

Research Article

Influence of Milling Conditions on the Behavior of AB₅-Type Materials as Metal Hydride Electrodes

Stanislava Todorova, Vesselina Rangelova, Veronika Koleva, and Tony Spassov 

Department of Applied Inorganic Chemistry, Faculty of Chemistry and Pharmacy, Sofia University, 1 James Bourchier, 1164 Sofia, Bulgaria

Correspondence should be addressed to Tony Spassov; tspassov@chem.uni-sofia.bg

Received 24 August 2018; Accepted 15 October 2018; Published 3 March 2019

Academic Editor: Jean M. Greneche

Copyright © 2019 Stanislava Todorova et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

A series of AB₅-type alloys with different particle and grain size were characterized electrochemically as materials for negative electrodes in Ni-MH batteries. Besides, the effect of alloy composition on the discharge capacity and cycle life was studied. Ball milling under hydrogen atmosphere was applied to reduce significantly the grain size of the alloys and to avoid the initial activation at the electrochemical charge/discharge cycling. The alloy morphology and microstructure after different mechanical treatments were characterized by XRD and SEM. The best effect in respect of discharge capacity and cycle life was achieved for the materials milled for 5 h under hydrogen atmosphere.

1. Introduction

Over decades, materials for negative electrodes in Ni-MH batteries are one of the most investigated topics in material science, the main reason being the growing need for new sources of energy and the few alternatives of the fossil fuels [1–3].

Among all types of hydrogen storage alloys for Ni-MH battery application, AB₅ type are of great importance, being even commercially implemented in rechargeable batteries for portable power tools and hybrid electrical vehicles (HEVs) due to their comparatively high energy density and low level of environmental toxicity [4–6]. The main drawback and limiting factor for the commercial application of LaNi₅ alloy is its low theoretical electrochemical capacity of 372 mAh/g and high cost [7]. A large number of investigation during the last decade have shown that substitution of La by Mm (Ce-rich or La-rich mish metal) and partial substitution of Ni by Co, Mn, Al, Cr, etc. lead to significant improvement of the electrochemical characteristics of LaNi₅ and reduce the price of the final product [8–10]. The addition of Co, Mn, Al, and other transition metals modifies the crystal structure of the LaNi₅ alloy thus increasing the

thermodynamic stability of the hydride phase and the alloy corrosion resistance, proving a long cycle life. The AB₅ alloys used in commercial Ni-MH batteries have typical composition of MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3} [11].

Another approach for improvement of the electrode characteristics is mechanical milling or alloying for the preparation of nanocrystalline AB₅ alloys and AB₅-TM (Transitional Metal) composites. Mechanical treatment is being used to obtain materials with smaller crystallite sizes and higher surface area thus improving the hydrating/dehydrating kinetics and hydrogen sorption capacities [12–14]. The microstructure of the alloys and composites synthesized using mechanical milling strongly depends on the conditions used—milling time and velocity, gas atmosphere, etc. However, there is no data if such treatment affects the electrochemical characteristics of the AB₅-TM composites and how it depends on the milling conditions.

In the present work, we have compared the electrochemical behavior of three AB₅-type materials—ball-milled MmNi₅, ball-milled MmNi_{4.1}Co_{0.6}Al_{0.3}, and MmNi₅-Ni composite obtained mechanically as well. The influence of both microstructure and composition on the electrochemical properties is studied. Ni is selected as additive to MmNi₅

because it is known to have a positive effect on the performance of the electrodes—forms unstable hydrides and has high electrocatalytic activity [4]. It is interesting to check if these positive characteristics can be observed electrochemically for materials synthesized mechanically because they are usually characterized through gas phase p-c absorption/desorption curves. The addition of other elements like Co and Al is also another way to improve the performance of the MmNi_5 alloy. In this case, the reduction of the grain size, i.e., the effect of grinding, is interesting to be analyzed as well. While milling hydrides instead of ductile metals is often used as the method for more pronounced particle size reduction of H-storage materials [15, 16], in this study, we apply milling of metals under hydrogen atmosphere, an approach which relies on the partial hydrogenation of the material, thus facilitating its deprecipitation during milling.

2. Materials and Methods

Two separate samples of as-received MmNi_5 alloy (Sigma-Aldrich Product no. 685976) are ball milled for 5 and 20 hours under hydrogen atmosphere in planetary-type mill Fritsch Pulverisette 6 with a rotation speed of 300 rpm and ball-to-powder mass ratio of 10:1. Stainless vial and milling balls were used. Hydrogen is used mainly to promote the grinding and ease the process of reducing the particle size. Milling time of 5 and 20 hours is selected for all other samples to study the effect of particle and grain size reduction on the electrochemical behavior of the materials as negative electrodes in Ni-MH batteries. MmNi_5 -Ni composite is obtained by adding 2 wt.% pure Ni powder (99.5%) to MmNi_5 using the same milling conditions. $\text{MmNi}_{4.1}\text{Co}_{0.6}\text{Al}_{0.3}$ was synthesized by high-frequency induction melting method.

The structure of all samples is determined using XRD (Co radiation). Morphology and particle size are studied using scanning electron microscope JEOL 5510.

The electrochemical behavior of the alloys during charge/discharge cycling is studied using three-electrode cell. The working electrode is prepared using 70 mg of the bulk or synthesized materials, 100 mg polytetrafluoroethylene (PTFE)/carbon black (Teflonized carbon), and heptane. The mixture is pressed at about 150 atm to form the electrode and left on air to dry. $\text{NiOOH}/\text{Ni}(\text{OH})_2$ is used as counter electrode and Ag/AgCl as reference. Each electrode is charged for 3 hours at 5 mA and discharged to 500 mV in 6 M KOH water solution.

3. Results and Discussion

X-ray powder diffraction revealing the microstructure of all studied samples is shown in Figure 1. It is clear that after milling for 5 hours MmNi_5 has sufficient reduction of the crystallite size from 88 nm for bulk MmNi_5 to 34 nm. Further milling for 20 hours leads to lower crystallite size of 10 nm and the sample loses partly its crystallinity (Figure 1). SEM images however show that the average particle size in both cases is nearly the same—about 2–3 μm . The particle size distribution being wide with both smaller separate particles and agglomerates consisting of much smaller particles is

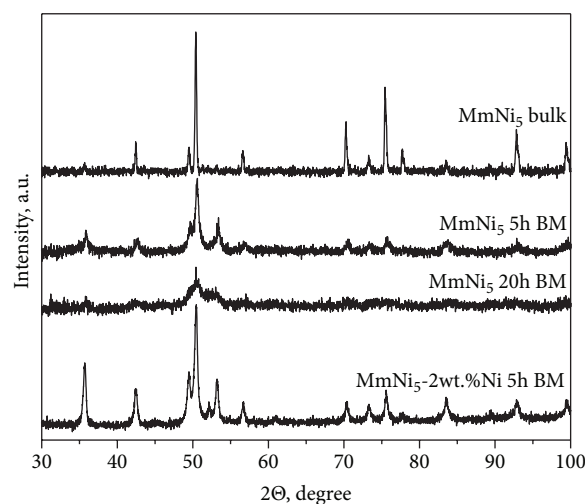


FIGURE 1: Powder diffraction patterns of MmNi_5 alloys—bulk and ball milled for 5 and 20 hours compared to the sample ball milled with 2 wt.% Ni for 5 hours.

presented in Figures 2(b) and 2(c). Milling of MmNi_5 with 2 wt.% Ni leads to the formation of a composite—the most intense peak of Ni at 52° being present at the pattern. Obviously, applying these milling conditions, nickel does not incorporate in the crystal lattice of MmNi_5 since there is no shift of the diffraction peaks. The broadening of the peaks in this case is smaller than in the sample milled for 5 hours without the addition of Ni and the crystallite size according to Scherrer's equation is 42 nm. It is interesting that only 2 wt.% Ni leads to a pattern with more intensive and better expressed crystal peaks from the sample milled for 5 hours without Ni (Figure 1). The SEM image of the composite (Figure 2(d)) reveals a wide particle size distribution with an average particle size of 12 μm . Bulk defects like cracks and fractures are not so well manifested; the particles retained the morphology of the bulk MmNi_5 but the particle size is reduced. All these effects result from the addition of 2 wt.% Ni. Srivastava and Panwar [13] have observed the same effect when adding nickel to MmNi_5 and milling for 3 hours. They explained it with respect to the hardness of the transition element added to MmNi_5 —less elastic metals preserve the morphology of the sample to some extent during mechanical processing.

Diffraction peaks in the pattern of bulk $\text{MmNi}_{4.1}\text{Co}_{0.6}\text{Al}_{0.3}$ are shifted towards smaller angles in comparison to bulk MmNi_5 (Figure 3) proving that the added Co and Mn substitute Ni atoms in the crystal lattice, thus changing only the cell size, but keeping the CaCu_5 structure type—the same as for MmNi_5 . The morphology of both alloys is similar (Figures 2(a) and 2(e))—particles with wide size distribution from 50 to 500 μm . Mechanical grinding of $\text{MmNi}_{4.1}\text{Co}_{0.6}\text{Al}_{0.3}$ for 5 hours leads to the significant lowering of the crystallite size from 90 nm for bulk material to 29 nm. Comparison of ball milled for 5 hours MmNi_5 and $\text{MmNi}_{4.1}\text{Co}_{0.6}\text{Al}_{0.3}$ shows similarity in the structure of both alloys—they are both nanocrystalline with similar crystallite size (Figure 3). There is no significant difference in the morphology as well— $\text{MmNi}_{4.1}\text{Co}_{0.6}\text{Al}_{0.3}$ milled for 5 hours

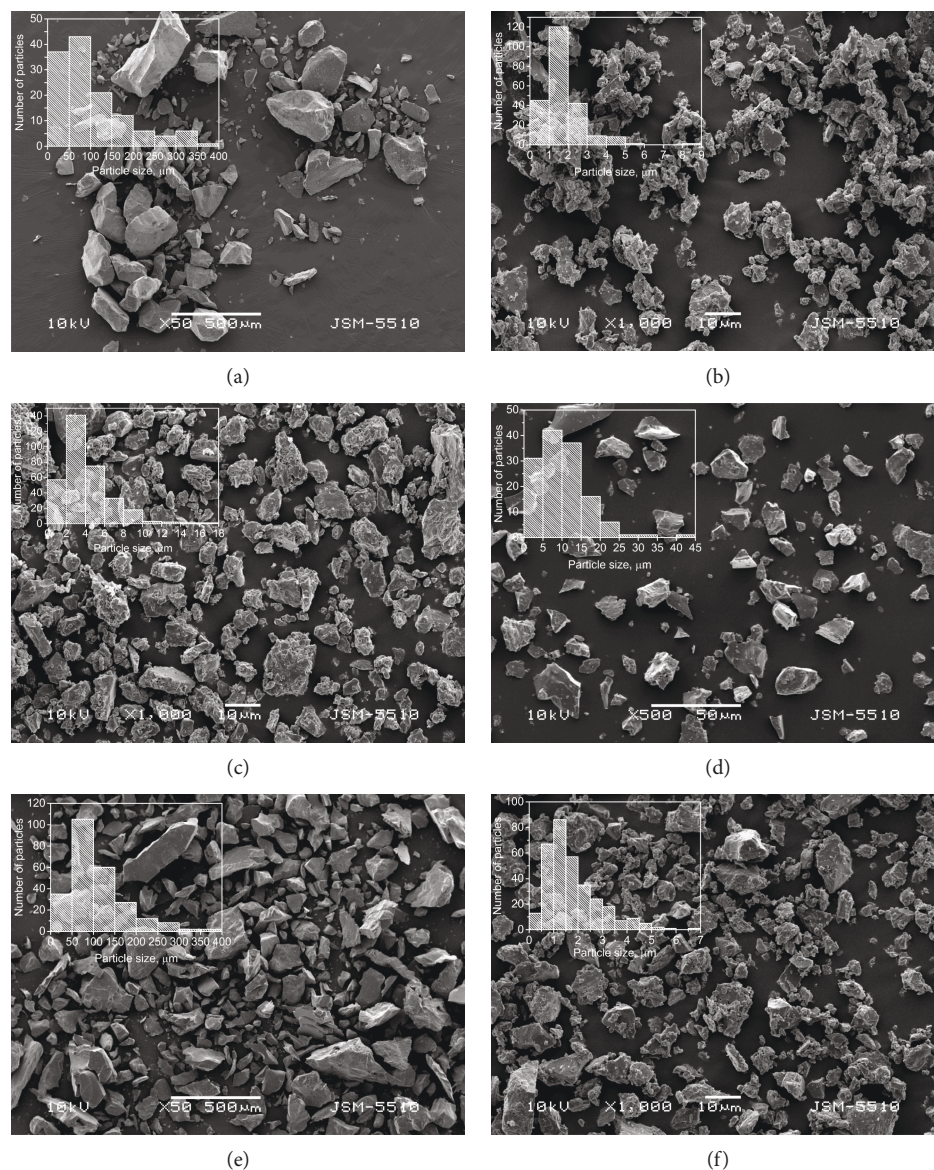


FIGURE 2: SEM images and corresponding histograms (inset) of bulk $MmNi_5$ (a); $MmNi_5$ ball milled for 5 h (b) and 20 h (c); $MmNi_5$ milled with 2 wt.% Ni for 5 h (d); and $MmNi_{4.1}Co_{0.6}Al_{0.3}$ bulk (e) and milled for 5 h (f).

has the same average particle size of about $2 \mu m$, but a little bit wider distribution in size (Figures 2(e) and 2(f)).

All of the ball-milled materials have nanocrystalline structure and reduced particle size and the influence of both microstructure and composition on their electrochemical properties is of high interest. The electrochemical discharge capacity of $MmNi_5$ alloys before and after milling is compared in Figure 4. The maximum discharge capacity of 78 mAh/g is measured for bulk $MmNi_5$ which drops in the second cycle to 36 mAh/g and becomes even lower with cycling reaching about 20 mAh/g . These results are close to those published by Jurczyk et al. [17]. Here, it has to be mentioned that the working electrode structure in our study was not optimized to maximize the electrode capacity but rather to achieve good reproducibility of the electrochemical results and to be able to compare them quantitatively (Figure 5). One possible explanation for the higher discharge capacity

obtained in this case than that of the milled samples can be the hydrogen atmosphere during grinding, which can cause formation of difficult to decompose cerium hydride and block some of the active centers on the surface of the particles of the milled $MmNi_5$ (mish metal used in the study is Ce-rich). Milled $MmNi_5$ for 5 and 20 hours has nearly the same initial discharge capacity of 35 and 37 mAh/g correspondingly, lower than that of the bulk alloy. The microstructure developed after mechanical grinding for 5 hours has the most positive effect on the discharge capacity. Despite the low values at the second and third cycles, there is a tendency for increase with cycling and the value for the last tenth cycle is 36 mAh/g . Milling for 20 hours leads to partial amorphization of the alloy but the discharge capacities vary with a minimum of 20 mAh/g at the third cycle to a maximum of 35 mAh/g at the sixth cycle, followed by a decay and a final capacity of 26 mAh/g . This is lower

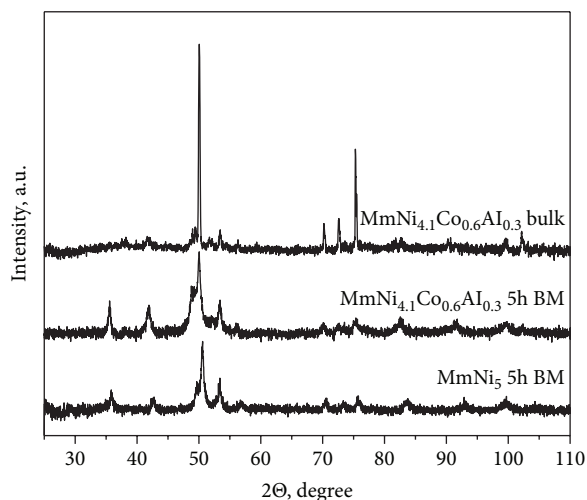


FIGURE 3: Powder diffraction patterns of bulk $\text{MmNi}_{4.1}\text{Co}_{0.6}\text{Al}_{0.3}$ and ball milled for 5 hours compared to MmNi_5 ball milled for 5 hours.

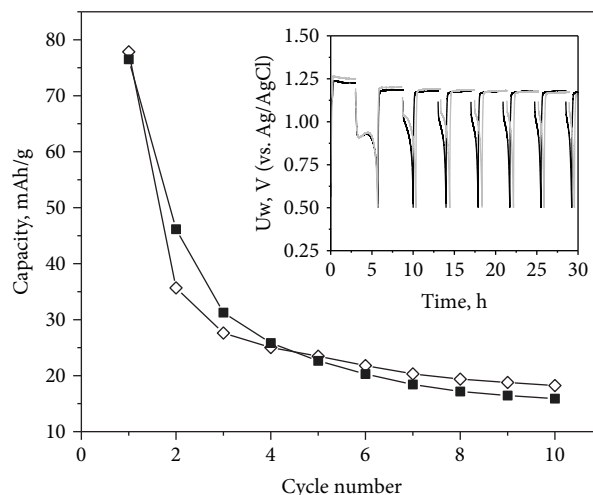


FIGURE 5: Discharge capacity as a function of the cycle number and initial charge/discharge curves (inset) for two electrodes with bulk MmNi_5 alloy, proving the reproducibility of the electrochemical experiments.

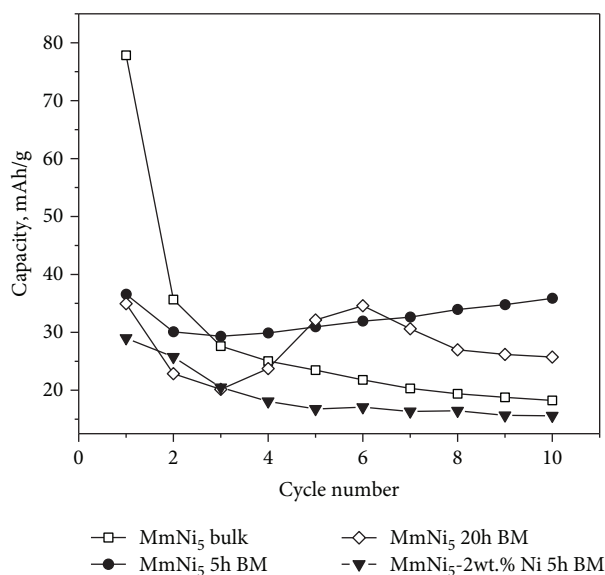


FIGURE 4: Discharge capacity as a function of cycle number for bulk MmNi_5 and ball milled for 5 and 20 hours compared to ball milled for 5 hours with 2 wt.% Ni.

than the final capacity of the sample milled for 5 hours, the main reason being partial agglomeration of the particles after such long grinding. For all materials, there is a clear tendency for a drop of the capacity in the second cycle which probably is due to corrosion processes on the surface of the electrode and difficult access to the particles of active material inside.

The lowest discharge capacities are obtained for the composite with 2 wt.% Ni—the lowest initial capacity of 27 mAh/g followed by additional decrease in the second cycle and constant value of 16 mAh/g (Figure 4). In this case, mechanical grinding, which is the activation process for MmNi_5 alloys [18], is suppressed due to nickel presence

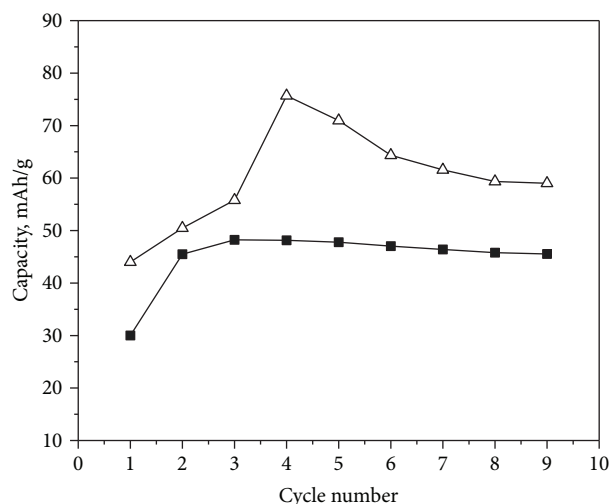


FIGURE 6: Discharge capacity as a function of cycle number for bulk $\text{MmNi}_{4.1}\text{Co}_{0.6}\text{Al}_{0.3}$ and ball milled for 5 hours.

and the larger particle and crystallite sizes cause difficulties in the electrochemical hydrogenation.

The electrochemical discharge curves for bulk $\text{MmNi}_{4.1}\text{Co}_{0.6}\text{Al}_{0.3}$ and milled for 5 hours are shown in Figure 6. They are both characterized by higher capacities than MmNi_5 samples. Co and Al are known for their positive effect on the electrochemical behavior of the metal hydride electrodes, namely, decrease in the corrosion rate, improvement in the cycle life, and increase in the amount of hydrogen stored [4]. These positive effects are true in our study as well. Bulk $\text{MmNi}_{4.1}\text{Co}_{0.6}\text{Al}_{0.3}$ has typical electrochemical behavior with the lowest initial discharge capacity of 35 mAh/g which becomes higher in the next cycles reaching a plateau of

45 mAh/g. Milling for five hours improves the microstructure and therefore the electrochemical performance of the electrode—initial discharge capacity of 45 mAh/g followed by a maximum of 75 mAh/g at the fourth cycle and a final one of 65 mAh/g.

4. Conclusions

Three nanocrystalline AB₅-type materials were obtained by mechanical grinding—MmNi₅, MmNi_{4.1}Co_{0.6}Al_{0.3}, and MmNi₅-2 wt.% Ni composite. The effective reduction of particle and crystallite sizes down to 2 μm and 34 nm, respectively, is observed after milling for 5 hours under hydrogen atmosphere. Grinding for 20 hours further reduces the size of the crystals to 10 nm without altering the average particle size due to their agglomeration. Adding 2 wt.% Ni to MmNi₅ during milling preserves the microstructure of the sample and the composite MmNi₅-2 wt.% Ni showed the least size reduction. The electrochemical performance of the materials showed that the discharge capacity strongly depends on particle and grain sizes and partial substitution of Ni by Co and Al. The highest discharge capacity was obtained for MmNi_{4.1}Co_{0.6}Al_{0.3} after milling for 5 hours.

Data Availability

All data are provided in Results and Discussion. Any additional information about the data used to support the findings of this study are available from the corresponding author upon request.

Disclosure

The research was performed as part of the employment of the authors (Sofia University “St. Kliment Ohridski”).

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

This work was supported by the European Union Horizon 2020 Project Materials Networking under Grant REP-692146-1 and European Regional Development Fund within the Operational Programme “Science and Education for Smart Growth 2014-2020” under the Project CoE “National Center of Mechatronics and Clean Technologies” (BG05M2OP001-1.001-0008-C01).

References

- [1] J. Chow, R. J. Kopp, and P. R. Portney, “Energy resources and global development,” *Science*, vol. 302, no. 5650, pp. 1528–1531, 2003.
- [2] K.-H. Young, “Research in nickel/metal hydride batteries 2017,” *Batteries*, vol. 4, no. 1, p. 9, 2018.
- [3] R. Zacharia and S. . Rather, “Review of solid state hydrogen storage methods adopting different kinds of novel materials,” *Journal of Nanomaterials*, vol. 2015, Article ID 914845, 18 pages, 2015.
- [4] J. Kleperis, G. Wójcik, A. Czerwinski, J. Skowronski, M. Kopczyk, and M. Beltowska-Brzezinska, “Electrochemical behavior of metal hydrides,” *Journal of Solid State Electrochemistry*, vol. 5, no. 4, pp. 229–249, 2001.
- [5] M. A. Fetcenko, S. R. Ovshinsky, B. Reichman et al., “Recent advances in NiMH battery technology,” *Journal of Power Sources*, vol. 165, no. 2, pp. 544–551, 2007.
- [6] Y. Liu, H. Pan, M. Gao, and Q. Wang, “Advanced hydrogen storage alloys for Ni/MH rechargeable batteries,” *Journal of Materials Chemistry*, vol. 21, no. 13, pp. 4743–4755, 2011.
- [7] J. H. N. Van Vucht, F. A. Kuijpers, and H. C. A. M. Bruning, “Reversible room-temperature absorption of large quantities of hydrogen by intermetallic compounds,” *Philips Research Reports*, vol. 25, pp. 133–140, 1970.
- [8] J.-M. Joubert, M. Latroche, and A. Percheron-Guégan, “Metallic hydrides II: materials for electrochemical storage,” *MRS Bulletin*, vol. 27, no. 9, pp. 694–698, 2002.
- [9] E. C. Souza and E. A. Ticianelli, “Effect of partial substitution of nickel by tin, aluminum, manganese and palladium on the properties of LaNi₅-type metal hydride alloys,” *Journal of the Brazilian Chemical Society*, vol. 14, no. 4, pp. 544–550, 2003.
- [10] W. C. Zhang, S. M. Han, J. S. Hao, Y. Li, T. Y. Bai, and J. W. Zhang, “Study on kinetics and electrochemical properties of low-Co AB₅-type alloys for high-power Ni/MH battery,” *Electrochimica Acta*, vol. 54, no. 4, pp. 1383–1387, 2009.
- [11] I. Rade and B. A. Andersson, “Requirement for metals of electric vehicle batteries,” *Journal of Power Sources*, vol. 93, no. 1-2, pp. 55–71, 2001.
- [12] S. Corré, M. Bououdina, N. Kuriyama, D. Fruchart, and G. Adachi, “Effects of mechanical grinding on the hydrogen storage and electrochemical properties of LaNi₅,” *Journal of Alloys and Compounds*, vol. 292, no. 1-2, pp. 166–173, 1999.
- [13] S. Srivastava and K. Panwar, “Effect of transition metals on ball-milled MmNi₅ hydrogen storage alloy,” *Materials for Renewable and Sustainable Energy*, vol. 4, no. 4, p. 19, 2015.
- [14] S. Srivastava and K. Panwar, “Investigations on microstructures of ball-milled MmNi₅ hydrogen storage alloy,” *Materials Research Bulletin*, vol. 73, pp. 284–289, 2016.
- [15] R. A. Varin, T. Czujko, and Z. Wronski, “Particle size, grain size and γ-MgH₂ effects on the desorption properties of nanocrystalline commercial magnesium hydride processed by controlled mechanical milling,” *Nanotechnology*, vol. 17, no. 15, pp. 3856–3865, 2006.
- [16] H. Simchi, A. Kafrou, and A. Simchi, “Structural characteristics and desorption properties of nanostructured MgH₂ synthesised by high energy mechanical milling,” *Powder Metallurgy*, vol. 54, no. 4, pp. 480–483, 2013.
- [17] M. Jurczyk, W. Rajewski, W. Majchrzycki, and G. Wojcik, “Mechanically alloyed MmNi₅-type materials for metal hydride electrodes,” *Journal of Alloys and Compounds*, vol. 290, no. 1-2, pp. 262–266, 1999.
- [18] J. J. Reilly, G. D. Adzic, J. R. Johnson, T. Vogt, S. Mukerjee, and J. McBreen, “The correlation between composition and electrochemical properties of metal hydride electrodes,” *Journal of Alloys and Compounds*, vol. 293-295, pp. 569–582, 1999.



Hindawi
Submit your manuscripts at
www.hindawi.com

