Mg-rich High Entropy Alloy as a Rare-Earth-Free Anode Material for Ni-MH Batteries and Hydrogen Storage Applications

Hakan Yüce[1], Gülhan Çakmak[1*], Eli Grigorova[2], Berke Pişkin[1], Fatih Pişkin[1]

1 Energy Materials Laboratory, Dept. of Metallurgical and Materials Engineering, Muğla Sıtkı Koçman University
2 Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

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The increasing demand for efficient and sustainable energy storage systems has driven research toward advanced rechargeable batteries, particularly Ni–MH systems. The performance of these batteries is largely determined by the hydrogen storage capability of the anode material. Conventional alloys, such as rare-earth-based AB_5 systems (e.g., $LaNi_5$), offer good kinetics but suffer from high cost and limited sustainability. Mg-based alloys provide high theoretical capacity but face challenges such as poor cycling stability and corrosion in alkaline environments. High entropy alloys (HEAs) have emerged as promising alternatives due to their multicomponent nature, tunable properties, and potential for improved hydrogen storage and electrochemical performance. In this study, a Mg-rich, rare-earth-free HEA was designed to combine high capacity with improved stability and cost-effectiveness for Ni–MH battery applications [1].

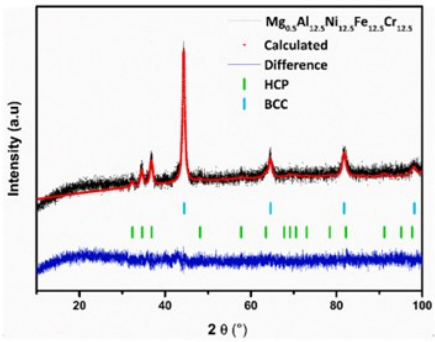


Figure 1. Powder XRD pattern of the arc-melted $Mg_{0.5}Al_{12.5}Ni_{12.5}Fe_{12.5}Cr_{12.5}$ high-entropy alloy, indicating the formation of a single-phase solid solution structure with a slight amount of HCP phase.

The $Mg_{0.5}Al_{12.5}Ni_{12.5}Fe_{12.5}Cr_{12.5}$ high-entropy alloy was synthesized using vacuum arc melting (VAM) under an argon atmosphere. To minimize Mg evaporation, a lamination strategy was applied, placing Mg at the center and surrounding it with higher melting point elements (Cr, Ni, Fe), which improved compositional stability and homogeneity. Prior to melting, the samples were subjected to vacuum and argon purging, and Ti was used as a sacrificial element to eliminate oxygen contamination. The alloy was remelted multiple times to ensure chemical uniformity. The resulting ingot was ground into 30–60 µm powders under an inert atmosphere to prevent oxidation.Structural and microstructural characterization were performed using XRD, SEM, TEM, and EDS analyses.Electrochemical measurements were conducted using a Swagelok cell with a three-electrode configuration in 6 M KOH electrolyte. The working electrode consisted of alloy powder mixed with Ni (3:1 ratio). Charge–discharge tests and EIS analysis were carried out to evaluate electrochemical performance. Hydrogen storage properties were investigated using a Sievert-type apparatus at temperatures between 25–300 °C over multiple hydrogenation/dehydrogenation cycles.

The $Mg_{0.5}Al_{12.5}Ni_{12.5}Fe_{12.5}Cr_{12.5}$ alloy exhibited a dominant BCC structure (~90.6 wt%) with a minor HCP phase, confirming successful Mg incorporation and improved homogeneity via lamination. TEM revealed nanoscale particles (5–20 nm), while SEM/EDS confirmed uniform composition without oxidation. The alloy delivered a maximum discharge capacity of 269 mAh/g, decreasing to 140 mAh/g after 50 cycles (51.85% retention), mainly due to surface degradation and $Mg(OH)_2$ formation, which limits hydrogen diffusion. EIS analysis showed that charge transfer resistance and hydrogen diffusion are the main limiting factors. Hydrogen storage reached 2.04 wt% at 300 °C with fast kinetics, while electrochemical results corresponded to ~1 wt%, indicating good consistency between methods.

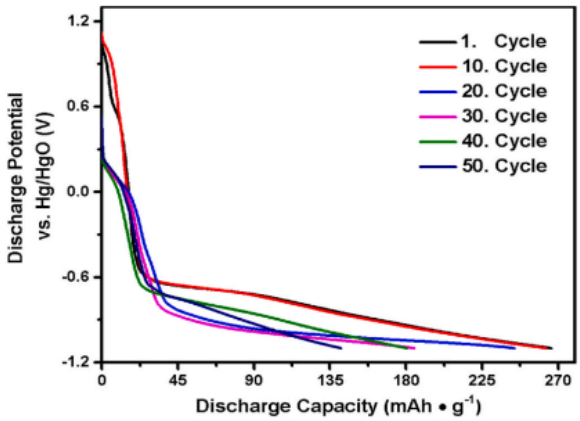


Figure 2. Discharge capacity as a function of cycle number for $Mg_{0.5}Al_{12.5}Ni_{12.5}Fe_{12.5}Cr_{12.5}$ alloy electrode at 273 K.

References

[1] Çakmak, G., Grigorova, E., Pişkin, B., Pişkin, F., & Yüce, H. (2025). Comparison of electrochemical and hydrogen storage performance of Mg-rich alloys as negative electrode materials in Ni-MH batteries. International Journal of Hydrogen Energy, 189, 151938. https://doi.org/10.1016/J.IJHYDENE.2025.151938



Hakan Yüce is currently a Master student in Metallurgical and Materials Engineering at Mugla Sıtkı Kocman University. He is working at Energy Materials Laboratory and his research areas are Energy Storage Materials, Ni-MH Battery, High Entropy Alloy, SOFC, EIS.

Presenting author: Hakan Yüce, **e-mail:** hakanyuce2@posta.mu.edu.tr **tel:** +90 531 526 4175