Magnetic Field Effects on Nickel Electrodes

for Nickel Metal Hydride and

Nickel Cadmium Batteries

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The nickel hydroxide electrode, $Ni(OH)_2/NiOOH$, has been used in commercial alkaline secondary batteries for more than 100 years. It serves as the positive electrode in Ni-Fe, Ni-Zn, Ni-Cd, and nickel metal hydride rechargeable batteries. The charge/discharge reaction for this electrode is

$$\beta\text{-}NiOOH + H_2O + e \leftrightarrows \beta\text{-}Ni(OH)_2 + OH^-$$

where the reduction is the discharge.

Recent work has shown that incorporation of magnetic microparticles into the electrode structure improves the power output of H_2/O_2 and H_2/air proton exchange membrane (PEM) fuel cells [1]. Magnetic particles also enhance the carbon monoxide tolerance of indirect reformation fuel cells [2].

Additives to nickel hydroxide include nickel and cobalt. Nickel and cobalt are ferromagnets. The question arose as to whether incorporation of magnetic microparticles into the nickel hydroxide electrode would improve the response of nickel hydroxide electrodes.

Magnetic microparticles range in diameter from 1 to 7 μm. The materials studied include magnetite (Fe_3O_4), samarium cobalt (Sm_2Co_7), and neodymium iron boron (NdFeB). Maximum energy product measures the strength of the magnetic material. For the materials studied here, the maximum energy product increases as Fe_3O_4 (1-5 MGO) < Sm_2Co_7 (12-24 MGO) < NdFeB (18-48 MGO). Glass particles of comparable size cannot be magnetized and serve as a control. The Fe_3O_4 and NdFeB microparticles were coated with silanes. The Sm_2Co_7 microparticles were uncoated.

A slurry of nickel hydroxide and, where appropriate, magnetic or glass microparticles was applied to a 0.459 cm^2 platinum disk electrode and allowed to dry. Magnetized electrodes are dried inside a hollow cylindrical magnet; once dried, the external magnet is removed [3]. All electrodes were charged and discharged at various scan rates in KOH electrolyte. The electrodes were then examined by cyclic voltammetry in the same electrolyte solution. Cathodic peak currents recorded at 200 mV/s are shown in the Table.

For $Ni(OH)_2$ containing no particles, electrodes dried in an external magnetic field yield currents that were 25% higher than similar electrodes dried with out the external field. As the film is and discharged, its structure is reformed and the enhancement is lost. In the following data, the non-magnetized $Ni(OH)_2$ electrode with no intercalated particles serves as the benchmark for nickel hydroxide electrodes that are not magnetized.

Additive (wt %)	i_p (μA) Non-mag	i_p (μA) Mag	i_p Ratio Mag/ nonmag	i_p Ratio Mag/ nonmag $Ni(OH)_2$
None	144	192	1.25	1.33
Glass (5)	9.9			
Fe_3O_4 (5)	211	267	1.71	1.85
Fe_3O_4 (10)	64.9	215	3.31	1.49
Fe_3O_4 (15)	41.1	~0		
NdFeB (5)	169	138	0.82	0.95
NdFeB (15)	62.0	~0		
Sm_2Co_7 (5)	122	334	2.63	2.32
Sm_2Co_7 (10)	176	~0		

From the Table, the addition of glass beads markedly diminishes electrode performance. Thus, the addition of particles alone does not improve performance.

Magnetite was added at 5, 10 and 15 wt %. For nonmagnetized electrodes, peak current decreases with increasing Fe_3O_4. For 5 and 10 wt % Fe_3O_4, magnetized electrodes yielded higher currents than the corresponding nonmagnetic electrodes by 70 and 230 %, respectively. When magnetized electrodes are compared to the nonmagnetized nickel hydroxide control electrode, the currents are enhanced 85 and 49 %, respectively.

For magnetized electrodes, as the magnetic content increased, film quality diminished because the magnetic particles clustered in the electrode center and did not provide a well distributed magnetic field. Particle clustering was most challenging for the strongest magnets, NdFeB, which under this electrode fabrication procedure did not enhance electrode performance.

Samarium cobalt at 5 wt % yielded the most substantial current enhancement. At this maximum energy product and loading, the best structure and field distribution were established. From the Table, magnetized Sm_2Co_7 yielded 163 % higher current than the nonmagnetized Sm_2Co_7. Magnetized Sm_2Co_7 yielded more than double the current of the nonmagnetized nickel hydroxide control.

In summary:

- Magnetization of the nickel hydroxide electrode enhances the current, at least for a few cycles until the reformed electrode structure loses its magnetization.
- Addition of magnetic microparticles allows the magnetization to be sustained in the structure on prolonged cycling.
- As magnetic strength and content increases, and good electrode structure is maintained, incorporation of magnetic particles is found to increase voltammetric peak currents by a factor of as much as ~2.
- Results suggest that increased charge and discharge times can be achieved by incorporation of magnetic microparticles.

References:

[1] 39th Power Sources Proceedings, 2000, p. 144-147.
[2] 40th Power Sources Proceedings , 2002, p. 262-265.
[3] P. Zou, "Magnetic Field Effects on Nickel Electrodes for Nickel Metal Hydride Batteries," M.S. Thesis, University of Iowa, 2002.