# Ni-Based Powders for Rechargeable Batteries

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Outline

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- Nickel Hydroxide for NiMeH and NiCd Batteries
  - Process Comparison
  - Powder Morphology
  - Crystal Structure
  - Electrochemistry
- $LiNi_{1-x}Co_xO_2$ for Li-Ion- / Li-Polymer-Batteries
  - Process Comparison
  - Powder Morphology and Composition
  - Electrochemistry and Safety

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## Ni-Based Powders for Rechargeable Batteries

### A Survey from a Process and Materials Point of View

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H.C. Starck


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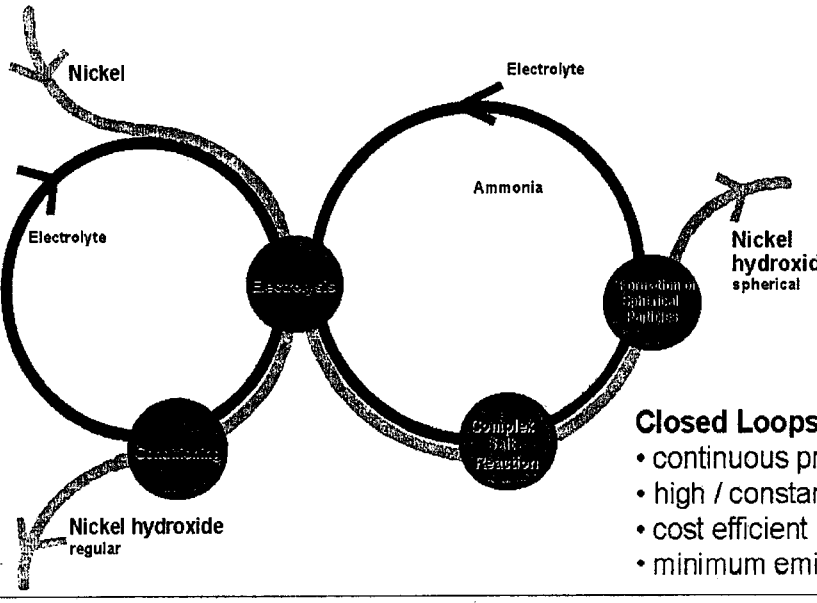
Nickel Hydroxide for NiMeH and NiCd Batteries H.C. Starck

Process Comparison

| ***The HCST Process*** | ***The Conventional Process*** |
|---|---|
| **The Chemistry** | |
| Nickel + Water ---> Nickel Hydroxide + Hydrogen | Nickel + Acids ---> Nickel Salts + Hydrogen<br>Nickel Salts + Caustic Soda ---> Nickel Hydroxide + Neutral Salts |
| 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<br>Minimum waste water and by - products. | Starting material is nickel in any form, dissolved in acids, chemically purified, excess acid need to be neutralized.<br>Nickel salts are precipitated with caustic soda in the presence of ammonia to form spherical nickel hydroxide.<br>Excess caustic is neutralized.<br>Waste water with neutral salts and heavy metals has to be discharged. |

## Nickel Hydroxide for NiMeH and NiCd Batteries H.C. Starck

### The H.C. Starck Process



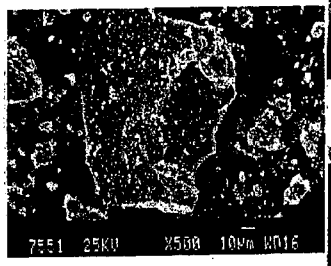

**Closed Loops:**

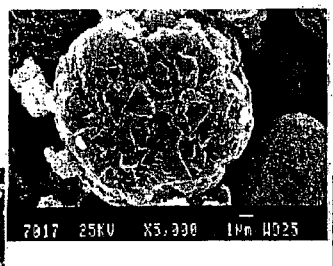
- continuous process
- high / constant quality
- cost efficient
- minimum emission

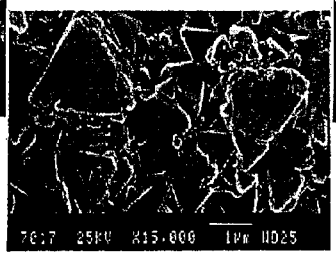
## Nickel Hydroxide for NiMeH and NiCd Batteries H.C. Starck

### Particle Morphology

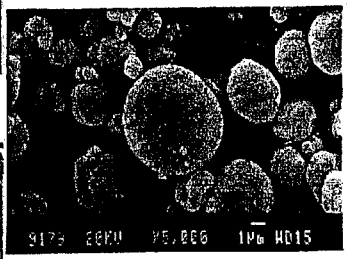
$Ni(OH)_2$ regular





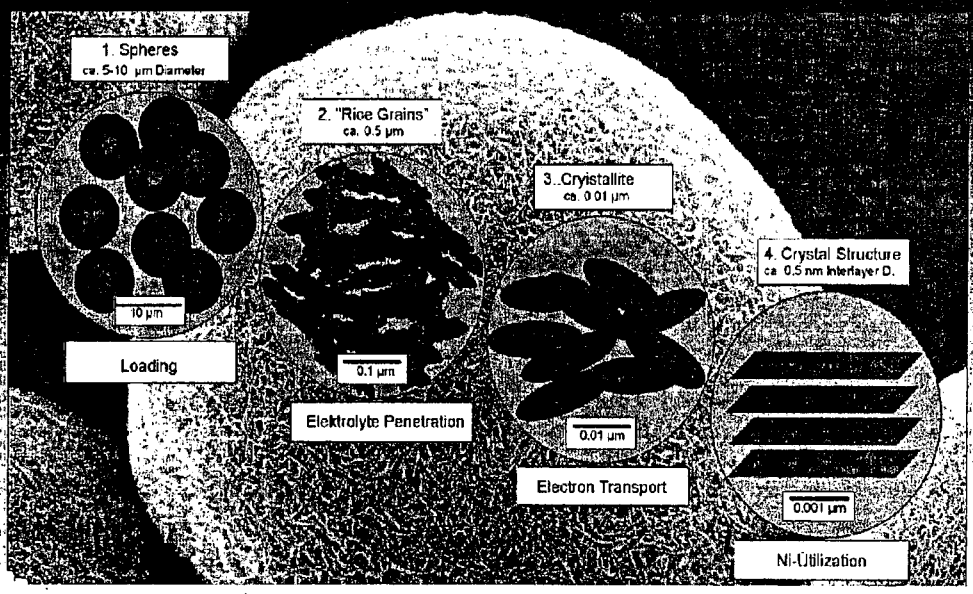


$Ni(OH)_2$ spherical



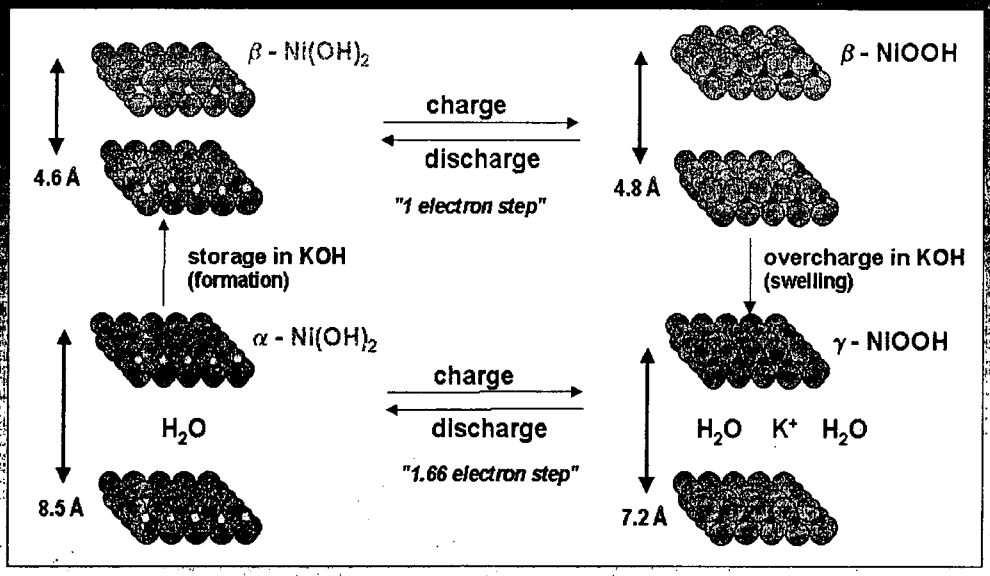
## Nickel Hydroxide for NiMeH and NiCd Batteries H.C. Starck

### 4 Structural Planes of Spherical $Ni(OH)_2$



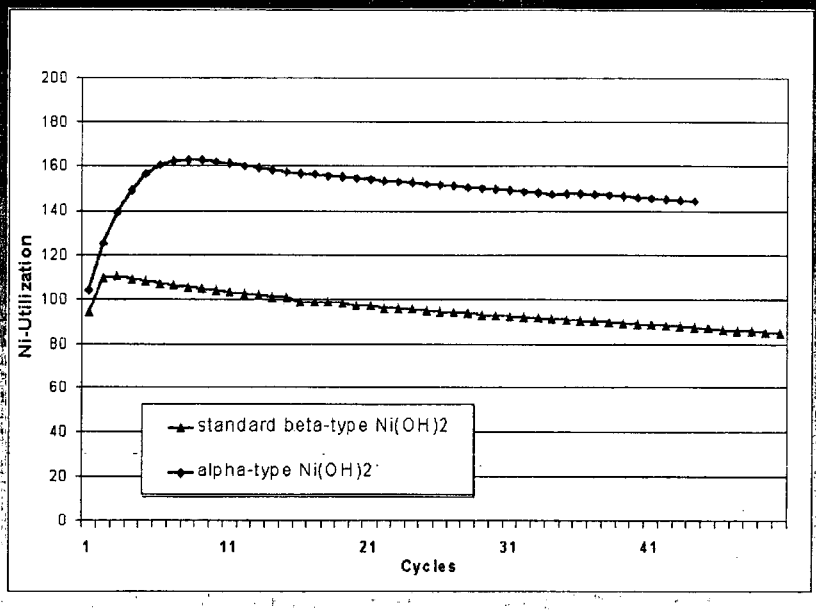

## Nickel Hydroxide for NiMeH and NiCd Batteries H.C. Starck

### Crystal Structure / Bode Diagram



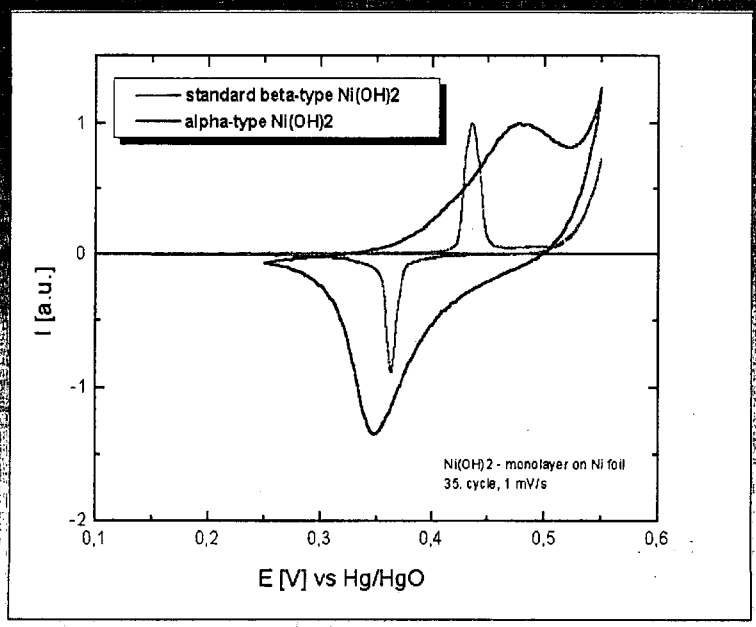
## Nickel Hydroxide for NiMeH and NiCd Batteries H.C. Starck

### Structure and Electrochemistry (I): Flooded cells




## Nickel Hydroxide for NiMeH and NiCd Batteries H.C. Starck

### Structure and Electrochemistry (II): CV



## Conclusion

- A flexible, economical and closed-cycle process for the production of $Ni(OH)_2$ powders has been developed.
- Particle morphology (shape, porosity, crystallinity, ...), as well as chemistry, can be controlled.
- The influence of the different structural planes of $Ni(OH)_2$ powders on the electrochemical performance in batteries was demonstrated.
- The electrochemical performance of different types of $Ni(OH)_2$ materials was presented. Beta type $Ni(OH)_2$ 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

H.C. Starck HCST

- **Nickel Hydroxide for NiMeH and NiCd Batteries**
  - **Process Comparison**
  - **Powder Morphology**
  - **Crystal Structure**
  - **Electrochemistry**
- **$LiNi_{1-x}Co_xO_2$ for Li-Ion / Li-Polymer Batteries**
  - **Process Comparison**
  - **Powder Morphology and Composition**
  - **Electrochemistry and Thermal Stability**

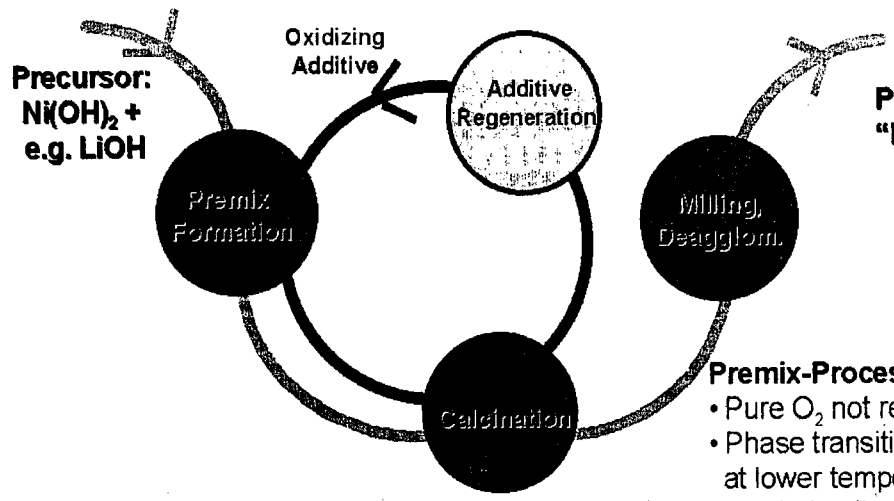
## $LiNi_{1-x}Co_xO_2$ for Li-Ion / Li-Polymer Batteries — H.C. Starck

### Process Comparison

| ***The HCST Process*** | ***The Conventional Process*** |
|---|---|
| The Chemistry | |
| $Ni(OH)_2 + LiOH \xrightarrow[\Delta]{\text{"O"}} LiNiO_2 + 1.5\ H_2O$ | |
| 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. | 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. |

## $LiNi_{1-x}Co_xO_2$ for Li-Ion- / Li-Polymer-Batteries — H.C. Starck

### The H.C. Starck Process

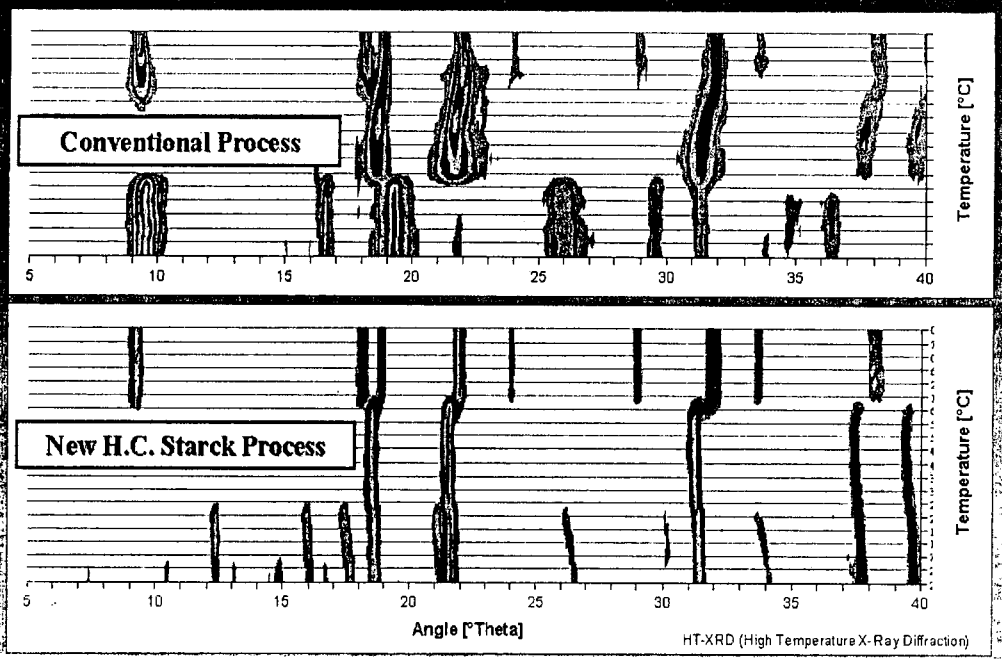



**Premix-Process:**

- Pure $O_2$ not required
- Phase transition occurs at lower temperatures due to in-situ oxidation
- Recycling of additive

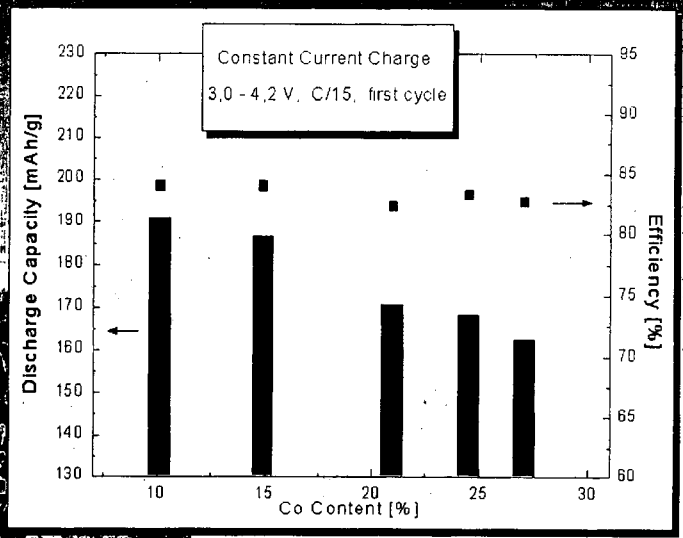
## $LiNi_{1-x}Co_xO_2$ for Li-Ion- / Li-Polymer-Batteries — H.C. Starck

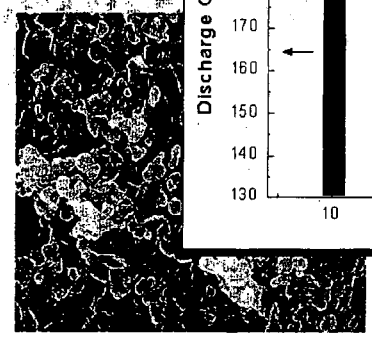
### Process Comparison




## $LiNi_{1-x}Co_xO_2$ for Li-Ion / Li-Polymer Batteries — H.C. Starck

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

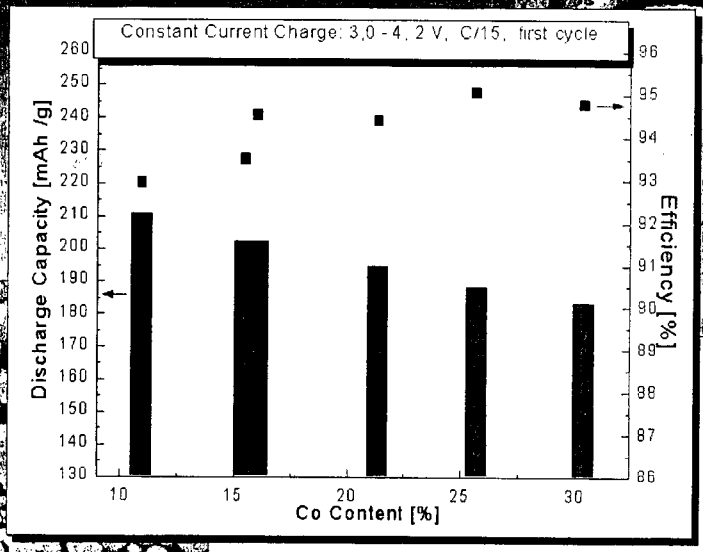


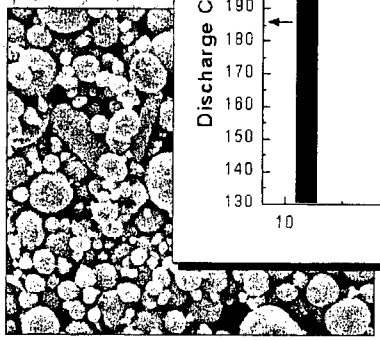



**Regular $Ni(OH)_2$ Precursor**

## $LiNi_{1-x}Co_xO_2$ for Li-Ion / Li-Polymer Batteries — H.C. Starck

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

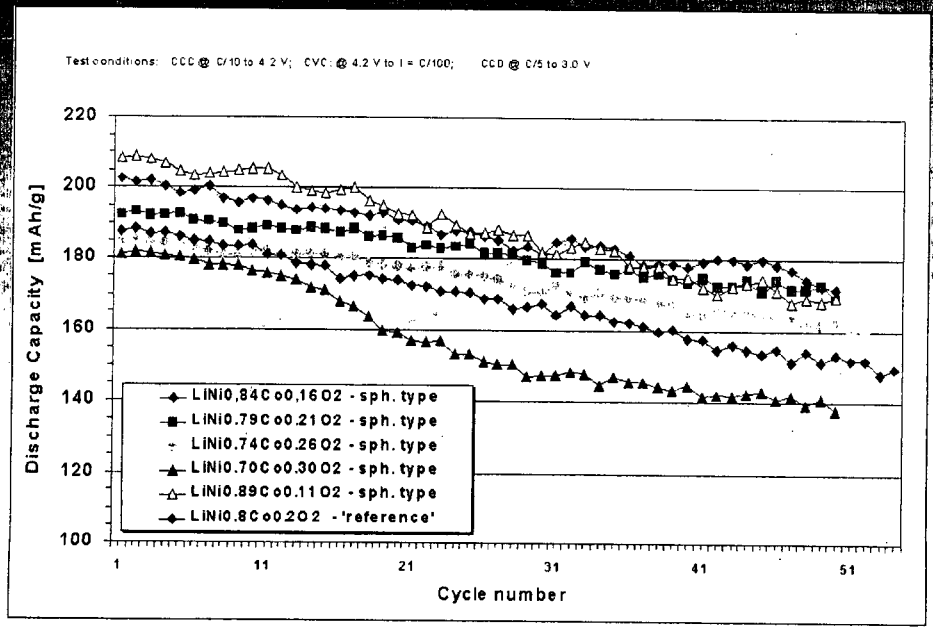


**Spherical $Ni(OH)_2$ Precursor**

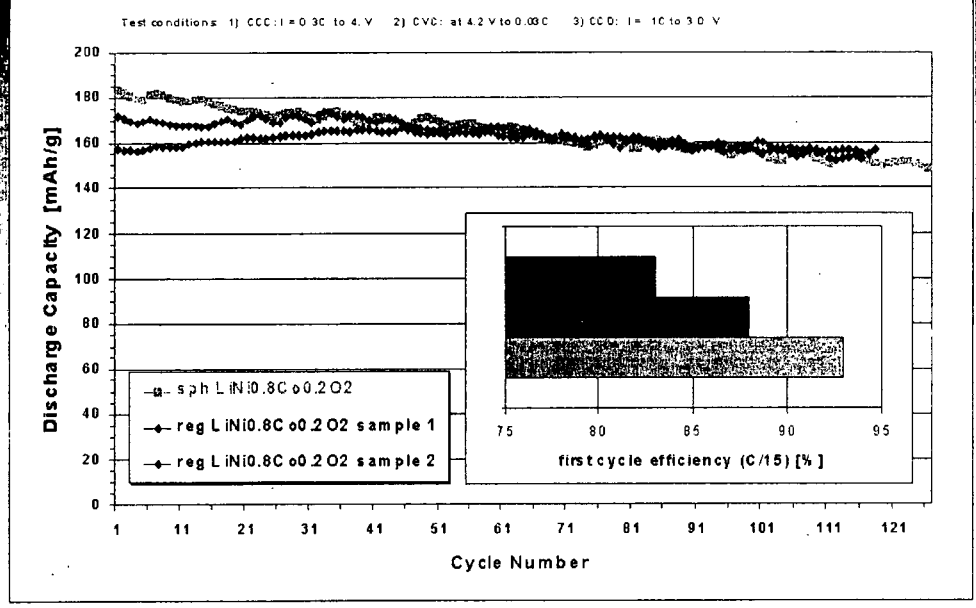
## $LiNi_{1-x}Co_xO_2$ for Li-Ion / Li-Polymer Batteries — H.C. Starck

### Composition and Cycle Performance: Li-Half-Cells



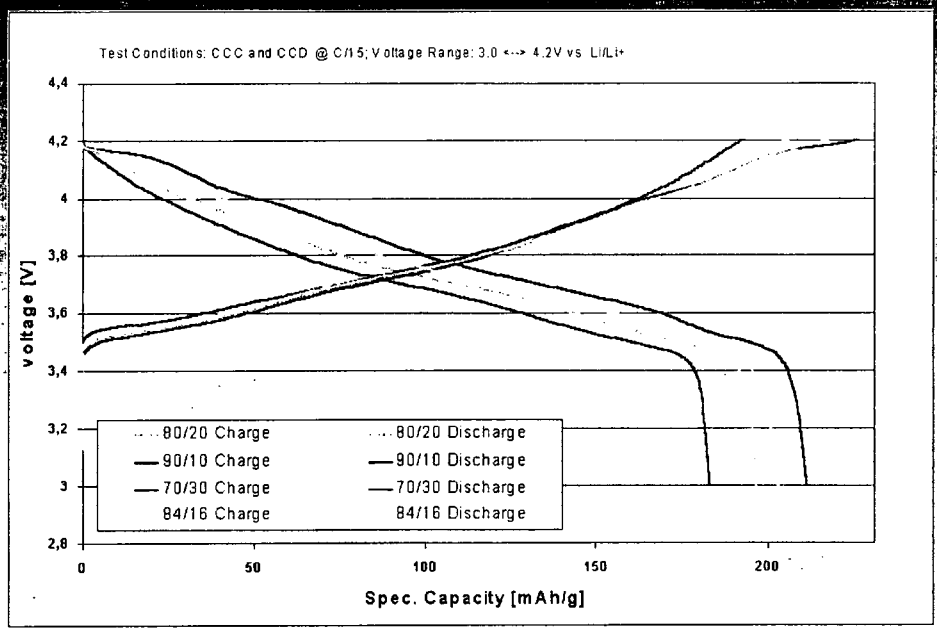
## $LiNi_{1-x}Co_xO_2$ for Li-Ion / Li-Polymer Batteries — H.C. Starck

### Structure and Cycle Performance: Li-Half-Cells



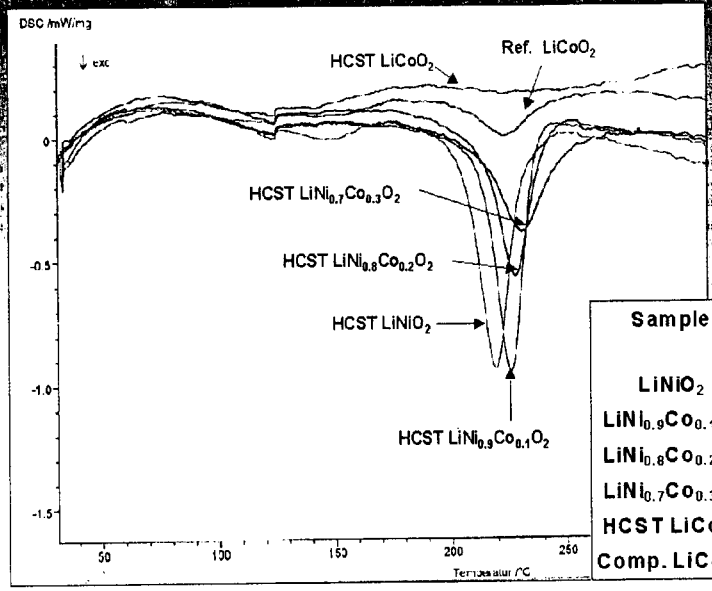

## $LiNi_{1-x}Co_xO_2$ for Li-Ion / Li-Polymer Batteries — H.C. Starck

### Composition and Electrochemistry: Li-Half-Cells



## $LiNi_{1-x}Co_xO_2$ for Li-Ion / Li-Polymer Batteries — H.C. Starck

### Thermal Stability: DSC-Comparison $LiNiO_2$ - $LiNi_{1-x}Co_xO_2$ - $LiCoO_2$




**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

| Sample | dH J/g | $T_{onset}$ °C | $T_{max}$ °C | $C_{charge}$ mAh/g |
|---|---|---|---|---|
| $LiNiO_2$ | 106 | 205 | 218 | 257 |
| $LiNi_{0.9}Co_{0.1}O_2$ | 99 | 213 | 225 | 243 |
| $LiNi_{0.8}Co_{0.2}O_2$ | 75 | 215 | 227 | 218 |
| $LiNi_{0.7}Co_{0.3}O_2$ | 63 | 213 | 231 | 204 |
| HCST $LiCoO_2$ | ~20 | ~200 | ~250 | 165 |
| Comp. $LiCoO_2$ | 23 | 204 | 222 | 165 |

## $LiNi_{1-x}Co_xO_2$ for Li-Ion / Li-Polymer Batteries — H.C. Starck

### Conclusion

- A process for the production of well ordered Ni-based cathode materials was developed. $LiNiO_2$ 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 $LiNiO_2$ materials have been produced and the influence of composition and morphology on electrochemical performance and thermal stability was tested.

- $LiNi_{1-x}Co_xO_2$ materials with low Co-content (<15%) behave similar to pure $LiNiO_2$ whereas materials with higher Co content show improved cycling performance and thermal stability.

- A comparison of $LiCoO_2$ 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.