UNIVERSITÀ DI TORINO

Dipartimento di Chimica

2023 - 2027 DIPARTIMENTO DI ECCELLENZA
Ministero dell'Università e della Ricerca

Nanomaterials for Industry and Sustainability

International Workshop & NIS colloquium

Explainable Machine learning: A closed-loop feedback approach for metal hydrides design and discovery

September 20th, 2024
Aula 14, Via Quarello 15/A, Torino

Attendance is free but registration is required:
NIS Colloquium UniTO (by 16/09/2024)
For any further information please write to: erikamichela.dematteis@unito.it

9.30-10.00
Welcome coffee (Aula 12)

10.00-10.15
Gabriele Ricchiardi - *Director of NIS Interdepartmental Centre - Università di Torino*
Marcello Baricco - *President of NIS Interdepartmental Centre - Università di Torino*
Welcome address

Morning session

Chair**: Marcello Baricco**

10.15-10.30
Erika Michela Dematteis
Università di Torino, Department of Chemistry, Torino (Italy)
An introduction and overview of the EX-MACHINA project

10.30-11.15
Vitalie Stavila
Sandia National Laboratories (USA)
Machine Learning Driven Design of High-Capacity Metal Hydrides

11.15-11.45
Mauro Palumbo
Università di Torino, Department of Chemistry, Torino (Italy)
Machine Learning-Driven Development of Metallic Hydrides: promises and challenges

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11.45-12.15
Ebert Alvares
Helmholtz Zentrum Hereon (Germany)
Evaluation of Multicomponent Thermodynamic Modeling Strategy for FeTi-based Alloys for Hydrogen Storage

11.45-12.15
Marta Corno
Università di Torino, Department of Chemistry, Torino (Italy)
Modeling Metal Hydrides: A Review of First Principle Calculation Challenges

13.00-14.00
Light Lunch & Group Picture (Aula 12)

Afternoon session

Chair**: Mauro Palumbo**

14.00-14.30
Luca Pasquini
Università di Bologna (Italy)
Thermodynamics, kinetics, and activation properties of $TiFe_{1-x}Ni_x$ intermetallics

14.30-15.00
Paola Rizzi
Università di Torino, Department of Chemistry, Torino (Italy)
TiFe from recycled materials: influence of side elements on sorption properties

15.00-15.15
Young researchers' 5-minute Pitch

- *Valentina Fiume – University of Turin, Italy*
- *Francesca Garelli – University of Turin, Italy*
- *Luca Leoni – University of Bologna, Italy*
- *Samia Rachidi – Rabat University, Morocco*

15.15-15.30
Erika Michela Dematteis
Università di Torino, Department of Chemistry, Torino (Italy)
Closing of the workshop - EX-MACHINA project: outlook and closing remarks

Online connection available at:

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Nanomaterials for Industry and Sustainability

An introduction and overview of the EX-MACHINA project

Climate change poses serious risks for ecosystems, human health, and economy. Energy production, storage and usage need sweeping changes to increase renewable energy (RE) applications and reduce dependence from fossil fuels. Hydrogen, H_2, as an attractive energy carrier, is suggested for energy storage from RE and for grids balancing. Metal Hydrides (MH) are efficient H_2 carriers in terms of tuneable H_2 delivery pressure-temperature, reversibility, and volumetric density. As strongly supported by the International Energy Agency (IEA), to reach the EU Fuel Cell and Hydrogen Joint Undertaking (FCH-JU) and US Department of Energy (DOE) targets for the development of an H_2 infrastructure, an efficient and safe storage of H_2 is necessary, which can be obtained in intermetallic compounds (IMC). Significant research efforts have been devoted to defining new compositions or MH materials, but there is a need of a public database including thermodynamic and structural data, nowadays dispersed in the literature. Hence, the open question is "Which design rules exist that dictate thermodynamic properties across the wide chemical and crystallographic space?". Computer modelling and data-driven approaches can address such challenging material science question but require significant computational and experimental efforts. Knowledge-driven materials design enabled by Machine Learning (ML) is a suitable approach. It uses algorithms trained on large amount of data to predict physical and chemical properties. Regression and classification methods are often used as "black boxes", so the discovery of hidden relationships is limited. Understanding ML decisions would improve models' accuracies and derive insights in complex phenomena (e.g., H_2 uptake and release in MHs). Explainable ML approaches extract feature's importance when training a model by suitable prediction methods and mapping directly interpretable by design.
EX-MACHINA aims to develop and apply an integrated experimental-theoretical closed-loop feedback method for developing new metal hydride materials by explainable machine learning and providing structure-property relationships. This will enable the development of sustainable and suitable materials for green hydrogen storage and handling.

Erika Michela Dematteis obtained the title of PhD cum laude in Chemical and Materials Sciences in 2018 at the University of Turin. She is currently a researcher at the Chemistry department of the University of Turin, and she studies metallic and inorganic materials for energy management. Her studies address the development of materials for batteries and for large-scale renewable hydrogen storage, combining theoretical and machine learning approaches and advanced synthesis and characterization methods. In 2022 she was the winner of the Hydrogen Europe Research "Best Researcher of the Year" award.

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Machine Learning Driven Design of High-Capacity Metal Hydrides

Vitalie Stavila,[1] *Matthew D. Witman,*[1] *Mark D. Allendorf*[1]

[1] *Sandia National Laboratories, Livermore, California, 94550, USA*

Hydrogen is a promising zero-carbon energy carrier poised to play a crucial role in future energy systems. However, safe and cost-effective storage and transportation remain challenging. Storing hydrogen in solid metal hydrides offers safety benefits due to low-pressure operation and higher volumetric density compared to high-pressure storage. We developed a machine learning approach to design interstitial and high entropy alloys with a high hydrogen-to-metal ratio and tunable equilibrium plateau pressures. Using a gradient boosting tree model, we established simple, physics-based design rules that govern the thermodynamic properties of metal hydrides across diverse structures and compositions. Our analysis revealed that the equilibrium H_2 pressure of metal hydrides strongly depends on several descriptors derived from the alloy's elemental composition and crystal packing. We synthesized dozens of new hydride materials using high-energy ball-milling and arc-melting techniques, spanning a wide range of pressure and temperature conditions for reversible hydrogen uptake and release. These materials were characterized by X-ray diffraction, scanning and transmission electron microscopy, and X-ray photoelectron spectroscopy. Hydrogen storage properties were assessed using the Sieverts method, with Pressure-Composition-Temperature measurements determining the enthalpy and entropy of hydrogen uptake and release in the most promising materials. We demonstrated that the complex chemical environments in hydrides composed of multiple atom types significantly influence the thermodynamics and kinetics of chemical processes, which can be harnessed for sustainable hydrogen storage applications.

Vitalie Stavila is a Staff Scientist at Sandia National Laboratories in Livermore, CA working on the development of materials solutions for energy generation and storage. In his current research Dr. Stavila uses various X-ray scattering and diffraction techniques to solve fundamental and applied materials science problems related to bulk and nanostructured metal hydrides, borides, oxides, chalcogenides, and metal-organic frameworks. A central theme in Dr. Stavila's research is the rational design of new materials by changing the chemical composition, the arrangement of the atoms or molecules in crystalline or amorphous configurations, and the size, shape, and orientation of nanoparticles and thin films. Dr. Stavila has edited two books, co-authored 15 patents and published more than 240 research papers.

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Machine Learning-Driven Development of Metallic Hydrides: promises and challenges

Giancarlo Beltrame[0], Matthew Witman[1], Erika Dematteis[0], Vitalie Stavila[1], ***Mauro Palumbo[0]***

[0]Department of Chemistry, University of Turin, Turin, Italy
[1]Sandia National Laboratories, Livermore, California

Machine learning (ML) is playing an increasingly important role in the development of metallic hydrides for hydrogen storage, a key aspect of advancing clean energy technologies. The primary focus of ML applications in this area is to discover and optimize new hydride materials that can store hydrogen efficiently and safely, while minimizing energy losses.
This study advances machine learning models to improve the accuracy of predicting standard equilibrium pressure during hydrogenation—a crucial factor in selecting materials for specific hydrogen storage applications. Building on foundational models from Sandia National Laboratories [1], this work enhances prediction accuracy and contributes to optimizing hydrogen storage technologies. Several machine learning algorithms, including Random Forests and Support Vector Machines from the Scikit-learn library, were employed on a dataset containing both experimental and computed thermophysical data on metal hydrides. This dataset was developed through a collaborative effort between the University of Turin and Sandia National Laboratories. Additionally, the study applied a novel data augmentation method known as PAirwise Difference Regression (PADRE) [2], which significantly expanded the dataset. The effectiveness of this augmentation technique is analyzed and compared to results obtained by adding new experimental data to the dataset. Finally, we will highlight the challenges to further enhance the model predictions and possible new future work on the topic.

[1] Extracting an Empirical Intermetallic Hydride Design Principle from limited data via interpretable machine learning, M. Witman et al., The Journal of Physical Chemistry, 2019
[2] Pairwise Difference Regression: A Machine Learning Meta-algorithm for Improved Prediction and Uncertainty Quantification in Chemical Search. Michael Tynes, Wenhao Gao, Daniel J. Burrill, Enrique R. Batista, Danny Perez, Ping Yang, and Nicholas Lubbers, Journal of Chemical Information and Modeling, 2021

Mauro Palumbo graduated in Materials Science at the University of Turin, Italy, in 2001. From 2001 to 2004, he pursued a Ph.D. in Materials Science at the Department of Chemistry, University of Turin. Between 2004 and 2020, he worked in various research centers in Italy and abroad, including the National Institute for Materials Science (Tsukuba, Japan), the International Center for Advanced Materials Simulations (Ruhr Universität Bochum, Bochum, Germany), and Scuola Internazionale di Studi Avanzati (Trieste, Italy). Since 2020, he has been an associate professor in “Scienza e Tecnologia dei Materiali” (Materials Science and Technology, ING-IND/22) at the Department of Chemistry, University of Turin. He teaches courses on metallic materials and computational methods to students of Materials Science and Chemistry. He is the author of 63 publications in peer-reviewed journals (1351 citations, h-index 20, source Scopus).

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Evaluation of Multicomponent Thermodynamic Modeling Strategy for FeTi-based Alloys for Hydrogen Storage

Hydrogen, with its high energy density, is considered a promising next-generation energy carrier as it may be produced cleanly through electrolysis of water powered by renewable energy sources. However, the volumetric energy density of liquid and gaseous hydrogen is poor, making it challenging to develop efficient storage. Solid-state storage using FeTi-based metal hydrides is considered as a suitable solution, owing to their near-ambient operating conditions, higher volumetric capacity, and safety.

Hydrogenation of metal hydrides is governed by their entropic and enthalpic properties, which combined determine the temperature and pressure conditions for hydrogenation. Therefore, tuning their composition through alloying is crucial for tailoring their thermodynamics for technological use. Multicomponent thermodynamic modeling is a well-suited approach for guiding these materials' development.

From the computational perspective, while the widely accepted bcc order-disorder model has been successfully employed in many systems, complexities arise when used for AB metals and their hydrides, particularly when A and B elements have vastly different hydrogen affinities. We recently addressed this problem by modeling the FeTi-H system using an analytical expression for the Gibbs free energy derived from the perfectly ordered state of the bcc order-disorder model[1]. This ensured the model was compatible with the metallic system, but its extrapolation to multicomponent alloys remained elusive.

In this presentation, we propose a comprehensive framework for modeling the thermodynamics of FeTi-based multicomponent AB-type interstitial hydrogen storage materials. We will focus on the requirements for describing the paraequilibrium, a specific equilibrium state relevant to the interstitial hydrogenation of alloys. The model is simplified further by using density functional theory point-defect calculations to determine the site preferences for substitutional impurities in the FeTi sublattices, which in turn allows us to choose only the necessary model parameters required to evaluate phase equilibria in the FeTi-based multicomponent system, paving the way for future FeTi-based multicomponent thermodynamic model assessments.

[1] E. Alvares, P. Jerabek, Y. Shang, A. Santhosh, C. Pistidda, T. W. Heo, B. Sundman, M. Dornheim, Modeling the thermodynamics of the FeTi hydrogenation under para-equilibrium: An ab-initio and experimental study, Calphad 77 (2022) 102426. doi:10.1016/J.CALPHAD. 2022.102426.

Ebert Alvares has obtained an M.Sc.-Ing. degree in materials science & engineering from the Grenoble Alpes University in France and the Federal University of Sao Carlos in Brazil. Currently, he is pursuing a doctoral degree at the Institute of Hydrogen Technology of the Helmholtz-Zentrum Hereon. Ebert focuses on developing computational methods for the multiscale modeling of solid-state hydrogen storage materials for application in the sustainable energy sector. His expertise lies in computational thermodynamics, bridging atomistic and phase-field simulations to design new materials with better performance under operating conditions.

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Modeling Metal Hydrides: A Review of First Principle Calculation Challenges

Density Functional Theory (DFT) plays a crucial role in complementing experimental studies on the structure and dynamics of hydrogen in metal hydrides.
This contribution aims to review the challenges and advancements in applying DFT to model hydrogen diffusion and adsorption in metal systems, with a glimpse into the potential integration of machine-learning techniques.
Chemists have long recognized the need for metal hydrides to achieve a stability 'sweet spot': too stable and insufficient hydrogen is released at low temperatures; too unstable and the reaction may not be reversible under practical conditions. Fortunately, DFT-based methods enable the assessment of this stability by predicting thermodynamic properties, equilibrium reaction pathways, and phase diagrams for candidate metal hydride systems with reasonable accuracy. [1]
By using only proposed crystal structures and compositions, millions of mixtures of pure metals, metal hydrides, and alloys have been efficiently screened to identify promising reaction schemes.
DFT has been successfully used to predict hydrogen hopping rates in various metal matrices, including pure metals, ordered alloys, and disordered alloys. Recently, theoretical works have corroborated the evidence that nanostructured metal borohydrides show advantages for energy storage applications compared to their bulk counterparts and that the role of additives as the doping with transition metals (e.g. Ni) can further facilitate the release of H_2. [2,3]

[1] Gulino, V.; Dematteis, E.M.; Corno, M.; Palumbo, M.; Baricco, M. Theoretical and Experimental Studies of $LiBH_4$–LiBr Phase Diagram *ACS Appl. Energy Mater.* **2021**, *4*, 732.

[2] Albanese, E.; Corno, M.; Baricco, M.; Civalleri, B. Simulation of nanosizing effects in the decomposition of $Ca(BH_4)_2$ through atomistic thin film models. *Res. Chem. Intermediat.* **2021**, *47*, 345.

[3] Pantaleone, S.; Albanese, E.; Donà, L.; Corno, M.; Baricco, M. Theoretical prediction of nanosizing effects and role of additives in the decomposition of $Mg(BH_4)_2$. *RSC Adv.* **2024**, *14*, 6398.

Marta Corno earned a Ph.D. in Chemical Sciences in 2007 at the University of Turin and is currently associate professor in Physical Chemistry at the Chemistry Department of the same University. As a computational chemist, she applies quantum mechanical methods to model advanced materials for energy storage applications. Her research includes interactions of biomolecules with inorganic surfaces for biomaterials and pharmaceuticals, and prebiotic chemistry. She is author of 80 articles in international peer-reviewed journals and passionate about scientific communication.

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Thermodynamics, kinetics, and activation properties of $TiFe_{1-x}Ni_x$ intermetallics

E. Pericoli,[1] V. Ferretti,[1] D. Verna,[1] E. Dematteis,[2] P. Rizzi,[2] M. Baricco,[2] and L. Pasquini[1]

[1] Department of Physics and Astronomy, University of Bologna, Bologna, Italy
[2] Department of Chemistry, University of Turin, Turin, Italy

The TiFe intermetallic alloy has proven to be a good candidate for hydrogen storage applications, thanks to the raw material abundance and good gravimetric and volumetric density (1.87 wt.% and 105 kg_{H2} m^{-3}, respectively) [1]. Over the past decades, the effect of stoichiometric tailoring by elemental substitution on TiFe thermodynamic and hydride-forming properties has been extensively investigated, highlighting the promising aspects of ternary $TiFe_{1-x}M_x$ (M being a transition metal) compounds for large-scale solid-state hydrogen storage applications. Notably, Ni substitution appears to have a significant impact in lowering the first plateau pressure, bringing milder conditions for the activation and enhancing resistance to poisoning [2-3].
The present work aims to investigate the effect of Fe partial replacement with Ni and Ti on the thermodynamics and kinetics of hydride formation and on the required activation conditions, drawing a general picture where structural and thermodynamic parameters are correlated. More specifically, we have carried out elemental substitution within the homogeneity range of the TiFe phase, varying Ni content from 0 to 30 at.% and Ti content from 50 to 53 at.%. Samples have been prepared by arc melting; structural, microstructural and hydrogen sorption properties have been determined by x-ray diffraction with Rietveld refinement, electron microscopy, Sievert apparatus and high-pressure differential scanning calorimetry. In addition, phase stabilities have been calculated by the Calphad method.
By establishing a correlation between the tailored compositions and the unit cell volume of the crystal, we aim to discuss the implications on hydride stability (enthalpy and entropy of formation and decomposition), hysteresis, activation conditions and equilibrium pressure, providing a comprehensive picture of the dependence of hydrogen storage properties on the specific stoichiometry.

[1] E. M. Dematteis,N. Berti, F. Cuevas, M. Latroche and M. Baricco, Mater. Adv., 2 (2021) 2524-2560
[2] K. D. Ćirić, A. Kocjan, A. Gradišek, V. J. Koteski, A. M. Kalijadis, V. N. Ivanovski, Z. V. Laušević, D. Lj. Stoijć, Int. J. of Hydrogen Energy, 37 (2012) 8408-8417
[3] Yaqin Li, H. Shang, Y. Zhang, P. Li, Y. Qi, D. Zhao, Int. J. of Hydrogen Energy, 44 (2019) 4240-4252

Luca Pasquini obtained the PhD title in condensed matter physics in 2000 from the University of Bologna, where he is currently professor at the Department of Physics and Astronomy. His research interests focus on materials for solid-state hydrogen storage and artificial photosynthesis based on photoelectrochemical processes. His studies combine several experimental methods for synthesis, structural analysis and characterization of physico-chemical properties of materials. He is the group leader of N-REX: Nanomaterials for Renewable Energy Conversion and Storage (site.unibo.it/n-rex/).

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TiFe from recycled materials: influence of side elements on sorption properties

Paola Rizzi[1], Francesca Garelli[1], Erika Michela Dematteis[1], Vitalie Stavila[2], Marcello Baricco[1]

[1]*University of Torino, Department of Chemistry and NIS, Via Giuria 7, Torino, Italy*

[2] *Sandia National Laboratories, USA*

In 2020 the European Commission, by the Circular Economy Action Plan, has defined the path to follow to achieve a more sustainable model for economic development. In this view, materials used for hydrogen storage must be included in a circular economy perspective. TiFe is a promising compound for hydrogen storage due to its high volumetric density, good sorption kinetic, reversibility and possibility to work in mild temperature and pressure conditions. As promising scraps candidates for TiFe production are Ti6Al4V and stainless steels, it is of importance to consider the influence of side elements like Al, Cr, Co and Cu on the sorption properties of TiFe.
$TiFe_{0.80}X_{0.20}$ (X = Al, Cr, Co, Cu) alloys were synthetised by arc melting and their chemical, structural, and microstructural characterizations were performed by XRD, SEM and EDX analyses, while H_2 absorption properties by PCT measurements with a Sievert volumetric apparatus.
The addition of Al influences the crystal structure and impacts on absorption kinetics and PCT curves, notably exhibiting steep plateau, caused by alloy inhomogeneity, with composition variations in the matrix. Equilibrium pressures are higher with respect to TiFe metal hydride.
In $TiFe_{0.80}Cr_{0.20}$ alloy, the presence of the $Ti(Fe,Cr)_2$ and $Ti_4Fe_2O_{1-x}$ phases was detected. The latter phase was also identified in $TiFe_{0.80}Co_{0.20}$ alloy. In $TiFe_{0.80}Cu_{0.20}$ alloy, the formation of the $Ti_4Fe_2O_{1-x}$ oxide was identified, with a small amount of the β-$Ti_{80}(Fe,Cu)_{20}$ phase. Also in this case, a lattice expansion for the TiFe compound was observed.
Sorption properties are significantly affected by substitutions, often resulting in a decrease in hydrogen storage capacity. Hydrogen sorption results can be utilized to assess suitable temperatures and pressures for storage usage in view of potential real-world applications.

Paola Rizzi, PhD in Chemistry, is now full professor of Materials science and technology. She teaches courses on metallic materials in Materials Science and Chemistry courses. Her research activity is focused on: 1) development of advanced materials for hydrogen storage and compression and design of integrated systems; 2) production and properties of amorphous and metastable metallic materials for advanced applications; 3) synthesis and properties of nanoporous metals. She is author of more than 120 publications on international journals.

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Nanomaterials for Industry and Sustainability

Young Researchers' 5-minute Pitch

Valentina Fiume - University of Turin, Italy

PhD student in Chemical and Material Science with a focus on metal hydride and polymer composites for hydrogen storage. Master's degree in Clinical, Forensic and Sport Chemistry.

Polyethylene as a binder for metal hydride pellets for hydrogen storage

AB_5 compounds are promising for hydrogen storage, but present activation difficulties. This study shows that AB_5 and polyethylene pellets maintain hydrogen storage properties while providing good mechanical strength and stable absorption properties.

Francesca Garelli - University of Turin, Italy

I am a PhD candidate in Chemistry and Materials Science, working on the influence of various elements in TiFe alloys on hydrogen storage ans aiming to develop recycled metal scrap alloys for sustainable energy applications.

Hydrogen storage from a circular economy perspective using $TiFe_{0.8}X_{0.2}$ (X = Al, Cr, Co, Cu) alloys potentially derived from scrap materials

This study investigates how common impurities in scrap metals (Al, Cr, Co, Cu) affect TiFe alloys' hydrogen sorption properties. Substitutions impacts on crystal structure, storage capacity, and activation, with potential implications for alloy design and recycling in a circular economy.

Luca Leoni - Univeristy of Bologna, Italy

PhD candidate at the university of Bologna under the supervision of Prof. Cesare Franchini. Works in the field of ab-initio material modeling investigating innovative ML applications.

Hydrogen diffustion in Magnesium using Machine Learning Potentials

We present a computational study of hydrogen diffusion properties in magnesium using machine learning (ML) accelerated molecular dynamics simulations. By fine-tuning state-of-the-art universal ML potentials on an actively learned database, we achieve results that agree exceptionally well with experimental data. Our approach not only surpasses previous computational works based on Nudged Elastic Bands in accuracy but also in computational cost and applicability.

Samia Rachidi – Rabat University, Morocco

I'm a PhD candidate at MV University Rabat, Morocco, at the laboratory of condensed matter and interdisciplinary sciences, specializing in hydrogen storage materials. My research integrates DFT and experimental techniques to advance hydride-based storage solutions.

Investigation of diffusion of hydrogen through $FeTiH_2$ using DFT calculations

We investigated FeTi material degradation and found promising results using biaxial strain calculations, achieving ΔH values of -39 and -42 kJ/mol·H2 with desorption temperatures of 285.36K and 330.53K, aligning with DOE hydrogen storage criteria. AIMD simulations confirmed structural stability under strain, while first-principles calculations identified favorable hydrogen diffusion pathways, with the (2c)-site as the most stable, explaining degradation during hydrogenation cycles.