

## Layered Nanocrystals for Electrochemical Power Sources: Nanostructured Layered Ni Hydroxides for the Positive Electrode in NiMH Cells.

Zbigniew .S. Wronski, Daniel. Martineau, and Graham J. Carpenter  
CANMET's Materials Technology Laboratory, Natural Resources Canada,  
568 Booth Street, Ottawa, Ontario,  
K1A 0G1 Canada

Inducing protonic conductivity in otherwise poor electronic-conductor metal oxides and hydroxides is a common challenge one can encounter while studying both, electrochemical energy storage in hydrogen batteries and energy conversion in hydrogen fuel cells. This is because protons must be efficiently delivered to the active mass, which is an *interface material*, where electrons and electric current are generated in redox reactions at the interface between electron-conducting electrode and ion-conducting electrolyte. Traditionally, efficient proton delivery--which is either reversible in a rechargeable hydrogen (alkaline) battery cell or irreversible in hydrogen fuel cells-- is achieved by increase in the active interface material volume, lowering the activation energy via use of catalyst, and increase mobility of ionic carriers in solid oxides. The increased ionic mobility is often induced in defected crystalline oxide structure. The increased volume and improved mixing of a catalyst is usually met in fine powders.

We showed previously that further increase in the mobility of protons in fine Ni(OH)<sub>2</sub> powders, as used in the positive electrode of rechargeable alkaline cell, depends on the presence of stacking fault disorder in the compact packing of Ni-O hexagonal basal planes and subsequent fragmentation of these oxides into mosaic structure of *layered nanocrystals*. In this study we discuss two alternative routes for preparation of such a *mosaic crystal nanostructure*: (i) mechanochemical grinding of layered hydroxides, in which mechanical action and thus induced Shockley partial dislocations give rise to the net positive charge of Ni-O planes and donation of protons from OH group; whereby the proton conductivity is improved, (ii) electrochemical grinding, in which similar effect on proton mobility is induced by chemical doping of Ni hydroxide with allivalent redox metal, and inducing the cycling charging of the planes at each discharge of the Ni (+2 → +3)Co(+3)(OH)<sub>2</sub> active mass. Layered double hydroxides (LDH), containing of NiAl of varying M(+2):M(+3), ratios, where M(+3) is nonredox metal, have also been prepared, as to compare them with the NiCo containing hydroxide.

High-resolution electron microscopy with 200KV FEG TEM and EELS spectrometer was used for direct lattice imaging of the structure in the mosaic nanocrystals. The electrodes made of these nanomaterials were charge/discharge cycled in 24%KOH-1%LiOH electrolyte at charge rate C/4 and discharge rate C. At each 10<sup>th</sup> cycle slow discharging at C/5 rate was forced. Since the electron removal must be balanced by the proton de-insertion from the electrode this procedure gave some insight into proton mobility in the material. A new method of

electro-dilatometry, was used to correlate the charge and discharge voltage changes with simultaneous swelling of the material on proton insertion and de-insertion into the oxide structure.

It was observed that layered Ni hydroxides which performed poorly in electrode cycling experiments exhibit 10-20 % improvement in the discharge capacity when processed into the mosaic nanostructure consisting of layered nanocrystals.. Also, the *in-situ* collected electro-dilatometric patterns for the nanostructured electrodes consistently exhibit fast, almost linear response of the swelling to the potential change. This swelling is highly reversible without the extra component of the cumulative (irreversible swelling). This means that the nanostructured material is more receptive for insertion and de-insertion of ionic species, in this case H<sup>+</sup> ions. This can explain lower losses in the discharge capacity on cycling. Indeed, the Ni positive electrode, prepared from the nanostructured material, maintained 100% of its discharge capacity at the discharge rate C/5 and above 90% when being discharged fast rate, up to 800cycles.

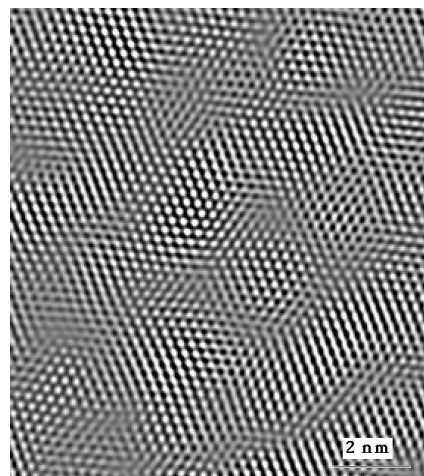
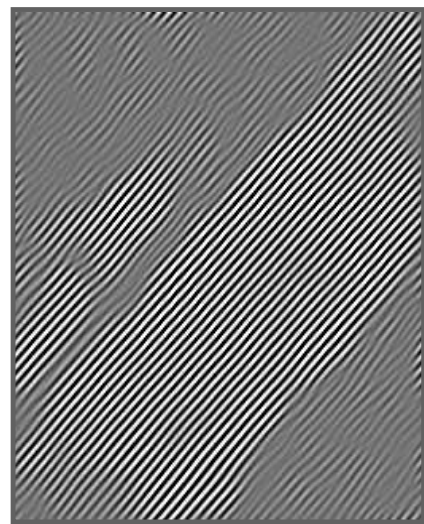


Fig. Regular (TOP) and nanostructured (BOTTOM) Ni hydroxide battery material. HR lattice imaging in FEG-TEM reveals extensive sheet-like crystallographic habitat in the not-processed material and a mosaic of layered nanocrystals with sizes as low as 2 nm in the nanostructured. The nanostructured materials combines highly ordered

layered nanocrystals with large fraction of disordered interface material; this provides high storage capacity for inserted ionic species (viz.  $H^+$ ) combined with good kinetics for insertion/de-insertion reactions.