STRUCTURAL AND ELECTROCHEMICAL HYDROGENATION CHARACTERISTICS OF Y-CONTAINING $R\mathrm{Ni}_{3-x}\mathrm{Mn}_x$ (R = Y and lanthanides; x = 0…2) ALLOYS

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Y-containing $R\mathrm{Ni}_{3-x}\mathrm{Mn}_x$ intermetallic compounds were synthesized for Ni-MH batteries negative electrode applications. X-ray powder diffraction confirmed $\mathrm{LaY_2Ni_9}$-type structure. Mn substitution enhanced initial discharge capacities but reduced cycling stability. Mn-free alloys showed superior cycling stability and high-rate performance. Results reveal a trade-off between capacity enhancement and cyclic stability, providing insights for optimizing Y-containing compounds for energy storage.

Keywords: nickel-metal hydride batteries, intermetallic compounds, hydrogen storage, electrochemical properties

Introduction. In recent decades, the demand for high-performance energy storage and autonomous solutions has driven extensive research into novel materials for energy production, storage and distribution, with special attention devoted to alternative energy sources and advanced battery technologies, particularly nickel-metal hydride (Ni-MH) batteries, which offer superior environmental compatibility and safety compared to conventional systems. Among promising electrode materials, Y-containing and Mg-free AB_3 intermetallic compounds have emerged as breakthrough candidates due to their exceptional electrochemical hydrogen sorption capabilities and high discharge capacities, with especially remarkable high-rate dischargeability (HRD) parameter characteristics that make them ideal for high-current applications where rapid energy delivery is critical [1–4].

As a continuation of our previous research, this study examines the electrochemical properties of Y-containing $R\mathrm{Ni}_{3-x}\mathrm{Mn}_x$ (R = rare-earths) alloys, focusing on optimal rare-earths compositions and whether Ni replacement can optimize hydrogen storage performance and cycling stability for energy storage applications.

Experimental details. The samples were synthesized by arc melting under argon atmosphere, followed by annealing at 600°C for three weeks in evacuated quartz tubes. Structural characterization was conducted using X-ray powder diffraction with Cu-$K\alpha$ radiation. Electrochemical performance of synthesized samples was evaluated in a three-electrode cell with metal hydride (MH) working, platinum counter, and Ag/AgCl reference electrodes. MH-electrodes were prepared by mixing the prepared alloy powder with carbonyl Ni as a conductive additive at a 1:3 mass ratio. Galvanostatic cycling tests were performed at 50 mA/g, while HRD measurements were conducted after 50 cycles, starting at 1 A/g with gradually decreasing current densities.

Results and discussions. The X-ray diffraction analysis showed that the alloys were synthesized as multi-phase materials with the dominant LaY_2Ni_9-type crystal structure (*R*-3*m* space group), confirming successful formation of the target phase alongside minor secondary phases.

Electrochemical characterization demonstrated that Mn-substituted compounds exhibit significantly enhanced discharge capacities compared to their non-substituted counterparts. While Mn-containing alloys achieved the highest initial discharge capacities, these materials showed noticeable capacity degradation during extended cycling. In contrast, AB_3 alloys, where the *B*-site is occupied specifically by Ni, displayed better cycling stability despite lower maximum capacities. To establish composition-structure-property relationships, not only was the impact of elemental composition on electrochemical characteristics examined, but also the correlation between maximum discharge capacity and unit cell volume was investigated.

High-rate discharge (HRD) measurements clearly demonstrate that increasing Mn content negatively impacts discharge kinetics. The optimal HRD performance was achieved by the Mn-free composition, which retained a substantial portion of its maximum capacity even at elevated current densities. These results indicate a fundamental trade-off between capacity enhancement through Mn substitution and the preservation of high-rate discharge capability and long-term cycling stability.

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