



- **Nickel Hydroxide for NiMH and NiCd Batteries**
 - Process Comparison
 - Powder Morphology
 - Crystal Structure
 - Electrochemistry
- **$\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ for Li-Ion- / Li-Polymer-Batteries**
 - Process Comparison
 - Powder Morphology and Composition
 - Electrochemistry and Safety



Ni-Based Powders for Rechargeable Batteries
A Survey from a Process and Materials Point of View

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Process Comparison

The HCST Process**The Chemistry**

Nickel + Water --->
 Nickel Hydroxide
 + Hydrogen

Starting material are nickel cathodes readily available from various sources. Cathodes are electrochemically dissolved in water. The resulting Ni(OH)₂ is transferred into the spherical form in the presence of ammonia
 Minimum waste water and by - products.

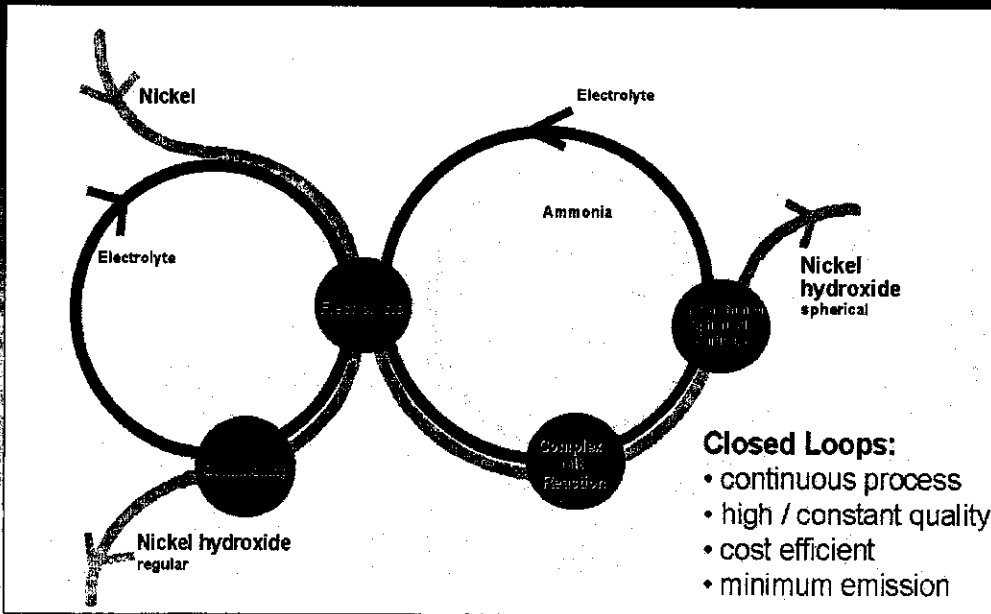
The Conventional Process

Nickel + Acids --->
 Nickel Salts + Hydrogen
 Nickel Salts + Caustic Soda --->
 Nickel Hydroxide +
 Neutral Salts

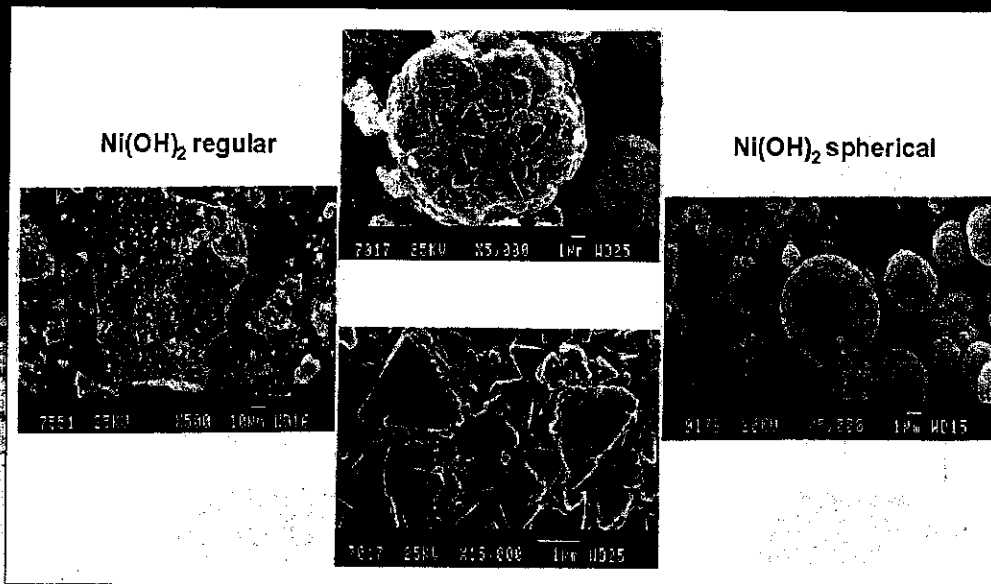
Starting material is nickel in any form, dissolved in acids, chemically purified, excess acid need to be neutralized. Nickel salts are precipitated with caustic soda in the presence of ammonia to form spherical nickel hydroxide.
 Excess caustic is neutralized.
 Waste water with neutral salts and heavy metals has to be discharged.



The H.C. Starck Process

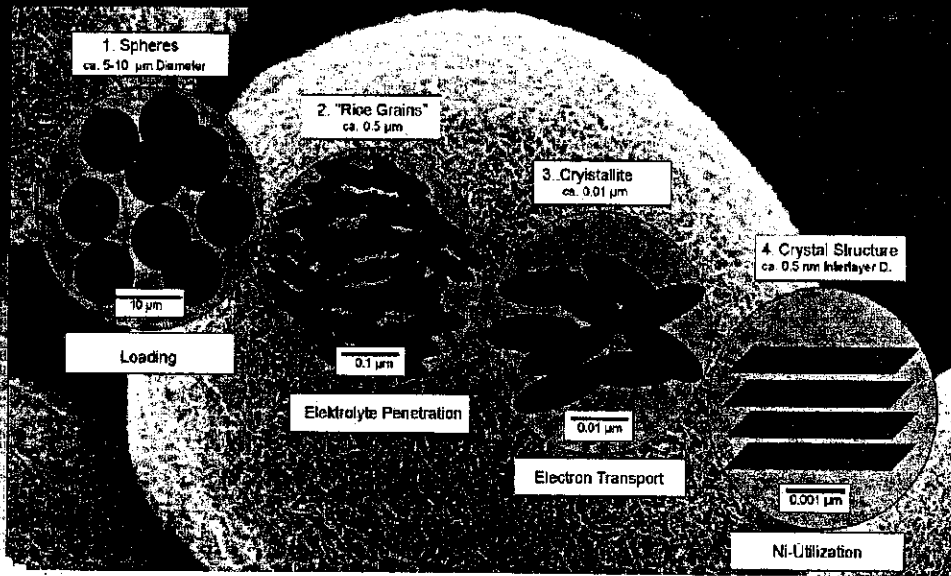


Particle Morphology

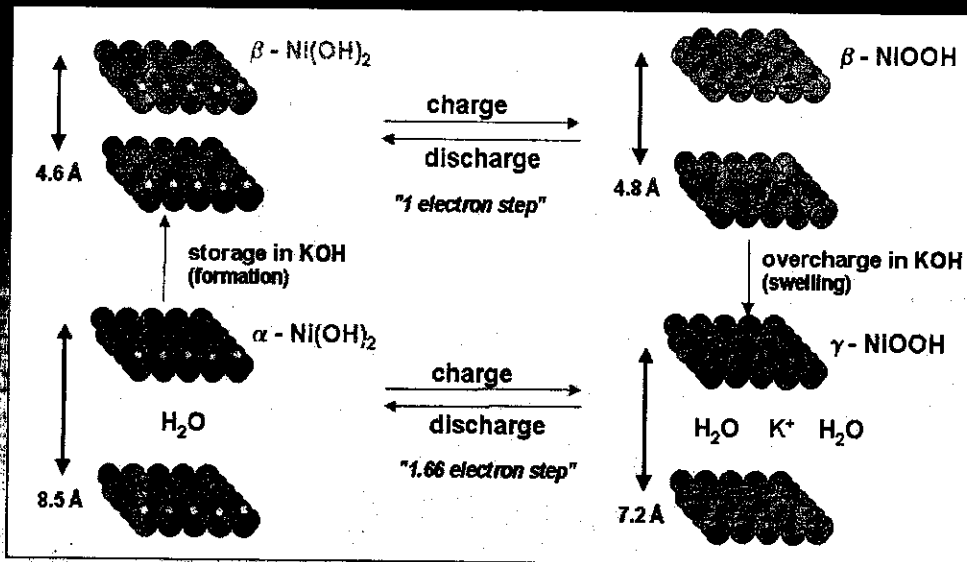


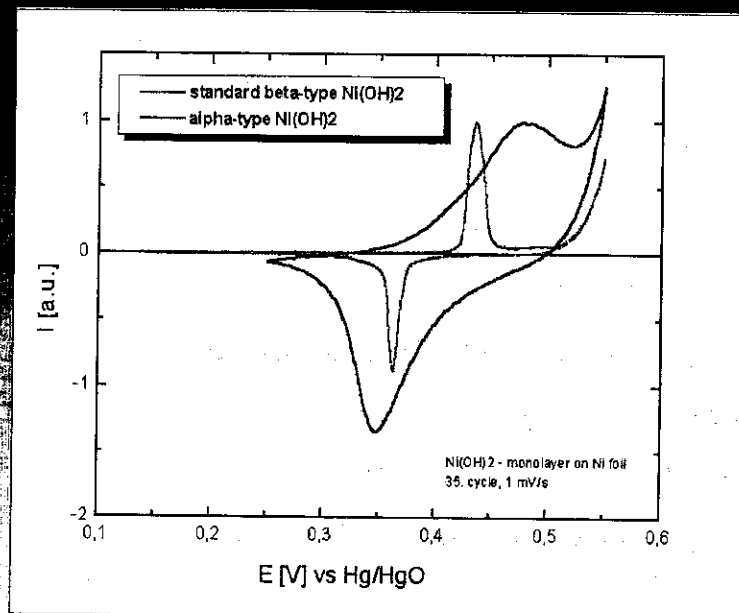
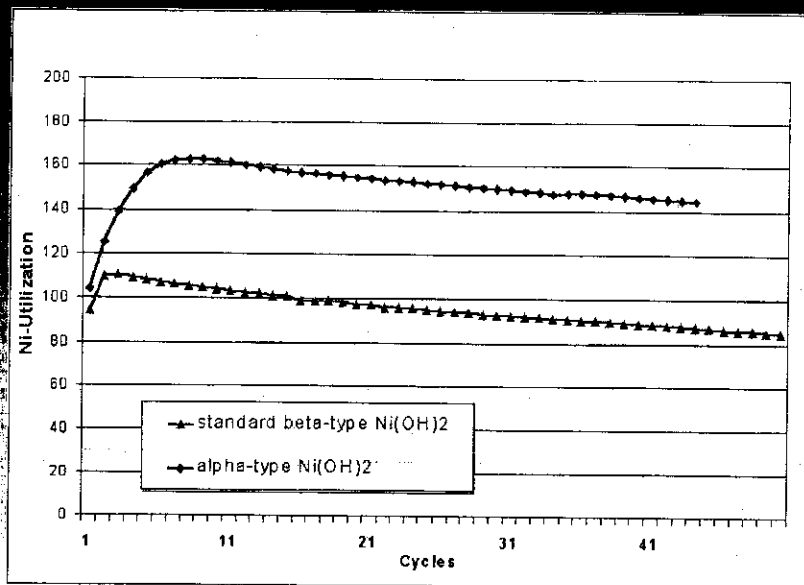


4 Structural Planes of Spherical Ni(OH)₂



Crystal Structure / Bode Diagram







Conclusion

- A flexible, economical and closed-cycle process for the production of $\text{Ni}(\text{OH})_2$ powders has been developed.
- Particle morphology (shape, porosity, crystallinity, ...), as well as chemistry, can be controlled.
- The influence of the different structural planes of $\text{Ni}(\text{OH})_2$ powders on the electrochemical performance in batteries was demonstrated.
- The electrochemical performance of different types of $\text{Ni}(\text{OH})_2$ materials was presented. Beta type $\text{Ni}(\text{OH})_2$ Hydroxides are capable of Ni-utilizations up to 110%, whereas alpha type materials can deliver values around 160%. Both show also different charge and discharge kinetics.

Outline



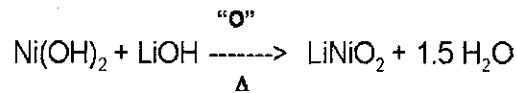
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 - **Electrochemistry and Thermal Stability**



Process Comparison

The HCST Process

The Chemistry



Starting material are Nickel Hydroxides (in house) which are homogeneously mixed with lithium salts like LiOH and oxidizing additives (premix). This mix can be calcined at relatively low temperatures and reduced reaction times to avoid the decomposition of the product.

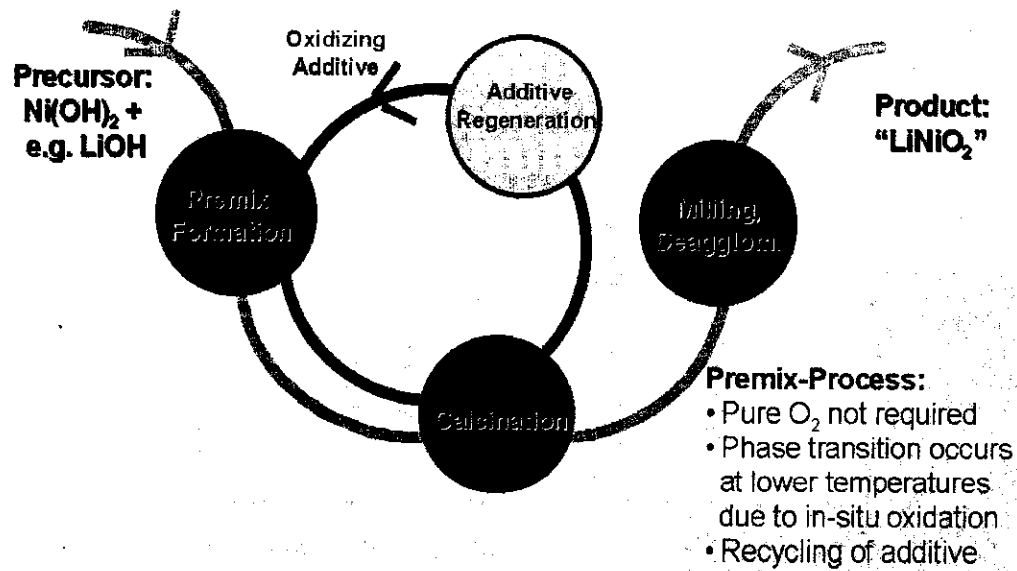
The deagglomeration of the particles is easy and the shape of the product can be controlled.

The Conventional Process

Starting materials are nickel salts like Ni(OH)₂ or NiO in any form and lithium salts like LiOH. These materials are mechanically mixed and calcined in oxygen atmosphere. Calcination temperatures are in the range of 700 to 850 °C and reaction times usually exceed 10h.

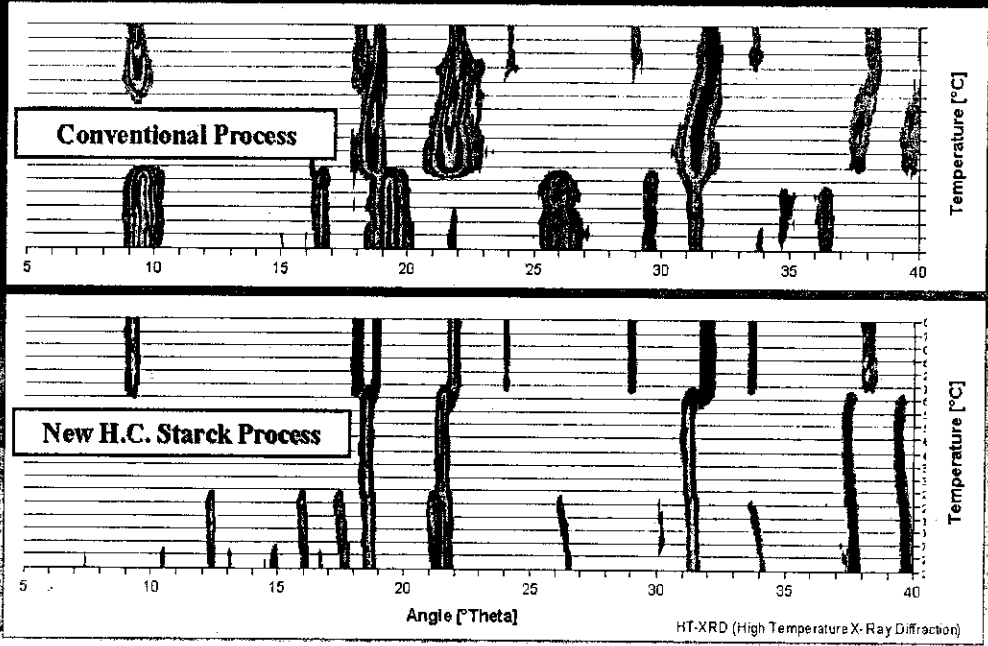


The H.C. Starck Process

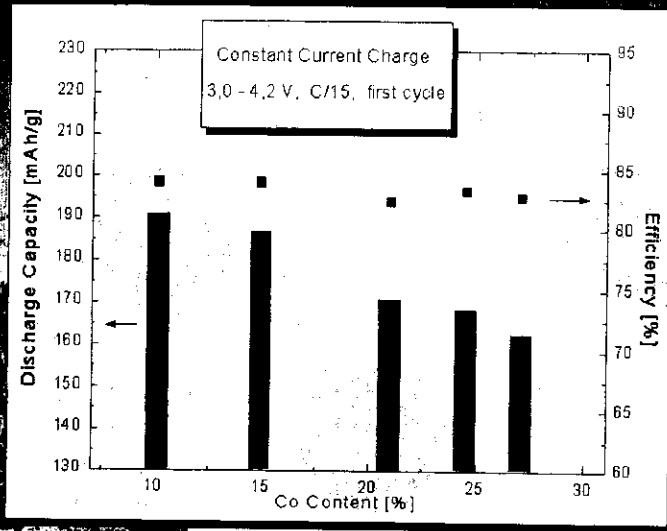




Process Comparison



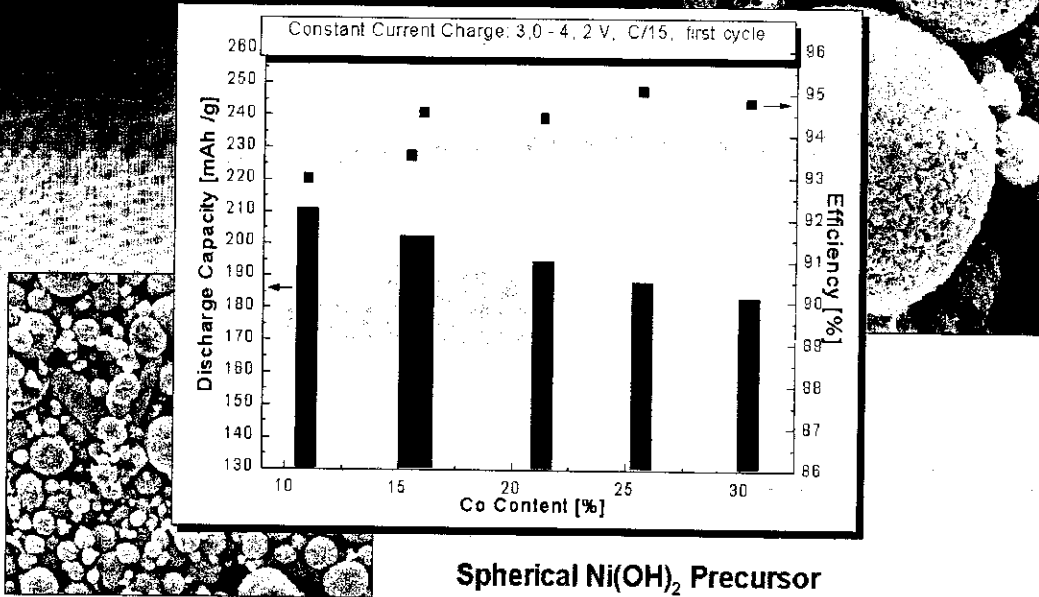
Composition and Electrochemistry (I): Li-Half-Cells



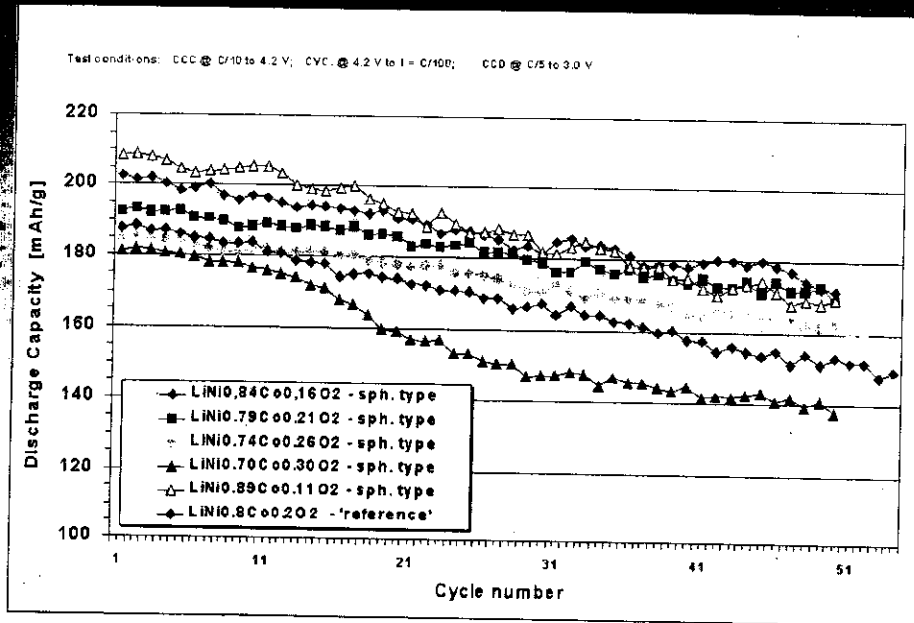
Regular Ni(OH)₂ Precursor



Composition and Electrochemistry (I): Li-Half-Cells

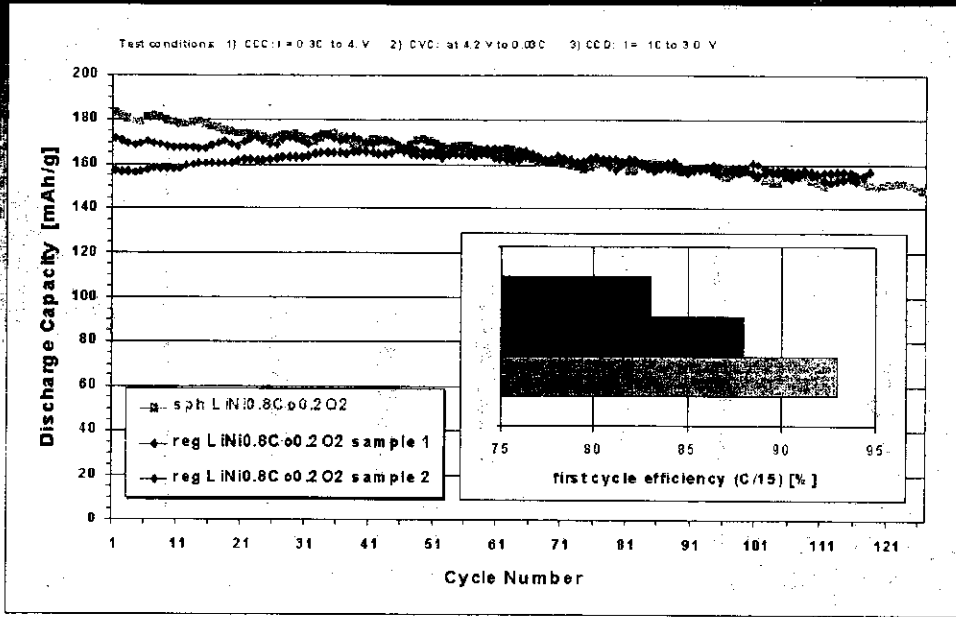


Composition and Cycle Performance: Li-Half-Cells

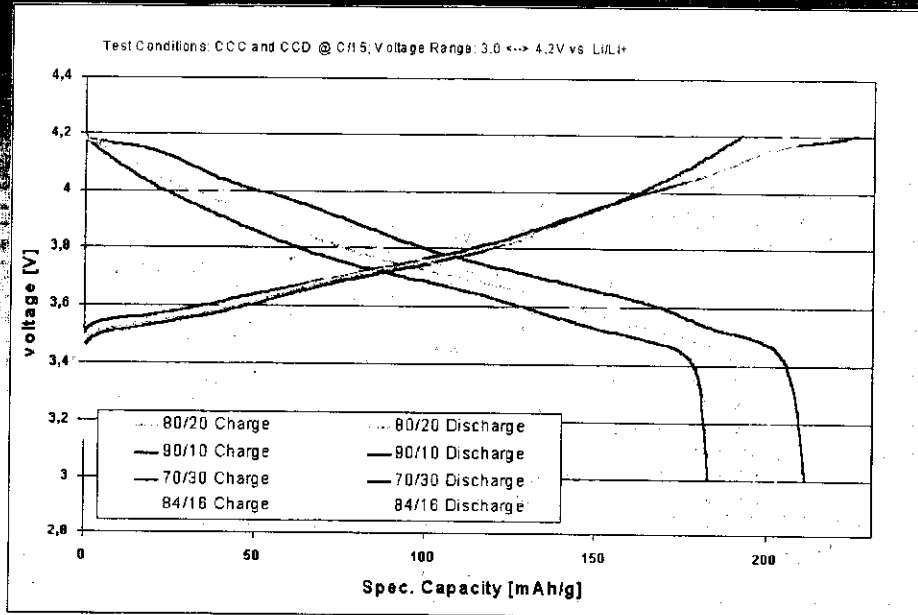




Structure and Cycle Performance: Li-Half-Cells

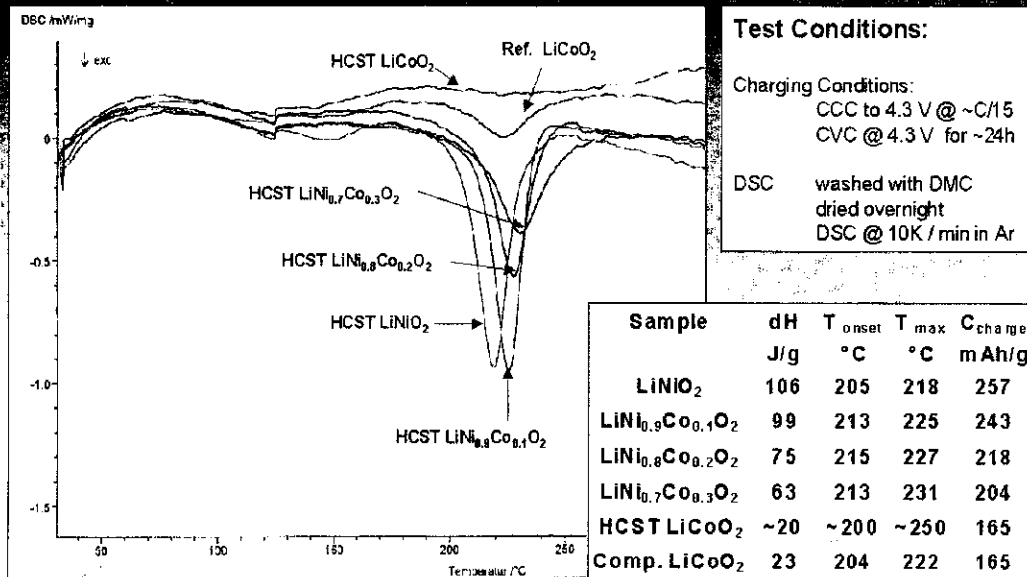


Composition and Electrochemistry: Li-Half-Cells





Thermal Stability: DSC-Comparison LiNiO₂ - LiNi_{1-x}Co_xO₂ - LiCoO₂



Test Conditions:
 Charging Conditions:
 CCC to 4.3 V @ ~C/15
 CVC @ 4.3 V for ~24h
 DSC washed with DMC
 dried overnight
 DSC @ 10K / min in Ar



Conclusion

- A process for the production of well ordered Ni-based cathode materials was developed. LiNiO₂ materials can be produced at moderate reaction temperatures. The reactive premix is directly transformed to the final product at a well defined reaction temperature and without forming intermediate phases.
- Various Co doped LiNiO₂ materials have been produced and the influence of composition and morphology on electrochemical performance and thermal stability was tested.
- LiNi_{1-x}Co_xO₂ materials with low Co-content (<15%) behave similar to pure LiNiO₂ whereas materials with higher Co content show improved cycling performance and thermal stability.
- A comparison of LiCoO₂ showed, that not only the chemical composition has an influence on the thermal stability but also the "particle morphology" which is mainly influenced by the manufacturing process and the process parameters.