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Editor
Milica Vlahović

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FOREWORD

The conditions created by the development of technologies in which modern man lives have led to a complex and paradoxical effect: that by removing obstacles on the way to a more comfortable, simpler, faster and more efficient life and way of working, man also generates numerous misfortunes, attracting dark clouds of threats to the survival of the planet and humanity. The question that concerns and affects all of us - all people, all living beings, systems in which life takes place, large and small, strong and weak - boils down to the problem of the negative impact of man on the environment; this issue invites us to an urgent solution by looking at the causes, proposing solutions, evaluating them, changing approaches and ways of thinking, as well as drawing correct conclusions. Simply put, by adapting nature to one's own needs, man threatens and damages it. That is why, with the joint efforts of all of us, individuals, organizations and states, it is necessary to take all possible measures to immediately prevent the negative effects that are ahead of us.

The importance of renewable sources of electricity, which this international conference focuses on, is noticeable from two angles: the first - it is certain that fossil fuels as a resource will disappear and it is necessary to find alternative sources, the second - the use of renewable energy sources by its essence implies "clean" technology that significantly contributes to reducing CO₂ emissions and thus mitigating climate change and reducing pollution, while encouraging social and economic development in all spheres of life.

The 11th International Conference on Renewable Electrical Power Sources is organized by the Society for Renewable Electrical Power Sources (DOIEE) at SMEITS, with co-organizers: The Institute of Architecture and Urban & Spatial Planning of Serbia (IAUS) and the Chamber of Commerce and Industry of Serbia, with the support of the Ministry of Science, Technological Development and Innovation of the Republic of Serbia.

The registered participants designed their papers according to the given conference topics:

- Energy sources and energy storage;*
- Energy efficiency in the context of use of renewable energy sources (RES);*
- Environment, sustainability and policy;*
- Applications and services.*

Eminent authors - scientists, teachers, experts in this field from fifteen different countries: Algeria, Belgium, Bosnia and Herzegovina, China, Croatia, Greece, Hungary, India, Portugal, Saudi Arabia, Serbia, Slovenia, Spain, the United Arab Emirates, and Ukraine, contributed to the conference through sixty-nine papers that were reviewed by the Scientific Committee of the Conference, and after the review process were accepted for presentation at the conference and for publication in the proceedings.

At the end of this short message and at the beginning of the proceedings I believe that it can be proudly said that scientists, researchers, policy makers and industry experts gathered in one place, in order to exchange experiences and knowledge with the aim of promoting scientific and professional ideas and results of research, technology improvement for the use of RES, promoting the rational use of electricity, affirming and proposing inventive solutions in the field of sustainable sources of electricity.

*Belgrade,
November 2023*

Milica Vlahović

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ISPITIVANJE LIF/B SISTEMA KORIŠĆENJEM NEGATIVNOG MODA LDI MS: MOGUĆI SISTEM ZA SKLADIŠTENJE VODONIKA

INVESTIGATION OF LIF/B SYSTEM USING THE NEGATIVE MODE LDI MS: A POSSIBLE HYDROGEN STORAGE SYSTEM

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Apstrakt

Mnogi teorijski proračuni su pokazali da su litijumom dekorisni borani (B_xH_y) ili klasteri bora (B_n) potencijalni materijali za skladištenje vodonika. Pored toga, pokazalo se da klasteri litijumfluorida poboljšavaju kapacitet skladištenja vodonika bolje od samog litijuma. Međutim, broj eksperimentalnih studija je mnogo manji. Zbog toga je u ovom radu ispitivana mogućnost interakcije klastera litijuma ili litijumfluorida sa boranima, metodom laserske desorpcione/ionizacione masenespektrometrije (LDI MS). Preliminarni rezultati su pokazali da negativni mod LDI maseni spektri suspenzije LiF/B (1:3) u dejonizovanoj vodi sadrži $Li_2(BH_{18})^-$, $LiF_2(BH_3)^-$, $LiB_2(BH_3)_2^-$, $LiF_2LiB(BH_4)_2^-$ jone. Smanjenje sadržaja bora u LiF/B sistemu (1:1) rezultira malo izmenjenim masenim spektrom. Intenzitet $Li_2(BH_{18})^-$ i $LiF_2(BH_3)^-$ opada, dok druga dva jona pokazuju blago izmenjen sastav: $Li_2F(B_3H_2)^-$ i $LiF_2(BH_5)_3^-$. Rezultati pokazuju da klasteri Li_2 i “superhalogen” LiF_2 mogu da interaguju sa boranima. U oba slučaja, najintenzivniji joni su bili kompleksi između „superhalogena” $-LiF_2$ i borana.

Ključne reči: Litijum-borani; “Superhalogen”-boran klasteri; Borhidridi; Skladištenje vodonika; LDIMS

Abstract

Many theoretical calculations have shown that lithium decoration of borane (B_xH_y) or boron (B_n) clusters are potential materials for hydrogen storage. In addition, lithium fluoride clusters have been shown to improve hydrogen storage capacity better than lithium itself. However, the number of experimental studies is much smaller. Therefore, in this work, the possibility of interaction of lithium or lithium fluoride clusters with boranes was investigated by laser desorption/ionization mass spectrometry (LDI MS). The preliminary results have shown that the negative mode LDI mass spectra of the suspension of LiF/B (1:3) in deionized water include $Li_2(BH_{18})^-$, $LiF_2(BH_3)^-$, $LiB_2(BH_3)_2^-$, $LiF_2LiB(BH_4)_2^-$ ions. The reducing the boron content in the LiF/B system (1:1) results in a little changed mass spectrum. The intensities of $Li_2(BH_{18})^-$ and $LiF_2(BH_3)^-$ decrease, while two other ions show a slightly changed composition: $Li_2F(B_3H_2)^-$ and $LiF_2(BH_5)_3^-$. The results show that the Li_2 and “superhalogen” LiF_2 clusters can interact with boranes. In both cases, the most intense ions were complexes between “superhalogen” $-LiF_2$ and boranes.

Key words: (English) Lithium-boran; “Superhalogen”-boran clusters; Borohydrides; Hydrogen storage; LDI MS

1 Introduction

Hydrogen, which has large resources and is not harmful to the environment, is an excellent candidate for renewable energy sources. Finding effective materials for hydrogen storage is one of the biggest challenges.

Nanostructured clusters of carbon or boron are potential candidates for hydrogen storage. Metal-decorated fullerenes and nanotubes of carbon and boron could also be good candidates [1-10]. For example, it has been found that lithium, as the lightest metal, can definitely facilitate the improvement of hydrogen storage capacity of nanostructured clusters. It is well known that lithium borohydride, LiBH_4 , is a good choice for efficient hydrogen storage. However, there are limitations in using LiBH_4 , such as high operating temperatures, slow kinetics, and poor reversibility [11]. Therefore, continuous efforts are being made to develop new materials for hydrogen storage based on Li-B complex. Theoretical research has shown that many complexes can be considered as potential materials for hydrogen storage: the lithium decoration of B_{40} borospheres, borane clusters decorated with lithium ($\text{B}_n\text{H}_n\text{Li}_6$, $n = 5-7$), binary boron-lithium clusters B_{12}Li_n ($n = 1-14$), and $\text{LiBH}_4 \cdot x(\text{BH}_4)_x$ ($x = 1-4$) complexes [12-15]. Theoretical calculations also showed that heterogeneous lithium fluoride clusters improve hydrogen storage capacity better than homogeneous lithium clusters [16].

The aim of this work is to investigate the possibilities of experimental formation of complexes/clusters of lithium or lithium fluoride clusters with boranes. Here we have studied the LiF/B system using the method LDI MS.

2 Experimental

The mass spectra recorded in this work were obtained using a commercially matrix-assisted laser desorption/ionization mass spectrometer (MALDI MS), Voyager- DE PRO (Sciex, USA). This instrument is equipped with a nitrogen laser (with 20 Hz pulse frequency, a wavelength of 337 nm and pulse duration of 3 ns). The mass analyzer is a time-of-flight (TOF) analyzer that can operate in linear or reflector mode as standard. Here, the mass spectra were acquired in negative reflectron mode. The instrumental parameters were: Accelerating voltage 25000 V, grid voltage 85%, laser intensity 3300 a.u. and number of laser beats 200, with a delayed extraction time of 100 ns.

All mass spectra were obtained without matrix using the method LDI MS. The sample was a suspension of LiF/B (1:3 and 1:1 ratio) in 50 μl of deionized water; 1 μl of the sample was applied directly to a stainless steel plate and dried at room temperature before being added to the mass spectrometer.

3 Results and discussion

The full mechanism of ion generation in LDI MS is still being explored, but it is known that the sample is rapidly heated and a gas cloud forms that is rich in H^+ ions, electrons, and other ions and neutrals from the sample. In a complex process involving ion-molecule reactions, dissociation reactions and a simple proton transfer, the detected ions are formed. Thank you to the ease of hydrogen transfer, the LDI MS method can be used to explore the possibilities of bonding hydrogen with lithium, lithium fluoride, or lithium boride clusters without the need to introduce additional hydrogen into the system.

Figure 1 shows the LDI mass spectrum of the suspension of LiF/B in deionized water (the amount of boron was three times greater than the amount of lithium fluoride).

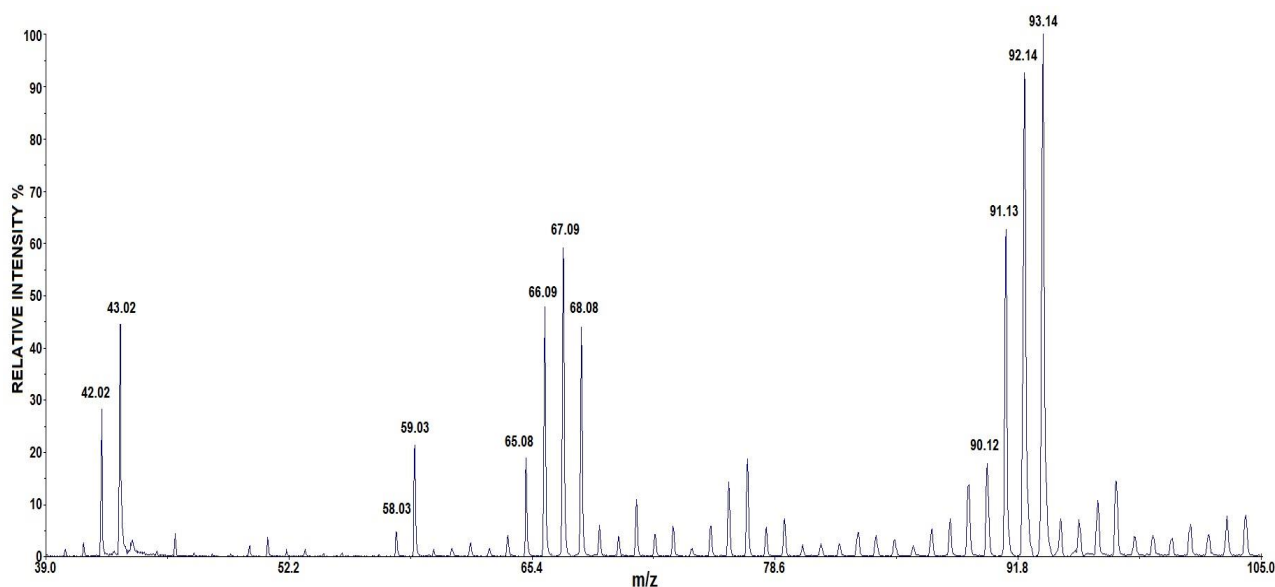


Figure 1. The LDI mass spectrum of the suspension of LiF/B (1:3) in deionized water.

In this mass spectrum, there are four groups of peaks identified as follows: m/z 42.02, 43.02 indicates the presence of $\text{Li}_2(\text{BH}_{18})^-$ ions (calcd 42.18, 43.18), m/z 58.03, 59.03 indicates the presence of $\text{LiF}_2(\text{BH}_3)^-$ (calcd 58.05, 59.05), m/z 65.08, 66.09, 67.09, 68.08 indicates the presence of LiB_5H_6^- ($\text{LiB}_2(\text{BH}_3)_2^-$) (calcd 65.12, 66.12, 67.11, 68.11) together with $\text{LiF}(\text{B}_2\text{H}_{18})^-$ (calcd 65.17, 66.17), while the most intensity group of peak at m/z 90.12, 91.14, 92.14, 93.14 indicates the presence of $\text{LiF}_2\text{LiB}(\text{BH}_4)_2^-$ (calcd 90.12, 91.12, 92.12, 93.11) together with $\text{Li}_2\text{F}_3(\text{BH}_9)^-$ (calcd 90.11, 91.11).

Figure 2 shows the LDI mass spectrum of the suspension of LiF/B in deionized water at a 1:1 ratio.

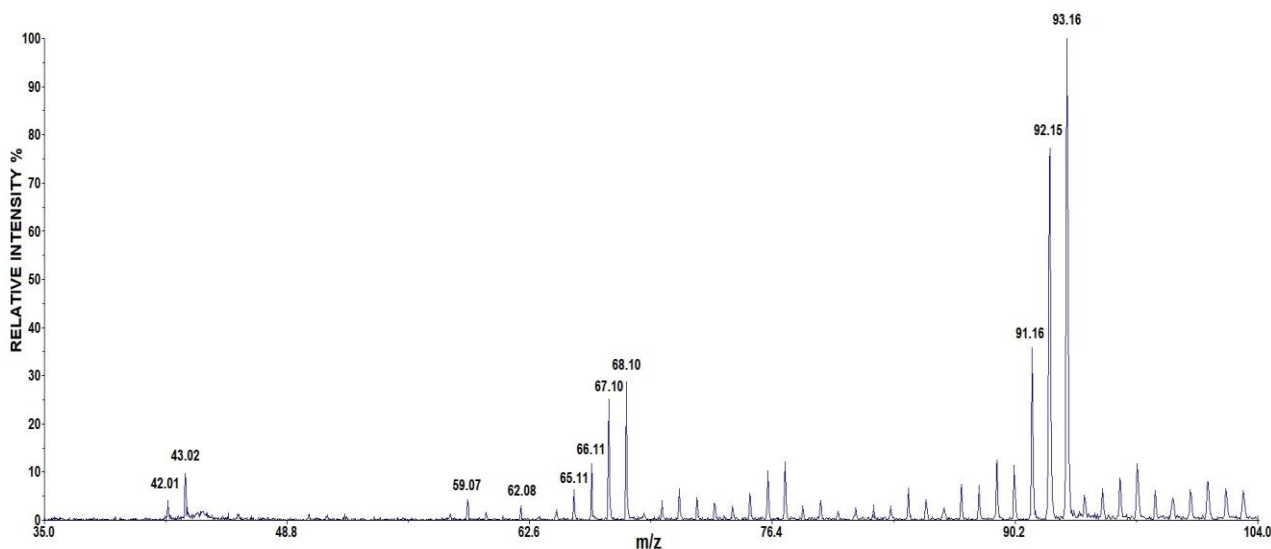


Figure 2 The LDI mass spectrum of the suspension of LiF/B (1:1) in deionized water.

The comparison of Figures 1 and 2 shows that the reduction of the boron content in the LiF/B system leads to a change in the mass spectra. The intensities of the peaks around m/z 43 and 59 in Figure 2 are lower than the corresponding intensities in Figure 1. The isotopic composition around m/z 68 and 93 is also different in Figure 1 and Figure 2. In Figure 2, the relative intensity of the peaks m/z 65.11, 66.11, 67.11, 68.11 and m/z 90.15, 91.16, 92.16, 93.16 indicates the presence of $\text{Li}_2\text{F}(\text{B}_3\text{H}_2)^-$ (calcd 65.08, 66.08, 67.08, 68.08) and $\text{LiF}_2(\text{BH}_5)_3^-$ (calcd 90.16, 91.16, 92.16, 93.16) ions, respectively.

The results show that in both cases the most stable ions are formed between the “superhalogen” LiF_2 cluster and the boron compound.

4 Conclusion

The preliminary results of the study of the LiF/B system by the method LDI MS show that the homogeneous Li₂ cluster and the heterogeneous “superhalogen” LiF₂ cluster can interact with boranes. Under these experimental conditions, the “superhalogen” LiF₂ cluster forms a more stable complex with boranes, i.e. the group of peaks around m/z 93 is of the highest intensity in the LDI mass spectra of the LiF/B system in both cases.

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