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Nickel hydroxide and other nanophase cathode materials for rechargeable batteries

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Abstract

The staff of US Nanocorp, Inc. are developing unique nanostructured materials for a wide range of applications in the areas of energy storage (batteries and ultracapacitors) and energy conversion (fuel cells and thermoelectric) devices. Many of the preparations of these materials exploit a wet synthesis process (patent pending) that is scaleable to large volume manufacturing and anticipated to be low in cost. Specifically, both the β-form of nickel hydroxide and the hollandite form of manganese dioxide have been synthesized. The hexagonal $Ni(OH)_2$ is anticipated to significantly boost energy densities in nickel–alkaline batteries, including nickel/cadmium, nickel/metal hydride and nickel/zinc. The nanophase MnO_2 microstructure exhibits an unusual tunnelled tubular geometry within a 'bird's nest' superstructure, and is expected to be of interest as an intercalation cathode material in lithium-ion systems as well as a catalyst for fuel cells. Characterization of these materials has been by the techniques of high resolution SEM and TEM, as well as XRD. Both Hg porosimetry and BET surface measurements for conventional and spherical nickel hydroxides are summarized. Pore distribution and electrochemical activity for the nanophase materials will be examined in the future.

1. Introduction

The rate of market penetration of the nickel/metal hydride and lithium-ion rechargeable battery systems has been unprecedented. Despite higher cost and incidents related to safety, rechargeable lithium systems have found application in high-technology notebook computer and cellular phones so rapidly that a considerable market share has been denied the nickel/metal hydride system, attributable to a significant, but not overwhelming volumetric energy density advantage. This advantage could be mitigated in the event that considerable improvements were made in the energy density of nickel alkaline active material. Moreover, volume ratios of active materials in nickel alkaline cells continue to improve. It has been several years since Matsushita Corp. reported [1] at least 51% of active material (including Co additive) by volume in the positive electrode in cylindrical nickel/cadmium cells containing open-porosity foam-nickel substrates, compared to 35% in cells with traditional sintered positive electrodes. The implications in larger batteries, for example,

EV and HV, where first costs and safety issues are paramount, are critical.

US Nanocorp, Inc. is developing [2,3] nanostructured $Ni(OH)_2$ that is expected to yield at least a 20% improvement in cathode energy content.

2. Nickel hydroxide

The electrochemical utilization and practical capacity of battery active materials are directly affected by their morphology and surface area, by the lattice defect structure, and the catalyzed nature of the surface (for charge transfer). In the case of nickel hydroxide, recent changes in the preparation have provided the potential for a significant leap in energy density $(Wh\ dm^{-3})$.

Chemically prepared β-$Ni(OH)_2$ consists of a hexagonal sandwich type (brucite) structure with a plane of Ni atoms between an array of O atoms (OH) [4]. The theoretical X-ray density of active β-$Ni(OH)_2$ material is 4.15 g ml^{-1} [5]. In the most common charged state, β-NiOOH, the same lattice habitat is maintained, but the X-ray density increases to 4.6 g ml^{-1}. However, the traditional material used in bat-
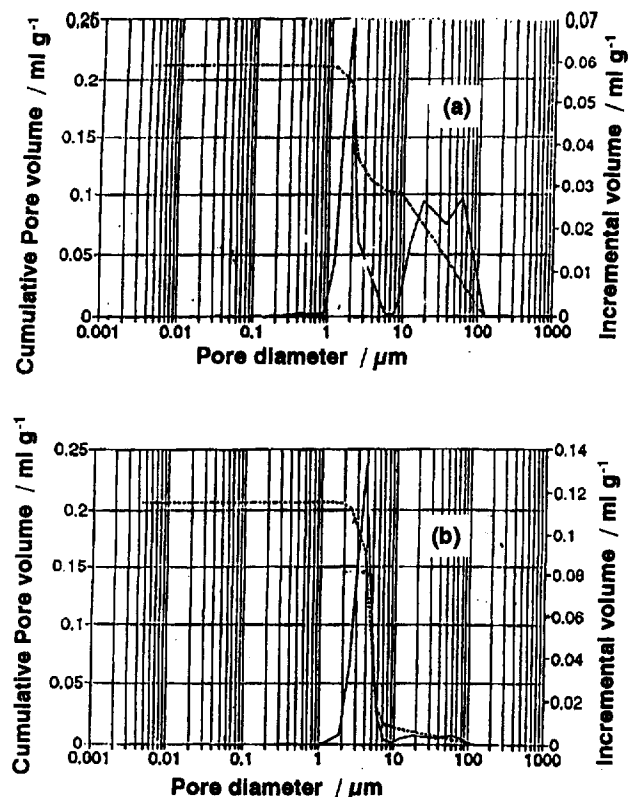
Fig. 1. Pore structure analysis of conventional (a) and spherical (b) nickel hydroxides: · · ·, cumulative volume; ——, incremental volume.

Table 1

Comparison of Hg porosimetry results and BET surface areas for two types of nickel hydroxide

	Conventional	Spherical
Median pore diameter (volume) (μm)	5.07	4.71
Median pore diameter (area) (μm)	2.11	4.16
Bulk (geometric) density (g ml^{-1})	1.24	1.73
Apparent (skeletal) density (g ml^{-1})	1.69	2.69
Specific surface area (m^2 g^{-1})	0.24	0.21
BET specific surface area (m^2 g^{-1})	45.7	17.9

teries for over 90 years usually has over 50% pores. As shown in the pore-size analysis (Fig. 1), there are a significant number of large pores which are not needed for electrochemical efficiency. Yuasa Battery Co. pioneered the use of spherical nickel hydroxide, resulting in improved packing efficiency [6]. This type of material was compared with standard nickel hydroxide at Rutgers University by Hg porosimetry (at 60 000 psi) and BET surface analysis. Pore diameters are defined relative to the diameters at which 50% of the pore volume and area are occupied, the latter calculated from the thermodynamic work function. The latter technique yields much higher values, likely due to the presence of pores of diameter less than 0.0045 μm which cannot be detected by Hg intrusion. The results are summarized in Table 1.

To achieve high electrochemical efficiency, nickel hydroxide is normally catalyzed with 5–10 wt.% cobalt, a costly additive. It has been shown [7,8] that the deposition of cobalt on the surface of nickel hydroxide rather than as a co-deposit results in improved catalytic activity. This observation was confirmed at Rutgers University [9,10] in the fabrication of fiber-mat substrate electrodes. Preliminary experiments indicate that lower levels of Co may still be effective and would likely carry over to nanophase material. This is critical in establishing cost effectiveness with respect to lithium technologies.

Finally, the percent active material can be further increased by the use of non-graphitic plastic-bonded (PB) electrodes which preclude the need for additional conductive diluents

[11], especially in low and medium rate applications, including EV (but not HV) batteries.

Clearly, it would be desirable from an energy density standpoint to achieve practical material densities comparable to the theoretical density, notwithstanding the requirement for some porosity to allow for electrolyte irrigation. It is well known in the field of material science that such densities can be realized in practice for nanophase hard ceramics and intermetallic materials, under conditions of superplasticity, even at low temperatures (including ambient). Specifically, TiO_2 has been shown [12] to achieve the theoretical density at less than half the melting point. Likewise, the metal oxides such as $Ni(OH)_2$ and MnO_2 are expected to exhibit similar properties. Therefore, a modest increase in tapping density of 15–20% ought to retain desirable electrolyte distribution and be well within achievable yields, while boosting considerably the effective energy densities. US Nanocorp has initiated this approach by developing a wet chemical synthesis method for these active battery materials and, whilst doing so, has obtained SEM and TEM images.

The as-synthesized nanophase powder has a β-$Ni(OH)_2$ structure, as indicated by X-ray diffraction data. The resultant product is a mixture of highly porous (nanoporous) fibers and equi-axed grain particles (see Fig. 2). The fibers are approximately 2–5 nm in diameter by 15–50 nm long, while the average particle size is approximately 5 nm. In order to be a useful battery material, the nanophase powder is re-agglomerated to a dimension of 10–12 μm.

As shown in Table 2, the actual density of the conventional material is about 1.6 g ml^{-1}. With a high surface area, this
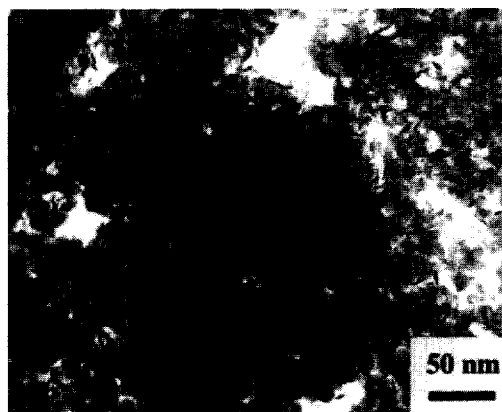

Fig. 2. TEM photograph of nanophase nickel hydroxide.

Table 2
Salient physical properties of Ni(OH)₂

Type	Av. particle size (μm)	Packing density (g ml⁻¹)	Energy density (mAh ml⁻¹)
Conventional	50	1.6–1.8	400 [a]
Spherical	10–20	2.0–2.1	500 [a]
Nanophase	0.005–2.2	2.3–2.5 (est.)	700 [b] (est.)

[a] Including 10% cobalt.
[b] Including 5% cobalt.

can go up to 1.8 g ml⁻¹. The present advanced spherical powders can have a packing density up to 2.1 g ml⁻¹. Nanophase Ni(OH)₂ offers the potential for a greatly improved packing density.

3. Nanophase manganese dioxide

Nanophase MnO₂ was synthesized using a similar wet chemistry synthesis route. The resultant reaction product is a hollandite structure, which exhibits an unusual 'bird's nest' morphology. It is anticipated that this geometry may have application as an intercalation material [13] in lithium-ion rechargeable batteries (similar to the spinel phase currently under development) as well as in zinc/manganese dioxide rechargeable alkaline cells. This structure is shown in Fig. 3. Each 'bird's nest' is about 10 μm in diameter, comprised of an assemblage of many individual nanofibers with diameters from 5 to 25 nm.

4. Conclusions

Nanophase active materials for batteries offer the potential for boosting the performance of both nickel alkaline and lithium rechargeable batteries in a cost-effective manner. These ultrafine particle-size materials must be re-agglomerated to be useful battery materials. The resultant materials have extremely homogeneous porosity and a narrow pore size distribution. Future work will characterize these properties in a quantitative fashion and electrochemical evaluations will be initiated.

Acknowledgements

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Fig. 3. Hollandite nanophase MnO₂ 'bird's-nest' structure.

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[13] Q. Feng, H. Kanoh, K. Ooi, M. Tani and Y. Nakacho, Synthesis of hollandite-type manganese dioxide with H+ form for Li rechargeable batteries, J. 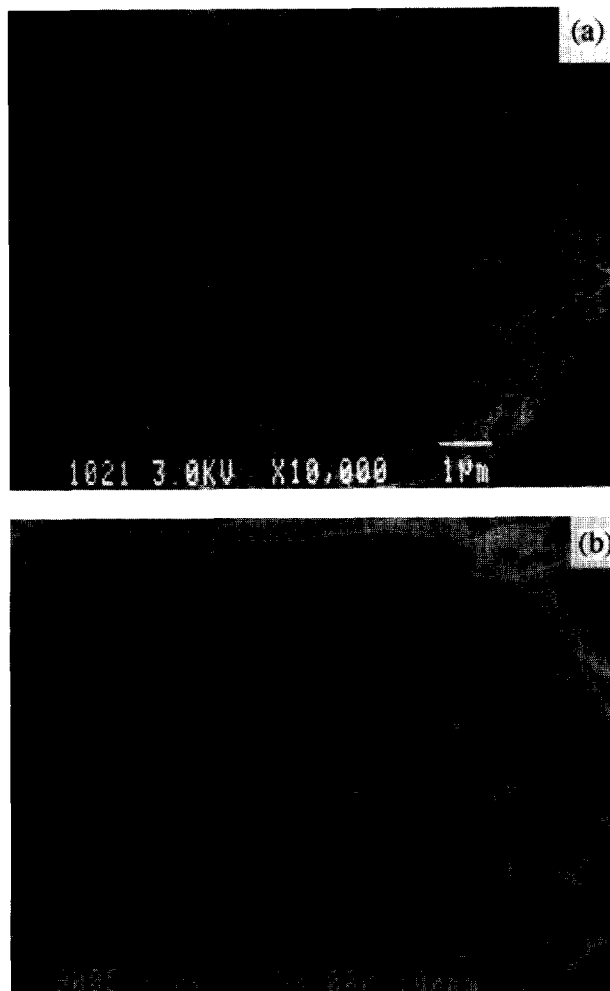Electrochem. Soc., 141 (1994) L135.