NiMH batteries will outperform Li batteries by utilizing H_2 and O_2 gas reactions combined with an α/ϒ- Ni(OH)/NiOOH-electrode

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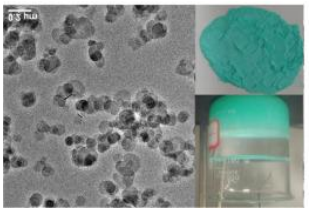
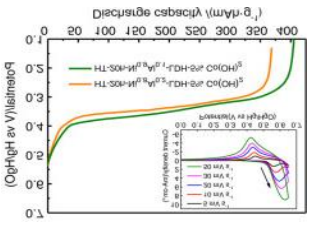
Rechargeable electrochemical cells and the resulting batteries are complicated and development is slow as rechargeable batteries form chaotic systems as they undergo charge-discharge cycling. All reactions (including parasitic side reactions) occurring in both electrodes must be as reversible as possible, else the battery will derail upon cycling. Although several thousand of redox reactions have been characterized and described in various tables and chemical textbooks very few redox reactions have been realized in rechargeable batteries. Lead acid-, NiCd-, NiMH- and Li-ion batteries are still the dominating rechargeable battery chemistries.

Nickel-hydrogen batteries (NiH_2) combine a nickel hydroxide electrode with a hydrogen electrode. They have the longest cycle life of all batteries and are used in space application. In a NiMH battery a metal hydride is both a hydrogen electrode and a solid-state hydrogen storage leading to a significantly better volumetric capacity.

The charge carrier hydrogen is shuttled between the electrodes by water molecules during charge and discharge. The NiMH battery can also be charged and discharge by gaseous additions of H_2 and O_2 respectively.[1] These gaseous additions can be used to mitigate performance deterioration by electrolyte dry out by replenishing the amount of water in the electrolyte and also rebalance the electrode capacities. [2] This mitigates pressure, build ups during overcharge and overdischarge states that in practical battery packs can be difficult to avoid. Improved understanding of the reaction kinetics at the metal hydride surfaces have thus led to NiMH-batteries with the largest capacity-throughput of all present battery chemistries. (Capacity-throughput = cycle life*cell capacity) as the gas additions will significantly increase the cycle life. The cell capacity, however, remains the same.

From these findings we could also collude that the MH-alloy powder in spent NiMH batteries can be used to make new batteries if the corroded surface is cleaned from $Mm(OH)_3$ corrosion products. This cleaning can be made by a simple grinding process where the $Mm(OH)_3$ corrosion products are washed away. NiMH cells made by using such treated and reconditioned MH-powders showed superior reaction kinetics as well as longer life time as the reconditioned powder are already activated and covered by an active as well as protective surface.[3,4]





A way to increase the cell capacity is to utilize the α/γ $Ni(OH)_2$ /Ni(III)OOH redox couple for the Ni-electrode. Commercial Ni-electrodes presently use the β/$Ni(II)(OH)_2$ + OH^- ↔

Al stabilized Ni-hydroxide Al. stabilized Ni-electrode

β/Ni(III)OOH + H_2O + e^- redox reaction. This corresponds to a capacity of 289 mAh/gram.[5]

An interesting aspect of the nickel oxidation state in the α/γ $Ni(OH)_2$ /Ni(III)OOH redox couple can possibly reach 3.67 upon charging. This would correspond to a capacity increase to 482 mAh/gram. If this can be implemented as a stable redox couple NiMH batteries will reach the capacity of Li-ion batteries.

The α/γ $Ni(OH)_2$ /$Ni(3.67?)OOH_{0.33?}$ redox couple is possible to stabilize via intercalation of anions such as OH^-, $NO3^-$, CO_3^{2-} as well as cations Al^{3+}, Co^{2+}, Fe^{3+}.[6]

The problem with a Ni-electrode based on the α/γ redox couple is that has been shown to be unstable and reverts back to the β/β redox couple. This makes it difficult to build battery packs as the cells in the pack can get different capacities in the battery string. Work is underway to address these issues.

[1] Ye, Z.; Noréus, D. Oxygen and hydrogen gas recombination in NiMH cell, *Journal of Power Sources*, **2012**, 208, 232–236

[2] Shen, Y.; Noréus, D.; Starborg, S. Increasing NiMH battery cycle life with oxygen. *Int. J. Hydrog. Energy* **2018**, 43C 18626–18631.

[3] Shen, Y.; Peng, F.S.; Kontos, S.; Noréus, D. Improved NiMH performance by a surface treatment that creates magnetic Ni-clusters. *Int. J. Hydrog. Energy* **2016**, 41, 9933–9938.

[4] Shen, Y.; Svensson-Grape, E.; Noréus, D.; Widenkvist, E.; Starborg, S. Upcycling of Spent NiMH Battery Material-Reconditioned Battery Alloys Show Faster Activation and Reaction Kinetics than Pristine Alloys. *Molecules* **2020**, 25, 2338.

[5] Zhou, F.; Wu, M.; Hu, W-K; Jiang, Z-G.; Noréus, D. Alpha nickel hydroxide electrodes improve aqueous rechargeable batteries capacity, *Materials Research Bulletin*, **2024**, **179**, 112967-

[6] Lskavian, D. N.; Diakonov, A.K.; Sinitsyn P.A.; Kokin, A. A.; Levin E.E.; Nikitina V.A. Quantifying polarization losses in undoped and Co-doped $Ni(OH)_2$ electrodeposits. *Electrochimica Acta*, **2026**, 545, 147736-48.

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