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High-temperature combustion synthesis and electrochemical characterization of LiNiO$_2$, LiCoO$_2$ and LiMn$_2$O$_4$ for lithium-ion secondary batteries

Abstract Lithium nickelate (Li$_{0.88}$Ni$_{1.12}$O$_2$), lithium cobaltate (LiCoO$_2$) and lithium manganate (LiMn$_2$O$_4$) were synthesized by fast self-propagating high-temperature combustion and their phase purity and composition were characterized by X-ray diffraction and inductively coupled plasma spectroscopy. The electrochemical behaviour of these oxides was investigated with regard to potential use as cathode materials in lithium-ion secondary batteries. The cyclic voltammograms of these cathode materials recorded in 1 M LiClO$_4$ in propylene carbonate at scan rates of 0.1 and 0.01 mV s^{-1} showed a single set of redox peaks. Charge-discharge capacities of these materials were calculated from the cyclic voltammograms at different scan rates. The highest discharge capacity was observed in the case of Li$_{0.88}$Ni$_{1.12}$O$_2$. In all the cases, at a very slow scan rate (0.01 mV s^{-1}) the capacity of the charging (oxidation) process was higher than the discharging (reduction) process. A strong influence of current density on the charge-discharge capacity was observed during galvanostatic cycling of Li$_{0.88}$Ni$_{1.12}$O$_2$ and LiMn$_2$O$_4$ cathode materials. LiMn$_2$O$_4$ can be used as cathode material even at higher current densities (1.0 mA cm^{-2}), whereas in the case of Li$_{0.88}$Ni$_{1.12}$O$_2$ a useful capacity was found only at lower current density (0.2 mA cm^{-2}). For the fast estimation of the cycling behaviour of LiMn$_2$O$_4$, a screening method was used employing a simple technique for immobilizing microparticles on an electrode surface.

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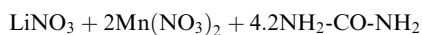Meinsberg, Germany

Introduction

LiNiO$_2$, LiCoO$_2$ and LiMn$_2$O$_4$ are the three most popular 4 V cathode materials tested in lithium-ion batteries. These batteries are currently the state-of-the-art of commercial cells used in consumer electronics. They have the inherent advantages of high energy density, long cycle life and moderate rate capabilities. However, the electrochemical performance of these oxide materials largely depends on the method by which they are synthesized, as the composition, structure and morphology are concurrently affected by it [1]. Conventionally, these oxide materials are prepared by a solid state method [2, 3, 4, 5], which is a tedious and time-consuming process involving prolonged heating and intermittent cooling and grinding of the powders. Recently, soft-chemistry methods such as sol-gel [6], metal-inorganic/ organic precursors [7, 8] and ion-exchange reactions [9] have been tried.

The research on LiCoO$_2$ and LiMn$_2$O$_4$ is more advanced because of the simplicity of preparing these materials. The theoretical capacity of LiCoO$_2$ is 274 Ah kg^{-1}; however, the available capacity is limited to less than ca. 120 Ah kg^{-1} owing to the irreversible loss of rechargeable capacity [10]. When more than 50% of the Li content of LiCoO$_2$ was withdrawn, severe degradation was reported [11]. Oxidation of the electrolyte and the structural instability of Li$_x$CoO$_2$ ($x < 0.5$) were reported to be responsible for the reduction in capacity with cycling [12]. A comparative study of these compounds [13] reveals that LiNiO$_2$ is a better candidate in view of its higher capacity, better reversibility and maximum voltage, which does not endanger the
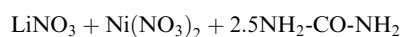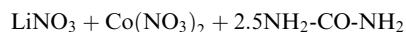
electrolyte stability during cycling. It has been repeatedly shown that stoichiometric and electrochemically active $LiNiO_2$ is difficult to prepare unless proper processing methods are employed [3, 14]. The $LiNiO_2$ particle size effect was studied with respect to the charge and discharge recycling process and it was found that smaller agglomerates give better cycle-life stability [15]. The theoretical energy density of $LiCoO_2$ and $LiNiO_2$ is twice as high as that of $LiMn_2O_4$, but in practice only half of the Li content can be removed, thus leading to the same order of useable energy density for the three materials. High cell voltage, long shelf life, wide operating temperature range, low cost and the use of non-toxic electrode materials are thought to be advantageous, so many researchers pay a great deal of attention to $LiMn_2O_4$. Attempts to make a thin film $LiMn_2O_4$ cathode for rechargeable lithium microbatteries were shown to be very promising [16]. The synthesis and electrochemical characterization of spinel $LiMn_2O_4$ remains the focal point of much research, with the aim to improve the performance of $LiMn_2O_4$/carbon rechargeable cells [17, 18]. Tarascon and co-workers [19, 20] have investigated the electrochemical behaviour, synthesis, operating temperature and cut-off voltage of a $LiMn_2O_4$ cathode.

To solve the problems encountered with these oxides, efforts are mainly focused on new synthesis routes, which tend to modify the electrochemical properties. In the present work, we report the synthesis of $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$ by self-propagating high-temperature combustion (SPHTC). We have already reported some details with respect to the synthesis of these materials and their electrochemical behaviour in conjunction with aqueous electrolytes [21, 22]. The main advantage of this method of preparation, compared to solid state sintering and other methods, is that the experiment is completed within 10 min. The basic principle of the synthesis is the decomposition of an oxidizer, e.g., a metal nitrate, in the presence of a fuel. These oxide materials prepared by SPHTC were characterized electrochemically in a non-aqueous electrolyte using cyclic voltammetry and charge/discharge studies. The phase formation and composition of these oxide materials were ascertained by X-ray diffraction (XRD) studies and inductively coupled plasma (ICP) spectroscopy. Scanning electron microscopy was used to study the morphology of the compounds.

Experimental

Synthesis of oxide materials

The oxide materials $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$ were prepared by SPHTC [21]. For the syntheses the stoichiometries of the reaction mixtures were taken as follows:

$$LiNO_3 + Co(NO_3)_2 + 2.5NH_2\text{-}CO\text{-}NH_2$$

$$LiNO_3 + Ni(NO_3)_2 + 2.5NH_2\text{-}CO\text{-}NH_2$$

$$LiNO_3 + 2Mn(NO_3)_2 + 4.2NH_2\text{-}CO\text{-}NH_2$$

The nitrate is responsible for the oxidation of urea to yield a high temperature, and also for the oxidation of the transition metals. The required amounts of metal nitrates and urea (the fuel) were dissolved in a minimum amount of distilled water in a quartz beaker. The beaker with the solution was subjected to heating in a muffle furnace at 500 °C. After a few minutes the solution boiled, underwent rapid dehydration followed by decomposition with an intense flame to yield a black fine powder. The exact reaction pathway has not yet been elucidated.

The oxide materials were analysed by XRD using a HZG 4 (Cu K_α) diffractometer (Seifert-SPM, Germany). A scanning electron microscope (Leo 440, Germany) equipped with an Econ 4 detector (EDAX, USA) was used to obtain the morphology of the particles. The lithium and metal contents were determined by means of ICP spectroscopy.

Electrochemical characterization

Electrochemical studies were carried out using a three-electrode system. The cathode was made by pressing a mixture of 80 wt% of oxide material, 10 wt% of graphite powder (Lonza KS 6) and 10 wt% of polytetrafluoroethylene powder (Aldrich) on a nickel mesh. The pressed electrode had an area of 1 cm². Lithium metal was used as reference and counter electrodes. The electrolyte used was a solution of 1 M $LiClO_4$ in propylene carbonate (PC).

For cyclic voltammetry an Autolab (ECO-Chemie, Utrecht, Netherlands) controlled by a personal computer was used. A galvanostat PS 5 (Sensortechnik Meinsberg) was employed for charge-discharge studies. All the experiments were recorded at 22 ± 1 °C and were carried out in an argon atmosphere.

Results and discussion

XRD and ICP studies

The XRD patterns of the $Li_{0.88}Ni_{1.12}O_2$, $LiCoO_2$ and $LiMn_2O_4$ samples (Fig. 1) prepared by SPHTC are comparable with the standard data and show the formation of single-phase compounds. Lithium nickelate and lithium cobaltate are reported to have a rhombohedral lattice with lithium and nickel (or cobalt) ions occupying the octahedral sites of the fcc oxygen packing. They crystallize in the rhombohedral system (space group $R3m$) with a layered structure. This enables a facile intercalation and deintercalation of lithium ions in the inter-slab space, which in turn determines the charge and discharge efficiency of the batteries. It has been reported in the literature that $Li_{1-x}CoO_2$ and $Li_{1-x}NiO_2$ with $0 \le x \le 0.5$ still have a layered structure and can be used as electrode materials. $LiMn_2O_4$ is also known to intercalate lithium ions reversibly. Unlike the two other oxides, it has a spinel structure. The oxygen atoms form a cubic close-packed array, the transition metal atom in the interstices with six nearest neighbour atoms forming an octahedron, and the lithium atoms reside in interstices, with four oxygen atoms as nearest neighbours forming a tetrahedron. This gives rise to a three-dimensional network of channels in which the lithium atoms are located and through which they can diffuse. The presence of such channels is thought to be necessary for the intercalation and deintercalation of lithium from $LiMn_2O_4$ [17].

To determine the exact stoichiometry of these oxide materials prepared by SPHTC, the metal contents of the samples were analysed by ICP spectroscopy. According to this analysis, the compounds have the following composition: $LiCoO_2$, $Li_{0.88}Ni_{1.12}O_2$ and $LiMn_2O_4$. The non-stoichiometric formation of $Li_{0.88}Ni_{1.12}O_2$ was due to difficulties in oxidation of Ni(II) to Ni(III). Scanning electron microscopic images of these compounds are shown in Fig. 2. The SPHTC process produces particles of a very uniform size (1–4 μm) with a spherical shape.
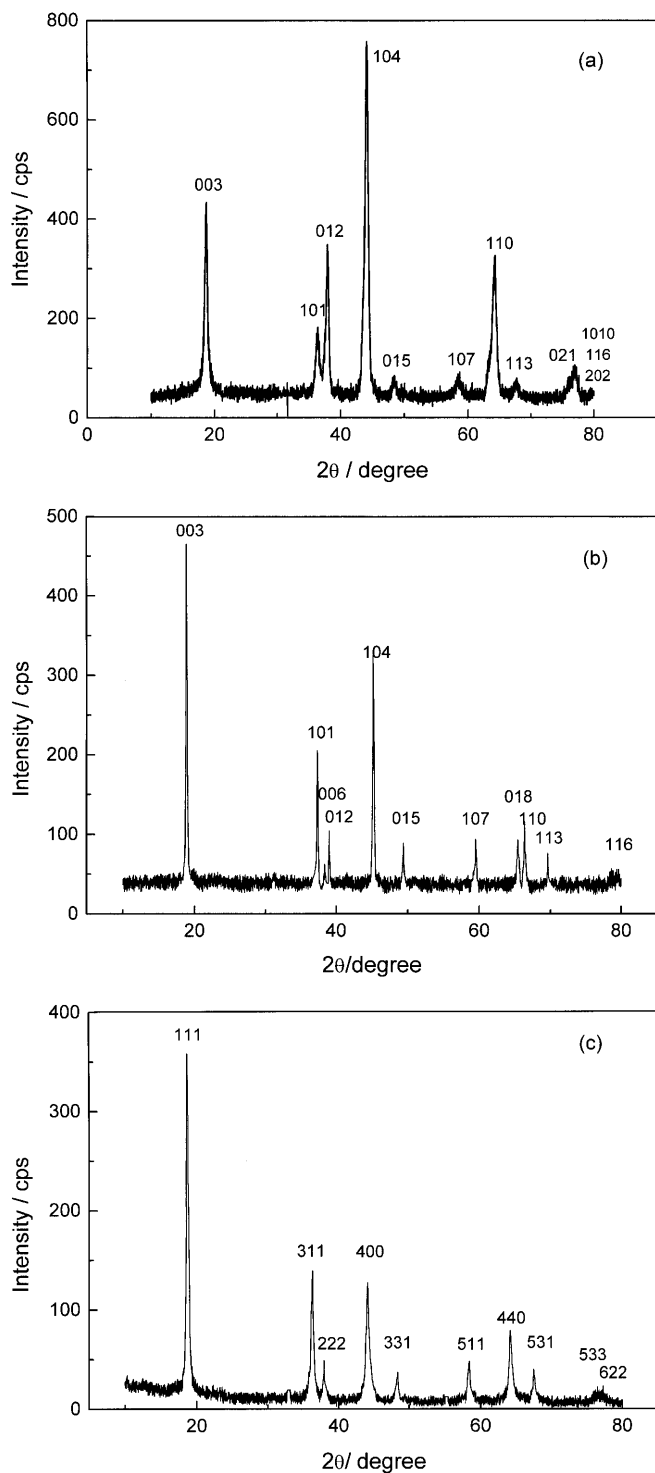

Fig. 1 XRD patterns of **a** $Li_{0.88}Ni_{1.12}O_2$, **b** $LiCoO_2$ and **c** $LiMn_2O_4$. Indices according to JCPDS 85-166, 16-0427 and 64-1524
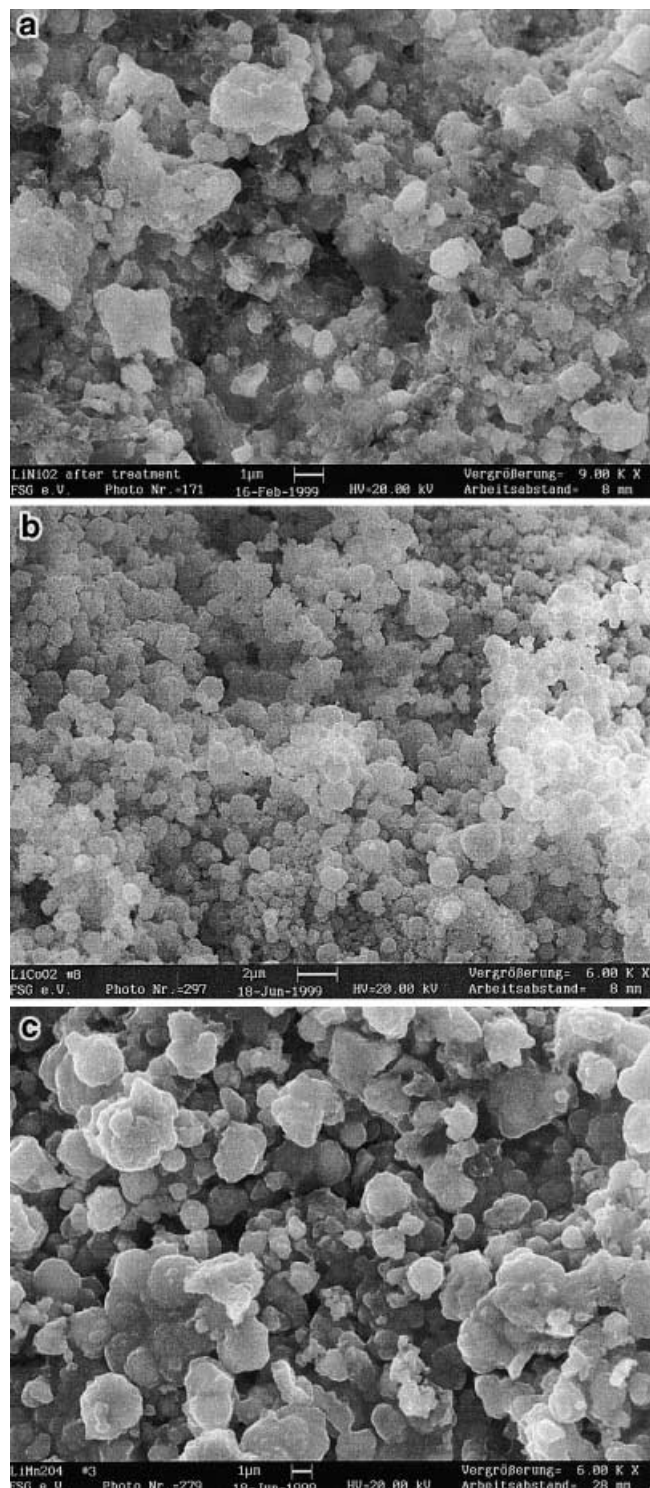

Fig. 2 SEM photographs of **a** $Li_{0.88}Ni_{1.12}O_2$, **b** $LiCoO_2$ and **c** $LiMn_2O_4$

Electrochemical characterization

The oxide materials were characterized with regard to their potential application as cathode materials in lithium-ion secondary batteries by cyclic voltammetry (CV) and galvanostatic cycling.

Cyclic voltammetry

For cycling of the pressed $Li_{0.88}Ni_{1.12}O_2$ electrode in 1 M $LiClO_4$/PC electrolyte solution the potential limits 3.0 V and 4.4 V vs. Li/Li^+ were chosen. Figure 3a and b shows the cyclic voltammograms obtained at two scan rates of 0.1 and 0.01 mV s^{-1}, respectively. At 0.1 mV s^{-1} an anodic peak at 4.0 V and a corresponding cathodic peak at 3.5 V were observed (cf. Fig. 3a). At 0.01 mV s^{-1}, two anodic peaks and a single cathodic peak appeared in the first scan (cf. Fig. 3b). In the second scan, one anodic and one cathodic peak are visible; however, both exhibit some fine structure. Such changes with cycling are
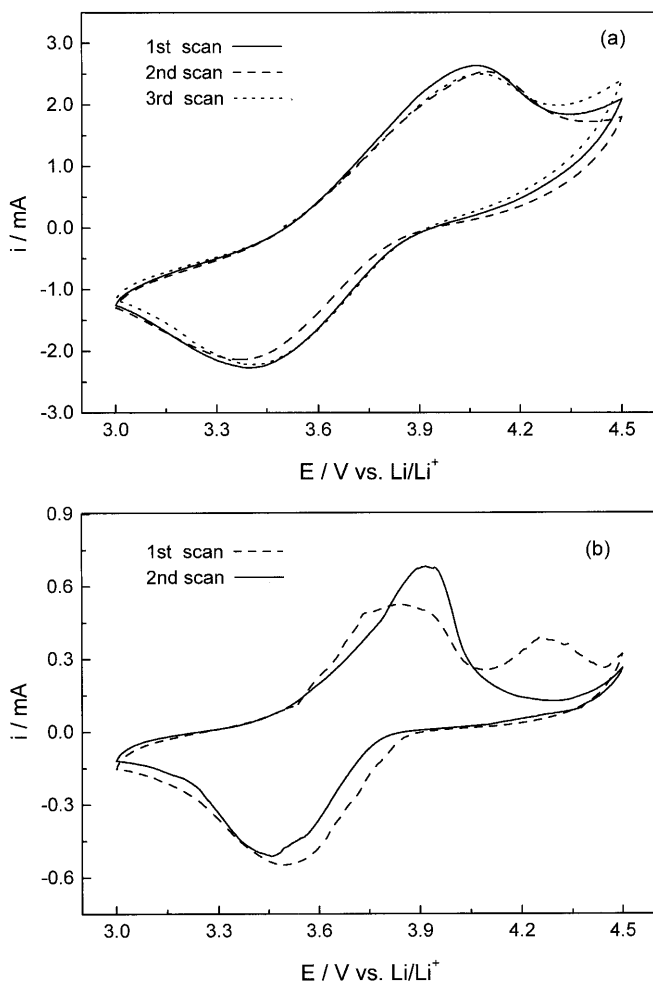
usually attributed to structural changes, which improve the performance of the oxide material [23, 24]. The reaction responsible for the redox peaks is:

$$Li_{0.88}Ni_{1.12}O_2 \rightleftharpoons Li_{0.88} - xNi_{1.12}O_2 + xLi^+ + xe^- \qquad (1)$$

Figure 4a and b shows the cyclic voltammograms obtained for $LiCoO_2$ pressed electrodes at scan rates of 0.1 and 0.01 mV s^{-1}, respectively. As in the case of $Li_{0.88}Ni_{1.12}O_2$, an anodic peak at 4.3 V and a cathodic peak at 3.5 V were observed (cf. Fig. 4a). However, in contrast to $Li_{0.88}Ni_{1.12}O_2$, the peak currents decreased considerably at a scan rate of 0.01 mV s^{-1} in the second cycle (see Fig. 4b).

Comparing the CV curves obtained for both $Li_{0.88}Ni_{1.12}O_2$ and $LiCoO_2$, the potential separation between the redox peaks remains constant at both scan rates, i.e. 0.5 V for $Li_{0.88}Ni_{1.12}O_2$ and 0.7 V for $LiCoO_2$. Such a peak separation at slow scan rates is indicative of the insertion and extraction process of lithium being associated with an over-voltage due to the bulk transport processes. The deteriorating cyclic voltammogram at
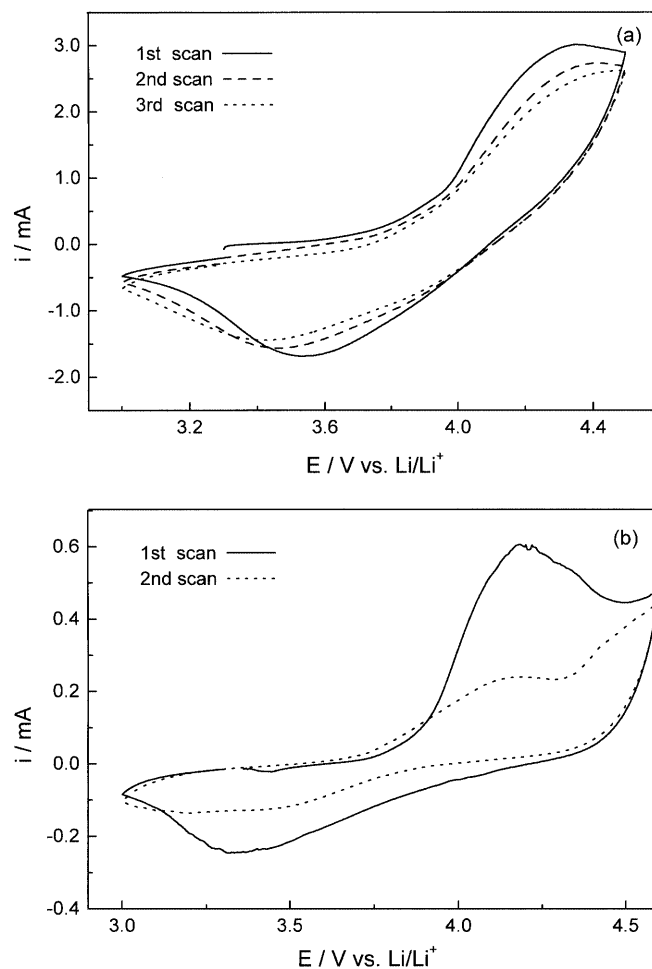

Fig. 3 Cyclic voltammograms of the $Li_{0.88}Ni_{1.12}O_2$ electrode at scan rates of **a** 0.1 mV s^{-1} and **b** 0.01 mV s^{-1}, with 1 M $LiClO_4$ in PC as the electrolyte

Fig. 4 Cyclic voltammograms of the $LiCoO_2$ electrode at scan rates of **a** 0.1 mV s^{-1} and **b** 0.01 mV s^{-1}, with 1 M $LiClO_4$ in PC as the electrolyte

0.01 mV s^{-1} for the LiCoO$_2$ electrode depicted in Fig. 4b distinctly demonstrates that its crystal structure undergoes an irreversible change if its potential exceeds 4.2 V. This process is also responsible for the decrease of peak currents measured at 0.1 mV s^{-1} for LiCoO$_2$ (cf. Fig. 4a) with subsequent cycling. In contrast, the peak currents were almost constant in the case of Li$_{0.88}$Ni$_{1.12}$O$_2$ at all cycles.

A LiMn$_2$O$_4$ pressed electrode in 1 M LiClO$_4$/PC electrolyte solution gives cyclic voltammograms as shown in Fig. 5a and b for two scan rates. At 0.1 mV s^{-1}, there was a broadened anodic peak at 4.4 V and a cathodic peak at 3.8 V. There was no change in peak currents with cycling. The CV at 0.01 mV s^{-1} (Fig. 5b) was distinctly different from that at 0.1 mV s^{-1} (Fig. 5a). At the lower scan rate, the anodic peak appeared with a preceding hump and the cathodic peak was broadened. It is known that cycling of only one Li$^+$ in the concentration range $0 < x \leq 1$ occurs in the potential range of about 3.5–4.5 V. Also, the system is reported to be stable and allows the insertion and extraction of Li$^+$ to take place in two steps [19]. Although, in the present study, we do not observe such distinct two peaks during the oxidation and reduction scans, the broadened peaks in the cyclic voltammograms show that the process occurs in two steps. Also, the peak separation (0.3 V), which is considerably less than that of Li$_{0.88}$Ni$_{1.12}$O$_2$ and LiCoO$_2$, indicates that the lithium intercalation and deintercalation process is much easier in the case of LiMn$_2$O$_4$.

Table 1 gives the charge-discharge capacities of these materials calculated from the cyclic voltammograms at different scan rates. The highest discharge capacity was observed in the case of Li$_{0.88}$Ni$_{1.12}$O$_2$. Always, at a very slow scan rate (0.01 mV s^{-1}), the capacity of the charging (oxidation) process is much higher than in the following discharging (reduction) process. This is due to electrolyte oxidation at higher potential (4.6 V) and longer duration of the experiment.

Charge-discharge studies

A LiMn$_2$O$_4$ pressed electrode was subjected to charge-discharge studies in 1 M LiClO$_4$/PC electrolyte solution. The electrode was cycled in the potential range of 3.6–4.2 V by applying a current density of 1 mA cm^{-2}. Figure 6 shows that about 35–40 Ah kg^{-1} could be reversibly cycled within the first 20 cycles. In the first cycle the efficiency apparently exceeds 100% ($Q_{discharge}$/
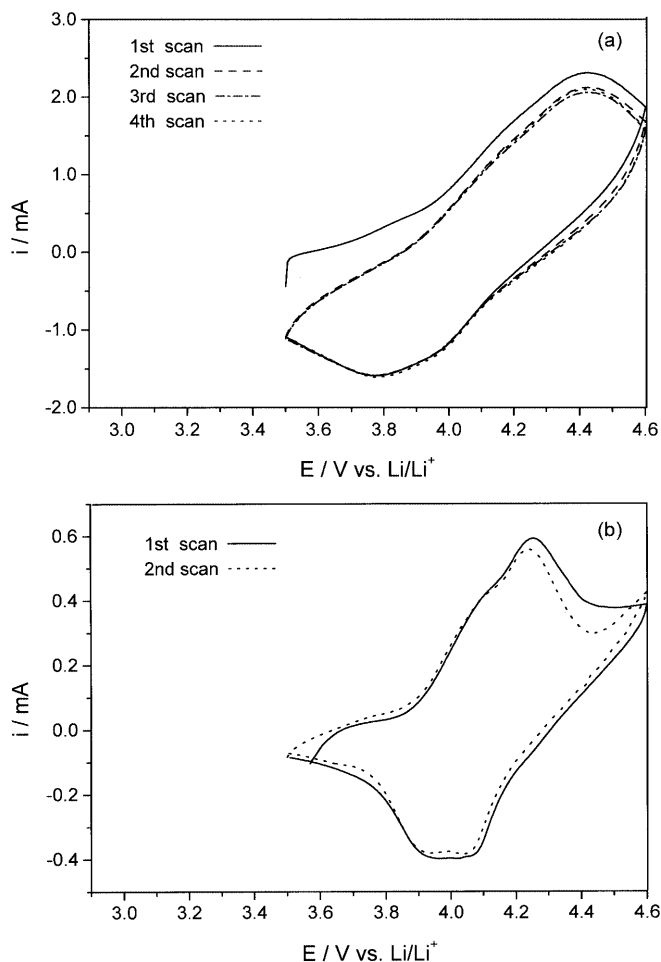

Fig. 5 Cyclic voltammograms of the LiMn$_2$O$_4$ electrode at scan rates of **a** 0.1 mV s^{-1} and **b** 0.01 mV s^{-1}, with 1 M LiClO$_4$ in PC as the electrolyte

Q_{charge}) and this is due to a partial oxidation of manganese ions during the synthesis of Li$_{0.92}$Mn$_2$O$_4$. In the following cycles the efficiency was about 100%.

Since charge-discharge studies with a pressed electrode were time consuming, we confined the experiments to 20 cycles only. For a quick estimation of the cycling behaviour of the cathode materials a screening method was used [25, 26], taking LiMn$_2$O$_4$ as an example. An amount of about 1–5 μg of solid microparticles was mechanically immobilized simply by pressing them on the tip of a platinum wire electrode ($A = 0.5$ mm^2) and subjected to charge-discharge studies galvanostatically

Table 1 Charge-discharge capacities of cathode materials calculated from the cyclic voltammograms at different scan rates

Scan rate (mV s^{-1})	Li Mn$_2$O$_4$		Li$_{0.88}$Ni$_{1.12}$O$_2$		LiCoO$_2$	
	CC^a (mA g^{-1})	DC^a (mA g^{-1})	CC (mA g^{-1})	DC (mA g^{-1})	CC (mA g^{-1})	DC (mA g^{-1})
0.10	39.18	34.72	49.98	54.01	61.93	41.93
0.01	112.4	61.50	97.01	83.81	107.1	63.64

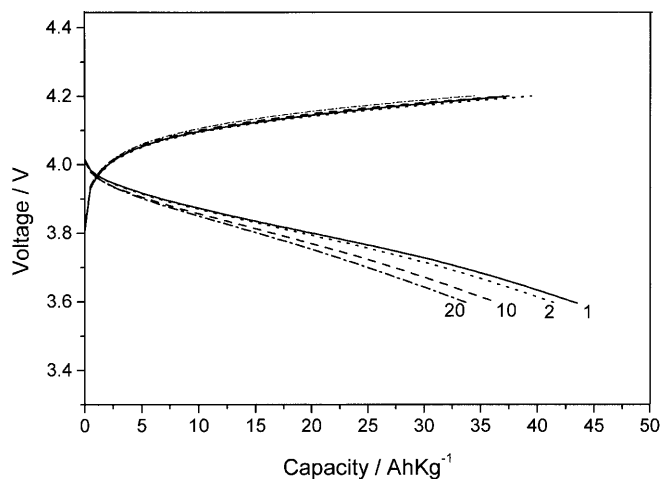^{a}CC, charge capacity; DC, discharge capacity

Fig. 6 Charge-discharge curves at the 1st, 2nd, 10th and 20th cycling of the LiMn$_2$O$_4$ electrode at 1 mA cm^{-2} current density and in the potential range of 3.6–4.2 V, with 1 M LiClO$_4$ in PC as the electrolyte
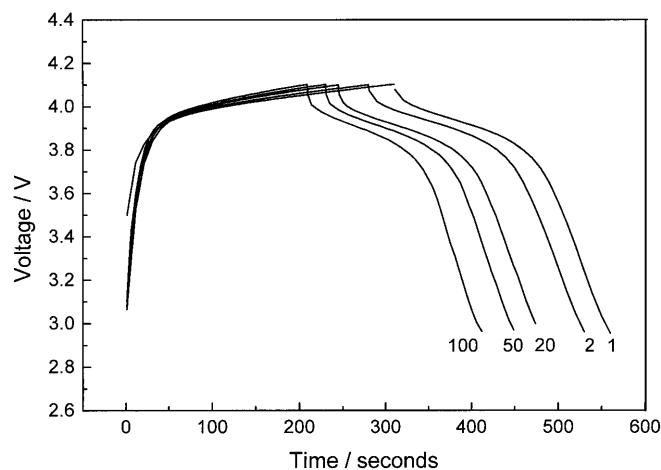

Fig. 7 Charge-discharge curves of mechanically immobilized LiMn$_2$O$_4$ microparticles on a platinum tip electrode. Number of cycles carried out: 100; current: 2 µA; potential range: 3.0–4.1 V; electrolyte: 1 M LiClO$_4$ in PC

with 2 µA current. This corresponds to a current density of about 0.1 A g^{-1}. Such a high current density is possible in this method because of the small particle size, the small amount of immobilized compound, and the absence of any binders and conducting materials (such as graphite). Such additives partly block the surface of the active material in pressed electrodes and could undergo oxidation at higher voltages. Figure 7 shows the charge-discharge behaviour of LiMn$_2$O$_4$ in the 100 cycles studied. Interestingly, the charging time decreases with increasing cycle number, whereas there is not much change in the discharge time. This may be due to structural changes in the material during cycling, as reported in literature [19, 20]. This simple method of immobilized solid microparticles on an electrode surface proved to be useful for a fast characterization of electrode materials for secondary batteries. Recently, Uchida et al. [27, 28, 29] have published an ingenious experiment to measure the electrochemistry of *single* microparticles and applied the new technique to lithium nickelate, cobaltate and manganate. This technique needs more sophisticated instrumentaion, but it yields highly important information which was not accessible with the screening method we used.

In the course of our experiments we observed that the current density has a very strong effect on the charge-discharge capacity of our materials. To illustrate this, a number of experiments were carried out with Li$_{0.88}$-Ni$_{1.12}$O$_2$ and LiMn$_2$O$_4$ cathode materials and the results are presented in Table 2. The experiments were carried out with pressed electrodes. Firstly, the electrode was oxidized and reduced with a current density of 1 mA cm^{-2}, which was subsequently reduced down to 0.2 mA cm^{-2}. From the table it is clear that the LiMn$_2$O$_4$ can be used as cathode material even at higher current densities, whereas in the case of Li$_{0.88}$Ni$_{1.12}$O$_2$ a useable capacity was found only at a lower current density (0.2 mA cm^{-2}).

Conclusions

The simple SPHTC method proved to be useful to prepare cathode materials for Li-ion secondary batteries within a short reaction time. The stoichiometric compounds LiCoO$_2$ and LiMn$_2$O$_4$ were easy to prepare by this method, whereas, as reported by many authors on different synthesis methods, stoichiometric LiNiO$_2$ could not be similarly obtained. Since there is a need for alternatives to the expensive LiCoO$_2$, in this paper we have concentrated on the synthesis and electrochemical characterization of Li$_{0.88}$Ni$_{1.12}$O$_2$ and LiMn$_2$O$_4$ cathode materials. LiMn$_2$O$_4$ exhibited good charge-discharge capacities (90.2/80.4 Ah kg^{-1} at the 14th cycle and at 0.3 mA cm^{-2} current density) and a better tolerance for higher current density and prolonged cycling. The unsatisfactory electrochemical behaviour of Li$_{0.88}$Ni$_{1.12}$O$_2$ is most probably due to non-stoichiometry and further experiments have to be carried out to optimize the reaction procedure.

Table 2 Effect of current density on the charge-discharge capacity of Li$_{0.88}$Ni$_{1.12}$O$_2$ and LiMn$_2$O$_4$ cathode materials

LiMn$_2$O$_4$			Li$_{0.88}$Ni$_{1.12}$O$_2$		
CD[a] (mA cm^{-2})	CC[a] (Ah kg^{-1})	DC[a] (Ah kg^{-1})	CD (mA cm^{-2})	CC (Ah kg^{-1})	DC (Ah kg^{-1})
1.0	35.6	29.4	1.0	2.0	1.5
0.9	36.5	31.9	0.9	2.3	1.8
0.8	39.9	34.8	0.8	2.5	2.1
0.7	45.6	39.4	0.7	2.9	2.6
0.6	52.4	43.9	0.6	3.7	3.4
0.5	86.0	72.6	0.5	5.1	4.7
0.3	90.2	80.4	0.3	13.0	12.7
0.2	131.8	94.0	0.2	60.0	47.0

[a]CD, current density; CC, charge capacity; DC, discharge capacity

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