Lithium Nickel Cobalt Oxides for Use in Lithium Ion Battery Cathodes

Battery Materials
Special and Fine Chemicals
Merck KGaA

1. Introduction

Insertion electrodes are of great interest to battery researchers and electrochemists. Some lithium ion insertion electrodes like $LiNiO_2$ and $LiCoO_2$ show higher operating voltages than the conventional 3 V systems. In today commercial available Li ion batteries typically $LiCoO_2$ is used.

The $LiCoO_2$ - system has some interesting advantages. The preparation of this system is easy to realize and it is a safe system. It shows a good reversibility and in comparison to the $LiNiO_2$- system it has a higher voltage working region because of the Co^{3+} / Co^{4+} redox system. The specific energy of this system is high. On the other hand there are some problems regarding availability and costs of the cobalt raw materials [1,2,3].

The advantage of the Li-Ni-system is that the cell voltage of the Ni-system is smaller. The preparation of this system causes some problems and at a lithium content of < 0.5 lithium per formula unit a structural rearrangement can occur. This irreversible modification of the material is also clearly visible in the electrochemical cell behavior. The system can be described more effective as $Li_{1-z}Ni_{1+z}O_2$, where z is the Ni-ion amount situated in the Li-ion layers [2].

The $LiCoO_2$ - and $LiNiO_2$ - system both show layered structures where the Li - ion is situated in alternate layers on octahedral sites. The metal-oxygen-framework can be described as a 2-dimensional structure. In the interstitial space the lithium mobility is high.
In general the layered MO_2 framework (M = Co, Ni) shows that the c axis of the layered materials expands rapidly on delithiation due to a decrease of the electrostatic binding energy of the lithium-depleted layers. Voltages higher than 4 V occur for low lithium contents and transform this cathode materials into a highly oxidizing state and therefore instable in many of the organic-based electrolytes.
A relationship between the level of operating voltage of transition metal oxides and their d-electron character has been recognized.
The order of operating voltage is approximately :
3d-metal oxides > 4d metal oxides (> sp-metal elements) [1].

The development of an alternative cathode with the advantages of both systems is a promising way. This new system should show a layered structure and as a possible candidate a solid solution of the $LiNiO_2$ and $LiCoO_2$ can be proposed [3-13]. This solid solution $LiCo_{1-x}Ni_xO_2$ with $0 \le x \le 1$ can be prepared in a temperature range of 500 - 1000°C [2,3,4].

Due to the preparation procedure a low-temperature (LT) and a high -temperature-product (HT) can be distinguished [6]. The electrochemical properties of these systems are different and should be adapted to the desired application tasks.

The HT- modification has a rock salt structure and shows a better electrochemical behavior than the pure systems. One disadvantage of this system is that it should be charged above 4 V, particularly at low lithium contents, which is outside the electrochemical stability window of many organic-based electrolytes.
The LT - solid solution Li-Ni-Co-systems (400°C) show a single-phase and a spinel like x-ray-pattern for $0 \leq x \leq 0.2$. In lithium cells the LT-$LiCo_{1-x}Ni_xO_2$ electrodes discharge most of their capacity at voltages approximately 0.5 V lower than the HT- phase electrodes [4]. In that case the electrochemical stability of the LT- phases is better.

Investigations on the mixed Ni-Co-system for batteries at Merck KGaA has been done since 3 years. Several mixtures were investigated and characterized under electrochemical and materials aspects. Solid solutions of Ni-Co systems with increasing Co or Ni content from 0 to 100% were prepared.

2. Preparation and Measurements

Different preparation procedures e.g. solid state reactions or wet chemistry techniques (sol-gel, precipitation reactions, ...) were tested in Merck laboratories to find a reproducible and stable reaction path. The final decision on an up scale ready process for industrial production was made on the base of a solid state reaction.

The characterization of the materials were performed in Merck laboratories to get structural and physical information of the powders (tap density, particle size distribution, specific area, x-ray diffraction, morphological investigations (HRSEM), ...). The special electrochemical battery relevant properties are tested in Merck application labs (capacity test, CV measurements, ac - impedance or dc conductivity measurements, ...).

The specific capacity of the materials is measured in two different cell arrangements. One is in special steel 2016 coin cells from Hohsen Corp. (Japan). Here a half cell versus metallic lithium is prepared using an electrolyte mixture EC/DMC (50:50 wt.%) with 1 molar $LiPF_6$ (1.10379 liquid battery electrolyte LP30 Selectipur from Merck KGaA). The standard charge and discharge rate is C/7 and D/7 respectively. The measured voltage range is from 2,5 V vs. Li/Li^+ to 4.2 V vs. Li/Li^+.
For more detailed investigation an open 3 electrode cell is used in an argon filled glove box. The reference and counter electrode is metallic lithium. The active material is pressed on an aluminum grid.
In both cases the cathode mix is a mixture of active material (85%), carbon black (10%) and PTFE (5%). For capacity measurements typically the constant current mode is used.

The open 3 electrode arrangement and button cells are also used for the slow scan CV investigations.

3. Results

The $LiNi_{0.8}Co_{0.2}O_2$ structure can be identified by XRD measurements. The main phase can be related to $LiNiO_2$ (JCPDS File: 9 - 0063). Possible non intensive $LiCoO_2$ pattern can be observed (JCPDS File: 16-0427). In diagram 1 the XRD patterns with the Cu - Kα and in diagram 2 with the Fe - Kα radiation are shown.
In the Merck lab the standard X-ray source Fe Kα radiation with $\lambda = 1{,}93604$ is used.

Physical data:
The following properties are investigated: tap density, particle size distribution, specific surface area. Typical data are presented in table 1:

Table 1:

Tap density [g/cm^3]	Particle size distribution [µm]			Spec. Surface area [m²/g]
	d10	d 50	d 90	
2.3	2.7	12	21	0.8

Electrochemical Data:

The following electrochemical measurements were performed with the final product.
- Capacity test in coin cells versus lithium at room temperature and 60°C
- Slow scan CV at room temperature

4. Discussion and Conclusions:

The cycling curve of $LiNi_{0.8}Co_{0.2}O_2$ shows two visible plateaus in the charge/discharge diagram (diagram 3). The first plateau can be indicated in the voltage range between 3.7 - 3.8 V vs. Li/Li^+. The second plateau is located at 4.3 V vs. Li/Li^+.

In the pure $LiCoO_2$ there is a plateau at 3.93 V vs. Li/Li^+ and further plateaus at 4.08 V and 4.2 V vs. Li/Li^+. The first plateau can be explained by the fist order transition from $LiCoO_2$ to $Li_{0.8}CoO_2$ and the other plateaus represent the transformation of the hexagonal structure to the monoclinic one [5].
The pure $LiNiO_2$ cathode shows a plateau at 3.8 V and a very weak one at 4 - 4.1 V vs. Li/Li^+.

In our standard $LiNi_{0.8}Co_{0.2}O_2$ material we observe a mixed curve between the pure Co and Ni material. The intercalation and deintercalation process is dominated by the Li-Ni system. This statement is exactly visible in the CV diagram (diagram 4) where the peaks of the solid solution are smoother than those of the pure Ni system. The voltage range is equal.

The constant current cycling results of the solid solution of $LiNi_{0.8}Co_{0.2}O_2$ (1.08750 cathode powder SNC8020 Selectipur form Merck KGaA) can be described as followed:

Room temperature measurements:		60°C measurements in coin cells:	
0.1 mA			
1.Charge capacity:	208 mAh/g	1. Charge capacity:	215 mAh/g
1. Discharge capacity:	196 mAh/g	1. Discharge capacity:	196 mAh/g
3. Charge capacity:	197 mAh/g	3. Charge capacity:	198 mAh/g
3. Discharge capacity:	196 mAh/g	3. Discharge capacity:	195 mAh/g
3 mA			
1. Charge capacity:	181 mAh/g		
1. Discharge capacity:	177 mAh/g		
3. Charge capacity:	177 mAh/g		
3. Discharge capacity:	176 mAh/g		

In diagram 5 the specific capacity at 60°C for 8 cycles is shown.
The total charge capacity loss after 8 cycles can be announced between 10 - 15%. The discharge capacity loss is roughly 5-6 %. The capacity loss per cycle is smaller than 1%.

Long term measurements are still in work. The results will be presented when available.

5. Summary:

Table of properties of cathode powder SNC8020 Selectipur.

Property:	**Typical Data:**
Tap density [g/cm^3]	2,3
Particle size distr.	
d10 [µm]	2,7
d50 [µm]	12
d90 [µm]	21
Specific surface area BET [m²/g]	0,8
Ni to Co ratio	4,0
pH	11,4
Li/(Ni/Co)	1,06
3. Discharge capacity [mAh/g] (0.1mA (RT))	197
3. Charge capacity [mAh/g] (0.1mA (RT))	196

Merck KGaA has already a lot of experience in preparation of mixed oxides with various Ni/Co ratios. Specific battery relevant datas are available for the ratios 100/0, 95/5, 85/15, 80/20, 67/33, 50/50, 33/67, and 0/100. Materials with other ratios are possible to investigate and to prepare using the already established pilot equipment up to several hundred kilograms.

In addition to these established procedures and materials showing the typical values of standard products, customer specific developments are welcome. Variation of particle size distribution for special fit to different electrode processing, variation of specific surface area and also multi doping is possible using the know how and equipment of a 300 year old pharmaceutical/chemical company producing more than 20.000 products from milligrams to thousands of metric tons.

Other cathode materials for lithium ion batteries available from Merck KGaA are manganese based oxides, nickel oxides and cobalt oxides.

Cooperation on battery materials with:

- Technical University Darmstadt, Germany;
- University Regensburg, Germany;
- University Duisburg, Germany;
- Center for Solar Energy and Hydrogen Research, Germany;
- Bar Ilan University, Israel;

Funded Research Cooperation:

Funded by the BMBF, Germany:	Materials for Lithium Ion Batteries with Liquid Electrolytes
Funded by the EC, Brussels:	Lithium Carbon Liquid Electrolyte Batteries (Performance Improvements and Cost Reduction)

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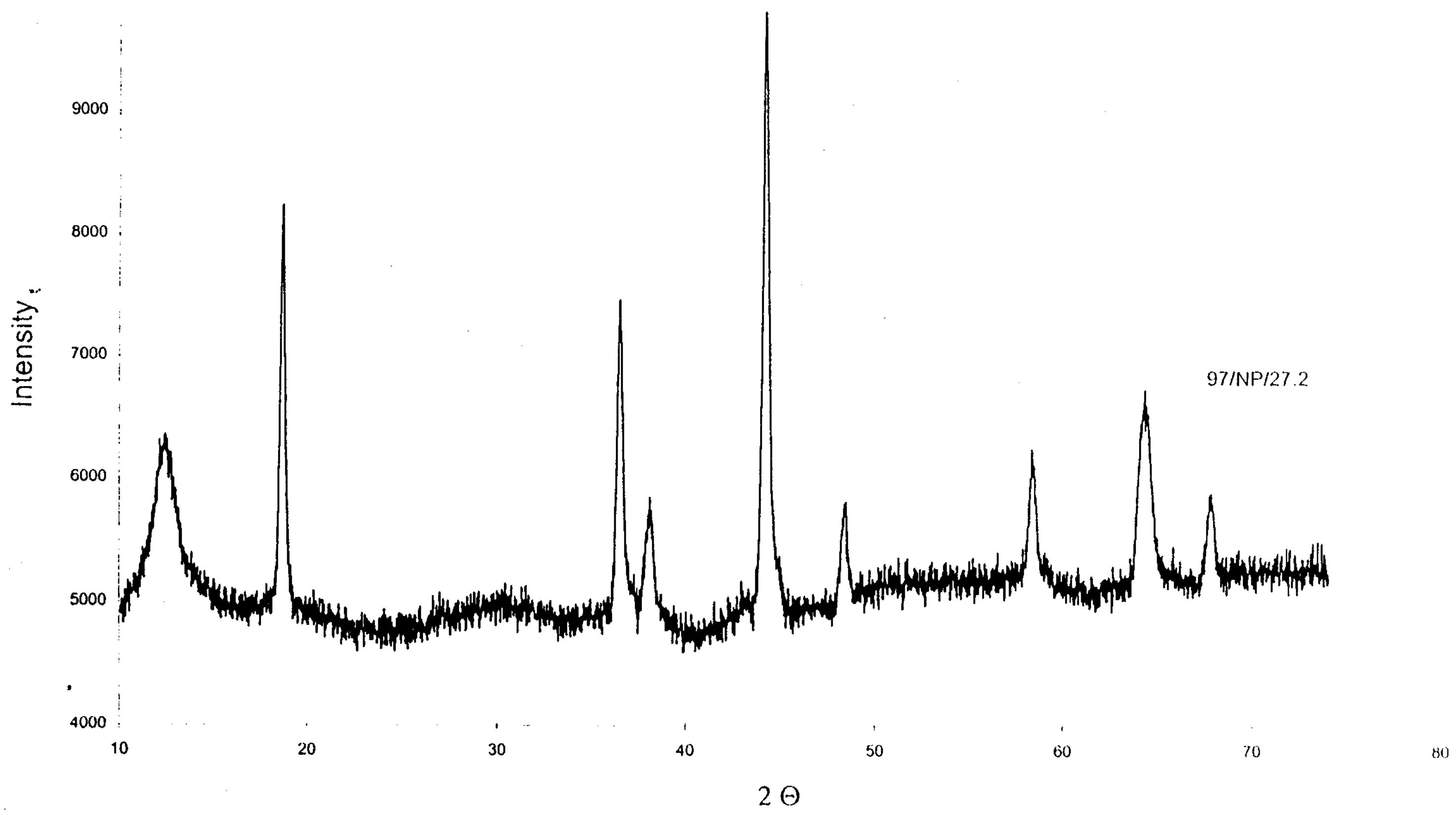

XRD Data of $LiNi_{0.8}Co_{0.2}O_2$ with Cu Kα radiation

Applikationslabor
Dr.L.Heider
19.08.1997

Diagram 1: XRD diagram of $LiNi_{0.8}Co_{0.2}O_2$

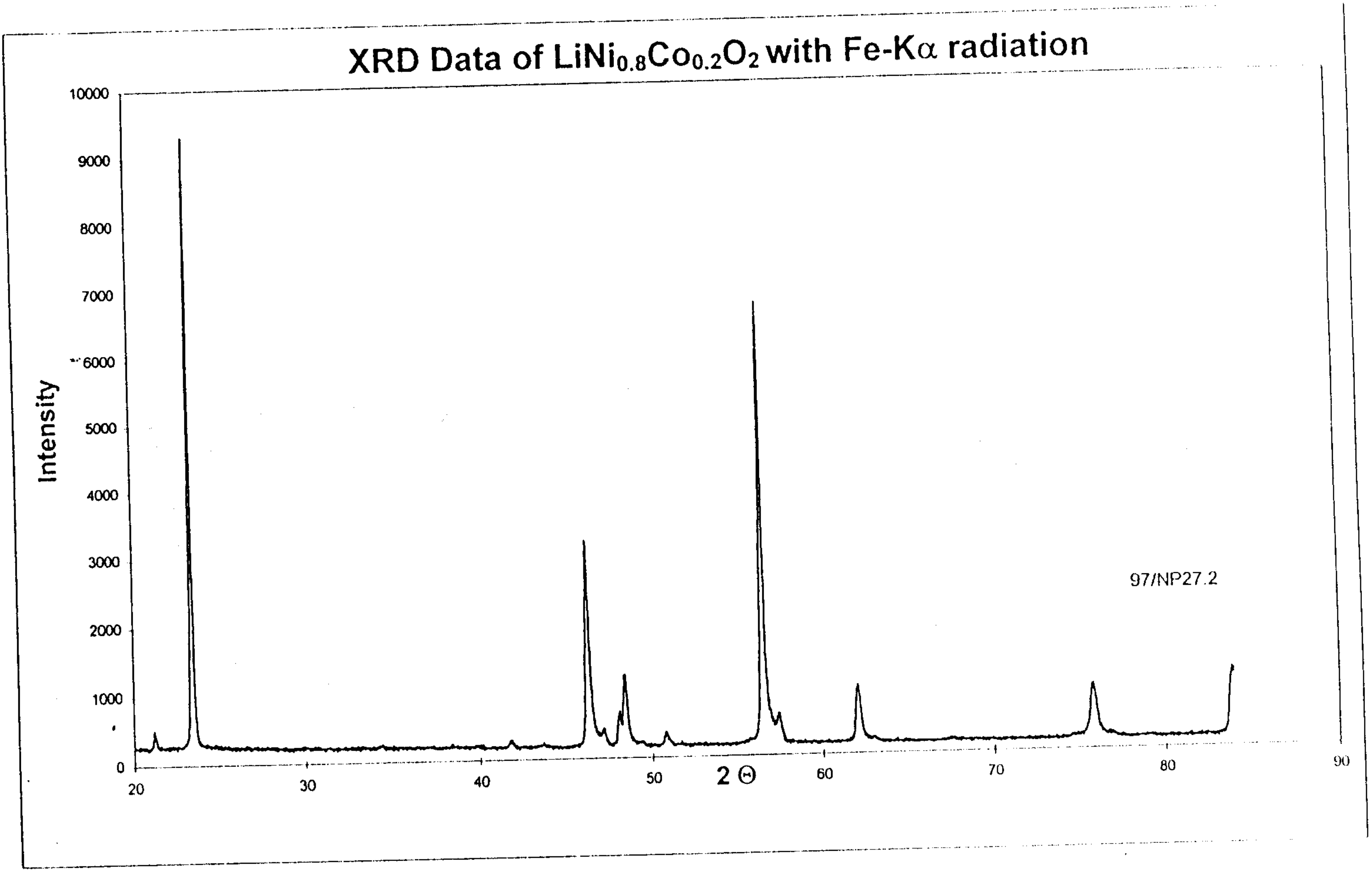

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Diagram 2: XRD diagram of $LiNi_{0.8}Co_{0.2}O_2$

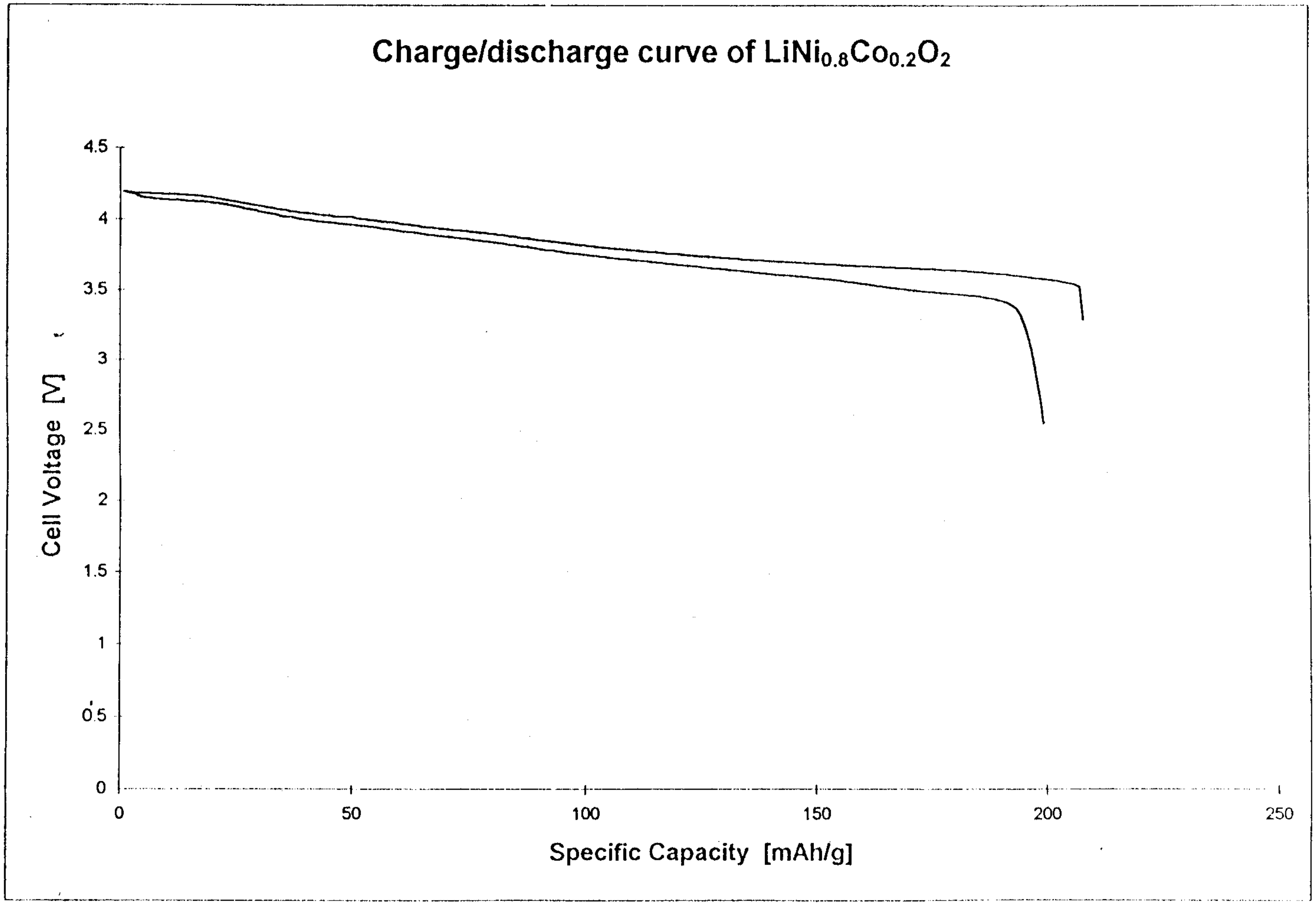

Diagram 3: Cycle curve versus capacity of $LiNi_{0.8}Co_{0.2}O_2$

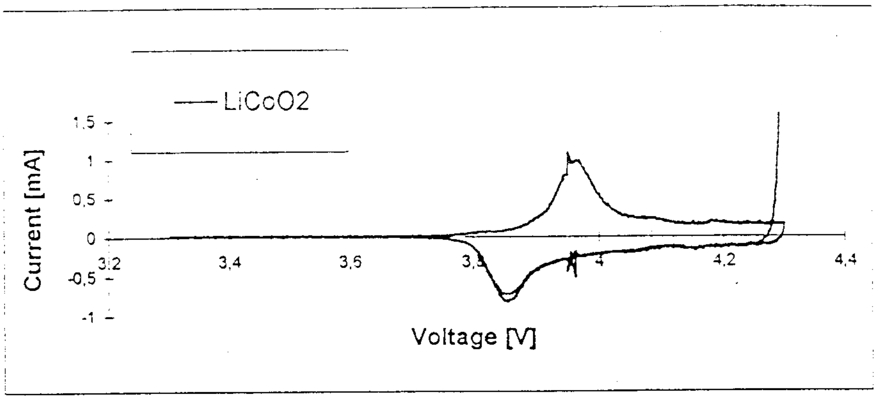

Diagram 4a: CV of $LiCoO_2$

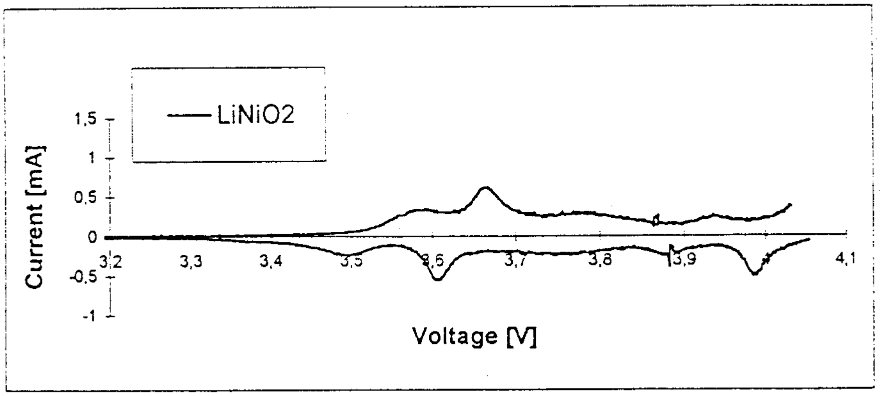

Diagram 4b: CV of $LiNiO_2$

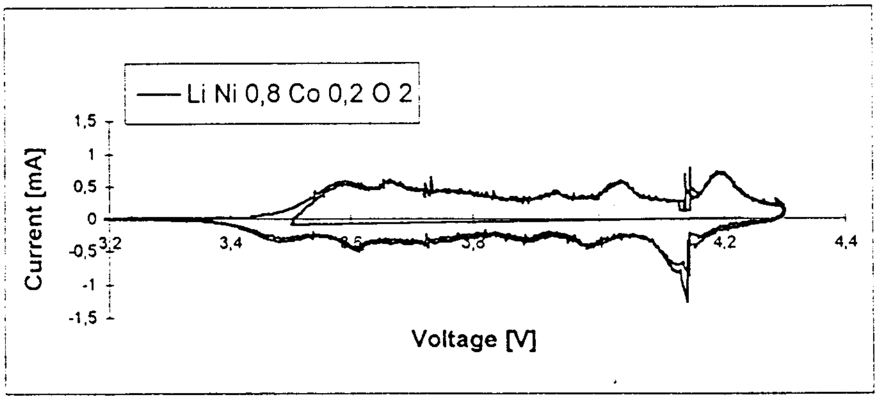

Diagram 4c: CV of $LiNi_{0.8}Co_{0.2}O_2$

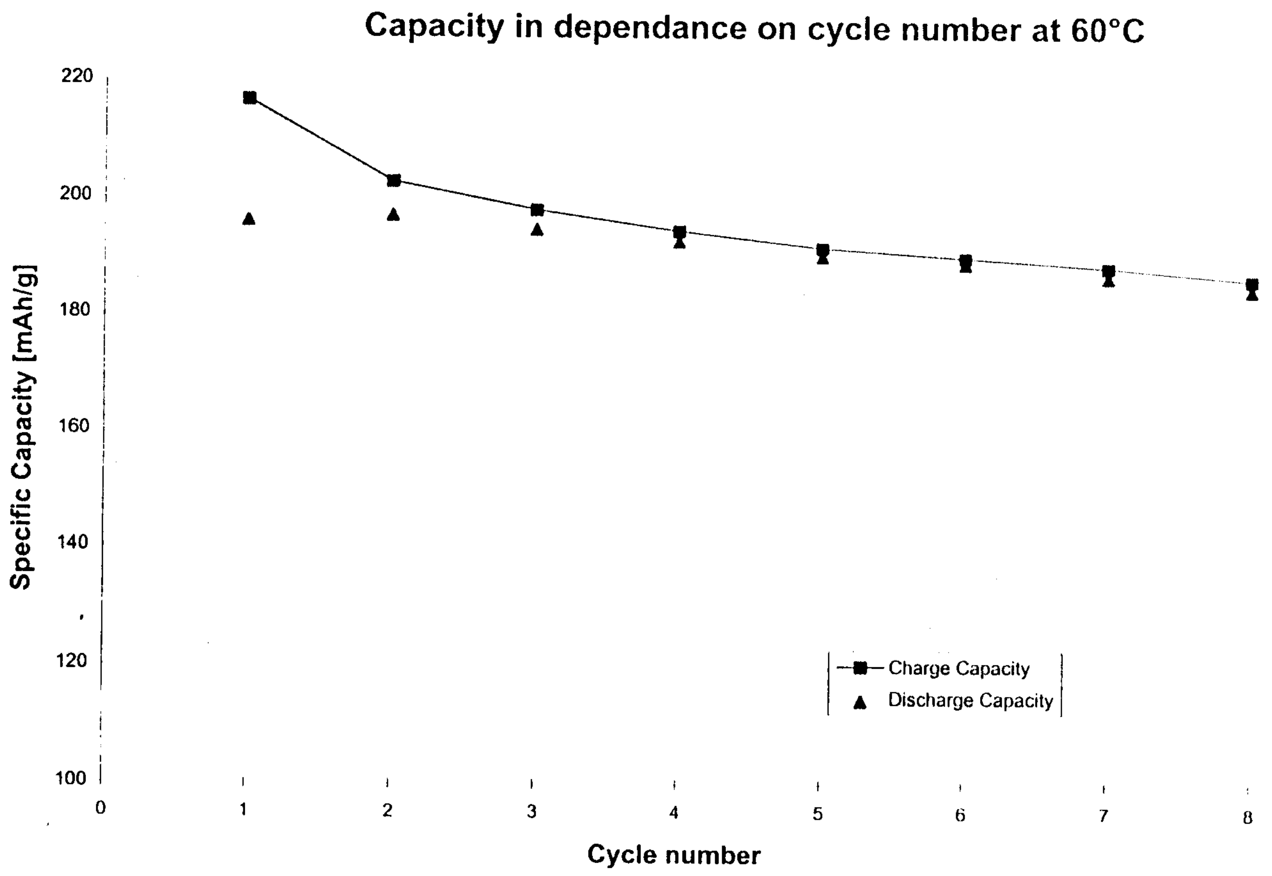

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Diagram 5: Capacity versus cycle number at 60°C of $LiNi_{0.8}Co_{0.2}O_2$