

## ORIGINAL PAPER

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## Intercalation materials for lithium rechargeable batteries

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**Abstract** An overview is given of intercalation materials for both the negative and the positive electrodes of lithium batteries, including the results of our own research. As well as lithium metal as a negative electrode, we consider insertion materials based on aluminium alloys. In the case of the positive electrode metal-oxides based on manganese, nickel and cobalt are discussed.

**Key words** Intercalation materials · Lithium battery

### Introduction

The realization of rechargeable lithium batteries with sufficient capacity requires an improvement in the cycleability of the negative and the positive electrodes. However, using lithium in secondary batteries is not without problems. High energy densities could only be observed in secondary batteries with pure lithium as the anode material. During charging, lithium is often deposited in a dendritic form.

A possibility for improving the cycleability of lithium batteries is the “swing” concept or the “lithium ion battery” concept.

This type of intercalation battery demands excellent host materials for the insertion/reinsertion of lithium and lithium ions. For the negative electrode, intercalation materials based on carbon or lithium alloys are used and for the positive electrode metal oxides, lithium spinels in particular, have been recommended.

### Anode materials

#### Metallic lithium

Lithium is a most reactive metal. It reacts immediately and irreversibly with many organic and inorganic solvents and electrolytes with formation of an inhomogeneous surface layer [1–8]. In electrolyte solutions it is generally recognized that the composition of the electrolyte solution determines the composition of the layer on the top of the lithium electrode [9, 10]. The existence of this “passivating” layer is the prerequisite for the use of lithium in battery systems. If we speak about the “passivity” of lithium we are referring to a kinetically hindered system. From a thermodynamic point of view, the lithium system is not stable.

Electrochemical *in situ* techniques such as impedance measurements or potentiostatic or galvanostatic transients combined with optical and surface analytical methods have been used to investigate the behaviour of the phase boundary lithium/electrolyte. It was found by FTIR, IR, XPS, SIMS, Raman and X-ray measurements [11–17] that, for instance, lithium in contact with propylene carbonate (PC) electrolytes forms a surface layer of decomposition products of the solvent and the anion of the electrolyte. Lithium alkylcarbonates have been detected as the main component of the layer. In the presence of traces of water, the alkylcarbonates react to form lithium carbonate, alcohol and carbon dioxide. It was found by electrochemical *in situ* techniques [18] that the surface layer is formed instantly upon contact of the metal with the solution. This means that metallic lithium also reacts with the anions of the electrolyte and traces of other components (such as H<sub>2</sub>O, O<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>O, N<sub>2</sub> etc.) forming many decomposition products [19–24].

The thickness of the freshly formed layer is determined by the electron-tunnelling range and changes with time. This layer acts as an interphase between the metal and the solution and has the properties of a solid electrolyte, with high electronic resistivity.

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Most of the investigations to improve the reversibility of the lithium electrode during cycling have been done by the trial and error principle. This means that proven concepts derived from electroplating (influence of inhibitors and other additives on the metal dissolution and deposition processes) have been transferred from the interacting system metal  $\leftrightarrow$  water to the interacting system lithium  $\leftrightarrow$  aprotic solvent, in the hope that the kinetics of lithium dissolution and deposition processes can be influenced positively in terms of long-term reversibility. According to our knowledge [25, 26], these concepts are doomed to failure for the following reasons:

- The reactive interaction between lithium and the solvent or the anion of the electrolyte leads to an irreversible formation of a surface layer in a time less than 100 ms.
- The solvent molecule and the electrolyte anion are decomposed by metallic lithium at different potentials and/or at different velocities.
- The reaction products exhibit inhomogeneity with respect to their chemical composition.
- The “passive” layer therefore shows many regions with variations in the electronic and ionic conductivity, causing a variation in the local layer thickness. These regions are the places where dendrites of metallic lithium are forming and growing.

#### Lithium insertion materials

The cycleability of the lithium electrode can be improved by the use of lithium-inserting substrates. The most common materials are lithium-carbon and lithium-aluminium. Other suitable alloying substrates are Sn, Pb, Bi, Sb, As and others.

The anodes based on LiAl alloys can be cycled up to 1000 times, depending on the cycling conditions. One should emphasize that the depth of discharge (DOD) reaches only 1–10% of that of the comparable primary lithium batteries.

Using substrate-forming alloys or intercalation compounds with lithium, the reactivity towards the electrolyte or the solvent can be decreased. Therefore, the lithium in the host material will be “shielded” and the formation of dendrites will be reduced or avoided if the diffusion velocity inside the host material is high enough. However, a potential shift occurs and leads to a decrease in the energy and power density. For some purposes, the increase in cycleability compensates for these disadvantages.

The diffusion of lithium in the alloy matrix determines the charge/discharge rate of the battery and limits its use as a low or high rate cell. The diffusion process itself is determined by the nature of the host material and its morphology.

The main problems of lithium alloy electrodes are connected with the significant differences in volume between the pure basic material and the lithium alloy

formed. Therefore, during cycling, mechanical stress and cracks are induced by these volume differences (LiAl 96.8% [27] in relation to the host lattice). In the case of carbon, the volume difference during the formation of  $\text{LiC}_6$  is only 9.4% [28]. Carbon has therefore been the most favoured host material in recent years.

#### Insertion into carbon

Carbon is a low-cost material for the battery industry. Many different kinds of carbonaceous materials have been developed, such as graphite, coke or carbon fibre materials [29]. Due to its layered structure, carbon can insert into lithium according to the following scheme



with  $0 < x \leq 1$ .

The higher the lithium content the lower is the potential of the carbon electrode (Fig. 1). Similar results are published in [30].

With increasing  $x$ , the potential approaches that of metallic lithium. This is another reason for choosing carbon as favoured host material.

During the first lithium uptake, an irreversible loss of capacity occurs. A surface layer similar to the layer formed on lithium is formed [31, 32]. After some cycles, a reversible response of the  $\text{Li}_x\text{C}_6$  electrode is observed (Fig. 2).

The kinetics of the electrochemical process are controlled by the diffusion of the lithium ion inside the host material. The measured chemical diffusion coefficient is in the order of  $D_{\text{Li}} = 10^{-9} \text{ cm}^2 \text{ s}^{-1}$  [33]. The specific capacity of the  $\text{Li}_x\text{C}_6$  electrode is 0.186 Ah/g ( $x = 0.5$ ). Compared to metallic lithium (3.86 Ah/g), it is lower by more than one order of magnitude.

Nevertheless, the disadvantages of metallic lithium during cycling can be avoided. However, it should be mentioned that all alloying materials (carbon, metals) have not as yet shown the high-energy-density properties

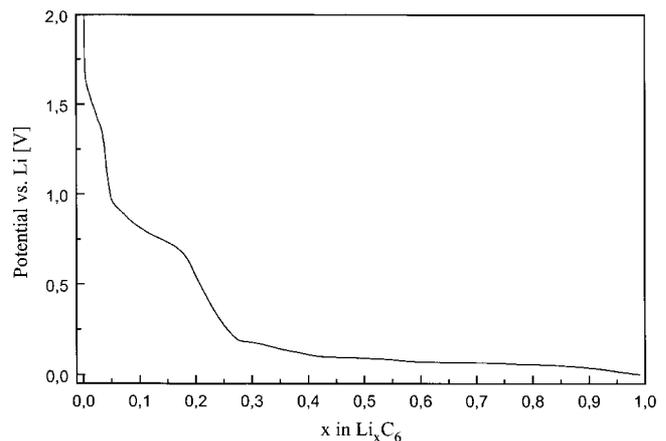
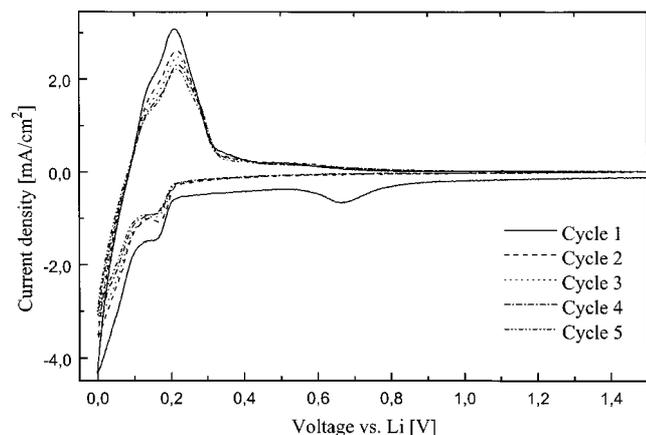


Fig. 1 The potential of an  $\text{Li}_x\text{C}_6$  electrode as a function of the composition

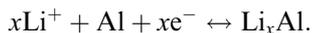


**Fig. 2** Cyclic voltammograms of an  $\text{Li}_x\text{C}_6$  electrode (graphite material) in propylene carbonate – 1 M  $\text{LiClO}_4$  electrolyte (sweep rate 0.1 mV/s)

that have been displayed by batteries based on lithium metal.

#### Insertion into aluminium alloys

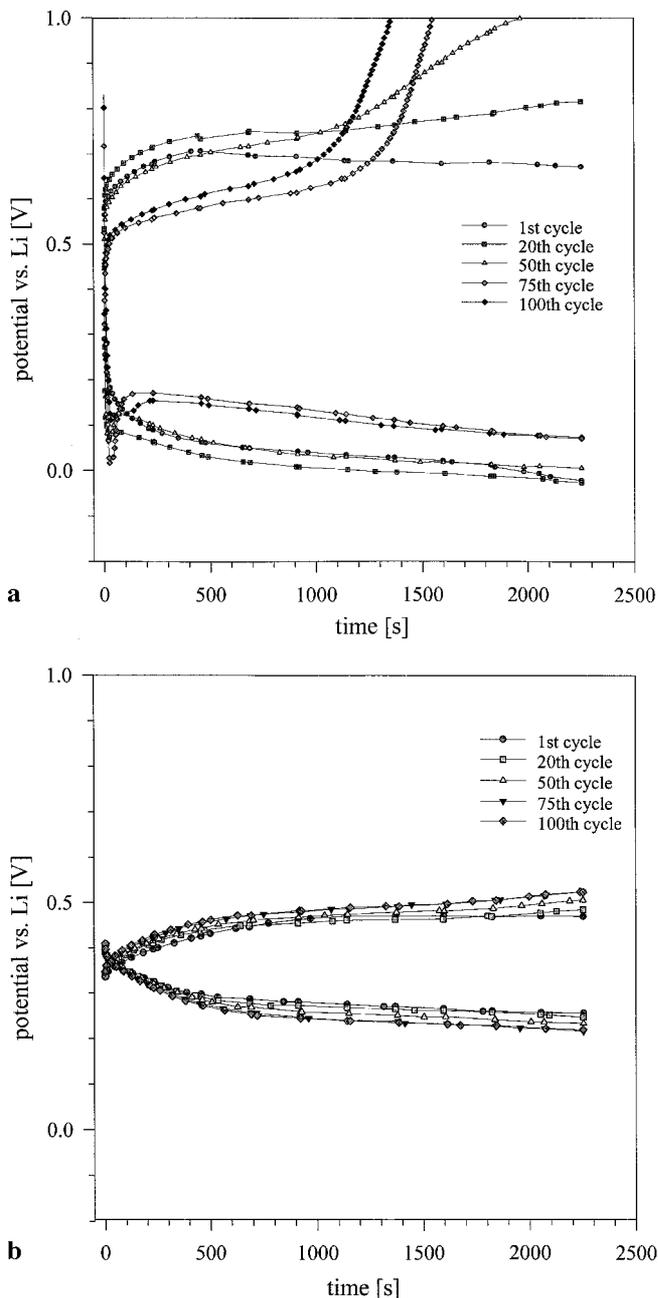
Alloys have been under investigation since Dey in 1971 [34] demonstrated the possibility of electrochemical alloying with lithium in organic electrolytes. The use of alloys as the negative electrode is based on the reversible insertion of lithium into the host material in accordance with the reaction



Anodes of this alloy can be cycled many times without side reactions such as the rapid decomposition of the organic electrolyte or dendrite formation. However, the anode is covered by a fairly stable, thin, passivating layer [35].

As in the case of lithium, the structure of the thin passivating surface layer is also strongly influenced by the composition of the electrolyte solution. Many researchers described the positive effect obtained by adding small amounts of organic or inorganic compounds.

Recently, we studied the effect of dilithium phthalocyanine on cycling efficiency, cycle life and corrosion behaviour of different anodes in 1 M  $\text{LiClO}_4$  – propylene carbonate solution [36]. It was shown by electrochemical impedance spectroscopy and current-potential measurements that the addition of dilithium phthalocyanine reduces the thickness of the surface layer. Probably, the freshly deposited lithium is either not as reactive or a modified film with enhanced migration properties for lithium ions is growing. In the case of lithium-aluminium alloy anodes, the addition of dilithium phthalocyanine has a positive influence on long term cycling (Fig. 3). In the electrolyte without additive, “normal” behaviour of the aluminium electrode is observed.



**Fig. 3a, b** Cycling behaviour of an Al substrate in propylene carbonate – 1 M  $\text{LiClO}_4$  solution, **a** without additive and **b** with addition of  $10^{-2}$  M  $\text{Li}_2$ -phthalocyanine

In the absence of an additive, the overvoltage increases during cycling because of hindered lithium transport through the surface film formed. After about 80 cycles, the lithium transfer is blocked and the aluminium electrode stops working as an insertion material. In the electrolyte with an additive, a modified surface film is obviously growing on top of the aluminium surface. This film shows no changes in its properties, but a small overvoltage is observed during subsequent cycling. The layer is not a hindrance to the transfer of lithium in the aluminium host material. It seems that the

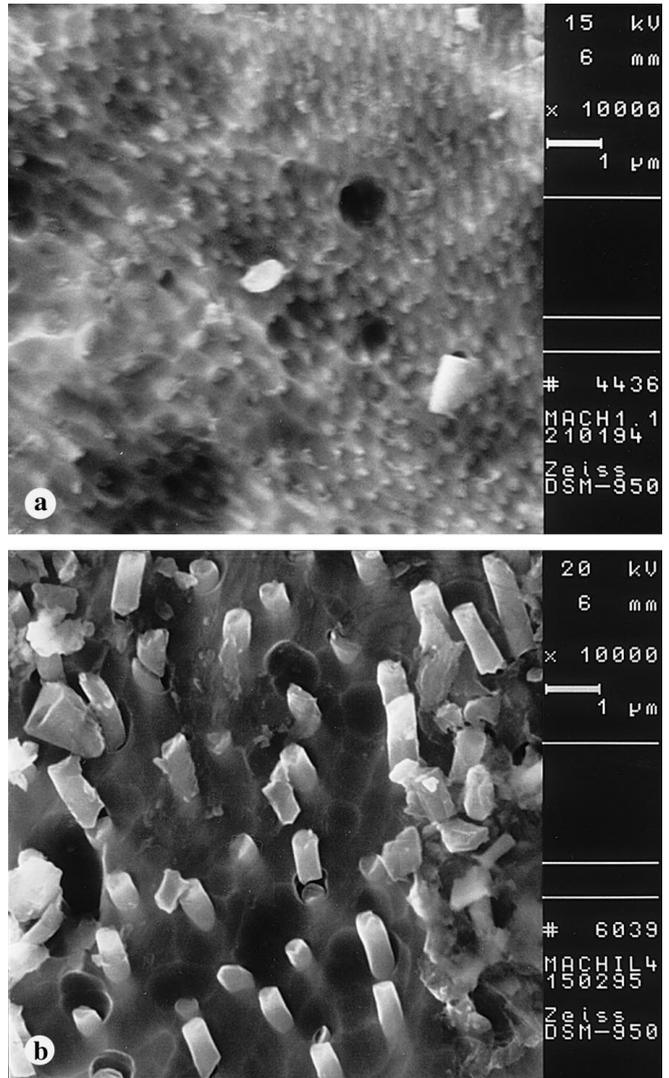
combination of lithium alloys and dilithium phthalocyanine gives a synergetic improvement in the lithium cycleability.

The change in volume due to changes in the morphology of LiAl and other  $\text{Li}_x\text{Me}$  alloys (Me = metal) is the central problem in the development of rechargeable negative electrodes for lithium cycling. Attempts have been made to avoid this problem by creating “dimension-stable” alloying electrodes in that way that (1) small particles of the active phase of  $\text{Li}_x\text{Me}$  are embedded in a stabilizing matrix [37, 38] or (2) the aluminium host has previously formed an alloy with other metals that are soluble in aluminium or form intermetallic compounds with it, but do not form alloys with lithium, e.g., nickel. In this way one creates an alloy matrix of modified grain size with stabilizing properties towards “mechanical stressing” during charge/discharge processes of lithium [39, 40].

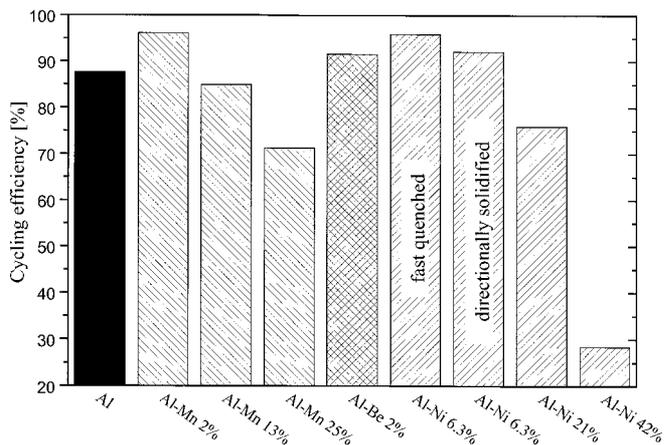
Therefore, the suitability of different binary Al-Ni, Al-Mn and Al-Be alloys as anode substrates in rechargeable lithium batteries has been tested, comparing these with pure aluminium. The changed composition on alloying aluminium with a second metal does dramatically influence the mechanical properties and the electrochemical behaviour. On the other hand, the electrochemical properties of these substrates are also determined by the macro- and microstructure. In particular, the eutectic mixture of Al-Ni (Al/ $\text{Al}_3\text{Ni}$ ) seems to be an interesting substrate material in rechargeable lithium batteries. The  $\text{Al}_3\text{Ni}$ -phase does not form an alloy with lithium and acts only in the improvement of the mechanical stability. The second phase of pure aluminium can receive the incorporated lithium. We investigated various forms of this eutectic mixture. By fast quenching one gets very finely spread segregations of the  $\text{Al}_3\text{Ni}$  phase (Fig. 4a). A direct heat flow (vertical Bridgeman method) leads to a directionally solidified rodlike Al- $\text{Al}_3\text{Ni}$  eutectic (Fig. 4b). This directionally solidified eutectic consists of an Al matrix containing faceted  $\text{Al}_3\text{Ni}$  rods grown into it nearly parallel to each other and in the direction of heat flow.

The diffusion coefficient of lithium in the aluminium host was estimated to be  $10^{-12} \text{ cm}^2 \text{ s}^{-1}$  in the  $\alpha\text{-AlLi}$  phase and  $4 \dots 8 \cdot 10^{-10} \text{ cm}^2 \text{ s}^{-1}$  in the  $\beta\text{-AlLi}$ -Phase [41]. It was found that lithium shows the highest mobility in the strongly disordered eutectic mixture, probably due to an increased number of grain boundaries.

The usefulness of a new anode material can be examined only under real conditions. The consumer is interested in the maximum number of charge/discharge cycles with the highest possible power density. Figure 3a presents a set of typical cycling curves of an aluminium substrate. The cycling efficiency was estimated to be 88% under the used conditions (DOD: 10%). The reversible behaviour is lost for cycle numbers much larger than 100. Comparable curves were obtained with the other substrates. With increasing content of manganese or nickel, the cycling efficiency decreases dramatically (Fig. 5).



**Fig. 4a, b** SEM pictures of Al-Ni (6.3 mass %) eutectic mixtures, **a** fast quenched and **b** directionally solidified by a vertical Bridgeman method ( $R = 50 \text{ mm/h}$ ), transversely cut



**Fig. 5** Average cycling efficiency of various substrates (composition in mass %)

## Cathode materials

### Lithium-manganese oxides

Manganese dioxide is an interesting material for battery applications. In principle it is suitable for the intercalation of small ions ( $H^+$ ,  $Li^+$ ), and it is also inexpensive, non-polluting and readily available. It occurs in various modifications, among which the most used for industrial purposes is  $\gamma$ - $MnO_2$ , which can be synthesized either chemically (CMD- $MnO_2$ ) or electrochemically (EMD- $MnO_2$ ).

This oxide is characterized by a tunnel structure formed by an alternating arrangement of two double chains and one single chain of  $MnO_6$  octahedrons. The reversibility of the lithium intercalation into  $MnO_2$  depends on the degree of discharge.

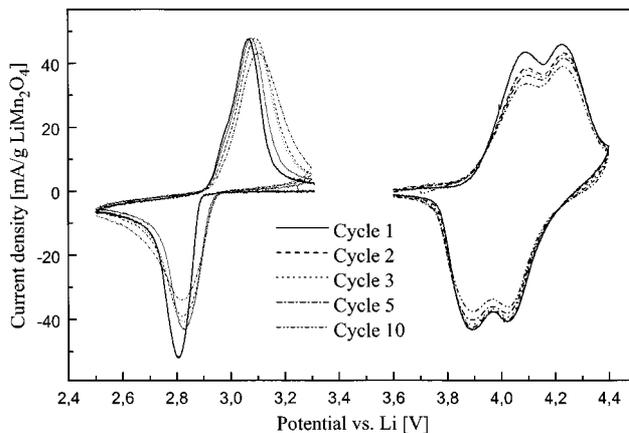


In  $\gamma$ - $MnO_2/Li$  cells, the lithium insertion during discharge occurs mainly into the  $(2 \times 1)$  tunnels. The intercalation of  $Li^+$  into the  $(1 \times 1)$  tunnels leads only to a ratio of 0.2  $Li^+/Mn$  in these domains. A higher lithium intercalation causes a change of the  $(1 \times 1)$  domains into an  $[Mn_2]O_4$ -spinel type lattice [42]. The original lattice is destroyed and cannot be renewed during recharge. However, the spinel type lattice shows a more or less reversible  $Li^+$  intercalation. For practical purposes this is insufficient. However, the properties of manganese dioxide described above have led to concerted efforts to synthesize  $MnO_2$  forms that could be suitable in secondary lithium batteries. That the spinel form is a lithium insertion compound was first shown by Hunter [43], who has reported lithium extraction from  $LiMn_2O_4$  by acid treatment. The resulting material was identified as  $\lambda$ - $MnO_2$ , where the  $[Mn_2O_4]$  framework remains as a spinel structure and allows the intercalation and deintercalation of  $Li^+$  ions.

Therefore, the lithium spinel  $Li[Mn_2O_4]$  is of great interest in the system Li-O-Mn. The transport of  $Li^+$  is achieved at interstitial places in the  $[Mn_2]O_4$  sublattice. The spinel itself is stable in a wide range of stoichiometry  $Li_x[Mn_2O_4]$  ( $0 \leq x \leq 2$ ). Starting from the  $LiMn_2O_4$  phase, there are two possibilities:

1. Intercalation of a second  $Li^+$  gives the composition  $1 < x \leq 2$ , which can be cycled in the potential range of about 2.5–3.5 V.
2. Cycling of only one  $Li^+$  in the composition range  $0 < x \leq 1$  occurs in the potential range of about 3.5–4.5 V.

In the first case, ( $1 < x \leq 2$ ), a Jahn-Teller distortion can be induced with increasing lithium content in accordance with an average manganese ion valency of below 3.5. The result is a transformation of the crystal symmetry from cubic to tetragonal. The width of this two-phase domain (characterized by a flat discharge curve) allows cycling in the composition range



**Fig. 6** Cyclic voltammograms of  $LiMn_2O_4$  in propylene carbonate – 1 M  $LiClO_4$  electrolyte (sweep rate 50  $\mu V/s$ )

$1.1 < x \leq 1.8$  [44]. In the second case ( $0 < x \leq 1$ ) the system is stable. The cubic structure remains and allows the insertion and reinsertion of  $Li^+$ . The insertion and reinsertion process occurs in two steps [45]. In the first step, lithium is approximately cycled in the range  $1 > x > 0.5$  and in the second step in the range  $0.5 > x > 0$ .

Figure 6 shows the cycling behaviour of  $LiMn_2O_4$  prepared by low-temperature synthesis via a formate precursor and freeze drying [46]. The two intercalation processes of lithium are clearly visible. Investigations in the range 3.5–4.5 V show the good reversibility of the spinel in this potential region and the electrolyte stability up to 4.5 V.

Although the spinel type manganese oxide is very promising, many investigations are being undertaken in order to improve the stability of the structure by doping with metal ions such as Ni, Co, Fe, Mg or Zn [47]. The complete exchange of manganese by nickel or cobalt leads to layered structures of the Li-metal oxides.

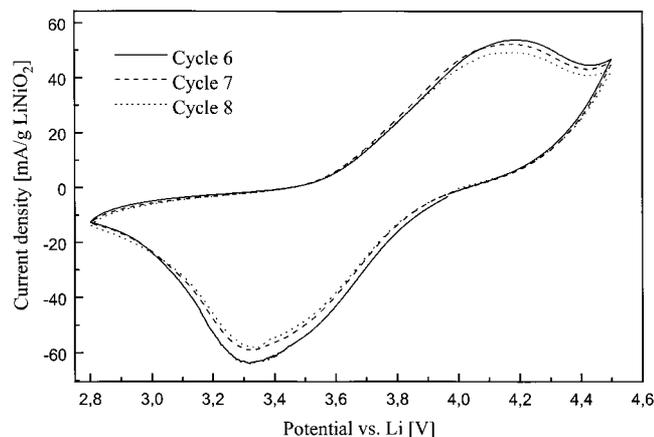
### Layered lithium-metal oxides

Lithiated nickel and cobalt oxides of the general formula  $LiMeO_2$  (where Me = Ni, Co or Ni/Co) are insertion compounds for high-voltage lithium batteries. These materials possess a layer structure where lithium and the transition metal ions fill alternating layers of octahedral sites in a cubic, close-packed lattice of oxygen ions.

The compounds  $Li_{1-x}NiO_2$  ( $0 \leq x \leq 0.5$ ) and  $Li_{1-x}CoO_2$  ( $0 \leq x \leq 0.5$ ) are suitable cathode materials for 4-V rechargeable lithium cells using a carbon anode (“lithium ion” battery). The cell reaction in the C/ $LiMeO_2$  systems can be summarized by the following electrochemical process:



Broussely et al. [48] investigated the mechanism of Li insertion/reinsertion by cyclic voltammetry. This mech-



**Fig. 7** Cyclic voltammograms of  $\text{LiNiO}_2$  in propylene carbonate – 1 M  $\text{LiClO}_4$  electrolyte (sweep rate 0.1 mV/s)

anisms for the nickel oxide and for the cobalt oxide are quite different. The first charge and discharge curve of an  $\text{LiNiO}_2$  cathode is totally different from that of subsequent cycles. The Li from  $\text{LiNiO}_2$  cannot be fully inserted during the subsequent reduction step because of a structural transformation to  $\text{Li}_{1-x}\text{NiO}_2$ . After a few cycles, the reversible reaction (shown in Fig. 7) can be described as follows:



The practical specific capacity of Li-Ni oxides is about 125–150 mAh/g [48, 49].

In contrast to these observations, in the case of  $\text{LiCoO}_2$ , the lithium after the first charging process is completely inserted during the following discharge process [48].

The overall reaction of the  $\text{LiCoO}_2$  charge/discharge is



Practical specific capacities of  $\text{Li}_x\text{CoO}_2$  cathodes correspond to the capacity range of the Li-Ni materials. Both compounds show a very pronounced plateau in the charge and discharge curve. The Li-Ni and Li-Co oxides possess a high structural stability in the voltage range investigated (4.1–3.0 V). This is the reason for the good reversibility in the charging/discharging process.

However, it seems that the price (6 \$/kg for  $\text{LiNiO}_2$  and 48 \$/kg for  $\text{LiCoO}_2$  [50]) and the resources of nickel and cobalt could limit their world-wide use in secondary batteries. From these considerations, it is considered that the Li-Mn spinels, in combination with carbon, may be the most promising systems for rechargeable lithium batteries.

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