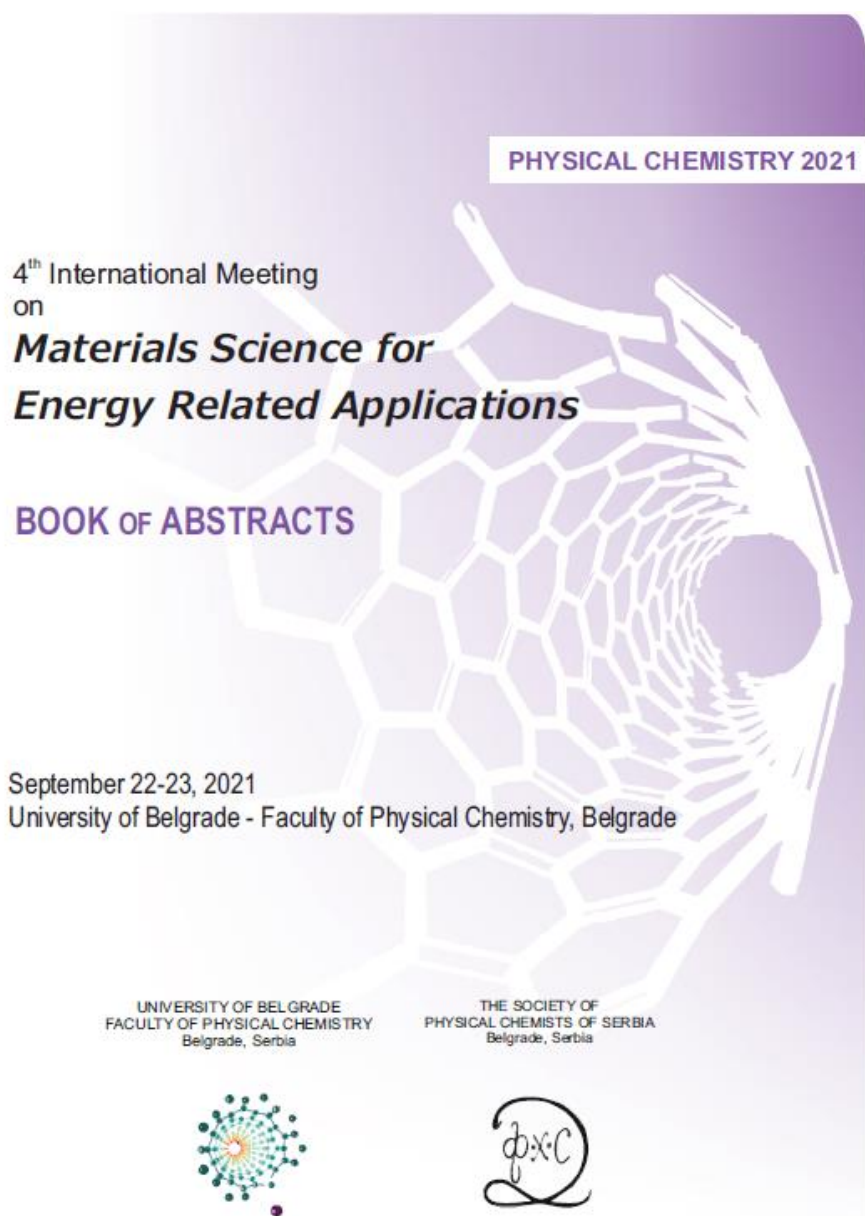


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1. **Bojana Paskaš Mamula**, Igor Milanović, Bojana Kuzmanović, Nikola Biliškov, Nikola Novaković; **Interaction of light alkali metals with ammonia borane: a theoretical study**; 4th International Meeting on Materials Science for Energy Related Applications, September 22-23, 2021, University of Belgrade - Faculty of Physical Chemistry; Book of abstracts p.17



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INTERACTION OF LIGHT ALKALI METALS WITH AMMONIA BORANE: A THEORETICAL STUDY

Bojana Paskaš Mamula¹, Igor Milanović¹, Bojana Kuzmanović¹, Nikola Biliškov², Nikola Novaković¹

¹ „VINČA” Institute of Nuclear Sciences - National Institute of the Republic of Serbia, University of Belgrade, Belgrade, Serbia

² Ruđer Bošković Institute, Zagreb, Croatia

Ammonia borane – AB (formula: $\text{NH}_3\text{-BH}_3$) has been known for its extraordinary gravimetric hydrogen capacity (nearly 20 wt.%) and is therefore considered as promising hydrogen storage material. However, there are several drawbacks to overcome, namely dehydrogenation kinetics is rather poor, and three-step desorption releases contaminated hydrogen with each subsequent step requiring significantly higher temperature. In addition, there are detrimental by-products (e.g., borasine, diborane) that also limit its practical application. Eliminating at least borasine release is possible through the reaction of alkali metal ($\text{M}=\text{Li}, \text{Na}$) with AB and producing monometallic amidoborane salts MAB.

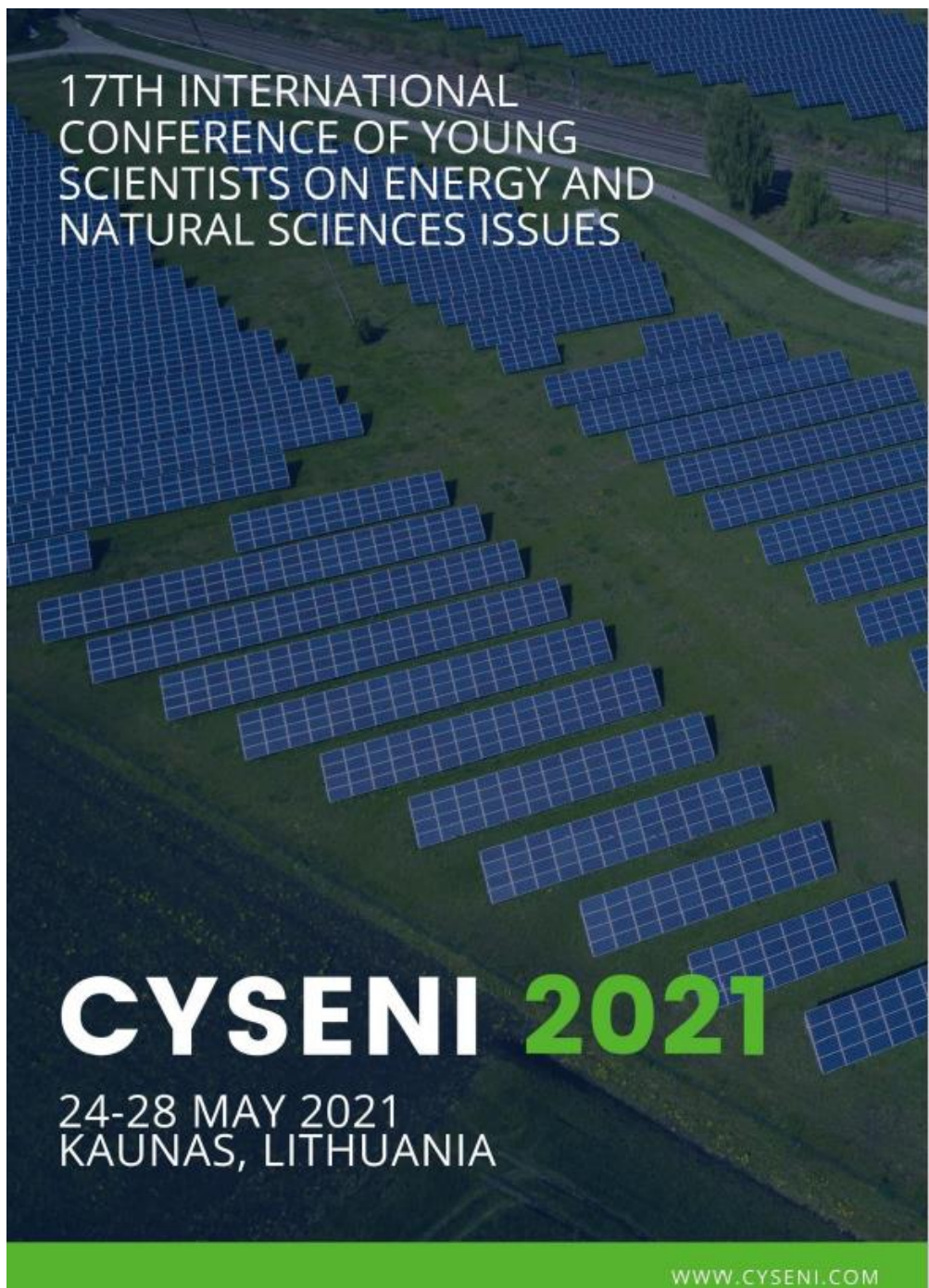
In this paper, electronic structure calculations and the analysis of charge density topology of pure AB, lithium, and sodium amidoboranes were performed in order to investigate cohesion and bonding nature. The influence of the specific alkali metal substitution will be assessed using calculated IR and Raman spectra and analysis of vibrational bands in comparison to pure AB.

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1. K. Batalović, J. Radaković, **B. Paskaš Mamula**; **Property prediction using machine learning – a case study of metal hydrides**; 17th International conference of young scientists on energy and natural sciences issues pg. 403-412, CYSENI 2021, May 24-28, 2021; Kaunas, Lithuania.



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PROPERTY PREDICTION USING MACHINE LEARNING – A CASE STUDY OF METAL HYDRIDES

K. Batalović, J. Radaković, B. Paskas Mamula

*Center of Excellence for Hydrogen and Renewable Energy
VINCA Institute of nuclear sciences – national institute of Republic of Serbia,
University of Belgrade
P.O.Box 522, 11 000 Belgrade, Serbia
Phone: +381113408599
Email: kciric@vin.bg.ac.rs*

ABSTRACT

Accurate prediction of reversible metal hydride formation enthalpy is one of the key requirements for a rapid design of new hydrogen storage and nickel-metal-hydride battery materials. In the last decades, DFT (density functional theory) approach showed good predictive potential for the ground state properties and accurate energies of hydride formation. However, calculating zero-point energy and temperature contributions in addition to 0K formation energy is computationally and time-consuming and therefore often avoided, hindering modelling of experimental behaviour.

Recently reported approach for universal machine learning in materials science based on a MatErials Graph Network (MEGNet), an implementation of DeepMind's graph networks, demonstrated very low prediction errors in a broad array of properties in both molecules and crystals, enabling hydride formation energy prediction with a DFT accuracy. In our work, we consider applications of this approach to the wide screening of potential dopants in reversible metal hydride materials, as well as the potential of transfer learning for the universal machine-learning model capable of addressing all contributions to hydrogen formation behaviour. Prediction of the formation energies for the Mg and Ni containing intermetallic hydrides, as well as the influence of various dopants, provides guide to the contribution of chemical nature and local structure to the destabilization of these hydrides.

Keywords: metal hydride, machine learning, DFT

INTRODUCTION

In the pursuit of renewable energy solutions in the last decades, special attention is dedicated to the investigation and design of novel materials, which can serve in energy conversion or storage processes. Among those, metal hydrides continue to attract interest, given their wide use in hydrogen storage, thermal energy conversion [1] hydrogen compressors [2], and nickel-metal hydride batteries [3]. The importance of Mg and Ni in the materials for these applications was also determined by the data science approach of Rahnama and Sridhar [4]. Magnesium is seen as a potential candidate for stationary and mobile hydrogen storage, but the high stability of magnesium hydride limits its applications [5]. In order to meet requirements in regards to the stability of the hydride, i.e., achieve hydrogen desorption at low temperatures, alloying or doping with other elements is studied as a way of hydride destabilization or improvement of sorption kinetics [6]. In particular, complex Mg hydrides are widely studied [7]. Mg_2NiH_4 complex hydride is seen as a compromise between hydrogen gravimetric density and hydride stability, where Ni acts to loosen the Mg-H bond. As opposed to the Mg_2NiH_4 , which can be formed by hydrogen absorption in the intermetallic compound Mg_2Ni , synthesis of Mg_2FeH_6 must be achieved in other ways, since the starting binary alloy is not stable. Mg_2FeH_6 forms a slightly more stable hydride than MgH_2 [8] which is of interest for thermochemical energy storage applications [9].

Regardless of the system in question, accurately predicting hydrogen formation/desorption enthalpy of some intermetallic compound, and also being able to determine the influence of various dopants on this property, has been a long-lasting goal of the research. Computational methods developed in the last century, especially the ones relying on the density functional theory (DFT), enabled accurate prediction of the electronic structure and stability of materials, providing tools for materials design which account not only the chemical nature (as seen in some empirical models) but also the crystal structure. In particular, predicting metal hydride enthalpies from the first principles within the error of 5-10 kJ/molH₂ is achievable for many metal hydride systems, given that the enthalpy changes in the hydride formation/decomposition reaction (at the temperatures close to the ambient one) can be reasonably approximated by the change in electronic energy calculated from the first principles [10] [11]. The contribution of the ZPE (zero-point energy) is not negligible, and must also be calculated in order to get the most accurate hydrogen absorption/desorption enthalpies [12].

Lately, development of the artificial neural networks (ANN) and machine learning (ML) applications in materials science promise new tools that can be trained on the large corpus of available DFT data to deliver predictions of properties of interest with high accuracy and much greater speed as compared to DFT calculations [13]. In our work, we demonstrate how DFT calculations can be complemented with a machine learning approach for a wide screening of suitable dopants for hydrogen storage applications of Mg₂NiH₄ and Mg₂FeH₆.

METHODOLOGY

DFT calculations

To model the effect of doping in Mg₂NiH₄ and Mg₂FeH₆, band structure calculations of these hydrides, as well as intermetallic Mg₂Ni, was done using a full potential (linearized) augmented plane-waves plus local orbitals (FP (L)APW + lo) method, as implemented in Wien2k program package [14] based on the density functional theory [15]. The exchange and correlation effects were included within the generalized gradient approximation, using the Perdew-Burke-Ernzerhof scheme. The radii of the muffin-tin non-overlapping spheres centered at the atomic nucleus were 2.0 bohr for Mg, 1.8 bohr for Fe and Ni, and 0.8 bohr for H. Mixed LAPW/APW+lo basis set was used, while the energy to separate core and valence states was -6Ry. The Brillouin zone integration was achieved via a tetrahedron method, using a mesh of 286 irreducible k-points for Mg₂FeH₆ and 128 irreducible k-points for Mg₂NiH₄. Self-consistency was achieved by demanding that the convergence of the integrated charge difference within 10⁻⁵. The unit cell parameters were optimized, and the investigated structures were relaxed until the forces acting on all atoms were less than 1 mRy/bohr.

The methodology of machine-learning-based predictions

Starting from the fully optimized unit cells of Mg₂NiH₄ and Mg₂FeH₆, models of doped hydrides were made, and dopants are selected among the 26 elements, mainly metals, of 4th or 5th period in Periodic system of elements (PSE). Substitution of Mg with other elements in Mg₂NiH₄ was modelled by creating the supercell Mg₇MNi₄H₁₆, where M represent substituting atoms listed in table 3. To model the substitution of iron by other metals, one of the four equivalent Fe atoms in the unit cell of Mg₂FeH₆ was replaced with substituting atoms (M) listed in table 2, resulting in hydrides with supercell formula Mg₈Fe₃MH₂₄. The unit cells of studied doped systems are shown in Fig.1. The resulting predictions for energies were scaled to the unit cells of formulas Mg_{2-x}M_xNiH₄ and Mg₂Fe_{3-y}M_yH₁₈ where required.

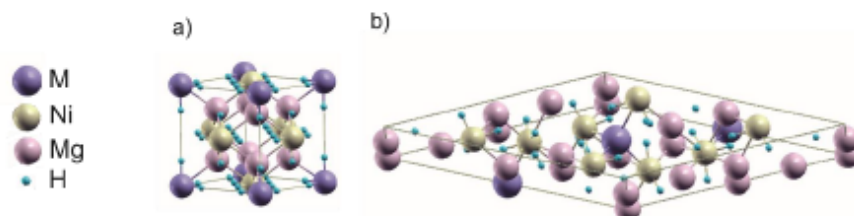


Fig. 1. Unit cell of doped hydrides a) $\text{Mg}_{7/8}\text{M}_{1/8}\text{NiH}_4$ b) $\text{Mg}_2\text{Fe}_{3/4}\text{M}_{1/4}\text{H}_6$

For the prediction of the stability of the studied doped hydrides, a MatErials Graph Network (MEGNet) [16], an implementation of DeepMind's graph networks [17], was used. MEGNet demonstrated low prediction errors in a broad array of properties in both molecules and crystals, enabling hydride formation energy prediction with a DFT accuracy. Here mp-2019.4.1 model, trained on data set containing 133,420 data from the Materials Project [18], was used. Predicted energy of formation is in reference to the constituent elements in their standard state, and the mean absolute error (MAE) of predicted formation energies is 0.026 eV/atom compared to the DFT calculated values.

RESULTS AND DISCUSSION

ML prediction of hydride formation energy

Prediction of the formation energy based on the graph made from the optimized structures is shown in Table 1 and compared to the DFT and experimental data. Formation energy for Mg_2Ni is also calculated to determine hydride formation energy since this intermetallic compound is a starting point for the formation of Mg_2NiH_4 (see equation 1, $x=0$).

Table 1. MEGNet prediction for the intermetallic stability (ΔE^{ML}) and hydrogen absorption energies ($\Delta E_{\text{hyd}}^{\text{ML}}$); comparison to DFT calculated values ($\Delta E_{\text{hyd}}^{\text{DFT}}$) and experimental values ($\Delta H_{\text{hyd}}^{\text{exp}}$)

	ΔE^{ML} (eV/atom)	$\Delta E_{\text{hyd}}^{\text{ML}}$ (kJ/molH ₂)	$\Delta E_{\text{hyd}}^{\text{DFT}}$ (kJ/molH ₂)	$\Delta \text{ZPE}_{\text{hyd}}$ (kJ/molH ₂)	$\Delta H_{\text{hyd}}^{\text{exp}}$ (kJ/molH ₂)
Mg_2FeH_6	-0.3841	-110.8	-106.05 [19] -93.4 [20]	+14.6 [20]	-98 ± 3 [21]
Mg_2NiH_4	-0.3140	-80.1	-81.0 [22]	+8.6 [23]	-64.0 [24]
Mg_2Ni	-0.1795				

The proposed graph neural network (GNN) approach was shown to reproduce accurately DFT formation energies, for both intermetallic and hydrides. Therefore, based on the optimized structure of hydrides and, if needed, the optimized structure of the starting intermetallic alloy, obtaining hydride formation energy is straightforward, and agreement with the DFT results is good, as seen in Table 1.

However, this approach relies on the knowledge of reaction mechanisms. For example, a comparison of the $\Delta E_{\text{hyd}}^{\text{ML}}$ to the experimentally reported enthalpy for Mg_2FeH_6 decomposition by Didisheim et al. [21] is very good, having in mind ZPE change in the reaction. However, other researchers report formation or decomposition of Mg_2FeH_6 through the intermediate step of MgH_2 formation, and in such case much smaller experimental enthalpies have also been reported, i.e. -77 kJ/molH₂ [8].

Further, we consider the effect of doping of various elements (labelled M) in two cases: substitution of Fe with dopant in Mg_2FeH_6 , and substitution of Mg with dopant in Mg_2NiH_4 , as shown in Fig.1. Parameters were optimized using DFT calculations for the pure hydrides,

Mg₂NiH₄ and Mg₂FeH₆, starting from the experimental values and allowing volume change, lattice parameters ratio change (for Mg₂NiH₄), and relaxation of atomic forces. Basically, the structure with minimal energy is selected for a ground state. In such a structure, one of the Mg atoms is replaced with the M atom, where M is one of the elements from the 4th or 5th period of PSE. Details of the supercells used to model these compounds are presented in Table 2.

Table 2. Details of the supercells used to model doping in the studied hydrides

	space group no.	lattice parameter (Å)	cell angle (°)	atom site
Mg ₅ Fe ₃ MH ₂₄	221	a=b=c=6.437	α=β=γ=90.0	Mg (0.250 0.250 0.250) M (0.000 0.000 0.000) Fe (0.500 0.500 0.000) H (0.242 0.000 0.000) H (0.742 0.500 0.000) H (0.500 0.500 0.242)
Mg ₇ MNi ₄ H ₁₆	1	a=13.2516	α=90.0	Mg (0.671 0.435 0.030) Mg (0.329 0.065 0.506) Mg (0.000 0.000 0.000) Mg (0.500 0.500 0.036) Mg (0.000 0.000 0.497) M (0.500 0.500 0.539)
		b=14.4283	β=90.0	Ni (0.668 0.288 0.287) Ni (0.332 0.212 0.249) H (0.553 0.343 0.321) H (0.873 0.510 0.200)
		c=6.4419	γ=153.2	H (0.127 0.990 0.336) H (0.699 0.208 0.233) H (0.301 0.292 0.303) H (0.674 0.300 0.529) H (0.326 0.200 0.008)

The formation energy of M doped Mg₂FeH₆ is equal to the predicted formation energy of the hydride, since it is calculated as:

$$\Delta E_{\text{hyd}} = E(\text{Mg}_2\text{Fe}_{1-x}\text{M}_x\text{H}_6) - 2E(\text{Mg}) - (1-x)E(\text{Fe}) - xE(\text{M}) - 3E(\text{H}_2) \quad (1)$$

Table 3 summarizes the obtained results. Comparing to the hydride formation energy of the pure Mg₂FeH₆, -110.8 kJ/mol, we can see that most of the studied elements (all except Ti and Zr) as dopants lead to the destabilization of the hydride. This trend is in agreement with earlier DFT reports for Mn, Ni and Co-doped hydride [20], however, the amount of destabilization is largely underestimated as compared to DFT. For example, Co doping was found to decrease hydride formation energy by 12.6 kJ/molH₂ [20], while only a 2.8 kJ/molH₂ decrease is seen in ML predicted energies.

Table 3. MEGNet prediction of formation energy of $\text{Mg}_2\text{Fe}_{1-x}\text{M}_x\text{H}_6$, $\Delta E_{\text{hyd}}^{\text{ML}}$.

M	ΔE^{ML} eV/atom	$\Delta E_{\text{hyd}}^{\text{ML}}$ kJ/molH ₂
Li	-0.3354	-97.1
Be	-0.3534	-102.3
Na	-0.3094	-89.6
Mg	-0.3430	-99.28
Al	-0.3505	-101.4
K	-0.2708	-78.4
Ca	-0.3359	-97.2
Sc	-0.3725	-107.8
Ti	-0.3861	-111.7
V	-0.3785	-109.6
Cr	-0.3703	-107.2
Mn	-0.3782	-109.4
Co	-0.3732	-108.0
Ni	-0.3505	-101.3
Cu	-0.3257	-94.3
Zn	-0.3235	-93.6
Ga	-0.3284	-95.1
Sr	-0.3264	-94.5
Y	-0.3617	-104.7
Zr	-0.4009	-116.0
Nb	-0.3751	-108.6
Mo	-0.3881	-112.3
Ru	-0.3804	-110.1
Rh	-0.3758	-108.8
Pd	-0.3744	-108.4
Ag	-0.3200	-92.6
In	-0.3323	-96.2

Further, we discuss the substitution of Mg in reversible hydride, Mg_2NiH_4 . Hydride is formed by hydrogen absorption in Mg_2Ni , and hydride formation energy of doped hydride is calculated as:

$$\Delta E_{\text{hyd}} = E(\text{Mg}_{2-x}\text{M}_x\text{NiH}_4) - E(\text{Mg}_{2-x}\text{M}_x\text{Ni}) - 2E(\text{H}_2). \quad (2)$$

Since formation energy prediction is in reference to the elements in their standard state, equation 2 becomes:

$$\Delta E_{\text{hyd}}^{\text{ML}} = \Delta E^{\text{ML}}(\text{Mg}_{2-x}\text{M}_x\text{NiH}_4) - \Delta E^{\text{ML}}(\text{Mg}_{2-x}\text{M}_x\text{Ni}). \quad (3)$$

The results are presented in Table 4. Comparison of the results to the DFT work shows excellent agreement for the Co and Cu doping: DFT calculated formation energy of -66.6 kJ/molH₂ and -65.6 kJ/molH₂ for Co and Cu doped Mg_2NiH_4 respectively, is reported [25]. However, one should have in mind that Mg is immiscible with V, Cr, and Fe, and therefore any ternary phases tend to decompose into more stable binary intermetallics upon cycling. Therefore, the approach we used for the prediction of hydride formation energy might lead to overestimation of the doped hydride stability in some cases.

Table 4. MEGNet prediction of formation energy (ΔE^{ML}) of $Mg_{2-x}M_xNiH_4$ and $Mg_{2-x}M_xNi$, and predicted hydride formation energy ΔE_{hyd}^{ML} .

M	$\Delta E^{ML}(Mg_{2-x}M_xNiH_4)$ eV/atom	$\Delta E^{ML}(Mg_{2-x}M_xNi)$ eV/atom	ΔE_{hyd}^{ML} kJ/molH ₂
Li	-0.3273	-0.1673	-86.3173
Be	-0.2240	-0.1275	-57.1927
Na	-0.3222	-0.1007	-94.234
Al	-0.2691	-0.2200	-59.0356
K	-0.2787	+0.0101	-95.58
Ca	-0.3395	-0.1096	-98.7882
Sc	-0.3705	-0.2572	-87.8948
Ti	-0.3461	-0.1908	-89.2649
V	-0.3114	-0.1321	-86.0423
Cr	-0.2947	-0.1046	-84.3827
Mn	-0.3002	-0.1198	-84.0402
Fe	-0.2699	-0.0852	-78.8154
Co	-0.2581	-0.1161	-70.3583
Cu	-0.2667	-0.1589	-67.0681
Zn	-0.2658	-0.1935	-61.7565
Ga	-0.2533	-0.2151	-54.409
Sr	-0.2999	-0.0370	-95.9226
Y	-0.3707	-0.2084	-95.0252
Zr	-0.3686	-0.2167	-93.1148
Nb	-0.3268	-0.1485	-88.8694
Mo	-0.2894	-0.0819	-85.8783
Ru	-0.2598	-0.1446	-66.8076
Rh	-0.2845	-0.2263	-63.3244
Pd	-0.2901	-0.2350	-63.9564
Ag	-0.2638	-0.1675	-64.8441
In	-0.2674	-0.2010	-61.2114

Figures 2 and 3 visualize the dopant effect in the studied cases, for the dopants belonging to the 4th and 5th periods.

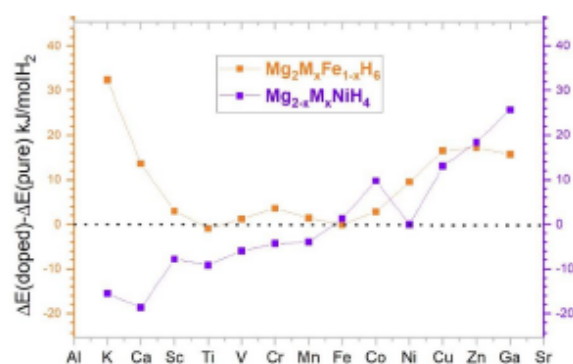


Fig. 2. Plot of the doping effect of 4th period elements on hydride formation energy for b) $Mg_2Fe_{3/4}M_{1/4}H_6$ (orange, left) and $Mg_{7/8}M_{1/8}NiH_4$ (purple, right)

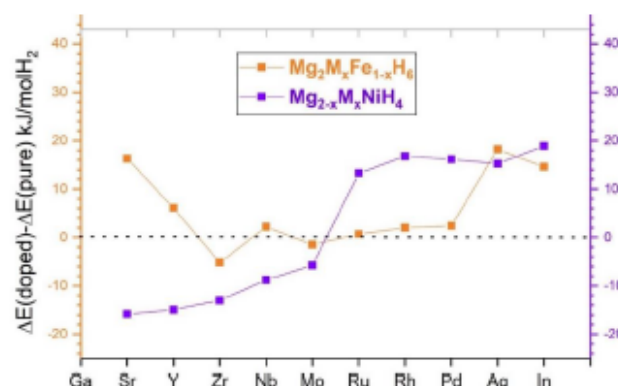


Fig. 3. Plot of the doping effect of 5th period elements on hydride formation energy for b) $\text{Mg}_2\text{Fe}_{1-x}\text{M}_x\text{H}_6$ (orange, left) and $\text{Mg}_{2-x}\text{M}_x\text{NiH}_4$ (purple, right)

Comparing the influence of dopants in Mg_2FeH_6 and Mg_2NiH_4 , we can conclude that due to the local structure and nature of the element being replaced (Mg or Fe) qualitatively different behaviour is seen, for both 4th and 5th-period elements as dopants. Choice of the substitution element in Mg_2NiH_4 can be made such to either destabilize or stabilize hydride and in general we see that elements from the left part of the period cause increase in the stability of the hydride, while larger destabilization is seen for the elements at the right end of the period. The main reason of such phenomena could be in the strength of the bond that such of the elements make with hydrogen – this trend resembles stability of binary hydrides, which decrease down the period. For the substitution of Fe in Mg_2FeH_6 , we can see that the larger the discrepancy of iron and dopant element electronic structure, the larger destabilization can be expected. However, given the coordination of 6 hydrogen atoms around Fe is related to the iron electronic structure, a change of the coordination in the doped hydrides is also expected. Looking at Figs. 2 and 3, we can also conclude that the graph approach of the used model is suitable for addressing the influence of both chemical nature and local structure. Reservation in regard to these results is related to the absence of relaxation of the doped structures, and significant quantitative difference between DFT calculated and ML predicted formation energies for the Mg_2FeH_6 doped systems. Therefore, further steps in machine learning for the structure optimization as well as the optimization of the GNN model would ensure the most accurate predictions of hydride formation enthalpies.

Discussion of the potential of transfer learning to the prediction of hydride formation enthalpy

In order to make a highly accurate prediction of the experimental values of hydride formation enthalpy, besides the prediction of DFT electronic energy, the contribution of ZPE should also be added. MEGNet models are trained to predict ZPE for molecules; however, these computations are very demanding for crystals, and results are reported for a small number of compounds. Instead of training on the calculated ZPE data, we considered training a model on experimental data available in the DOE SNL database [26] and listed in literature [12]. This corpus of experimental data related to the reversible metal hydrides is intersected with the Materials project database [18] to obtain structures and energies of the starting metal/alloy and corresponding hydride, and form a graph representation input of the hydride. However, this

search is limited only to the cases where a single, known, crystal structure of the alloy and hydride phase occurs, and this is not so often the case in experimental work. Therefore, only 34 hydrides were found, and the experimental enthalpy and DFT calculated hydride formation energy is presented in Fig. 4.

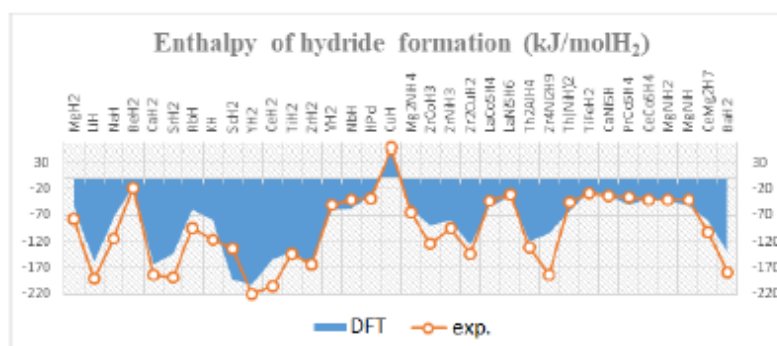


Fig. 4. Comparison of the literature values of hydride formation enthalpy and DFT calculated hydride formation energy from Materials project data [18]

On this dataset, we tried to apply transfer learning, relying on the embeddings obtained in the MEGNet model, to account for ZPE and other reasons for discrepancies. However, this dataset was shown to be too small for such a task, and overfitting during training could not be avoided, given that calculation of property such as ZPE requires a complex architecture of the ANN. An additional problem comes from the fact that ANN should also be trained to predict the most stable structure of the starting intermetallic compound (for example, in here studied case, to know that Mg_2FeH_6 will be formed directly from elements, while Mg_2NiH_4 will be formed starting from the stable Mg_2Ni intermetallic compound). Therefore, future work is expected to solve these problems and address adaptation of GNN for the complex problematics of hydride formation.

CONCLUSION

In this work, we consider the application of machine learning to the prediction of hydride formation energy. MEGNet model is used to predict the stability of Mg_2NiH_4 , Mg_2Ni , and Mg_2FeH_6 , as well as the hydride formation energy of $Mg_{2-x}M_xNiH_4$ and $Mg_2Fe_{1-x}M_xH_6$, where M is one of 26 elements, mainly metals. Good agreement with DFT results is seen for $Mg_{2-x}M_xNiH_4$ doped hydrides, while for $Mg_2Fe_{1-x}M_xH_6$ trend is predicted but the dopant effect is underestimated. Comparing the influence of dopants in Mg_2FeH_6 and Mg_2NiH_4 , we show how hydride formation energy can be tuned, and how, due to the local structure and nature of the element being replaced same dopants have different influence. Choice of the substitution element in Mg_2NiH_4 can be made such to either destabilize or stabilize hydride and in general we see that elements from the left part of the period cause increase in the stability of the hydride, while largest destabilization is seen for the elements at the right end of the period.

In order to predict experimental values with high accuracy, additional factors in addition to formation energy must be taken into account. In particular, temperature effect should be considered, and ZPE contribution should be added, given that vibrations of a light elements (such as Li or Mg) as well as hydrogen atom are not negligible in the hydrides. We propose that this can be done by using transfer learning and MEGNet embeddings in combination with experimental data. We demonstrate good accuracy for the fast screening of potential dopants,

and further steps in the application of this approach are related to the improvement of the model for the doped systems, as well as pre-step of machine learning relaxation of the doped structures prior to the prediction of hydride formation enthalpy.

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Microstructure and thermal behavior of Mg-V thin films for solid state hydrogen storage

T. PANTIĆ¹, K. ZAGAR SODERŽNIK², S. ŠTURM², S. DREV², A. MITROVIĆ¹, S. KURKO¹, B. PASKAŠ MAMULA¹, N. NOVAKOVIĆ¹, J. GRBOVIĆ NOVAKOVIĆ¹, I. MILANOVIĆ¹, S. MILOSEVIĆ GOVEDAROVIĆ¹

¹ Centre of Excellence for Renewable and Hydrogen Energy – CONVINCe, Vinča Institute of Nuclear Sciences, University of Belgrade, Serbia; ² Jožef Stefan Institute, Ljubljana, Slovenia

Introduction

The study on hydrogen storage properties of Mg-based thin films is widely conducted due to the fact that they enable controllable design of important properties such as the microstructure, interface, surface and particle size.

The advantages of thin film hydrides over bulk materials and powder [1-3]:

- larger surface area – faster kinetics of dehydrogenation
- lower pressure and temperature of desorption
- composition, interface and crystallinity can be accurately tailored on the nanoscale
- the hydrogen absorption and desorption mechanisms are also easily deduced by modeling and the fitting calculations
- protective coating could be done in order to improve the rate of hydrogenation and reduce the oxygen contamination
- additionally studied as “switchable mirrors” as they exhibit optical and electrical changes upon hydrogen absorption and desorption
- potential application as hydrogen sensors, energy-efficient windows, solar absorbers...

Experimental:

Nanocrystalline thin films were synthesized by non-equilibrium processing by co-deposition using a multi-source magnetron sputtering system Kurt J. Lesker (KJLC CMS-18)

In order to increase hydrogenation rate ion irradiation with H⁻ and Xe¹⁰⁺ ion has been applied. Irradiation were done on FAMA ion source at Vinča Institute of Nuclear Sciences. Distribution of defects (Frenkel pairs) in the near-surface region was estimated by Monte Carlo simulations

The samples for STEM analysis were prepared by conventional cross-section sample preparation technique. The samples were cut, ground, polished down to approx. 100 µm and, after dimpling, thinned down to electron transparency using Gatan PIPS ion-milling system.

For the structural and compositional studies, we used a probe Cs-corrected scanning transmission electron microscope (Jeol, ARM 200 CF, STEM) operated at 200 kV, equipped with electron dispersive X-ray (EDX) spectrometer (Jeol, Centurion SSD) and electron energy-loss (EEL) spectrometer (Gatan, Quantum ER Dual EELS).

TOF-ERDA measurements were done using 20 MeV ¹²⁷I⁶⁺ beam. Analysis of TOF-ERDA spectra was done using program Potku.

Results and discussion:

To investigate the microstructure and composition of Mg-V layered structure, STEM with EDX mapping were applied on irradiated and hydrogenated samples. Figure 1 shows Mg-V sample irradiated by H^+ ions. BF-STEM image (Fig. 1(a)) shows layered structure of Mg (appr. 25 nm thick) and V (appr. 1 nm thick) which is distorted due to the ion beam direction. The EDX mapping (Fig. 1(b-d)) shows presence of Mg and V elements. During the irradiation the V diffused into Mg.

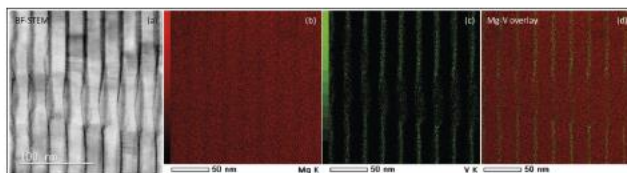


Figure 1. Mg-V irradiated with H^+ ions with fluence of 10^{17} ion/cm². (a) BF-STEM image of Mg and V layers. Bright area is Mg layer with thickness of appr. 25 nm, and black layer is V with approx. 1 nm thick layer. (b-c) EDX mapping, with (b) Mg-K line, (c) V-K line and (d) Mg-V overlap.

In contrast to non-hydrogenated sample the BF-STEM image of irradiated and hydrogenated sample shows completely different microstructure (Figure 2(a)). We observed severe microstructural changes. Mg and V layers were transformed to large crystals and the sample became beam sensitive and brittle. The EDX mapping from selected region (Fig. 2(b-d)) shows the presence of Mg, V and O. The samples are oxidized during sample treatment (?), but the results from TOF ERDA analysis shows successful hydrogen diffusion into samples.

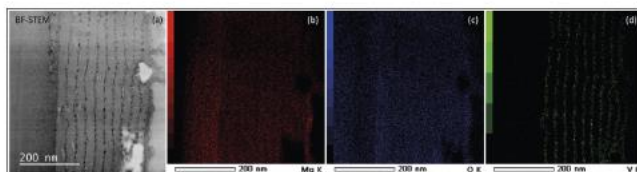


Figure 2. Mg-V irradiated and hydrogenated. (a) BF-STEM image of Mg and V layers. Bright area is Mg layer with thickness of appr. 25 nm, and black layer is V with approx. 1 nm thick layer. (b-c) EDX mapping, with (b) Mg-K line, (c) O-K line and (d) V-K line.

Quantitative depth profiles of TOF-ERDA show difference between irradiated only and irradiated plus hydrogenated films. While in irradiated samples hydrogen is observed on surface, hydrogenated films show hydrogen distribution through whole depth. Also, after hydrogenation there is mixing between layers and substrate, given that hydrogenation process leads to self-diffusion of metal atoms.

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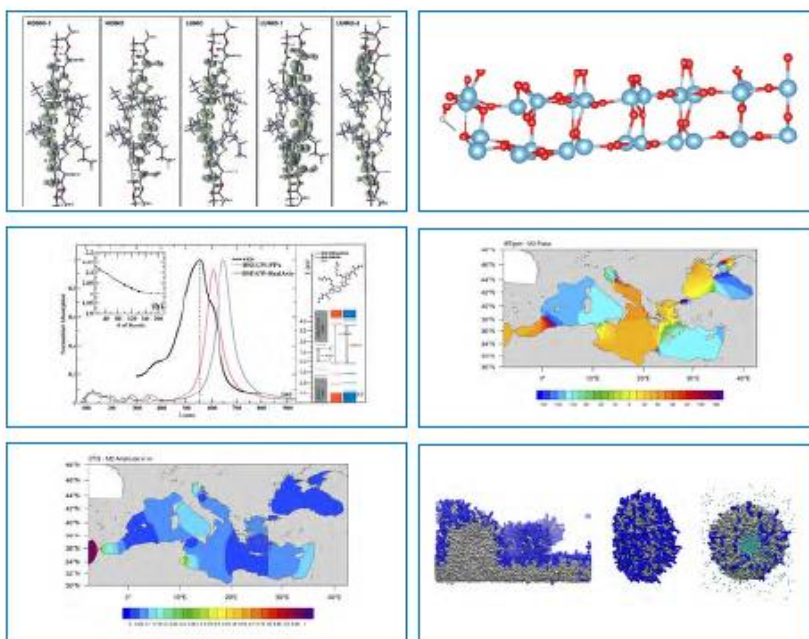
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HYDROGEN INTERACTION WITH TiO₂ SURFACE

Radojka Vujasin*, Bojana Paskaš Mamula,
Jasmina Grbović Novaković, Nikola Novaković

Vinča Institute of Nuclear Sciences, University of Belgrade, P.O. Box 522, 11001 Belgrade, Serbia

ABSTRACT. The hydrogen interaction with the rutile TiO₂ (110) surface has been investigated. Numerical model was set up to perform first principle calculations based on density functional theory, using CPMD code. Molecular dynamic simulations were performed to investigate the impact of hydrogen surface coverage on the properties and behavior of the system.

1 Introduction

Titanium dioxide attracts a lot of interest because of its low price, non-toxicity and safe usage. TiO₂ is material used in wide variety of industries, such as in environmental applications and electronic devices. Due to its electronic and optical properties, TiO₂ is known as a good catalyst. It was shown that addition of metal oxides can improve sorption properties of magnesium hydride, one of the most promising materials for hydrogen storage [1, 2]. Development of appropriate hydrogen storage materials is important for safe and sustainable implementation of hydrogen economy.

Studies on hydrogen behaviour and motion through oxide surface have been done to understand the mechanism of the reaction [3]. Yin et al. [4] have investigated hydrogen coverage on TiO₂ (110) surface under different experimental conditions of exposure to atomic hydrogen. They obtained that maximum H monolayer coverage on TiO₂ (110) surface is only 70% at room temperature, regardless of applied partial pressure of hydrogen. The same group confirmed that during heating of the hydrogenated sample, H atoms migrate into TiO₂ bulk. Kowalski et al. obtained the same results [5]. This is unusual behaviour, since desorption of H₂ (or H₂O) molecules into the gas phase is common characteristic of hydroxylated oxide surface.

Filippone et al. carried out research which showed that hydrogen behaves as a deep donor in rutile phase and forms an OH⁺ complex by interaction of H atom with oxygen vacancy, where H formed bond with a prevailing ionic character [6]. They have showed that electronic localization effects treatment have major influence on nature of bonding and charge distribution due to hydrogen incorporation. Also, Ti³⁺ species are formed as a result of localization of H and OH⁺ electronic levels on some Ti neighbours.

Theoretical investigations of rutile TiO₂ with one H and two H atoms adsorbed on the (110) surface were performed with the intention to examine its influence on hydrogen surface coverage on the properties of the system at different temperature.

* Corresponding author. E-mail: radojka.vujasin@gmail.com

2 Details of calculations and results

Numerical study is performed by CPMD (Car-Parrinello Molecular Dynamics) code [7, 8] which uses a plane wave/pseudopotential implementation of Density Functional Theory (DFT) [9, 10]. We use the CPMD compiled with Intel Fortran Compiler, MKL (Math Kernel Library), ACML (AMD Core Math Library) and MPI (Message Passing Interface) parallelization on the high performance ENEA CRESCO computing facilities [11].

Our system is TiO_2 slab supercell with 21 atomic layers with total of 84 atoms of TiO_2 and 1 or 2 H atoms. The surface of the supercells was separated from its periodic image in direction perpendicular to the (110) surface by 15 Å of vacuum. The cell parameters were $a = 5.9779$ Å, $b = 6.6124$ Å, $c = 37.0424$ Å. Three bottom layers were fixed to simulate the bulk. Troullier-Martins normconserving pseudopotentials with GGA-PBE exchange–correlation potential were used for all atoms [12, 13]. The electronic wave functions are expanded in plane-wave basis set with a kinetic energy cut-off equal to 70 Ry.

Two systems were investigated. The first one with one H atom (marked with $\text{TiO}_2\text{-1H}$ system), in the first atomic layer, has 50% of surface coverage. The second system (labelled with $\text{TiO}_2\text{-2H}$ system) has two H atoms and 100% of surface coverage. One H atom is positioned near O atom in the first atomic layer, and the other is positioned near O atom in the second atomic layer. H atoms are initially positioned at distances corresponding to short O–H bond (approximately 1 Å) in all cases (see Fig. 1).

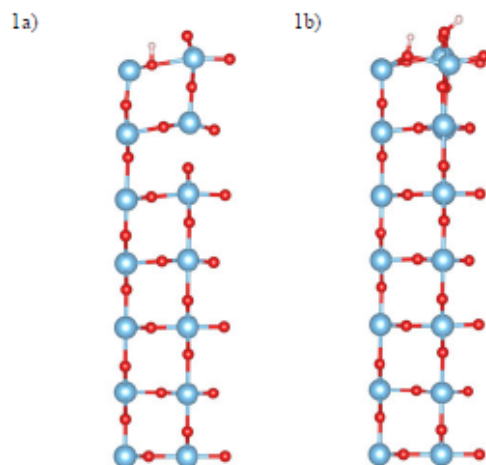


Fig. 1. Slab supercell of TiO_2 surface with H atoms on the surface after geometry optimization. a) $\text{TiO}_2\text{-1H}$ system, b) $\text{TiO}_2\text{-2H}$ system (Ti atoms – blue, O atoms – red, H atoms – white spheres).

Total energy calculation followed by geometry optimisation was performed for both systems. Structural analysis after geometry optimisation was analysed. In the Fig. 1a) and 1b) are shown supercells of systems after geometry optimization. Ionic relaxations show that there are no

differences in systems comparing to O-H distances, in both cases are 0.98 Å. The addition of the second H atom only slightly disordered the atoms in the first layer of the supercell.

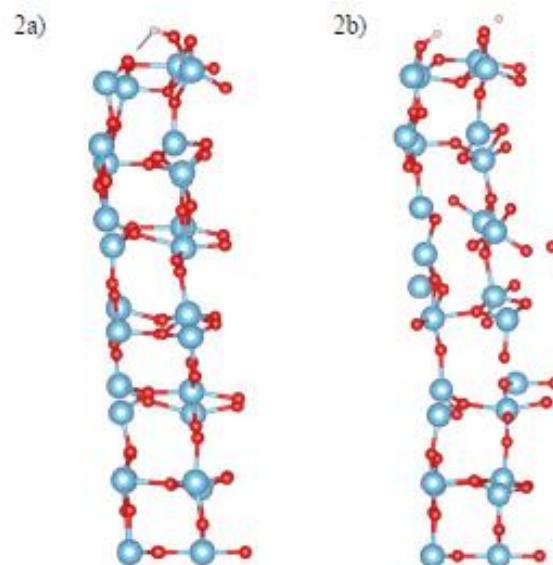


Fig. 2. Snapshot of the systems after 3 ps MD simulations at 450 K. a) TiO_2 -1H system, b) TiO_2 -2H system (Ti atoms – blue, O atoms – red, H atoms – white spheres).

MD simulations at constant temperature and constant volume were performed after geometry optimisation of the systems. Temperatures used in simulations were in range 200-500 K in steps of 50 K. MD simulations were performed for about 3 ps with timestep of 4 a.u. at each temperature and hydrogen atoms behavior were characterized. Snapshot of the systems after MD simulations at 450 K are shown in Fig. 2. Displacements of atoms in supercell structure are noticeable in both systems. H atoms are still on the surface near O atoms at the distance of about 1 Å.

To conclude, we performed geometry optimization and MD simulations of rutile TiO_2 (110) surface with adsorbed H atoms to investigate possibility for hydrogen uptake by titanium dioxide during the heating of the system. Heating the systems up to 500 K causes a disorder in both systems without changes H surface coverage.

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1. Tošić K., Grbović Novaković J., Mijaković S., Vujačić Nikezić A., Pantić T., Milošević Govedarović S., Paskaš Mamula B. **Characterization of pyrophyllite for potential use in water filtration.** The 2nd DIFENEW International Student Conference - DISC2022 December 6th 2022 Novi Sad, Serbia. Abstract book p.59. ISBN 978-86-6022-543-8.



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CHARACTERIZATION OF PYROPHYLLITE FOR POTENTIAL USE IN WATER FILTRATION

Tošić K.¹, Grbović Novaković J.¹, Mijaković S.¹, Vujačić Nikezić A.¹, Pantić T.¹, Milošević Govedarević S.¹, Paskaš Mamula B.¹

¹Centre of Excellence for Hydrogen and Renewable Energy, Vinča Institute of Nuclear Sciences - National Institute of the Republic of Serbia, University of Belgrade, Belgrade, Serbia

e-mail: katarina.tosic@vin.bg.ac.rs

Abstract: Water pollution has become a major source of concern and priority for society. So, it is important to find an adequate solution for its purification. Due to pyrophyllite's great physicochemical characteristics and distribution in nature, it is used in many industries as well as for wastewater treatment. In this study, the characterization of pyrophyllite was done with certain methods, in order to see the changes that occurred after modification, for possible use as a ceramic membrane for water filtration. Firstly, pyrophyllite was ultrasonically purified, then pastilles were made under the pressure of 50 MPa, and thermally treated at the temperature of 1050 °C in a time interval of 2-6 h. The methods that were used for the characterization were: X-ray structural analysis (XRD), infrared spectroscopy with Fourier transform (FTIR), scanning electron microscopy (SEM), Raman spectroscopy, as well as thermal analysis methods, thermogravimetric analysis (TGA) and differential thermal analysis (DSC). The thermal treatment removed impurities present in the sample and excess water was released. Also, amorphization and dehydroxylation were noticed, as well as a homogeneous arrangement of pores.

Keywords: Pyrophyllite; Water Pollution; Ceramic Membrane; Water Filtration.

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3. Katarina Batalović, **Bojana Paskaš Mamula**, Jana Radaković, Mirjana Medić Ilić, Bojana Kuzmanović. **Metal hydrides by design – insights from DFT and data science.** 6th Int. Symposium on Materials for Energy Storage and Conversion, 5.-8.7. 2022. Bol, Island of Brač, Croatia, Book of Abstracts, p. 14



The influence of defects on hydrogen sorption from magnesium-based composites and thin films

Tijana Pantić¹, Bojana Paskaš Mamula¹, Kristina Žagar Soderžnik², Igor Milanović¹, Nikola Novaković¹, Sanja Milošević Govedarović¹ and Jasmina Grbović Novaković¹

¹Department of Physics, Center of excellence for hydrogen and renewable energy (CONVINCE), "Vinča" Institute of Nuclear Sciences - National Institute of the Republic of Serbia, University of Belgrade, Mike Petrovića Alasa 12-14, 11351 Belgrade, Serbia

²Department for Nanostructured Materials, Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia

The kinetics and thermodynamics of hydrogen uptake/release remain the main drawback for the practical application of magnesium hydride (MgH_2) since its high thermal stability. There are possible ways of modification and destabilization of structure in order to improve hydrogen storage characteristics, such as mechanical milling, the presence of additives (metals, metal oxides, non-oxide ceramics, amides, amines, etc.), alloying, ion irradiation. Mechanical milling introduces defects into the material which leads to an improvement in reaction kinetics, especially hydrogen diffusion. Also, the particle size is reduced and the specific surface area of the material is increased, which shortens the desorption path of hydrogen, thereby accelerating the desorption process and reducing the desorption temperature. Ion bombardment introduces vacancies, dislocations, and micro-changes into the material surface layer, increasing the number of nucleation centers. While mechanical milling represents the simple and fast way for structure destabilization, thin films are a great way to monitor the influence of microstructure and/or additives on sorption properties under controlled conditions. They are particularly suitable because of the fact that ion bombardment can be used to control a certain concentration of defects at certain depths by simulation predictions. Milošević et al. showed that after milling MgH_2 with VO_2 , the kinetics of hydrogen sorption were significantly altered due to the presence of a multivalent V i.e. VO_2/VH system [1]. During mechanical milling, various additives are added to act as so-called catalysts and/or milling agents, which may produce additional defects, delay agglomeration, and thus improve the sorption properties of MgH_2 . Rašković - Lovre and her colleagues investigated the effect of modification of MgH_2 films by Ar^{+} ions, and it was found that ion bombardment introduced uniformly distributed vacancies in the surface layer of the film [2]. This study aims to investigate the effect of defects in the volume and on the surface of the material. The first part will deal with the influence of defects created in volume, on composites synthesized by mechanical milling at different parameters and different amounts of additives. The second part deals with the study of the influence of surface defects on sorption properties by bombarding thin films with H^{+} and Xe^{+} ions.

A series of MgH_2 composites with different weight percent of WO_3 additive (5, 10, and 15 wt.%) is synthesized under

different milling conditions in the SPEX 5100 and SPEX 8000M vibration mills. Milling is carried out in an argon atmosphere to avoid hydroxide formation due to the presence of moisture in the air. Microstructural characterization is performed by scanning electron microscopy (SEM), which will examine the change in particle morphology after milling, as well as the distribution of additives in MgH_2 . The change in particle size is monitored using a laser method for determining the particle size distribution (PSA). The desorption properties of the composite are tested by differential scanning calorimetry (DSC), temperature-programmed desorption (TPD), and the Sievert hydrogen sorption analysis method (HSA). The desorption process of H_2 from the composite is analyzed by fitting the experimental data using different kinetic models.

Thin films consisting of alternating Mg (30 nm) and V layers (1 nm) with 10 repetitions were synthesized by magnetron sputtering and modified by ion irradiation using H^{+} and Xe^{+} ions at FAMA ion source. Time-of-flight elastic recoil detection analysis (TOF-ERDA) shows the concentration of elements in the film, as well as their depth profiles. The microstructure and composition are examined by scanning transmission electron microscopy (STEM) with EDX mapping.

Mechanical milling and the addition of WO_3 introduced the defects into the MgH_2 bulk. The particle size is reduced and there is a decrease in desorption temperature compared to the as-received MgH_2 . Composites with a higher amount of additive show faster hydrogen sorption. TOF-ERDA results show that ion-irradiation induced defects improve hydrogen absorption. Surface defects play a major role in sorption reaction as they promote hydrogen dissociation.

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Tijana Pantić is a PhD candidate at the Faculty of Physical Chemistry, University of Belgrade and currently works as a research assistant at Vinča Institute of Nuclear Sciences. Her research is focused on materials for solid state hydrogen storage.

Presenting author: Tijana Pantić, e-mail: tjanap@vin.bg.ac.rs tel: +381 64 802 52 13

Metal hydrides by design – insights from DFT and data science

Katarina Batalović¹, Bojana Paskaš Mamula¹, Jana Radaković¹, Mirjana Medić Ilić¹, Bojana Kuzmanović¹

¹CONVINCE - Center of excellence for hydrogen and renewable energy, Laboratory of nuclear and plasma physics,
VINCA Institute of nuclear sciences – national institute of Republic of Serbia, University of Belgrade
P.O.Box 522, 11 000 Belgrade, Serbia

Clean energy solutions rely on various hydride materials, for both hydrogen storage and hydrogen production. In our work, we address the possibility of tuning the properties of the most attractive hydrides: Mg-based hydrides, AlH_3 and NaBH_4 , by doping.

Density functional theory (DFT) is used to address the stability and electronic structure of the studied doped hydrides. Incorporation of the dopant atoms as substitutional and/or interstitial impurities in the α - AlH_3 , β - AlH_3 , and MgH_2 is considered [1,2]. Fig.1. presents relaxed supercell of α - AlH_3 doped with Ti, which was demonstrated as one of the best dopants for stabilization of this hydride.

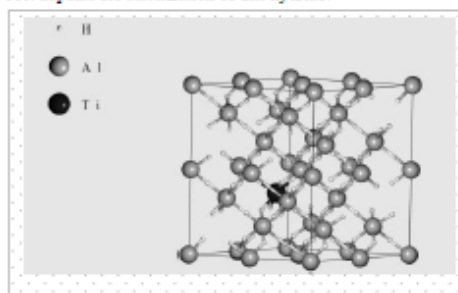


Figure 1. Supercell of Ti-doped α - AlH_3

For the studied AlH_3 polymorphs we found that their stability is determined by the chemical nature of the dopant rather than the crystal structure of the hydride.

In addition to DFT, data science tools offer new perspectives for design in materials science. In this work, we demonstrate an exploratory data science study, done using an unsupervised machine learning approach. Besides results obtained in our DFT studies, we assessed over 500 hydride calculation data found in the NOMAD archive [3] to understand the relevant inner structure of the hydride dataset containing AlH_3 , MgH_2 , and NaBH_4 hydrides.

Finally, we employ artificial neural network models based on the graph neural networks, including MEGNet [4] and our custom-developed model, to predict thermodynamical properties of the doped hydrides based solely on the hydride crystal structure or the crystal structure of the metal/intermetallic compound.

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Dr. Katarina Batalović is an associate research professor at the Vinča Institute. She obtained her Ph.D. in 2013. at the Faculty of physical chemistry, University of Belgrade. Her research interests are theoretical materials chemistry, density functional theory, and machine learning applied to hydrogen energy, energy conversion, and photocatalytic materials.

Presenting author: Katarina Batalović, e-mail: kbicir@vin.bg.ac.rs tel: +381113408599



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4. Katarina Tošić, **Bojana Paskaš Mamula**, Nikola Novaković, Mirjana Medić Ilić, Igor Milanović, Silvana Dimitrijević, Jasmina Grbović Novaković. **Thermally activated pyrophyllite as ceramic membrane**. Nineteenth Young Researchers' Conference Materials Science and Engineering, December 1-3, 2021, Belgrade, Program and the Book of Abstracts pg.27



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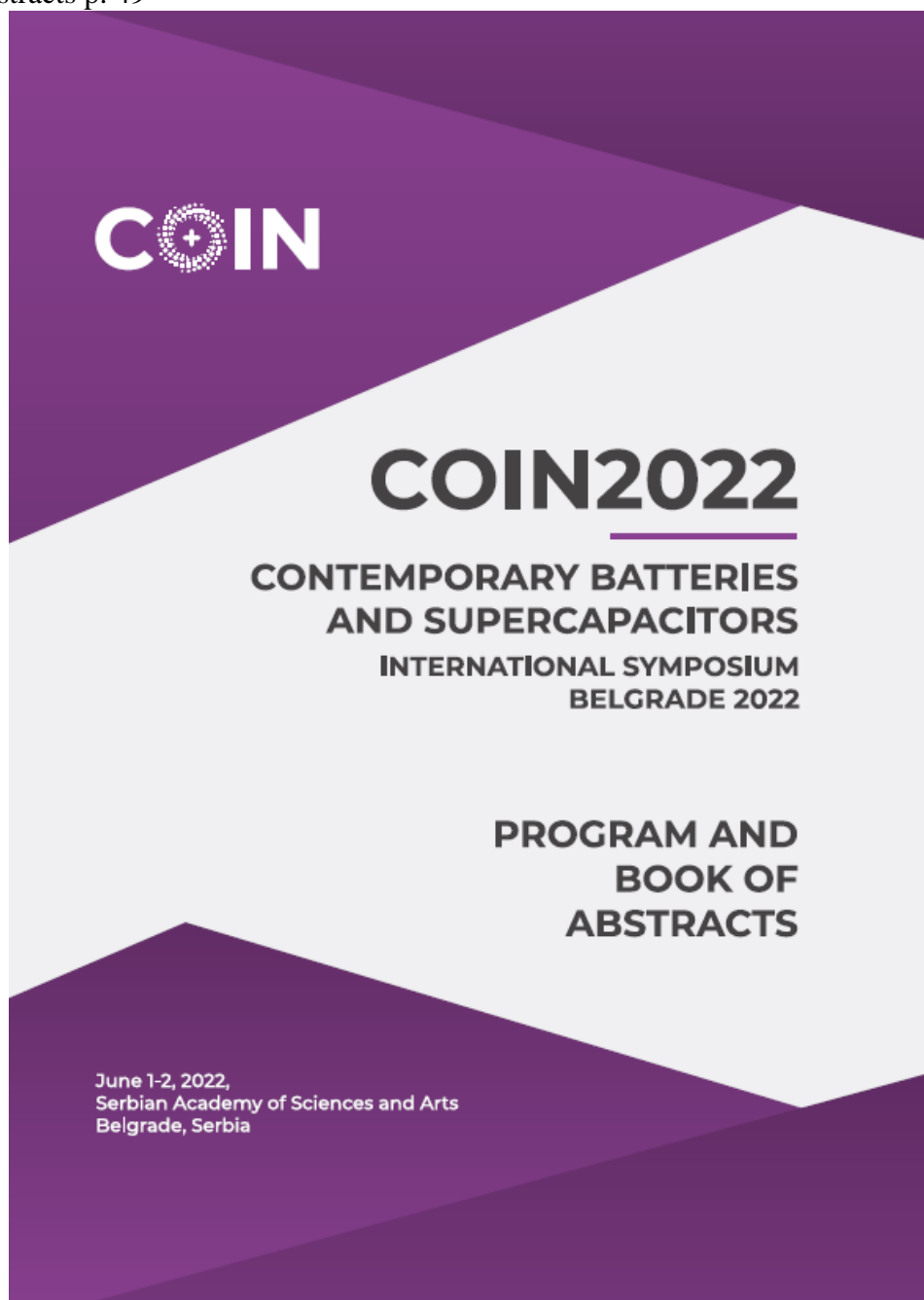
Thermally activated pyrophyllite as ceramic membrane

Katarina Tošić¹, Bojana Paskaš Mamula¹, Nikola Novaković¹, Mirjana Medić Ilić¹,
Igor Milanović¹, Silvana Dimitrijević², Jasmina Grbović Novaković¹

¹*Centre of Excellence for Hydrogen and Renewable Energy, Vinča Institute of Nuclear Sciences - National Institute of the Republic of Serbia, University of Belgrade, POB 522 Belgrade, Serbia,* ²*The Mining and Metallurgy Institute Bor, Zeleni bulevar 35, 19210 Bor, Serbia*

Due to pyrophyllite good physico-chemical characteristics, such as low electrical and thermal conductivity, good mechanical strength, low coefficient of expansion and excellent stability during heat treatment, it is widely used in many industries, such as industry paper, plastic, ceramics, rubber, plants, bricks and cosmetics, but also for waste treatment water. In this paper, the thermal modification of pyrophyllite is performed at a temperature of 1050 °C in a time interval of 2-6 h, under a pressure of 50 MPa, in order to obtain ceramic membranes for purification of pollutants in aqueous solutions. Prior to thermal treatment natural pyrophyllite clay is ultrasonically purified to remove other impurities. The changes that occurred after the thermal treatment were monitored: X-ray structural analysis (XRD), infrared spectroscopy with Fourier transform (FTIR), scanning electron microscopy (SEM), Raman spectroscopy, as well as thermal methods of analysis, which monitored the thermal stability of the obtained material.

5. Bojana Kuzmanović, Katarina Batalović, **Bojana Paskaš Mamula**, Mirjana Medić Ilić, Milica Vujković, **Al-ions Charge Storage Ability of the Conductive Polyaniline Emeraldine Salt**, Contemporary Batteries and Supercapacitors - International Symposium – June 1-2, 2022, Belgrade, Program and the Book of Abstracts p. 36
6. Katarina Batalović, Jana Radaković, Bojana Kuzmanović, Mirjana Medić Ilić, **Bojana Paskaš Mamula**, **Data-driven Design of New Mg-based Hydride Materials – A Synergy of Experiments and DFT**, Contemporary Batteries and Supercapacitors - International Symposium – June 1-2, 2022, Belgrade, Program and the Book of Abstracts p. 49



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a) Батерије - Апстракти

Al-ions Charge Storage Ability of the Conductive Polyaniline Emeraldine Salt

Bojana Kuzmanović¹, Katarina Batalović¹, Bojana Paskaš Mammula¹, Mirjana Medić Ilić¹ and Milica Vujković²

¹Vinča Institute of Nuclear Sciences – National Institute of Republic of Serbia, University of Belgrade
P.O.Box 522, 11 000 Belgrade, Serbia

²University of Belgrade – Faculty of Physical Chemistry, Studentski trg 12, Belgrade, 11000, Serbia
e-mail: kuzmob@vinca.rs

Development of new and attractive generation of polymer devices for application in the field of energy storage that meets the requirements of safety and environmental sustainability is an ongoing challenge. The majority of previous scientific results reported that polyaniline-based supercapacitors use only aqueous acid solutions as electrolyte. [1] The aim of this work is to examine the redox activity of polyaniline emeraldine salt (PANI-ES) in an aqueous electrolyte of aluminum salt, that have been studied to a lesser extent and lacking the characterization of charge storage behavior. The advantage of employing aluminum among various post-lithium rechargeable systems has the advantage in the fact that it is the most abundant metal element in the Earth's crust with one of the highest gravimetric and volumetric energy densities. By combining experimental (cyclic voltammetry, chronopotentiometry, galvanic charge/discharge, AFM - Atomic Force Microscopy) and theoretical approaches (density functional theory - DFT), the redox mechanism of polyaniline in the aqueous Al-salt solution is explained. [2] Polyaniline has been shown to have higher Coulombic capacitance at the same charge and discharge current in aqueous aluminum nitrate solution (1M Al(NO₃)₃) than in hydrogen chloride electrolyte solution (1M HCl), which makes it a suitable electrode for supercapacitors. From a practical point of view, a supercapacitor based on polyaniline and an aqueous solution of Al(NO₃)₃ was constructed and tested in terms of capacitance, cycle time, and self-discharge. The capacitor shows high charge and discharge capacity ($\approx 269 \text{ F g}^{-1}$ at a current density of 10 A g^{-1}) and relatively good capacity retention after 1000 charge and discharge cycles.

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Data-driven Design of New Mg-based Hydride Materials – A Synergy of Experiments and DFT

Katarina Batalović¹, Jana Radaković¹, Bojana Kuzmanović¹, Mirjana Medić Ilić¹, Bojana Paskaš Mamula¹

¹Laboratory for nuclear and plasma physics CONVINCE Center of excellence
for hydrogen and renewable energy VINCA Institute of the nuclear sciences –
national institute of the Republic of Serbia, University of Belgrade
e-mail: kciric@vin.bg.ac.rs

Hydrogen absorption/desorption is one of the key processes underlying many clean energy applications, such as thermal energy storage, hydrogen storage, hydrogen compression, and nickel-metal hydride batteries. For all those applications fast and reliable characterization of new materials, and in particular, information regarding energetics of hydride formation reaction is of main interest. In the last decades, DFT (density functional theory) approach showed good predictive potential for the ground state properties and calculation of hydride formation energies. Recently, MEGNet implementation [1] of graph neural networks showed promising results for fast and reliable prediction of formation energies for molecules and crystals. Here, we consider the development of a machine learning model based on the available DFT predicted structures and experimentally measured hydride formation enthalpies. The proposed model [2] is capable to predict hydride formation behavior for a wide variety of intermetallic compounds and distinguish the behavior of the polymorphs. In particular, based only on the crystal structure of the starting intermetallic compound, we were able to predict hydride formation enthalpy with accuracy comparable to DFT calculated values. Further, we demonstrate the application of this model for proposing new materials in Mg-Ni-M compound space with the desired enthalpy for hydrogen storage.

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7. Mirjana Medić Ilić, **Bojana Paskaš Mamula**, Bojana Kuzmanović, Jana Radaković, Nikola Novaković, Andela Mitrović, Jasmina Grbović Novaković; **Improvement of Hydrogen Storage Properties of MgH_2 by NaNH_2 addition**; Solid-State Science & Research Meeting; 10 & 11 June 2021, Zagreb, Croatia ; Book of abstracts p.69
8. K. Batalović, J.Radaković, **B. Paskaš Mamula**; **GNN and transfer learning for prediction of formation enthalpy of metal hydrides**; Solid-State Science & Research Meeting; 10 & 11 June 2021, Zagreb, Croatia ; Book of abstracts p.67



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P35 - Improvement of Hydrogen Storage Properties of MgH₂ by NaNH₂ addition

*M. Medić Ilić,¹ B. Paskaš Mamula,¹ B. Kuzmanović,¹ J. Radaković,¹
N. Novaković,¹ A. Mitrović,¹ J. Grbović Novaković¹*

¹University of Belgrade, Vinča Institute of Nuclear Sciences- National Institute of
Republic of Serbia, Centre of Excellence of Hydrogen and Renewable Energy,
Belgrade

e-mail: mirjanamedic@vinca.rs

MgH₂ based composites with addition of NaNH₂ (2 and 5 wt.%) as dopant were synthesized by mechanical milling using three different milling times. The hydrogen desorption properties and kinetic of these composites were examined using Thermal Desorption Spectroscopy (TDS), X-Ray Diffraction (XRD) for microstructure and particle size information and laser scattering method for estimation of particle size distribution (PSD) [1]. Samples with 5 wt.% of dopant and milling time of 15 and 30 minutes shows hydrogen desorption peaks shifting to lower temperatures in contrast to milled and as received MgH₂. All investigated composite samples shows enhanced kinetics with lowered E_a. Different Avrami parameter values were obtained for NaNH₂-MgH₂ composites and for pure MgH₂. With the milling time increasement (30 and 60 minutes) of the NaNH₂-MgH₂ composites, catalytic activity of NaNH₂ decreases which is followed by hydrogen desorption peaks shifting to higher temperatures.

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P33 - GNN and transfer learning for prediction of formation enthalpy of metal hydrides

K. Batalović,¹ J. Radaković,¹ B. Paskaš Mamula¹

¹Laboratory of nuclear and plasma physics, VINCA Institute of nuclear sciences,
University of Belgrade
e-mail: kciric@vin.bg.ac.rs

Prediction of metal hydride formation enthalpy is one of the key elements for a rapid screening and design of new hydrogen storage materials. In the last decades, DFT (density functional theory) approach showed good predictive potential for the ground state properties and calculation of hydride formation energies. Recently, graph neural network (GNN) implementations show promising results for fast and reliable prediction of formation energies for molecules and crystals. Here, we consider approach for universal machine learning based on a MatErials Graph Network (MEGNet) [1] that enable hydride formation energy prediction with a DFT accuracy. We demonstrate wide screening of potential dopants in Mg_2FeH_6 and Mg_2NiH_4 . In addition, we study the potential of transfer learning for building the universal machine-learning model capable of addressing experimentally reported hydride formation enthalpies.

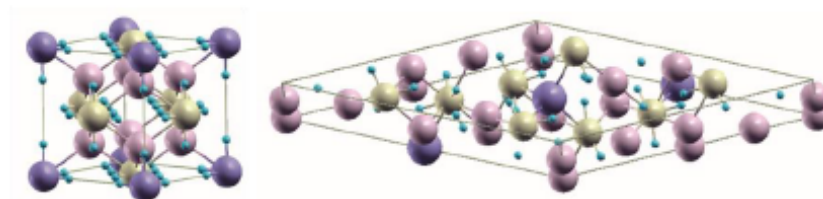
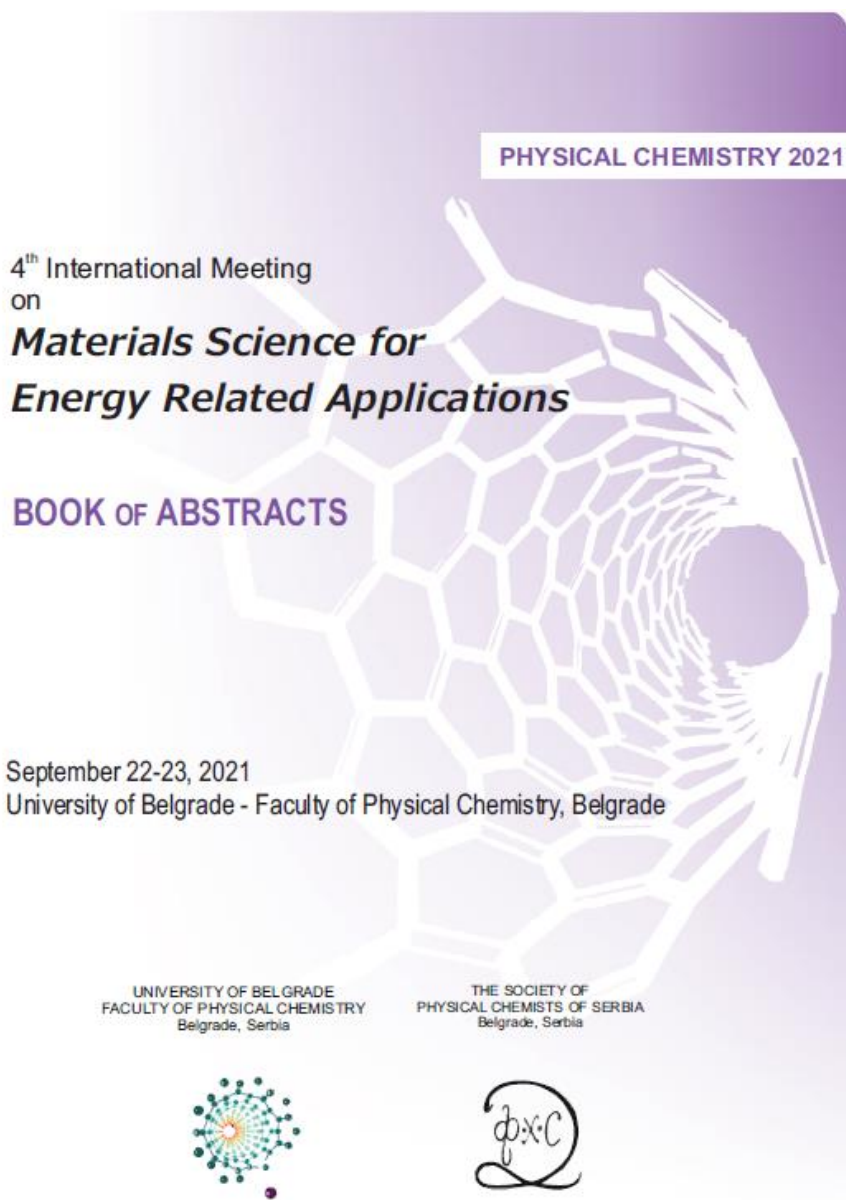


Figure 1 Unit cells of the doped Mg_2FeH_6 (left) and Mg_2NiH_4 (right)

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9. Katarina Batalović, Jana Radaković, **Bojana Paskaš Mamula**; **Data science and deep learning for the development of new hydrogen storage materials**; 4th International Meeting on Materials Science for Energy Related Applications, September 22-23, 2021, University of Belgrade - Faculty of Physical Chemistry; Book of abstracts p.18



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BOOK OF ABSTRACTS

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DATA SCIENCE AND DEEP LEARNING FOR THE DEVELOPMENT OF NEW HYDROGEN STORAGE MATERIALS

Katarina Batalović, Jana Radaković, Bojana Paskas Mamula

Laboratory of nuclear and plasma physics, VINCA Institute of nuclear sciences – national institute of the Republic of Serbia, University of Belgrade, Belgrade, Serbia

Prediction of metal hydride formation enthalpy is one of the key requirements for a rapid design of new hydrogen storage materials. In the last decades, DFT (density functional theory) approach showed good predictive potential for the ground state properties and accurate energies of hydride formation. However, calculating ZPE contribution and temperature effects in addition to formation energy at 0K is computationally and time-consuming and therefore often avoided, resulting in discrepancy to experiment.

The development of machine learning and, in particular, deep learning, opens a new perspective for predictive modeling of materials properties. Data collected through DFT calculations can be combined with experimental results in a predictive model, aiming to exploit unexplored compositional space. In this work, we consider the application of MatErials Graph Network (MEGNet) [1] to the prediction of hydrogen formation behavior, and screening of potential dopants in reversible metal hydride materials. Various approaches, relying on transfer learning and both experimental data and computational repositories (MP [2], NOMAD [3]) are proposed as a route to accurate prediction of a structure-property relation for hydrogen storage materials. Domains of applicability of these models are addressed.

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10. N. Novaković, **B. Paskaš Mamula**, I. Milanović. **Nature of bonding in amidoborane molecular chains and solids.** 4th International Symposium on Materials for Energy Storage and Conversion mESC-IS 2019, 11-13. September, Akyaka, Mugla, Turkey. The book of abstracts, pg. 93
11. Tijana Pantić, **Bojana Paskaš Mamula**, Sanja Milošević Govedarović, Sandra Kurko, Jasmina Grbović Novaković, Nikola Novaković. **Hydrogen in Mg-V thin films: TOF-ERDA characterization.** 4th International Symposium on Materials for Energy Storage and Conversion mESC-IS 2019, 11-13. September, Akyaka, Mugla, Turkey. The book of abstracts, pg.85



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Nature of bonding in amidoborane molecular chains and solids

Nikola Novaković, Bojana Paskaš Mamula, Igor Milanović

University of Belgrade, "Vinča" Institute of Nuclear Sciences, Centre of Excellence for Hydrogen and Renewable Energy, POB522, Belgrade 11000, Serbia

Ammonia borane ($\text{NH}_3\text{-BH}_3$ - AB) stands out as a perspective candidate material for hydrogen storage, with its high gravimetric density and low desorption temperature. Severe problems persist however, namely multiple-step irreversible desorption to stable polymeric species and contamination of desorbed hydrogen with unwanted substances in the process. At least one of many obstacles, like borasine poisoning, can be overcome with the substitution of amido group hydrogens with light alkaline metals, which gives amidoboranes, $\text{M}(\text{NH}_2\text{BH}_2)_x$ (x stands for charge of metal ion) or MAB. During the dehydrogenation process several desorption pathways are observed, one including the synthesis of alkali metal-($\text{BH}_2\text{-NH}_2\text{-BH}_2\text{-NH}_2\text{-BH}_2$) compound ($\text{M}(\text{B}_3\text{N}_2)$ for short). Another, non-substitutional, bonding mechanism is proposed [1] with alkaline metal ionically bind within tetrahedral environment of acidic hydrogens surrounding borane. We have performed systematic electronic structure calculations, vibrational analysis and analysis of charge density topology of AB, AB₂, A₂B₂ and A₂B₃ chains and their Li and Na - H substitutional counterparts with alkaline metal at symmetry allowed H positions on amide sites. Additionally, electronic structure of ($\text{BH}_2\text{-NH}_2\text{-BH}_2\text{-NH}_2\text{-BH}_2$)⁻ anion and $\text{Li}(\text{B}_3\text{N}_2)$ and $\text{Na}(\text{B}_3\text{N}_2)$ molecule have been calculated. Forces optimization of initial configurations have been performed, where single H atom in the first coordination of nitrogen (and boron) atoms have been substituted. The goal was to investigate trends in cohesion, bonding nature and strength of these mostly hypothetical molecules and to explain experimentally evident existence of at least some of them.

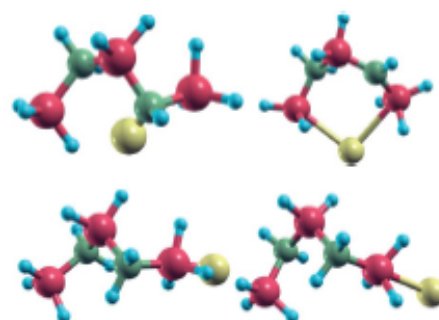


Figure 1. The molecular structures of Na-A₂B₃ with Na atom initially bounded at N (top) and B (bottom) atoms. Left) initial and right) final configurations are shown.

The obtained optimized structures of longer AB chains show strong deviation from alkane-like symmetry (C_{1v} , C_{2v} etc.), caused by acidic-protonic H interaction. The results show strong influence of alkali metal on deviation from alkane-like C_{2v} symmetry chains through strong interaction with both original substitution site and neighbor acidic hydrogens. All "higher" optimized structures are characterized with alkali atoms at the distances similar to distance in substituted AB system (around 2.3 for Na). Alkali atom in the systems with odd number of boron atoms causes distortion in order to position itself in equilibrium position between end boron atoms. In case of systems with even number of boron atoms, original shape of molecule tends to be preserved. In case of A₂B₃, Na-acidic H bonding prevails which can explain observed different nature of bonding in $\text{Na}(\text{B}_3\text{N}_2)$.

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Born in Belgrade, Serbia 20.12.1971. PhD in physics 2010, Belgrade University. Deputy director of laboratory for nuclear and plasma physics, VINČA Institute of nuclear sciences. Head of Laboratory for theoretical modeling of materials in Centre of Excellence for Hydrogen and Renewable energy, VINČA Institute of Nuclear Sciences. President of Hydrogen Economy Initiative Serbia NGO. Theoretical modelling of various metal-hydrogen solid and molecular systems (electronic structure calculations using state-of-art WIEN2k, Abinit, CPMD, Crystal and VASP codes) and local structures investigation of various semiconducting systems.

Corresponding author: Nikola Novaković, e-mail: novnik@vinca.com, tel:+381 64 26 23 565

Hydrogen in Mg-V thin films: TOF-ERDA characterization

Tijana Pantić, Bojana Paskaš Mamula, Sanja Milošević Govedarović, Sandra Kurko, Jasmina Grbović Novaković and Nikola Novaković

University of Belgrade, "Vinča" Institute of Nuclear Sciences, Centre of Excellence for Hydrogen and Renewable Energy, POB522, Belgrade 11000, Serbia

To develop sustainable hydrogen storage materials, a comprehensive knowledge of the mechanisms of hydrogen motion at atomic level is required. It is obvious that development of novel materials for solid state storage is related to tailoring of several properties such as alloy composition, surface properties, microstructure and grain size. Even though the final goal is to produce large amounts of materials that can reversibly store hydrogen, thin film processing is an optional method that offers the possibility to produce material with well-defined microstructures and dimensions. Thin films allow investigating in detail the surface state (presence of oxides, hydroxides) on H-absorption/desorption steps. Magnesium obtained significant attention as hydrogen storage material due to high gravimetric and volumetric capacity, low cost and high availability. However, the majority of the studies are related to materials obtained by ball-milling which prevents detailed surface sensitive characterization. Mg prepared in form of thin films does not suffer from embrittlement and/or decrepitation as bulk materials do. This allows the study of cyclic absorption and desorption. The problem of pure Mg thin films is that for hydrogenation the elevated temperature and pressures are needed. Capping the Mg thin films with Pd is proposed to overcome some drawbacks. Due to capping with palladium, the films exhibit a fast dissociation rate and good transport properties. The problem of capped films on the other hand is that the rate of absorption decrease with the increase of pressure and this is attributed to the fact that there is a MgH_2 layer formed at the interface. This hydride layer hinders further uptake of hydrogen due to the fact that hydrogen diffusion in magnesium hydride is the rate limiting step. To avoid this interface problem we have used alternating layers of Mg and V with 10 nm and 1 nm thickness respectively. Vanadium was used because it is known that the diffusivity of hydrogen in this element is extremely high even at ambient temperature. Further, to increase the hydrogenation rate and to introduce defects (Frenkel pairs) in the near-surface region, ion irradiation with H^+ ions at 3keV and ion fluence of 10^{17} ion/cm² has been applied. Ion irradiation with hydrogen was performed at FAMA ion source at Vinča Institute of Nuclear Sciences. The hydrogenation of thin films was done at HAS-UNLS sorption analyzer for 3h at 300 °C.

To investigate the H content depth profile in hydride, ERDA (Elastic Recoil Detection Analysis) equipped with time of flight (TOF) detector has been applied. The major advantages of TOF-ERDA spectroscopy is the ability to distinguish contributions in the spectrum that come from different ions having same energies. In the present work hydrogen content in Mg-V thin films has been investigated by TOF-ERDA using 20 MeV $^{127}I^{6+}$ beam. Preliminary results for irradiated

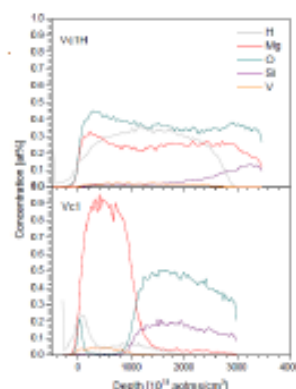


Figure 1. TOF-ERDA depth profile of 300 nm films.

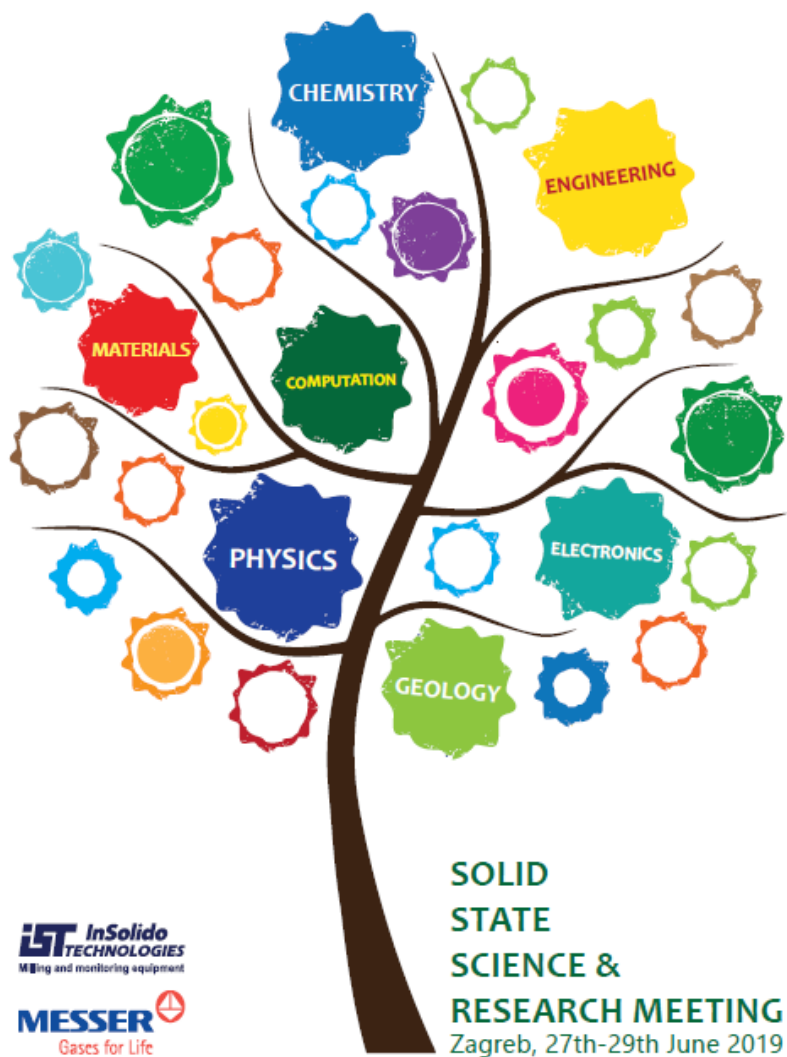
only 300 nm sample (Fig. 1 down) show predominance of Mg in the film, as expected, while the distribution of V is uniform, the consequence of insufficient resolution and probably pronounced Mg-V diffusion. The H concentration exhibits typical, two peaks behavior: sharp surface peak followed by more diffused bulk peak, the latter corresponding to theoretical SRIM calculated depth profile. After hydrogenation (Figure 1 up), the situation is substantially different: H concentration now has uniform distribution through entire film, while relative concentrations of other elements have decreased. The change of film width is the consequence of hydride volume expansion and change in film density (metallic Mg vs. MgH_2). It can be concluded that sandwich Mg-V thin films are fully hydrogenated at given conditions.



Born in Belgrade, Serbia 29.09.1973. B.Sc in physical chemistry 1999, M.Sc in physical chemistry 2003, PhD in physical chemistry 2005. From 2018 Head of Centre of Excellence for Hydrogen and Renewable energy at Vinča Institute of Nuclear Sciences, President of Serbian Society for Microscopy from 2010. 2009 awarded from International Association of Hydrogen Energy with IJHE outstanding Service Award. Guest Editor: Novel Perspectives on Hydrogen Storage in Solid Media and International Journal of Hydrogen Energy. Mum of 3.

Corresponding author: Jasmina Grbović Novaković, e-mail: jasnagn@gmail.com, tel:+381 64 16 96 253

12. T. Pantić, B. Paskaš Mamula, N. Novaković, S. Milošević Govedarović, S. Kurko, M. Micetić, J. Grbović Novaković. **TOF-ERDA measurements of hydrogen content and depth profile in Mg-V irradiated thin films.** Solid state science and research conference, 26-29.06.2019, Zagreb, Croatia, The book of abstracts, pg. 107.



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P45: TOF-ERDA measurements of hydrogen content and depth profile in Mg-V irradiated thin films

T.Pantić¹, B. Paskaš Mamula¹, N. Novaković¹, S. Milošević Govedarović¹, S. Kurko¹, M. Mičetić², J. Grbović Novaković¹

¹Centre of Excellence for Hydrogen and Renewable Energy, University of Belgrade, Belgrade

²Division of Materials Physics, Ruđer Bošković Institute, Zagreb
e-mail: tijanap@vinca.rs

Thin films, as materials for solid state hydrogen storage, show various advantages over bulk materials and powders. Faster dehydrogenation kinetics and lower desorption temperatures, as well as the possibility of better control of structure and composition are the reasons for their exhaustive research. In this study we've investigated thin films consisting of alternating Mg (30 nm) and V layers (1 nm) with 10 repetitions. Synthesized nanocrystalline thin films were modified by ion irradiation using of H⁺ and Xe⁸⁺ ions. TOF-ERDA measurements were done using 20 MeV ¹²⁷I⁶⁺ beam. TOF-ERDA results are presented in Figure 1 and 2. The results show that ion-irradiation induced defects improved hydrogen desorption and reduced desorption temperature.

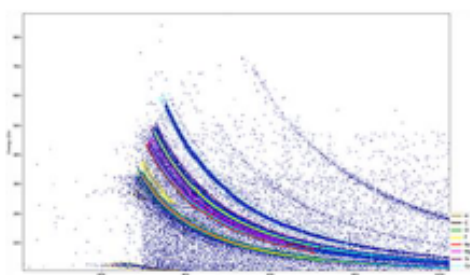


Figure 1. TOF-ERDA results of film irradiated by H⁺ ions, fluence 10⁻¹⁶ ions/cm³.

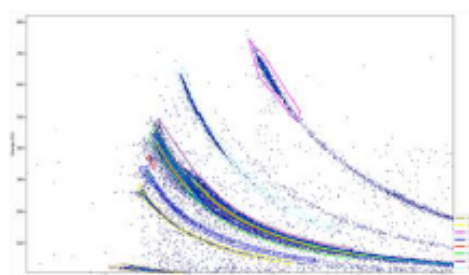


Figure 2. TOF-ERDA results of film irradiated by Xe⁸⁺ ions, fluence 10⁻¹⁶ ions/cm³.

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13. Jasmina Grbović Novaković, **Bojana Paskaš Mamula**, Sandra Kurko, Sanja Milošević Govedarović, Jelena Rmuš, Tijana Pantić, Mirjana Medić Ilić, Nikola Novaković. **Toward destabilization of MgH_2 structure – the combined theoretical and experimental study**. Gordon Research Conference, Hydrogen-Metal Systems, Understanding the Interaction of Hydrogen with Materials from the Atomic Level to Systems, June 30 - July 5, 2019, Castelldefels, Spain, poster 41.M/U.

Hydrogen-Metal Systems

Gordon Research Conference

Understanding the Interaction of Hydrogen with Materials from the Atomic Level to Systems

June 30 - July 5, 2019
Rey Don Jaime Grand Hotel
Castelldefels, Spain

Chairs: Ned T. Stetson and Michael Hirscher
Vice Chairs: Tom Autrey and Ping Chen

Contributors



#	Session	Name	Affiliation	Poster Title
31	Mon/Tue	Fujinami, Masanori	Chiba University	Positron annihilation spectroscopy of the crucial defects induced in austenitic stainless steel upon hydrogen embrittlement
32	Mon/Tue	Gaboriau, Dorian	CEA	TBD
33	Mon/Tue	Gemma, Ryota	Tokai University	Mechanochemical CO ₂ methanation over LaNi-based alloys
34	Mon/Tue	Gerber, Alexander	Tel Aviv University	Detection of hydrogen by the extraordinary Hall effect in CoPd systems
35	Mon/Tue	Gigante, Angelina	University of Geneva	A safe synthesis of alkali metal triboranes and decaboranes (M(B ₃ H ₈) ₂) and MB ₁₀ H ₁₀ (M=Na, Mg,Ca) . The role as intermediates for hydrogen storage.
36	Mon/Tue	Gizer, Gökhan	Helmholtz Zentrum Geesthacht	Tri-component amide-hydride-borohydride RHC system with superior hydrogen storage properties
37	Mon/Tue	Gomez, Maria A	Mount Holyoke College	Defects shape the proton conduction landscape in doped barium zirconate
38	Mon/Tue	Gomez, Osmar J	CSU-Northridge	Photoluminescent Properties of Hydrogen Storage Materials
39	Mon/Tue	Götz, Maximilian	DLR Institute of Networked Energy Systems	Switchable Optical Cavity Based on Magnesium-Hydrogen Interaction for Tunable Photo-Current Generation
40	Mon/Tue	Gray, Evan	Griffith University	TBD
41	Mon/Tue	Grbovic Novakovic, Jasmina	University of Belgrade	Toward destabilization of MgH ₂ structure – the combined theoretical and experimental study
42	Mon/Tue	Griessen, Ronald	VU University Amsterdam	Quality Factor for Enthalpy-Entropy Compensation, Isoequilibrium and Isokinetic Relationships
43	Mon/Tue	Grinderslev, Jakob B	Aarhus University - Chemistry and Nano	Dihydrogen Bonding and Dynamics in Ammonium Borohydride
44	Mon/Tue	Grünwald, Patrick A	Saarland University	Hydrogen embrittlement of grain boundaries investigated by a combination of Scanning Kelvin Probe and in situ mechanical tests in the SEM
45	Mon/Tue	Ha, Taejun	Korea Institute of Science and Technology	Characteristics of TiFe hydrogen storage alloy
46	Mon/Tue	Hagemann, Hans R	University of Geneva	Thermodynamic properties of boron hydrogen species
47	Mon/Tue	Hajiyev, Parviz	CEA LITEN, Université Grenoble Alpes	Effects of alkali cations and ammonia borane additive on the dehydrogenation properties of ammine zinc borohydrides

Jasmina Grbović Novaković, Bojana Paskaš Mamula, Sandra Kurko, Sanja Milošević Govedarović, Jelena Rmuš, Tijana Pantić, Mirjana Medić Ilić, Nikola Novaković, **Toward destabilization of MgH₂ structure – the combined theoretical and experimental study**, Hydrogen-Metal Systems, Gordon Research Conference, Understanding the Interaction of Hydrogen with Materials from the Atomic Level to Systems, June 30 - July 5, 2019, Castelldefels, Spain, poster 41.M/U

Toward destabilization of MgH₂ structure – the combined theoretical and experimental study

Jasmina Grbović Novaković, Bojana Paskaš Mamula, Sandra Kurko, Sanja Milošević Govedarović, Jelena Rmuš, Tijana Pantić, Mirjana Medić Ilić, Nikola Novaković

VINČA Institute of Nuclear Sciences, POB 522, 11001 Belgrade, Serbia

Straightforward way of destabilization of Mg-based metal hydride systems is weakening of the host lattice by various defects introduction (neutral and charged vacancies, displaced atoms of host lattice and substitutional and interstitial dopants). The experimental characterization of the induced material modifications and changes in the physical and chemical properties of interest is usually coupled with complementary theoretical approach i.e. theoretical *ab initio* material modelling. The experimental methods for synthesis and modification of materials include mechanosynthesis and composites, ion irradiation, severe plastic deformation methods (ECAP, Fast-Forging) and others. For theoretical description of induced changes, the various calculation methods were used, such as DFT based pseudopotential and linear all-electron methods applied on cluster, bulk, surface, single interface and multilayer models. The results show that improvement of (de)sorption properties using defects introduction can in principle be already explained using relatively simple theoretical models. Hydrogen storage properties can be tailored by addition of small amount of transition metals (Ti, V, Fe, Co, Ni, Cu and Pd), transition metal oxides (TiO₂, CeO₂), halides (FeF₃) or borides (TiB₂). We have used both, theoretical and experimental approach to study reaction mechanism in powder and thin films material.

Processes taking place during hydrogen desorption from Mg/MgH₂ thin films upon modification by ion irradiation were investigated. Irradiation was used to produce exact quantity of point defects within well-defined depth distribution. It was shown that the size, shape, and concentration of Mg nuclei formed during hydrogen desorption from MgH₂ thin films depend on the characteristics and distribution of the induced defects. In non-irradiated samples the shape of Mg nuclei is spherical, while in irradiated samples it is highly irregular. Variations in

sample color were observed during hydrogen desorption and before the creation of Mg nuclei. DFT calculations showed that the observed variations in the optical properties of samples can be explained by changes in MgH_2 electronic structure and the appearance of an H-vacancy band within the MgH_2 energy gap. On the other hand, the modification induced by capping with TiO_2 does not affect the shape of nuclei. The shape is rather spherical and do not depend on film thickness. The size and concentration of nuclei is related to the thickness of films. Both modifications (thin film capping with oxides and point defects) lead to reduction of temperature onset for desorption and improved kinetics.

Experimental characterization of MgH_2 doped with various 3d transition metals covered both desorption temperature and kinetics measurements using DTA and DSC methods. They show both desorption temperature decrease down to 70 °C and substantial kinetics improvement. Chemical bonding and stability of simple metal hydrides and transition metal doped MgH_2 have been assessed theoretically by means of charge density topology analysis on the both local (Bader concept of "atoms in molecules") and integral (concept of non-covalent interactions) level. Complex structure of NCI reduced charge density gradient in ionic MgH_2 with first and second neighbor bonded atoms is replaced with more pronounced directional first neighbor bonding in transition metal doped MgH_2 - 3d TM's (with the exception of Sc) tend to form shorter and stronger bonds with their first coordination H atoms. The shortest bonds are found for Fe and Co (~1.65 Å), while the longest (and of comparable length as Mg-H in pure MgH_2 , (~1.95 Å) for Sc and Zn. The distribution of so called bonding critical points (obtained from zero charge density gradient and specific saddle point configuration conditions) and bonding paths connecting two atomic sites gives us information about the existence, strength and nature of atomic interactions in the system. Beside expected Mg-H nearest neighbour (NN) bonds, charge density topology analysis of pure MgH_2 reveals existence of second neighbour (SN) longer H-H bond with directional character and possible contribution to and impact on overall stability of this system. Introduction of TM changes this picture. NN bonding paths persist while SN H-H bonds are missing in all TM doped systems. We conclude that the bonding is more directional with significant redistribution of available charge (TM are acting as electron donors) towards NN TM-H direction. The rise of charge density values in bonding critical points goes in favour of such a conclusion. Rise of covalent contribution of these bonds should be accompanied with specific properties of charge density laplacian. The value of this property is connected to the ionic-covalence ratio in chemical bonding. The trend obtained does not follow the trend in TM-H bond lengths and in-between bCP's charge density values. The reason for this could be spatial localization of 3d orbitals and specifics of $sp^3d^1-d^2$ hybridization.

14. J. Grbović Novaković, S. Kurko, S. Milošević Govedarović, T. Pantić, **B. Paskaš Mamula**, M. Medić, N. Novaković. **Theoretical and experimental approach to destabilization methods for improvement of hydrogen sorption kinetics in Mg based systems.** 22nd Conference “New Cryogenic and Isotope Technologies for Energy and Environment” EnergEn2018 BăileGovora, Romania, October 24 – 26, 2018 pg. 134-135.



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THEORETICAL AND EXPERIMENTAL APPROACH TO DESTABILIZATION METHODS FOR IMPROVEMENT OF HYDROGEN SORPTION KINETICS IN Mg BASED SYSTEMS

Jasmina Grbović Novaković, Sandra Kurko, Sanja Milošević Govedarović, Tijana
Pantić, Bojana Paskaš Mamula, Mirjana Medić, Nikola Novaković

*University of Belgrade, Vinča Institute of Nuclear Sciences, CONVINCE –Centre of Excellence for
Renewable and Hydrogen Energy, POB522, Belgrade 11000, Serbia
Corresponding author: jasnagn@gmail.com, jasnag@vin.bg.ac.rs*

Magnesium hydride (MgH_2) is considered as one of the most promising candidates for solid state hydrogen storage due to its high theoretical hydrogen capacity (7.6 wt.%), good reversibility, and relatively low cost. MgH_2 is also considered for thermal energy storage applications. However, several factors have hindered its application: (1) the thermodynamic stability of MgH_2 leads to its dehydrogenation temperature being as high as 350–400°C; (2) the kinetic rates of both dehydrogenation and hydrogenation reactions of Mg are usually poor and require high temperature conditions. The H storage properties can be tailored by addition of small amount of transition metals (Ti, V, Fe, Co, Ni, Cu and Pd), transition metal oxides (TiO_2 , CeO_2 , V_2O_5 , WO_3), halides (FeF_3) or borides (TiB_2). We have used both, theoretical and experimental approach to study reaction mechanism in powder and thin films material (Kurko, 2013; Montone, 2006; Paskas Mamula, 2014).

Processes taking place during hydrogen desorption from Mg/ MgH_2 thin films upon modification either by TiO_2 capped layer or by ion irradiation were investigated. Irradiation was used to produce controlled quantity of point defects with well-defined depth distribution. It was shown that the size, shape, and concentration of Mg nuclei formed during hydrogen desorption from MgH_2 thin films depend on the characteristics and distribution of the induced defects. In non-irradiated samples the shape of Mg nuclei is spherical, while in irradiated samples it is highly irregular. Variations in sample colour were observed during hydrogen desorption and before the creation of Mg nuclei. DFT calculations showed that the observed variations in the optical properties of samples can be explained by changes in MgH_2 electronic structure and the appearance of an H-vacancy band within the MgH_2 energy gap. On the other hand, the modification induced by capping with TiO_2 does not affect the shape of nuclei. The shape is rather spherical and do not depend on film thickness. The size and concentration of nuclei is related to the thickness of films. Both modifications (addition of additives or point defects) lead to reduction of temperature onset for desorption and improved kinetics.

On the other hand it is well known that energetic ball milling of hydrides substantially refines their particle size and forms nanometric grains within the particles. In the mechanical (ball) milling process there is always a connected reduction of the powder particle size which accompanies the reduction of grain size of the phases residing within the particle. Those changes has an effect on desorption properties of hydrides. This lecture will discuss in details those effects.

Keywords: hydrogen storage, magnesium based hydrides, DFT theory, ball milling, ion irradiation, kinetics.

Acknowledgments The work is supported by Ministry of Education, Science and Technological development under grant III45012 and III45003

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15. Tijana Pantić, Nenad Filipović, Sandra Kurko, **Bojana Paskaš Mamula**, Jasmina Grbović Novaković, Nikola Novaković, Sanja Milošević Govedarović. **Combined effects of mechanical milling and addition of WO₃ on hydrogen desorption from MgH₂**. 3rd Int. Symposium on Materials for Energy Storage and Conversion mESC-IS 2018, 10-12. September, Belgrade, Serbia. Programme & the book of Abstracts pg. 97.
16. **Bojana Paskaš Mamula**, Jasmina Grbović Novaković, Igor Milanović, Bojana Kuzmanović, Nikola Biliškov, Nikola Novaković. **Interaction of amidoborane molecular chains with alkali metals: a theoretical study**. 3rd Int. Symposium on Materials for Energy Storage and Conversion mESC-IS 2018, 10-12. September, Belgrade, Serbia, Programme & the book of Abstracts pg. 100.
17. Jelena S. Milićević, Sandra Kurko, **Bojana Paskaš Mamula**, Nikola Novaković, Tijana Pantić, Sanja Milošević Govedarović, Atif Hodžić, Jasmina Grbović Novaković. **Electrochemical behaviour of pyrophyllite carbon paste composite electrode**. 3rd Int. Symposium on Materials for Energy Storage and Conversion mESC-IS 2018, 10-12. September, Belgrade, Serbia, Programme & the book of Abstracts pg.95.

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Dr. Sanja Milošević Govedarović
Dr. Jasmina Grbović Novaković

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Combined effects of mechanical milling and addition of WO₃ on hydrogen desorption from MgH₂

Tijana Pantić¹, Nenad Filipović², Sandra Kučko¹, Bojana Paskaš Mamula¹, Jasmina Grbović Novaković¹, Nikola Novaković¹ and Sanja Milošević Govedarović¹

¹University of Belgrade, Vinča Institute of Nuclear Sciences, Centre of Excellence for Hydrogen and Renewable Energy POB 552, 11000 Belgrade, Serbia

²Institute of Technical Sciences of The SASA, Knez Mihailova 35/IV, Belgrade 11000, Serbia

Magnesium hydride as the most promising material for solid state hydrogen storage has been investigated for decades. In order to improve the sorption characteristic various modification methods has been applied: ion bombardment, mechanical milling, with addition of different oxides, halides etc [1]. Sluggish kinetics and high desorption temperature as the main drawbacks were drastically improved by mechanical milling with oxides of d-block elements such as vanadium, niobium, tantalum, nickel etc. Tungsten is also d-block metal so it is expected to have a similar effect on MgH₂. Tungsten-oxide powder were used in small concentrations: 5% (MW5), 10% (MW10), 15% (MW15) as additives to MgH₂ and milled together for 30 minutes in SPEX 5100 mill with BPR 10:1 in Ar atmosphere.

Effect of WO₃ addition on desorption temperature followed by differential scanning calorimetry (DSC-Figure 1) and temperature programmed desorption (TPD-Figure 2) were reported in this paper. Isoconversional kinetic analysis was applied in order to determine the kinetic behavior of material (Table 1).

Table 1. Kinetic parameters of commercial MgH₂, milled MgH₂, MW10, MW15 in θ range from 0.20-0.80

Sample	Tp [°C]	Ea [kJ/mol]	Avrami-Erofeev $g(\theta)=[-\ln(1-\theta)]^{1/n}$
com. MgH ₂	445	106	[$-\ln(1-\theta)$] ^{1/4}
milled MgH ₂	419	50	
MW5	393	66	
	366	64	
MW10	400	88	
	372	124	
MW15	415	141	
	447	168	

Both DSC and TPD curves of all milled samples demonstrate change in mechanism of desorption and the reduction of temperature. The onset of temperature desorption is reduced for 150°C. DSC curves of sample milled with 5% of WO₃ shows two desorption peaks as a result of different particles sizes. The reduction of desorption temperature maxima is up to 30 °C Two desorption peaks are visible also in MW10 sample too. In this case, desorption temperature is reduced

for about 40°C. Composite sample obtained with 15% of WO₃ (MW15) demonstrate unusual behavior: three desorption peaks appears: at 355, 385 and 440°C. This can be attributed to both inhomogeneous dispersion of catalyst, phase change of WO₃ during mechanical milling. The H₂ desorption process from composites was analyzed by fitting the experimental data using different kinetic models and the best fit was obtained by non-isothermal Avrami-Erofeev model (see Table 1). The analysis of the TPD curves indicates that the H₂ desorption from MgH₂ in the composites is controlled by nucleation and growth mechanisms with reaction order $n=4$.

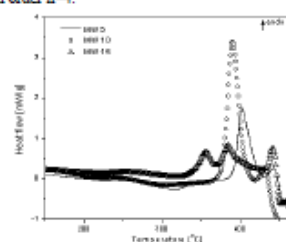


Figure 1. Hydrogen desorption obtained by DSC measurements for milled composite samples

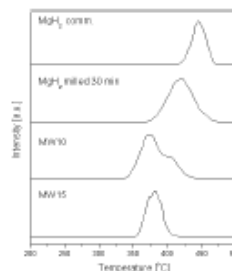


Figure 2. Hydrogen desorption obtained from TPD measurements of commercial MgH₂, MgH₂ milled for 30 minutes, and composite samples with different WO₃ content 10 and 15%



Sanja Milošević Govedarović

Sanja is Doctor of Physical Chemistry and she works as a Research Associate at the Laboratory of Physics, INS Vinča in Belgrade. Her research area covers various materials for solid state hydrogen storage and electrode materials for Li-ion batteries. Her presentations at international events were noticed and rewarded. Corresponding author: Sanja, e-mail: sanjam@vinca.rs tel: +381 11 3408 373

Interaction of amidoborane molecular chains with alkali metals: a theoretical study

Bojana Paskaš Mamula¹, Jasmina Grbović Novaković¹, Igor Milanović^{1,2}, Bojana Kuzmanović¹, Nikola Biliškov², Nikola Novaković¹

¹ VINČA Institute of nuclear sciences, University of Belgrade, POB 522, 11001 Belgrade, Serbia

² Rudjer Bošković Institute, Bijenička Cesta 54, 10000 Zagreb, Croatia

Ammonia borane ($\text{NH}_2\text{-BH}_3$ - AB) stands out as a perspective candidate material for hydrogen storage, with its high gravimetric density and low desorption temperature. Severe problems persist however, namely multiple-step irreversible desorption to stable polymeric species and contamination of desorbed hydrogen with unwanted substances in the process. At least one of many obstacles, like borasine poisoning, can be overcome with the substitution of amido group hydrogens with light alkaline metals, which gives amidoboranes, $\text{M}(\text{NH}_2\text{BH}_2)_x$ (x stands for charge of metal ion) or MAB. During the dehydrogenation process several desorption pathways are observed, one including the synthesis of alkali metal- $(\text{BH}_2\text{-NH}_2\text{-BH}_2\text{-NH}_2\text{-BH}_2)_n$ compound ($\text{M}(\text{B3N2})$ for short). Another, non-substitutional, bonding mechanism is proposed [1] with alkaline metal ionically bind within tetrahedral environment of acidic hydrogens surrounding borane. In this paper, we have performed systematic electronic structure calculations and the analysis of charge density topology of AB, AB2, A2B2 and A2B3 chains and their Na - H substitutional counterparts with alkaline metal at symmetry allowed H positions on amide sites. Additionally, electronic structure of $(\text{BH}_2\text{-NH}_2\text{-BH}_2\text{-NH}_2\text{-BH}_2)^+$ anion and $\text{Na}(\text{B3N2})$ molecule have been calculated. The goal is to investigate trends in cohesion, bonding nature and strength of these mostly hypothetical molecules and to explain experimentally evident existence of at least some of them.

The obtained optimized structures of longer AB chains show strong deviation from alkane-like symmetry (C_{2v} , C_{2v} etc.), caused by acidic-protonic H interaction. The results show strong influence of alkali metal on deviation from alkane-like C_{2v} symmetry chains through strong interaction with both original substitution site and neighbor acidic hydrogens. In case of A2B3, Na-acidic H bonding prevails which can explain observed different nature of bonding in $\text{Na}(\text{B3N2})$.

References:

- [1] K.J.Fijalkowski et al, *PCCP* 16, 23340-23346 (2014)

Electrochemical behaviour of pyrophyllite carbon paste composite electrode

Jelena S. Milićević¹, Sandra Kurko, Bojana Paskaš Mamula, Nikola Novaković, Tijana Pantić, Sanja Milošević Govadarović, Atif Hodžić², Jasmina Grbović Novaković¹

¹Vinča Institute of Nuclear Sciences, University of Belgrade, 11000 Belgrade, Serbia

²AD Harbi d.o.o Sarajevo, Bosnia and Herzegovina

Abstract

Pyrophyllite. Besides traditional applications, large pyrophyllite reserves have the potential for being used also in more sophisticated non-traditional fields. This study aimed to examine pyrophyllite for its potential application for the purification of real water systems. Its electrochemical characteristics were examined by using cyclic voltammetry (CV) of sulfuric acid (H_2SO_4) and potassium ferrocyanide ($K_4Fe(CN)_6$), a redox model compound. Due to its specific structure, surface groups and morphology of pyrophyllite carbon paste electrode exhibited electrocatalytic activity.

Electrochemical set up and measurements

Carbon paste electrode (CPE) are widely used electrodes in the fields of electrochemistry, due to their attractive advantages, such as low-cost implementation, simple preparation, low background current and wide potential window.

Pyrophyllite carbon paste electrodes have been investigated by cyclic voltammetry measurement in 0.5 M H_2SO_4 as acidic supporting electrolyte, with potential range from -0.5 V to +1.1 V vs Ag/AgCl (saturated KCl) reference electrode. In addition, 1 mM $K_4Fe(CN)_6$ in 0.1 M KCl was used as redox model compound. Parallel examinations were conducted with carbon paste electrode (CPE), containing only graphite and liquid binder (paraffin oil (P) and tricresyl phosphate (TCP)) by using 797 VA Computrace analyzer. The parameters for CV measurement were as follows: initial potential -0.5 V, end potential 1 V, sweep rate 0.1 V/s, initial purge time 60 s and scan rate 50 mV/s.

Results and discussion

Cyclic voltammograms obtained at PGP and PGTCP shows the cathodic and anodic peaks with good symmetry and peak to peak separations which is higher for PGTCP indicating reversible electrode processes (Fig. 1). The peak to peak separations indicate a significant electrocatalytic activity of PGTCP and PGP which is much better than GP and PP (Fig. 2).

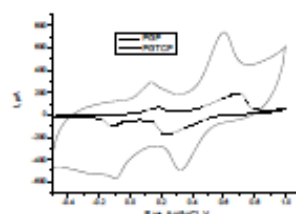


Fig. 1. Cyclic voltammograms at pyrophyllite graphite paraffin (PGP) and pyrophyllite graphite tricresyl phosphate (PGTCP) carbon paste electrode in 0.5 M H_2SO_4 at scan rate 50 mV/s.

It is clear that pyrophyllite can be used as electrochemically active component. The obtained results open a new field for further investigations which concern pyrophyllite as a sensor for the detection of water pollutants.

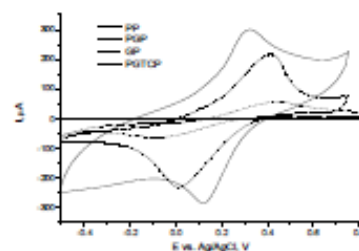


Fig. 2. Voltammograms obtained for 1 mM $K_4Fe(CN)_6$ in 0.1 M KCl at pyrophyllite paraffin (PP), pyrophyllite graphite paraffin (PGP), graphite paraffin (GP) and pyrophyllite graphite tricresyl phosphate (PGTCP) carbon paste electrode.

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Jelena S. Milićević

Jelena S. Milićević is working at Vinča Institute of Nuclear Sciences as a research associate. Her scientific areas of interest are: separation chemistry, environmental protection and voltammetric determination of pesticides. Until now, she has published 15 papers in international journals, 1 book chapter, 1 monograph and 25 conference papers, and she has been cited more than 100 times. Besides, she attended several summer schools and environmental protection courses. She attended short study visit at the Department of Analytical Chemistry at the University of Pardubice, Czech Republic within the CEEPUS Project, and at the Department of Ecology, University of Liverpool, UK within the COST action.

Corresponding author: Jelena S. Milićević, e-mail: jdmilic@vinca.rs tel: +381-11-644-7700

18. **Bojana Paskaš Mamula, Nenad Ivanović, Nikola Novaković. Properties of charge density topology of simple and transition metal doped metal hydrides – characterization of bond nature and strength using non-covalent interactions and Bader charge density analysis.** E-MRS Spring Meeting 2018, Strasbourg, France, 18-22. June, 2018, B-14
- **Konferencija ne objavljuje knjigu apstrakata već učesnici dobijaju samo knjigu programa.**



14:00	Structure/function comparisons of multifunctional Metal Phosphides supported Pt and Ir catalysts for Fuel Cell and Electrolysers Shuang Wu Department of Chemistry, Imperial College London	B P2.29
14:00	Detecting Genuine Entanglement using the Wigner Function Ziane mustapha, morad el baz, yassine hassouni Um5 rabat	B P2.30
14:00	Ab-Initio and DFT Study of the Isomerisation Kinetics of Substituted Icosadeca-ene Z. SKANDER ¹ , Y. BOUZAHER ¹ , A. DJEBAILI ^{1*} , ILHEM. R. KRIBA ² , Y. AHMANE ³ 1 Laboratory of chemistry and environmental chemistry L.C.C.E - University of Batna 1- Algeria 2 Faculty of Sciences- Department of Physics - University of Batna 2- 05000- Algeria 3 Faculty of Sciences- Department of Chemistry - University of Biskra- Algeria	B P2.31
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14:00	Theoretical analysis of electronic properties of porous germanium A.N. Sosa, A. Trejo, M. Cruz-Irisson Instituto Politécnico Nacional	B P2.33
14:00	Molecular dynamics study of water evaporation enhancement through a capillary graphene bilayer with tunable hydrophilicity Hieu Trung Kieu, Adrian Wing-Keung Law Environmental Process Modelling Centre, Nanyang Environment and Water Research Institute, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore, Interdisciplinary Graduate School, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore	B P2.34
14:00	Graphene oxide supported on ceramics for CO ₂ capture M.L. Grilli*, M. R. Mancini*, S. Stendardo *marialuisa.grilli@enea.it, rita.mancini@enea.it ENEA, Casaccia Research Centre, Via Anguillarese 301, 00123 Rome (Italy)	B P2.35
14:00	Light Driven Organic Transformations to Enhance Hydrogen Production William Yau Imperial College London	B P2.36
14:00	Effect of the core thickness on the physical properties of ZnO/TiO ₂ core/shell nanostructures: First-principles study 1) Slimane Haffad, 2) Madani Samah, 3) Khaled Boufaia 1) Département de technologie, faculté de Technologie, université de Bejaia, Algérie, 2) Département de biologie, faculté de biologie, université de Bejaia, Algérie, 3) Département de physique, faculté des sciences exactes, université de Bejaia, Algérie	B P2.37
14:00	Ionization equilibrium of c-band electrons and hydrogen-like donors in semiconductors under quantizing magnetic field N.A. Poklonski, A.N. Dzeraviah, S.A. Vyrko Belarusian State University, Physics Department, Nezavisimosti Ave. 4, Minsk 220030, Belarus, poklonski@bsu.by	B P2.38
14:00	Properties of charge density topology of simple and transition metal doped metal hydrides - characterization of bond nature and stability Bojana Paska*, Mamula, Nenad Ivanovic, Nikola Novakovic VINCA Institute of nuclear sciences - University of Belgrade, PGB 522, 11001 Belgrade, Serbia	B P2.39
14:00	Optimization study of new ZnO/Si/Cu ₂ O solar cell structure using one dimensional AMPS modeling simulation Samah BOUDOUR ^{1,2} , Idris BOUCHAMA ^{2,3} , Moudi HADJAB ¹ , S. LAIDOU ^{1,4} 1Research Center in Industrial Technologies CRTI, P.O. Box 64, Cheraga 16014, Algiers, Algeria. 2Electronic Department, Faculty of Technology, Mouhamed Boudiaf University of Mslia, 28000, Mslia - Algeria. 3Inorganic Materials Laboratory, Mouhamed Boudiaf University of Mslia, 28000, Mslia - Algeria. 4Laboratoire de Chimie, Ingénierie Moléculaire et Nanostructures, Université Ferhat Abbas-Sétif 1, Sétif 19000, Algérie	B P2.40


1. Katarina Tošić, Sara Mijaković, Sanja Milošević Govedarović, Ana Vujačić Nikezić, Anđela Mitrović Rajić, Jasmina Grbović Novaković, **Bojana Paskaš Mamula. Prirodna ruda pirofilit kao potencijalni materijal za prečišćavanje otpadnih voda.** 10. Memorijalni naučni skup iz zaštite životne sredine „DOCENT DR MILENA DALMACIJA“ 30-31.03.2023. Knjiga radova V-4, str. 1-6.
2. Anđela Mitrović Rajić, Katarina Tošić, Sara Mijaković, Sanja Milošević Govedarović, Ana Vujačić Nikezić, **Bojana Paskaš Mamula, Jasmina Grbović Novaković. Detekcija fungicida karbendazima u vodi primenom elektrode od ugljenične paste modifikovane pirofilitom.** 10. Memorijalni naučni skup iz zaštite životne sredine „DOCENT DR MILENA DALMACIJA“ 30-31.03.2023. Knjiga radova V-5, str. 1-6.



**10. MEMORIJALNI NAUČNI SKUP IZ ZAŠTITE ŽIVOTNE SREDINE
„DOCENT DR MILENA DALMACIJA“
30. - 31.03.2023.**

KNJIGA RADOVA





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PRIRODNA RUDA PIROFILIT KAO POTENCIJALNI MATERIJAL ZA PREČIŠĆAVANJE OTPADNIH VODA

Katarina Tošić, Sara Mijaković, Sanja Milošević Govedarović, Ana Vujačić Nikezić, Anđela Mitrović Rajić, Jasmina Grbović Novaković, Bojana Paskaš Mamula

Centar izuzetnih vrednosti za vodoničnu energetiku i obnovljive izvore energije, Institut za nuklearne nauke „Vinča“, Institut od nacionalnog značaja za Republiku Srbiju, Univerzitet u Beogradu, POB 522, Beograd, Srbija, katarina.tosic@vin.bg.ac.rs

Izvod

U radu je ispitivana prečišćena ruda pirofilit, u cilju dobijanja keramičkih membrana koje bi služile za prečišćavanje otpadnih voda. Uzorci prirodne rude pirofilit koji potiču iz rudnika Parsovići, Bosna i Hercegovina su ultrazvučno prečišćeni i od njih su napravljene pastile pod pritiskom od 50 MPa. Pastile su zatim termički tretirane na temperaturi od 1050 °C u trajanju od 2h, a infracrvenom spektroskopijom sa Furijeovom transformacijom (FTIR), ramanskom spektroskopijom ispitane su mikrostrukturne osobine materijala dok je ponašanje materijala nakon termičkog tretmana ispitano termogravimetrijskom analizom i diferencijalnom termalnom analizom. Rezultati ukazuju da je već 2 sata termičke obrade dovoljno da dođe do dehidroksilacije pirofilita odnosno oslobađanja OH grupa i stvaranja porozne strukture pogodno za dobijanje keramičkih membrana.

Ključne reči: pirofilit, keramičke membrane, mikrostruktura, FTIR, Ramanska spektroskopija, DTA.

Uvod

Potreba za razvojem efikasnih i ekološki prihvatljivih metoda za prečišćavanje kontaminiranih voda i smanjenje ili potpuno eliminisanje zagađivača [1-4] je sve izraženija. Svaki tretman ima svoja ograničenja ne samo u pogledu troškova, već i u pogledu izvodljivosti, efikasnosti, pouzdanosti kao i uticaja na životnu sredinu. Među različitim postupcima koji se trenutno primenjuju u tretmanu otpadnih voda, samo nekoliko se obično koristi u industriji, iz tehnoloških i ekonomskih razloga [2, 4]. Jedan od njih je adsorpcija koja se pokazala kao najbolji proces prečišćavanja vode i smatra se vrlo efikasnom metodom za kontrolu zagađenja uopšte. Tehnike adsorpcije karakteriše široka dostupnost, niska cena, velika efikasnost, jedinstvenost rada, kao i isplativost. Ključno za tehnologiju adsorpcije je da se primene ekološki, jeftini i efikasni adsorbenti [5] pa je u tom smislu prepoznata i razvijana upotreba glina. Prednosti glina su niska cena, visoka specifična površina, dostupnost, veliki potencijal za izmenu jona, odlična adsorpciona svojstva i netoksičnost. Jedna od bitnih karakteristika je i to što sadrži lako izmenljive jone na svojoj površini, pa je zbog toga veoma interesantna u primeni vezanoj za prečišćavanje i zadržavanje naelektrisanih štetnih vrsta prisutnih u zagađenim vodama [6]. Termičkom, hemijskom ili mehaničkom modifikacijom moguće je poboljšati njena adsorpciona svojstva jer se utiče na zapreminu pora, specifičnu površinu, kao i na broj katalitički aktivnih mesta koji povećavaju sposobnost adsorpcije zagađujućih supstanci, nakon obrade ili modifikacije [5].

Jedan od najzastupljenijih prirodnih glinenih materijala je pirofilit, teorijske formule $\text{Al}_2[\text{Si}_4\text{O}_{10}](\text{OH})_2$. Pirofilit sa svojom 2:1 dioktaedarskom strukturom sadrži ploču oktaedra $\text{Al-O}(\text{OH})$ koja se nalazi u „sendviču“ između dva sloja SiO_4 tetraedra koja su povezana [7]. Slojevi pirofilita su elektroneutralni i zato, za razliku od mika i smektita, pirofilit u svojim međuslojevima ne sadrži katjone i molekule vode [8]. Karakterišu ga niska električna i toplotna provodljivost, nisko reverzibilno termalno širenje i koeficijent širenja, kao i odlična stabilnost pri zagrevanju [9]. Zbog svoje velike rasprostranjenosti u prirodi, u poslednje vreme privlači veliko interesovanje [10].

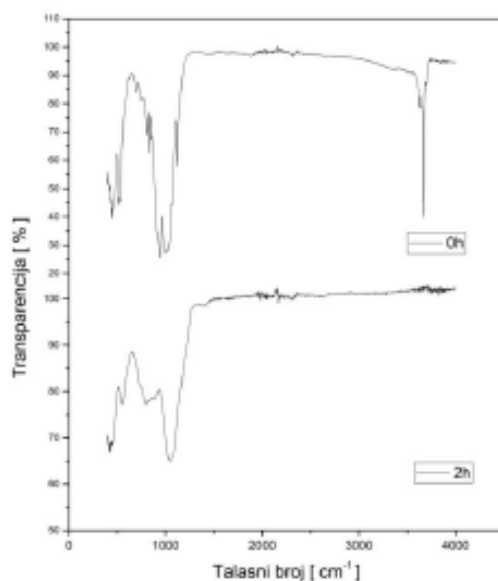
Eksperimentalni deo

Polazni uzorci prirodne rude pirofilita dobijeni su iz rudnika Parsovići, Bosna i Hercegovina. Uzorak pirofilita najpre je rastvoren u dejonizovanoj vodi, a zatim tretiran 30 minuta u ultrazvučnoj kadi da bi se na taj način odstranile nepotrebne faze. Od prečišćenog pirofilita napravljene su pastile pod pritiskom od 50 MPa koje su termički tretirane 2h na temperaturi od 1050 °C i koje su dalje ispitivane.

FTIR-ATR analiza je urađena na uređaju Thermo Scientific Nicolet iS10 Spectrometer. Spektri su snimani u opsegu od 400-4000 cm^{-1} , sa rezolucijom od 4 cm^{-1} . Ramanski spektri u ovom radu snimljeni su na DXR Raman mikroskopu sa laserom 532 nm, pri snazi od 8 mW. Spektri su korigovani na fluorescenciju u programu Omnic korišćenjem polinoma petog reda. DTA-TGA uređaj bio je SETARAM apparatus (Setsys Evolution). Uzorci su stavljani u posude od aluminijuma i zagrevani do 1000 °C, sa brzinom zagrevanja od 10 °C/min. Radna atmosfera bio je sintetički vazduh.

Rezultati i diskusija

Na slici 1 prikazani su ATR-FTIR spektri uzorka pirofilita pre i nakon termičkog tretiranja u trajanju od 2h. Uočava se da traka na 3673 cm^{-1} koja se pripisuje vibraciji veze Al-OH [10-15] nestaje nakon termičkog tretmana. Na 3619 cm^{-1} nalazi se OH istežuća vibracija [10] koja takođe nestaje ako se uzorak zagreje na 1050 °C. Nestajanje navedenih vibracija u kojima učestvuje OH grupa iz spektra termički tretiranog uzorka sugerise da se odigrala dehidroksilacija pirofilita. Traka na 1119 cm^{-1} pripada Si-O vibraciji u ravni [16] i nestaje nakon termičkog tretmana, dok se traka koja potiče od Si-O veze, karakteristične za aluminosilikate, nakon 2h, pomerila na 1046 cm^{-1} (tabela 1). Dve trake prisutne samo kod čistog pirofilita na 942 cm^{-1} i 998 cm^{-1} potiču od savijajućih vibracija Al-OH veze [17], odnosno istežućih vibracija Si-O i Si-O-Al [10-15]. Traka na 833 cm^{-1} pripada vibraciji savijanja Al-OH [11] i nestaje pri termičkom tretmanu, što ukazuje na to da su OH grupe koje koordinišu centralne atome Al , oslobođene i da dolazi do oštećenja oktaedarskih listova. Uočene oktaedarske vibracije AlO_6 [10] na 529 cm^{-1} pirofilita bez termičkog tretmana, koje nestaju nakon termičkog tretmana, kao što je slučaj i sa trakom na 514 cm^{-1} koja potiče od vibracija savijanja Si-O-Si veze ukazuju na narušavanje i tetraedarskih ploča. Prisustvo kvarca potvrđuje traka na 799 cm^{-1} [11].

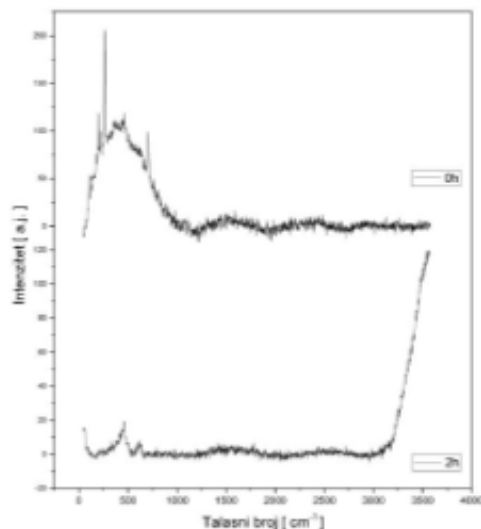


Slika 1. FTIR spektar uzorka pirofilita koji nije termički tretiran (0h) i koji je tretiran 2 sata (2h) na temperaturi od 1050°C

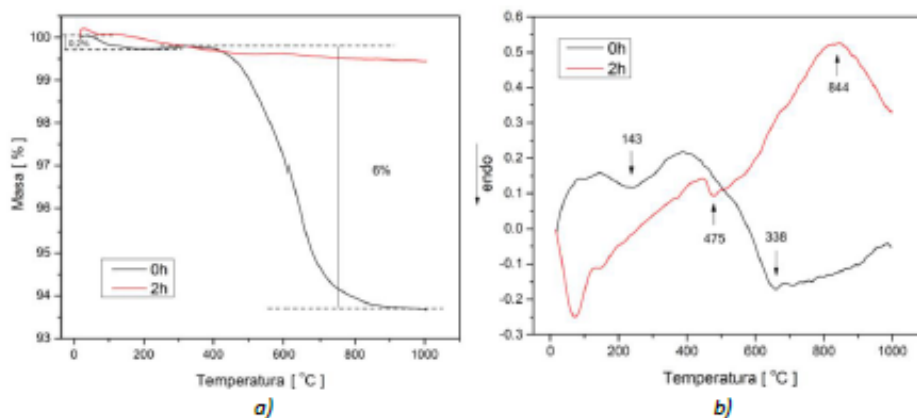
Tabela 1. Trake na FTIR spektru uzorka pirofilita koji nije termički tretiran (0h) i koji je tretiran 2 sata (2h)

Vreme trajanja termičke obrade		Vibracioni mod
0h	2h	
Vibracione trake		
[cm ⁻¹]	[cm ⁻¹]	
	417	
444	432	savijajuća Si-O [13]
514		vibracije savijanja Si-O-Si [11]
529		oktaedarske vibracije AlO ₆ ploča [10]
	553	
	799	kvarc [11]
811		prisustvo Si-O-Al gde je Al u tetraedarskoj koordinaciji [10]
		kvarc i kaolinit [15]
833		vibracije savijanja Al-OH [11]
	877	vibracije savijanja Al-OH [11]
942		vibracije savijanja Al-OH [11]
998		intenzivno istezanje Si-O i Si-O-Al [18]
1023		Si-O veza (karakteristično za alumosilikate) [10-15]
	1046	Si-O veza (karakteristično za alumosilikate) [10-15]
1119		Si-O istežuće vibracije [16]
3619		OH istezanje koje potiče od ilita i muskovita [10]
3673		OH vibracija veze Al-OH [10-15]

Na ramanskom spektru (slika 2) uzorka pirofilita koji nije termički tretiran, u opsegu od 0 - 800 cm^{-1} uočavaju se oštri maksimumi karakteristični za pirofilit [18]. Takođe, prisutna je široka traka u intervalu od 1200 - 2200 cm^{-1} , koja nestaje pri termičkom tretmanu. Uzrok može biti narušavanje strukture OH veze. Smanjenje intenziteta oštrog maksimuma u opsegu od 0 - 800 cm^{-1} i pojava novog na vrednostima talasne dužine od 438 cm^{-1} , pripisuje se dehidroksilaciji koja potiče od prisustva kaolinita i mulita [18].



Slika 2. Ramanski spektar uzorka pirofilita koji nije termički tretiran (0h) i koji je tretiran 2 sata (2h) na temperaturi od 1050°C



Slika 3: TGA i DTA krive uzorka pirofilita koji nije termički tretiran (0h) i koji je tretiran 2 sata (2h) na temperaturi od 1050°C

Strukturne promene uočene prethodnim metodama, jasno se vide i na DTA-TGA krivama. Termogravimetrijska analiza pirofilita koji nije termički tretiran pokazala je da se oko 0,2% mase gubi u temperaturnom intervalu između sobne temperature i 200 °C (slika 3a - crna kriva). Na DTA krivoj koja potiče od netretiranog uzorka vide se dva endotermna maksimuma (slika 3b - crna kriva). Prvi maksimum nalazi se u opsegu od 100 - 400 °C i može biti pripisan oslobađanju vezanih molekula vode sa površine, s obzirom da je gubitak mase 0,2% [19], dok se drugi maksimum koji se nalazi u opsegu od 600 - 800 °C povezuje sa dehidroksilacijom pirofilita [20]. Kod termički tretiranog pirofilita, oštar endotermni maksimum na 475 °C (slika 3b - crvena kriva) nastaje zbog prisustva kaolinita, koji počinje da se izdvaja prilikom dužeg zadržavanja na relativno visokim temperaturama [21]. Prema Sanchez-Soto i saradnicima [20], sav gubitak mase od skoro 6%, na TGA krivi netretiranog uzorka (slika 3a - crna kriva), pripisuje se dehidroksilaciji, odnosno gubitku strukturne vode. TGA kriva uzorka tretiranog 2h (slika 3a - crvena kriva) takođe pokazuje blagi gubitak mase, koji se pripisuje oslobađanju zaostale vode [20]. Na DTA krivoj istog uzorka, vidi se jedan egzotermni maksimum (slika 3b - crvena kriva) u opsegu temperatura od 700 - 1000 °C, za koji se pretpostavlja da nastaje usled transformacije kaolinitne u mulitnu fazu [20].

Zaključak

U ovom radu ispitane su strukturne promene prirodne rude pirofilit nastale nakon termičkog tretmana na temperaturi od 1050 °C u trajanju od 2h i pritisku od 50 MPa. Zaključeno je da termičkim tretmanom dolazi do dehidroksilacije, TGA analiza pokazala je da je ukupan gubitak mase iznosio 6%. Takođe, nakon 2h termičkog tretmana dolazi do narušavanja oktaedarskih i tetraedarskih ploča, što potvrđuje nestanak traka na FTIR spektru, koje potiču od vibracija savijanja Al-OH, oktaedarske vibracije AlO₆, kao i od vibracija savijanja Si-O-Si veze. Na osnovu navedenih rezultata, može se zaključiti da pirofilit pokazuje dobre predispozicije za pravljenje keramičkih membrana koje bi služile za prečišćavanje otpadnih voda.

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DETEKCIJA FUNGICIDA KARBENDAZIMA U VODI PRIMENOM ELEKTRODE OD UGLJENIČNE PASTE MODIFIKOVANE PIROFILITOM

Anđela Mitrović Rajić, Katarina Tošić, Sara Mijaković, Sanja Milošević Govedarović, Ana Vujačić Nikezić, Bojana Paskas Mamula, Jasmina Grbović Novaković

Centar izuzetnih vrednosti za vodoničnu energetiku i obnovljive izvore energije, Institut za nuklearne nauke „Vinča”, Institut od nacionalnog značaja za Republiku Srbiju, Univerzitet u Beogradu, POB 522, Beograd, Srbija, andjela.mitrovic@vin.bg.ac.rs

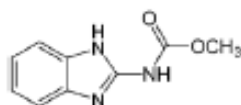
Izvod

Ovaj rad ima za cilj da dizajnira elektrodu od ugljenične paste modifikovanu pirofilitom za potencijalnu upotrebu za detekciju pesticida u vodenim rastvorima. Strukturna i morfološka karakterizacija prirodne gline pirofilit i mehanički modifikovanog pirofilita urađena je rendgenostrukturnom analizom i skenirajućom elektronskom mikroskopijom. Elektrohemijske karakteristike ove elektrode ispitivane su cikličnom voltametrijom u 1 mM $K_4Fe(CN)_6$ u 0,1 M KCl i 0,5 M H_2SO_4 i diferencijalnom pulsnom „striping“ voltametrijom u Briton-Robinsonovom puferu na pH 4. Pokazano je da maksimum na + 0,96 V u odnosu na Ag/AgCl elektrodu potiče od oksidacije karbendazima na pH 4 u Briton-Robinsonovom puferu. Dobru stabilnost i osetljivost pokazala je elektroda koja je sadržala 50% ugljenične paste i 50% pirofilita mehanički modifikovanog 15 minuta u mlinu sa kuglama. Razvijena metoda je linearna u opsegu od 1 ppm do 10 ppm sa $r = 0,999$ i granicom detekcije od 0,3 ppm.

Ključne reči: glina, mikrostruktura, elektroda, pesticid, senzor, voltametrija

Uvod

Pesticidi su supstance prirodnog ili sintetičkog porekla koje se koriste za suzbijanje štetočina koje šire bolesti, uništavaju imovinu i useve. Ova jedinjenja lako dospevaju u životnu sredinu. Fungicidi se koriste za suzbijanje različitih biljnih bolesti. Karbendazim (metil 1H-1,3 benzimidazole-2-il karbamat) (slika 1.) je benzimidiazol fungicid koji se široko koristi za suzbijanje biljnih bolesti [1].



Slika 1. Karbendazim – strukturna formula

Karbendazim ima toksičan efekat na sisare. Zbog toga je njegova kontrola i detekcija jako važna. U dosadašnjoj detekciji, najčešće su korišćene hromatografske tehnike, UV-Vis, spektroskopija, fluorometrija, ramanska spektroskopija, a takođe su korišćeni različiti materijali za pravljenje elektroda za voltametrijsko određivanje karbendazima [2-6]. U novije vreme, elektrode od ugljenične paste modifikovane različitim glinama se koriste za kvantitativnu i kvalitativnu detekciju različitih materijala rastvorenih u vodenim rastvorima [7, 8]. Pirofilit je mineral iz glupe filosilikata hemijske formule $Al_2Si_4O_{10}(OH)_2$. Kristalna rešetka pirofilita se sastoji od dve SiO_4 ploče između kojih se nalazi oktaedar $AlO_4(OH)_2$, pa on ima 2:1 strukturu [9].

Ova glina pokazuje jako dobre fizičke i hemijske osobine kao što su inertnost, mekoća, niska električna provodljivost, visoka toplotna provodljivost i visoka tačka topljenja. Zbog svih ovih karakteristika, pirofilit je našao veliku primenu kao adsorbens zagađivača životne sredine, keramici [10-12]. Pirofilit ima slojevit strukturu, a veze između slojeva su slabe van der Valsove i mogu se lako raskinuti, pa slojevi klize jedan preko drugog. Ovo svojstvo pirofilita je jako važno za njegovu modifikaciju. Mehanohemijaska modifikacija pirofilita dovodi do značajnih promena u njegovoj strukturi, do smanjenja veličine čestica, promene morfologije i povećanja specifične površine. Ovaj način modifikacije predstavlja zelenu metodu modifikacije jer ne koristi rastvarače.

U ovom radu je za kvalitativno i kvantitativno određivanje karbendazima kao radna elektroda korišćena elektroda od ugljenične paste modifikovana pirofilitom. Pirofilit je prethodno mehanohemijski aktiviran kako bi se povećala osetljivost elektrode.

Eksperimentalni deo

Ratvor karbendazima koncentracije 2000 ppm (97%, Sigma-Aldrich) je dobijen rastvaranjem ovog pesticida u metanolu. Briton-Robinsonov pufer je dobijen mešanjem 0,04 M H_3BO_3 , 0,04 M CH_3COOH , 0,04 M H_3PO_4 i 0,2 M NaOH. Sve hemikalije su nabavljene od Sigma-Aldrich. Glina pirofilit je iz rudnika Parsović, Bosna i Hercegovina. Mehanohemijaska modifikacija pirofilita urađena je u SPEX Mixer mlinu 5100 sa kuglama. Vreme mlevenja je bilo između 0 i 120 minuta. U tabeli 1. date su oznake uzoraka i vremena mlevenja. Ispitivanja kristalne strukture su urađena na difraktometru Rigaku Ultima IV, Japan. Korišćeni rendgenski snop je bio nikl-filtriran $CuK\alpha_1$, talasne dužine $\lambda=0,1540$ nm, koji radi na 40 kV u 40 mA. Merenja su rađena od 5 do 80° (2 θ), dok je brzina skeniranja bila 5°/min sa korakom od 2°. Morfologija uzoraka ispitivana je SEM-EDS korišćenjem JEOL JSM6610LV. Sva elektrohemijaska merenja urađena su na Gamry potentiostat Interface 1010E (Gamry Instruments, Warminster, PA, USA) u troelektrodnom sistemu.

Tabela 1. Oznaka uzorka i vreme mlevenja pirofilita

Oznaka uzorka	Vreme mlevenja (min)
P-0	0
P-15	15
P-30	30
P-120	120

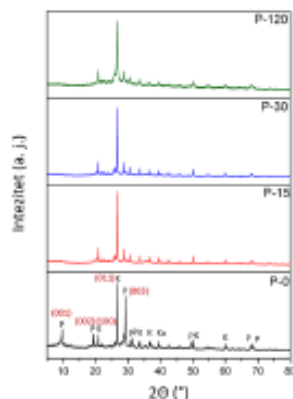
Kao referentna elektroda je korišćena Ag/AgCl elektroda, kao pomoćna platinska žica, dok je kao radna elektroda korišćena konstruisana elektroda od ugljenične paste modifikovana pirofilitom. Ova elektroda se sastoji od bakarne žice koja je provodnik i poliacetilena kao kućišta koje se puni pastom koja se pravi od pirofilita i ugljenika, a kao vezujuća tečnost korišćeno je parafinsko ulje. Kod ciklične voltametrije kao elektroliti su korišćeni 0,5 M H_2SO_4 i 0,1 M KCl kome je dodat 1 mM $K_4Fe(CN)_6$. Merenja su vršena u opsegu potencijala od - 0,5 V do + 1,1 V, dok je brzina skeniranja u oba slučaja iznosila 50 mV/s. Diferencijalna pulsna stripping voltametrija rađena je u Briton-Robinsonovom puferu na različitim pH vrednostima od 4-8.

Merenja su vršena u opsegu potencijala od +0,2 V do +1,2 V, akumulacioni potencijal je iznosio -0,15 V, akumulaciono vreme bilo 60 s i brzina skeniranja 50 mV/s, a kroz rastvor je sve vreme prodivavan azot. Opseg koncentracije karbendazima u kome je rađeno merenje bio je od 1 ppm do 10 ppm.

Rezultati i diskusija

Rendegonastrukturalna analiza

Strukturne promene izazvane različitim trajanjem mehaničkog mlevenja od 0 i 120 minuta date su na slici 2.

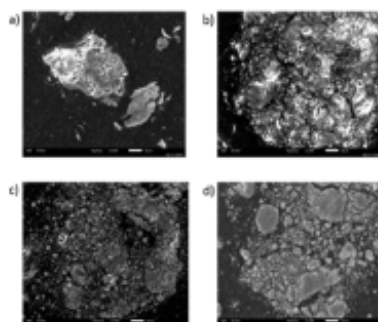


Slika 2. Difraktogrami uzorka koji su mleveni 0 (P-0), 15 (P-15), 20 (P-20) i 120 (P-120) minuta

Dve osnovne faze prisutne u rudi pirofilita iz rudnika Parsović sa karakterističnim refleksijama na uglovima 2θ su: pirofilit na $9,68^\circ$ (odgovara (001) refleksiji) i $29,21^\circ$ (003) i kvarc na $20,94^\circ$ (100) i $26,72^\circ$ (011). Karakteristična d vrednost za pirofilit za (001) refleksiju je $9,13 \text{ \AA}$, za (003) $3,06 \text{ \AA}$, dok za kvarc ona iznosi $4,24 \text{ \AA}$ (refleksija (100)) i $3,31 \text{ \AA}$ (refleksija (011)). U toku mehanohemijske modifikacije, dolazi do promene u kristalnoj strukturi pirofilita, što se u difraktogramu može videti kao širenje tipičnih refleksija koje pripadaju pirofilitu ili potpunom nestanku istih. Nakon 15 minuta mlevenja, intezitet refleksija se smanjuje, dok nakon 30 minuta refleksije (001), (002), (003) i (005) skoro da nestaju [13]. Refleksije koje pripadaju kvarcu su i dalje uočljive na difraktogramu zato što kvarc ima tvrdju strukturu od pirofilita, pa je potrebno i veće vreme mlevenja da bi se njegova stuktura promenila.

Skenirajuća elektronska mikroskopija

Morfologija uzoraka koji su mleveni 0, 15, 30 i 120 minuta ispitivane su skenirajućom elektronskom mikroskopijom (slika 3.)

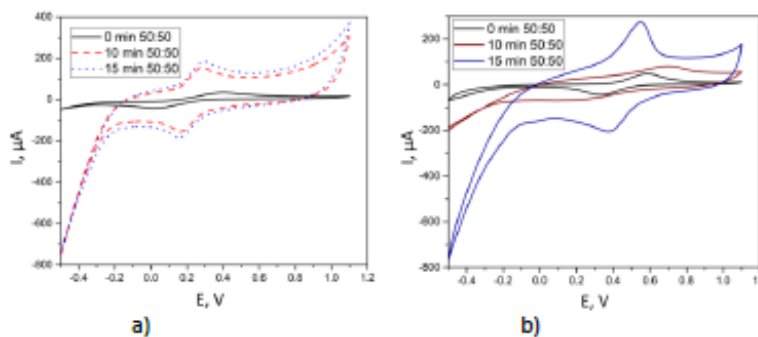


Slika 3. SEM mikografije uzoraka mlevenih a) 0 (P-0) b) 15 (P-15) c) 30 (P-30) i d) 120 minuta (P-120)

Sa slike 3. uočava se da čestice pirofilita imaju laminarnu strukturu, hrapave su površine i različite su veličine. Mehanohemijska modifikacija dovodi do smanjenja veličine čestica, a samim tim i do promena u morfologiji. Čestice više nemaju slojevit strukturu, već postaju zaobljene sa hrapavom površinom. Nakon 15 minuta mlevenja, dolazi do smanjenja veličine čestica i povećanja specifične površine, a nakon 30 minuta mlevenja, dolazi do aglomeracije. Aglomeracija je izraženija kako raste vreme mlevenja. Ovi aglomerati se sastoje od velikog broja spletenih čestica, pa je zbog toga specifična površina značajno smanjena kako raste vreme mlevenja i smanjuje se veličine čestica [14].

Ciklična voltametrija

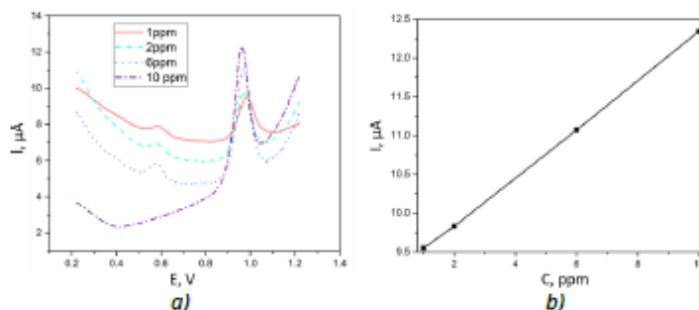
Na slici 4. dati su voltamogrami dobijeni u 1 mM $K_4Fe(CN)_6$ u 0,1 M KCl (slika 4a) i u 0,5 M H_2SO_4 (slika 4b) na elektrodi od ugljenične paste modifikovane pirofilitom sa parafinskim uljem kao vezujućom tečnošću gde je odnos ugljenika i pirofilita bio 50P:50C za mehanohemijski tretiran pirofilit u vremenu od 0 do 15 minuta. Sve tri elektrode su stabilne, a procesi koji se odigravaju na elektrodama su reverzibilni. Odvajanje od vrha maksimuma do vrha maksimuma je u vezi sa kinetikom prenosa elektrona i na osnovu slike se može zaključiti da su najreverzibilnije i najbrže elektrohemijske reakcije prenosa elektrona kada se koristi elektroda kod koje je pirofilit mehanohemijski tretiran 15 minuta. Ovo je posledica povećanja specifične površine pirofilita.



Slika 4. Voltamogrami dobijeni: a) u 1 mM $K_4Fe(CN)_6$ u 0,1 M KCl i b) 0,5 M H_2SO_4

Diferencijalna pulsna "striking" voltametrija

Na slici 5. dati su diferencijalno pulsni voltamogrami za određivanje karbendazima u Briton-Robinsonovom puferu na pH 4 (a) i kalibraciona kriva (b).



Slika 5. a) Diferencijalno pulsni voltamogrami za određivanje karbendazima u Briton-Robinsonovom puferu na pH 4 i b) kalibraciona kriva

Maksimum na +0,96 V odgovara oksidaciji karbendazima i raste sa porastom koncentracije ovog pesticida. Detekcija karbendazima rađena je u koncentracionom opsegu od 1 ppm do 10 ppm. U ovom koncentracionom intervalu moguće je izvršiti detekciju sa $r = 0,999$. Granica kvantifikacije je iznosila 1,03 ppm, limit detekcije 0,3 ppm, a relativna standardna devijacija 2,3 %.

Zaključak

Mikrostrukturalna i morfološka analiza dobijena rengenostрукturnom analizom i skenirajućom elektronskom mikroskopijom pokazuje da mehanohemijska modifikacija pirofilita dovodi do poboljšanja njegovih sorpcionih svojstva. Ovaj materijal je pokazao odličnu elektrohemijску aktivnost, pa se može koristiti kao komponenta u konstrukciji elektrohemijских senzora za detekciju karbendazima. Rezultati dobijeni cikličnom voltametrijom pokazuju da je elektroda konstruisana na ovaj način stabilna, jednostavna za konstrukciju i visoko osetljiva. Ovaj senzor je u Briton-Robinsonovom puferu na pH 4 pokazao najveću osetljivost u opsegu od 1 ppm do 10 ppm sa granicom detekcije od 0,3 ppm.

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Jelena MILOVANOVIĆ
Marko RODIĆ
Vuk FILIPOVIĆ
Života SELAKOVIĆ

Jelena KESIĆ
Mila LAZOVIĆ
Mihajlo JAKANOVSKI

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Characterization of pyrophyllite as a potential material for obtaining ceramic membranes

Katarina Ž. Tošić¹, Sara G. Mijaković¹, Bojana M. Paskaš Mamula¹,
Ana V. Vujačić Nikezić¹

¹ Vinča Institute of Nuclear Sciences, University of Belgrade, National Institute of the Republic of Serbia,
Belgrade, Serbia

Pyrophyllite is one of the most common natural clay materials and shows great physicochemical characteristics. Its low electrical and thermal conductivity, low coefficient of expansion, good mechanical strength, as well as excellent stability during heating, make it very suitable for use in different areas. Pyrophyllite is used in many industries, such as the paper and plastic industry, bricks, ceramics, cosmetics, plants, and rubber industry, but also for wastewater treatment. It is a potential material for obtaining ceramic membranes for water filtration [1, 2]. In our study, pyrophyllite was ultrasonically treated in order to remove other impurities, after which pastilles were made under the pressure of 50 MPa, and thermally modified at the temperature of 1050 °C in a time interval of 2-6 h. After the modification, the changes were monitored by different methods: X-ray structural analysis (XRD), infrared spectroscopy with Fourier transform (FTIR), scanning electron microscopy (SEM), Raman spectroscopy, as well as thermal analysis methods, thermogravimetric analysis (TGA) and differential thermal analysis (DSC). It was shown that amorphization and dehydroxylation, as well as homogeneous arrangement of pores, occurred after the thermal treatment. Except for the release of excess water, the thermal treatment led to the removal of certain impurities present in the sample.

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Преглед истраживања о складиштењу водоника у оквиру Центра за водоничну енергетику и обновљиве изворе енергије - CONVINCЕ

Јасмина Грбовић Новаковић, Сања Милошевић Говедаровић, Сандра Курко, Игор Милановић, Бојана Паскаш Мамула, Никола Новаковић

Центар за водоничну енергетику и обновљиве изворе енергије – CONVINCЕ, Институт за нуклеарне науке „Винча” – институт од националног значаја за Републику Србију, Универзитет у Београду, Београд, Србија

Hydrogen Storage Research Overview within Center of Excellence for Hydrogen and Renewable Energy - CONVINCЕ

Jasmina Grbović Novaković, Sanja Milošević Govedarović, Sandra Kurko, Igor Milanović, Bojana Paskaš Mamula, Nikola Novaković

CONVINCE Center of Excellence for Hydrogen and Renewable Energy, VINČA Institute of the Nuclear Sciences, National Institute of the Republic of Serbia, University of Belgrade, Belgrade, Serbia

Док потенцијал водоника као извора енергије и кључног састојка у многим перспективним пољима људског рада остаје значајан, изазови у успостављању водоничне економије су и даље велики. Ово је углавном зато што препреке и недостаци морају да се решавају у оквиру свих компоненти водоничне економије истовремено: производње, складиштења, транспорта и дистрибуције. Складиштење водоника је кључ за развој сигурне и ефикасне водоничне економије. Водоник има највећу специфичну енергију од било ког горива; међутим мала запреминска густина при стандардним условима има за резултат ниску густину енергије, што захтева развој иновативних метода складиштења како би се постигла већа густина енергије. Водоник се физички може складиштити као гас или течност. Складиштење водоника као гаса обично захтева резервоаре под високим притиском (350-700 бара). Складиштење водоника у течном стању захтева ниске температуре јер је тачка кључања водоника при притиску једне атмосфере $-252,8^{\circ}\text{C}$. Водоник се такође може складиштити на површини чврстих супстанци (адсорпцијом) или унутар њих (апсорпцијом). Крајњи циљ за гравиметријски капацитет складиштења за мобилне примене, постављен од стране Министарства енергетике САД, је $2,2\text{ kW/kg}$ или $6\text{ wt.}\%$. Међу металним хидридима, магнезијум хидрид (MgH_2) може да испуни ове потребе. MgH_2 је један од материјала за складиштење водоника који највише обећава јер се

While the potential of hydrogen as an energy source and crucial ingredient in many prospective fields of human endeavor remains significant, the challenges in establishing a hydrogen economy are still significant. This is mostly because obstacles and drawbacks have to be addressed within all components of the hydrogen economy simultaneously: production, storage, transportation, and distribution. Hydrogen storage is the key for the development of safe and efficient hydrogen economy. Hydrogen has the highest energy per mass of any fuel; however, its low volumetric density at ambient temperature results in a low energy per unit volume, therefore requiring the development of innovative storage methods that have potential for higher energy density. Hydrogen can be stored physically as either a gas or a liquid. Storage of hydrogen as a gas typically requires high-pressure tanks (350–700 bar). Storage of hydrogen as a liquid requires cryogenic temperatures because the boiling point of hydrogen at one atmosphere pressure is $-252,8^{\circ}\text{C}$. Hydrogen can also be stored on the surfaces of solids (by adsorption) or within solids (by absorption). The ultimate goal for gravimetric storage capacity of mobile applications set by the U.S. Department of Energy (DOE) is 2.2 kW/kg or $6\text{ wt.}\%$. Among the metal hydrides, magnesium hydride (MgH_2) can fulfill this requirement. MgH_2 is one of the most promising hydrogen storage materials

директно формира реакцијом Mg са гасовитим водоником и достиже висок специфични капацитет (7,6 wt.%). Термодинамичке баријере у разградњи магнезијум хидрида у облику праха или танког филма су предмет многих научних истраживања, пре свега кроз процес дестабилизације структуре хидрида [1]. Најчешће коришћена метода за дестабилизацију хидрида је наноструктурирање механичким млевењем које доводи до смањења величине честица и кристалита праха MgH_2 . Методе озрачивања јонима се такође користе [2]. Наноструктурирање се често комбинује са додатком катализатора и формирањем композита [3-7]. Стога, својства складиштења водоника могу се прилагодити додавањем мале количине прелазних метала (Ti, V, Fe, Co, Ni, Cu), оксида прелазних метала (WO_3 , CeO_2 , VO_2 , TiO_2) или борида (TiB_2) [3-7]. У зависности од уложене енергије током процеса млевења, типично време млевења за магнезијум или магнезијум хидрид се креће од 15 min до 20 h за високоенергетске млинове и од 20 до 150 h за нискоенергетске млинове. Највећи део истраживања усмерен је на морфолошке, структурне и термодинамичке ефекте типичне за дуго време млевења, док су у овом раду праћене промене које се дешавају при кратком времену млевења.

Даље, процеси који се одвијају током десорпције водоника из танких филмова Mg/MgH₂ након модификације јонским озрачивањем су такође били у фокусу нашег истраживања. Зрачење је коришћено да се добије тачна количина тачкастих дефеката унутар добро дефинисане дубинске дистрибуције. Показано је да величина, облик и концентрација Mg језгара насталих током десорпције водоника из танких филмова MgH_2 зависе од карактеристика и дистрибуције индукованих дефеката. У неоозраченим узорцима облик језгара Mg је сферичан, док је у озраченим узорцима веома неправилан. Варијације у боји узорака су примећене током десорпције водоника и пре стварања Mg језгара. DFT прорачуни су показали да се уочене варијације у оптичким својствима узорака могу објаснити променама у електронској структури MgH_2 и појавом траке H-ваканције унутар енергетског

because it is directly formed from the reaction of Mg metal with gaseous hydrogen and reaches a high mass capacity (7.6 wt. %). A matter of thermodynamic barriers in the decomposition of magnesium hydride in both powder or thin film form is the subject of many scientific studies, primarily through the process of destabilization of the hydride structure [1]. The most commonly used method for hydride destabilization is nanostructuring by mechanical milling which leads to reduction in the particle and crystallite size of the MgH_2 powder. Further, ion irradiation is also used [2]. Nanostructuring is often combined with catalyst addition and composite formation [3-7]. Therefore, the H storage properties can be tailored by addition of small amount of transition metals (Ti, V, Fe, Co, Ni, Cu), transition metal oxides (WO_3 , CeO_2 , VO_2 , TiO_2), or borides (TiB_2) [3-7]. Depending on the energy input during the milling process, the typical milling time for magnesium or magnesium hydride ranges from 15 min to 20 h for high-energy mills and from 20 to 150 h for low-energy mills. Most of the research is focused on the morphological, structural and thermodynamic effects typical for long milling times, while we have followed the changes taking place under short milling time.

Further, processes taking place during hydrogen desorption from Mg/MgH₂ thin films upon modification by ion irradiation were also in focus of our investigation. Irradiation was used to produce exact quantities of point defects within well-defined depth distribution. It was shown that the size, shape, and concentration of Mg nuclei formed during hydrogen desorption from MgH_2 thin films depend on the characteristics and distribution of the induced defects. In non-irradiated samples the shape of Mg nuclei is spherical, while in irradiated samples it is highly irregular. Variations in sample color were observed during hydrogen desorption and before the creation of Mg nuclei. DFT calculations showed that the observed variations in the optical properties of samples can be explained by changes in MgH_2 electronic structure and the appearance of an H-

процеса MgH_2 . С друге стране, модификација изазвана затварањем са TiO_2 не утиче на облик језгара. Облик је сферичан и не зависи од дебљине филма. Величина и концентрација језгара је повезана са дебљином филмова. Обе модификације (додавање адитива или тачкастих дефеката) доводе до смањења почетне температуре за десорпцију и побољшања кинетике процеса [8].

Део нашег истраживања посвећен је процени хемијског везивања и стабилности једноставних металних хидрида и MgH_2 допираног прелазним металима путем анализе топологије густине наелектрисања како на локалном (Бадерова теорија атома у молекулима) тако и на интегралном (нековалентне интеракције) нивоу. Трендови у макроскопским својствима (температуре топљења, укупна термодинамичка стабилност, еластична својства итд.) уочени у серијама једињења као што су алкални хидриди и халогениди, могу се приписати постојању суптилних разлика у топологијама густине наелектрисања. Ове разлике на локалном нивоу могу се описати коришћењем различитог броја и дистрибуције стационарних (критичних) тачака густине наелектрисања. На широј скали, региони привлачних и одбојних интеракција могу се идентификовати коришћењем концепта нековалентних интеракција. Локални концепт је недовољан да опише тополошки прелаз између $\text{LiH} - \text{NaH} - \text{KH}$. Иако LiH и NaH припадају различитим тополошким класама, нелокални приступ открива да је NaH заправо прелазни случај, у ком привлачне H-H концентрације наелектрисања нису довољне да испуне услов везивања. Комплексна структура нековалентне интеракције смањеног градијента густине наелектрисања у јонском MgH_2 са првим и другим суседним атомима замењена је израженијим усмереним везивањем са првим суседним атомима у MgH_2 допираном прелазним металима.

vacancy band within the MgH_2 energy gap. On the other hand, the modification induced by capping with TiO_2 does not affect the shape of nuclei. The shape is rather spherical and does not depend on film thickness. The size and concentration of nuclei is related to the thickness of films. Both modifications (addition of additives or point defects) lead to reduction of temperature onset for desorption and improved kinetics [8].

The part of our research is devoted to assessment of chemical bonding and stability of simple metal hydrides and transition metal doped MgH_2 by means of charge density topology analysis on both local (Bader concept of atoms in molecules) and integral (concept of non-covalent interactions) level. Trends in macroscopic properties (melting temperatures and overall thermodynamic stability, elastic properties etc.) observed in compound series such as alkali hydrides and halides, could be attributed to the existence of subtle differences in charge density topologies. These differences on the local level can be described using different number and distribution of charge density stationary (critical) points. On the broader scale, regions of bonding attraction and repulsion can be identified using non-covalent interactions concept. The local concept is insufficient to describe topological transition between $\text{LiH} - \text{NaH} - \text{KH}$. Although LiH and NaH belong to different topological classes, the non-local approach reveals that NaH is actually a transition case, with attractive H-H charge concentrations not sufficient to fulfill bonding condition. Complex structure of non-covalent interaction reduced charge density gradient in ionic MgH_2 with first and second neighbor bonded atoms is replaced with more pronounced directional first neighbor bonding in transition metal doped MgH_2 .

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