predictive-quality density-functional theory (DFT) based molecular dynamics. We therefore engage in the development and first-principles validation of a polarizable force field for the LPS SSE. In particular, the Buckingham parametrization and polyanion models are discussed. We further give a perspective on how to improve our scheme by Gaussian approximation potentials (GAP).

[1] A. Hayashi, A. Sakuda, M. Tatsumisago, *Front. Energy Res., **2016**, 4, 25*

MM 22.7 Wed 12:00 H43

Elastic moduli of LISICON and garnet superionics from first-principles molecular dynamics variable cell — •Giuliana Materzanini and Nicola Marzari — Theory and Simulation of Materials (THEOS) and National Centre for Computational Design and Discovery of Novel Materials (MARVEL), École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

In this work we have calculated elastic moduli of different materials belonging to two of the most studied and most performing families of crystalline ionic conductors, namely the LISICONs and the garnets, LGPS ($\mathrm{Li_{10}GeP_2S_{12}}$), LGPO ($\mathrm{Li_{10}GeP_2O_{12}}$) and LLZO ($\mathrm{Li_7La_3Zr_2O_{12}}$), in their different phases. Sampling of the space-phase was performed according to Car-Parrinello molecular dynamics in the variable cell volume and shape NpT ensemble. From the MD trajectories the time-dependent cell and strain matrices were extracted and the strain fluctuations were calculated as block averages of the strain tensor cross-products, for which statistical convergence was carefully monitored. Results for the elastic moduli of the different materials and for their different phases were reported and discussed, on the light of the available experimental literature.

MM 22.8 Wed 12:15 H43

Cage-hopping mechanism of lithium cation diffusion in liquid thiophene-derivatives as revealed by AIMD simulations — •Pouya Partovi-Azar and Daniel Sebastiani — Martin-Luther Universität Halle-Wittenberg

Unraveling the diffusion mechanism of $\mathrm{Li^+}$ in thiophene-based liquids is of great importance in reaching optimal electrolyte compositions for Li-based energy-storage devices. However, the dynamics of $\mathrm{Li^+}$ in thiophene-based electrolytes is barely known at an atomistic level, which makes it hard to reveal the actual mechanism of the diffusion. Here, we report on DFT-based *ab initio* molecular dynamics simulations performed to study the fundamental processes occurring in the $\mathrm{Li^+}$/thiophene-based systems. We consider $\mathrm{Li^+}$ ions at 1M concentration in thiophene and 3,4-ethylenedioxythiophene (EDOT) liquids in the condensed phase. Our simulations reveal a cage-hopping mechanism for $\mathrm{Li^+}$ diffusion in both liquids. Each $\mathrm{Li^+}$ is surrounded by four liquid molecules in a cage structure, while being coordinated by four sulfur and four oxygen atoms in the case of thiophene and EDOT, respectively. The liquid molecules in a cage form a slightly deformed tetrahedron, where a “weak” part is formed due to repulsive interaction between two closer sulfur atoms, allowing the $\mathrm{Li^+}$ ion to escape the cage. This finding can be directly used to define proper collective variables for metadynamics or kinetic Monte-Carlo simulations. The thermal energy at 300K is found to be enough to trigger a $\mathrm{Li^+}$ hopping in the thiophene liquid, but falls short in the case of EDOT liquid, which possesses a stronger molecular network due to H bonding.

MM 22.9 Wed 12:30 H43

Dense storage of alkali metals between graphene bilayers: a computational study — •Mahdi Ghorbani-Asl[1], Ilia Chepkasov[1,2], and Arkady V. Krasheninnikov[1] — [1]Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf, 01314 Dresden, Germany — [2]Katanov Khakass State University, pr. Lenina 90, Abakan 655017, Russia

We study the intercalation of alkali metals, namely lithium and sodium, between graphene sheets using density functional theory calculations with the van der Waals correction. The structures and energetics of a different number of alkali layers with closed packed structure have been investigated for AB and AA stacking sequences of bilayer graphene. The intercalation energies suggested that the AA stacking is more favorable for the single-layer intercalation but it has less effect on the multilayered storage. Our calculations showed that there is a clear correlation between the intercalation energy and the electron transfer between the intercalate and graphene. While the higher values of charge transfer observed for the single layer intercalation, the charge transfer is noticeable only for the outer alkali layers in the multi-layer case. As a result, the intercalation energy reduces with increasing the number of the layer from double to triple layers. The present study can shed light on the design of high storage alkali batteries using two-dimensional layered materials as reported recently [1].

[1] M. Kühne, F. Börrnert, S. Fecher, M. Ghorbani-Asl, J. Biskupek, D. Samuelis, A. V. Krasheninnikov, U. Kaiser, J. H. Smet, Nature (2018). https://doi.org/10.1038/s41586-018-0754-2

MM 22.10 Wed 12:45 H43

A first-principles based LATP force-field for grain-boundary simulations — Simon Rittmeyer[1], Karsten Reuter[1], Rüdiger Eichel[2], and •Christoph Scheurer[1] — [1]Theoretische Chemie, TU München — [2]IEK-9, FZ Jülich

Superionic lithium-ion conductors of NASICON structure are promising solid-state electrolytes (SSE) for all solid-state batteries (ASSB). A detailed multi-modal experimental analysis of carefully sintered $\mathrm{Li}_{1+x}\mathrm{Al}_x\mathrm{Ti}_{2-x}(\mathrm{PO}_4)_3$ (LATP, $x = 0.3$) has yielded interesting structural insights and a surprisingly lower ionic conductivity in the amorphous grain boundary interphase than in the grain bulk.[1] Combined with high cycling stability observed in a LATP-based phosphate-backbone ASSB, these findings call for a detailed microscopic understanding. We have constructed a first-principles based force-field which covers stoichiometries $x = 0 \ldots 0.3$ and sampled surface slab models representing possible LATP mixed occupancies. DFT computations on large surface models yield first insights into the mechanisms behind the peculiar properties of this material.

[1] A. Mertens, S. Yu, N. Schön, D. Guenduez, H. Tempel, R. Schierholz, F. Hausen, H. Kungl, J. Granwehr, and R. Eichel, Solid state ionics **309** (2017), 180.

MM 22.11 Wed 13:00 H43

Effect of mixed surface terminations on the structural and electrochemical properties of two-dimensional $\mathbf{Ti_3C_2T_2}$ and $\mathbf{V_2CT_2}$ MXenes multilayers — •Nuala Mai Caffrey — School of Physics & CRANN, Trinity College, Dublin 2

MXenes, a family of layered transition metal carbides and nitrides, have shown great promise for use in emerging electrochemical energy storage devices, including batteries and supercapacitors [1]. However, MXene surfaces are terminated by randomly distributed –O, –F and –OH functional groups and there is considerable debate regarding how the intercalating alkali metal ions interact with these functional groups. For instance, their measured Li or Na capacity is far lower than that predicted by theoretical simulations, which generally assume uniformly terminated surfaces. The extent to which this structural simplification contributes to such discrepancies is unknown.

I address this issue by employing first-principles calculations to compare the structural, electronic and electrochemical properties of two common MXenes, namely $\mathrm{Ti_3C_2T_2}$ and $\mathrm{V_2CT_2}$, with both uniform terminating groups and explicitly mixed terminations [2]. I find that the redox reaction is confined to the terminating groups for low concentrations of intercalated metal ions, with the oxidation state of the metal atoms unaffected until higher concentrations are achieved, in excellent agreement with experiment.

[1] Anasori et al, Nature Reviews Materials **2** 16098 (2017)

[2] Caffrey, Nanoscale **10** 13520 (2018)