

The study of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ 5-V cathodes for Li-ion batteries

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Abstract

In this work, we studied cycling and storage behavior at elevated temperatures of substituted spinel–nickel electrodes $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ ($x = 0.5$) that can operate as cathodes in 5-V advanced lithium-ion batteries. A stable electrochemical performance and low capacity fading were found upon cycling and storage (charged state) of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes in DMC-EC/LiPF₆ solutions at elevated temperatures (60 °C). It was established that cycling/storage of these electrodes led to dissolution of manganese and nickel and reduction of Mn^{2+} and Ni^{2+} on the lithium counter electrode. These phenomena were studied by solution analysis (ICP) and surface chemistry and morphological measurements (ex situ X-ray photoelectron and Raman spectroscopies, and SEM) of the lithium and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes. Since these electrodes perform well during prolonged cycling, it is clear that the above changes relate to surface phenomena and not changes in the bulk of the active mass.

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1. Introduction

There are intensive efforts to develop new cathodes for Li-ion batteries. A major impetus is to find cheaper cathode materials than LiCoO_2 which is the main cathode material used in practical, commercial Li-ion batteries. Also, there is strong initiative to develop materials of better rate capability and high voltage, than those of existing available materials (LiCoO_2 , $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$, LiMn_2O_4 , etc.).

Among possible new cathode materials for Li-ion batteries, LiMn_2O_4 spinel compounds, in which manganese atoms are partially substituted by nickel, copper, chromium, titanium, or aluminum, have attracted much attention in recent years [1–7]. It has been established that electrodes, based on these materials, show quite reversible redox behavior around 5 V (versus Li/Li^+), and they also demonstrate significant improvements in repeated Li intercalation/deintercalation cycling and capacity retention in comparison with LiMn_2O_4 cathodes.

Several papers [8,9] have been devoted to spinel–nickel substituted electrodes $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, where it was shown

that lithium extraction from $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ occurs around 4.4–4.7 and 4.7–5.0 V corresponding to the redox reactions of $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Ni}^{3+}/\text{Ni}^{4+}$, respectively. Of special interest are reports on cycling performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes at elevated temperatures [10] since this issue is of practical importance due to frequent operating and storage of lithium batteries in high-temperature environment. In our recent paper [11], we have studied the stability and the capacity retention of 5-V $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes during prolonged cycling at temperatures between 25 and 60 °C using various charging protocols. It was found that (i) a possible decrease of capacity which may be observed upon prolonged cycling of these electrodes, was mostly due to sluggish kinetics and not due to any pronounced degradation of the electrode active mass, (ii) capacities close to the theoretical value (146.6 mAh g^{−1}) could be obtained during long-term cycling of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes in the constant current – constant voltage charging mode in a conventional solution comprising ethylene carbonate, dimethyl carbonate and LiPF₆.

The goals of the present work were to further investigate the electrochemical stability of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes in cycling and storage conditions at elevated temperatures, and to study possible electrodes' structural changes (surface,

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bulk), and changes in solution phase that may occur during prolonged operation of these cathodes.

2. Experimental

Composite $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes on an aluminum foil current collector (one-side loading) were obtained from LG Chem. They comprised the active material (90%), conductive carbon and PVdF binder. The particle size distribution of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powder measured by a Mastersizer 2000 (Malvern, UK) is as follows: D 0.1–7.06 μm , D 0.5–14.61 μm , D 0.9–35.11 μm . For electrochemical measurements, we used two- and three-electrode cells in a coin-type 2325 configuration (NRC, Canada) using polypropylene separator (Celgard). Lithium disk and lithium chip served as counter and reference electrodes. The mass and geometric surface area of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes exposed to the electrolyte solution were 13 mg and 1.54 cm^2 , respectively. Three-electrode flooded cells, including $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes, lithium foil counter electrodes in parallel plate configuration, and lithium wire reference electrodes were also used. Electrochemical cells were assembled in a glove box filled with pure argon (VAC Inc.). The electrolyte solution (Li-battery grade, Tomiyama Pure Chemical Industries Ltd.) was a mixture of dimethyl carbonate (DMC), ethylene carbonate (EC), 2:1 w/w and 1.5 M LiPF_6 . The concentration of HF in solutions was about 100 ppm and they could also contain 20 ppm of water. The electrochemical measurements were carried out using a battery test unit model 1470 coupled with a FRA model 1255 (Solartron Inc.), and a multichannel battery tester from Maccor Inc., model 2000. All the potentials are given versus Li/Li^+ . The impedance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes was measured in the 100 kHz to 5 mHz frequency range at equilibrium pre-determined potentials (OCV conditions). The alternating voltage amplitude was 3 mV. All the measurements were conducted in thermostats at 40–60 °C. SEM measurements were carried out using a JEOL model JSM-840 scanning electron microscope. Raman spectra of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes were collected ex situ, in a back-scattered configuration using micro-Raman spectrometer HR800 (Jobin Yvon Horiba), holographic grating 1800 grooves/mm, with an Ar-laser (excitation line 514.5 nm), objective 50 \times (numerical aperture 0.75). The spectra were obtained at least from three different points on the electrode sample. X-ray photoelectron spectroscopic (XPS) data were obtained with an HX Axis system (Kratos Inc.), using monochromic $\text{Al K}\alpha$ (1486.6 eV) X-ray beam. For XPS measurements, electrodes were prepared by pressing (15000 psi) of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powder (ca. 20 mg) onto both sides of an aluminum foil. By this mode of preparation, the particles of the active material were embedded on the current collector, and thus the electrodes did not contain any binder and carbon black conductive additive. Electrolyte solutions, collected after cycling and storage experiments were analyzed for manganese

and nickel content by the ICP technique (ICP-AES, model ‘Spectroflame Modula E’ from Spectro, Kleve, Germany).

3. Results and discussion

Fig. 1 shows slow scan rate cyclic voltammograms of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode recorded at 60 °C from the initial (fresh) cell, and of the same electrode that was cycled and stored afterwards for 4, 5 and 7 weeks, as indicated. The electrode demonstrates quite reversible electrochemical behavior, which is characterized by two pairs of redox transitions in the 5-V domain. During Li extraction, peak potentials at 4.73 and 4.77 V are attributed to the $\text{Ni}^{2+} - \text{e}^- \rightarrow \text{Ni}^{3+}$ and $\text{Ni}^{3+} - \text{e}^- \rightarrow \text{Ni}^{4+}$ oxidation reactions, respectively. The corresponding reduction processes (Li insertion) occur at potentials of 4.67 and 4.70 V. In the 4 V region (inset to Fig. 1), the electrode shows also some minor redox behavior, related to the $\text{Mn}^{3+}/\text{Mn}^{4+}$ couple, typical for the LiMn_2O_4 spinel material. These results are in agreement with the literature data obtained from thin $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes in a LiBF_4 -containing solution [9]. Electrodes cycled at 60 °C in a DMC-EC (2:1)/1.5 M LiPF_6 solution (Fig. 1) provided high charge/discharge capacities with Coulombic efficiencies around 98%. Even after prolonged storage in a charged state at 60 °C, the electrode demonstrated quite sufficient capacity retention (Table 1).

As it follows from Fig. 1 and Table 1, prolonged storage of these electrodes at elevated temperatures results in a slight shift of the cathodic peak potentials to more negative values indicating some changes (slow down) in kinetics of Li intercalation into the active mass.

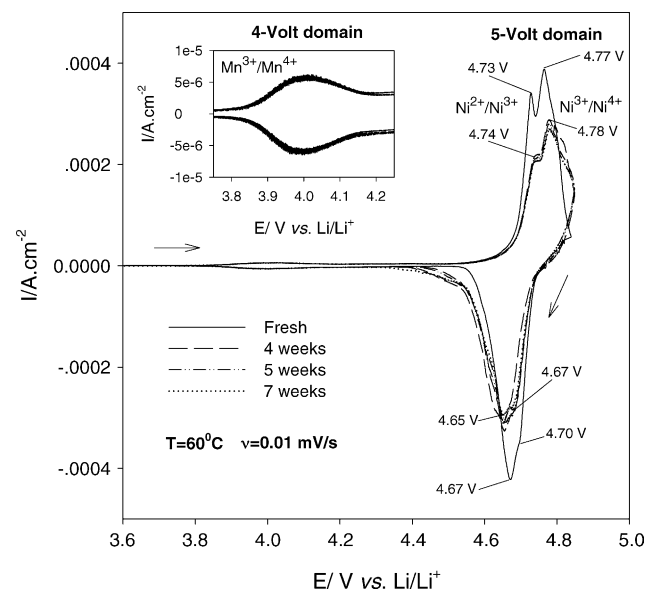


Fig. 1. Cyclic voltammograms measured at 60 °C from a pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode (stabilized by several initial voltammetric cycles) and from the same electrode stored at 60 °C in a $\text{Li}/\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cell (time of storage is indicated). Coin-type cell, the potential range was 3.50–4.85 V, the scan rate was 0.01 mV s^{-1} . DMC-EC (2:1)/1.5 M LiPF_6 solution.

Table 1

Capacities obtained from a $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode at 60°C in a DMC-EC (2:1)/1.5 M LiPF_6 solution

Li/LiNi _{0.5} Mn _{1.5} O ₄ cell	Charge capacity (mAh g ⁻¹)	Discharge capacity (mAh g ⁻¹)	Coulombic efficiency (%)	Discharge capacity loss (% per day)
Initial (fresh)	148	145	98.0	–
4 weeks storage	139	132	95.0	0.32
5 weeks (1st CV)	135	131	97.0	0.28
5 weeks (2nd CV)	130	129	99.2	0.31
7 weeks	133	127	95.6	0.25

Voltammetric cycling (scan rate, $\nu=0.01\text{ mV s}^{-1}$) in a potential range of 3.50–4.85 V was followed by storage at 60°C (charged state). The accuracy of the measurements is estimated as $\pm 5\%$.

It was shown that the capacity of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes in voltammetric charge–discharge cycling is nonlinearly depended on a potential scan rate (Fig. 2). The highest capacity (close to the theoretical one of 146.6 mAh g^{-1}) can be achieved with these electrodes at very low scan rates around 0.005 mV s^{-1} , which correspond to C/8–C/10 (the electrodes reach quasi-reversible conditions) using an upper cut-off potential of 4.85 V. In fact, 4.85 V is the maximum potential needed to extract all the available capacity from these electrodes. This potential seems to be low enough, so there is no interference of an oxidation of the electrolyte solution in the operational potential range of these electrodes. In this case, the capacity fading measured during storage (25 days, $T=60^\circ\text{C}$) was around 0.42 mAh g^{-1} per day (0.30% per day) indicating a stable behavior of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes. The electrochemical stability of these electrodes upon cycling at elevated temperatures ($T=40\text{--}60^\circ\text{C}$) was demonstrated also in repeated charge–discharge cycling in constant current mode followed by impedance measurements (after every five cycles) both at fully intercalated and partially deintercalated states. Fig. 3 shows a typical impedance spectrum obtained at $E=3.50\text{ V}$ from a pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode ('fresh' cell) and spectra recorded after the 10-th

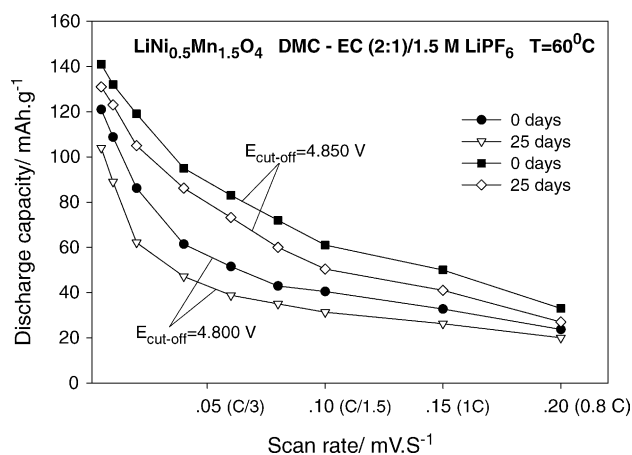


Fig. 2. Dependence of the discharge capacity of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes on scan rates in voltammetric cycling and on storage time (as indicated) at 60°C . Coin-type cell, cut-off potentials were 4.80 and 4.85 V, DMC-EC (2:1)/1.5 M LiPF_6 solution. On the X-axis, numbers in brackets denote the corresponding C rates (i.e. the duration in hours for delivering of the full capacity in the voltammetric experiments).

and 20-th galvanostatic cycles (constant current mode, C/10 rate). In this figure, impedance spectra obtained after electrode's storage at $T=40^\circ\text{C}$ for 50 and 100 h are also shown. These spectra exhibit depressed semicircle in the high-to-medium frequency range related to charge transfer and a straight line of a Warburg-type element, related to the lithium solid-state diffusion. After several initial cycles, the electrode's impedance decreases. We have no explanation yet to the changes in the electrodes' impedance that are measured during the first cycles. They can be related both to bulk structural rearrangements and to changes in the electrodes' surface. For instance, surface species that are present initially on the active mass (e.g. Li_2CO_3 or LiF which is formed on the surface immediately as the electrodes are immersed in solution and the lithiated metal oxides react with trace HF) are replaced by less resistive species formed by nucleophilic reactions between oxides and the electrophilic

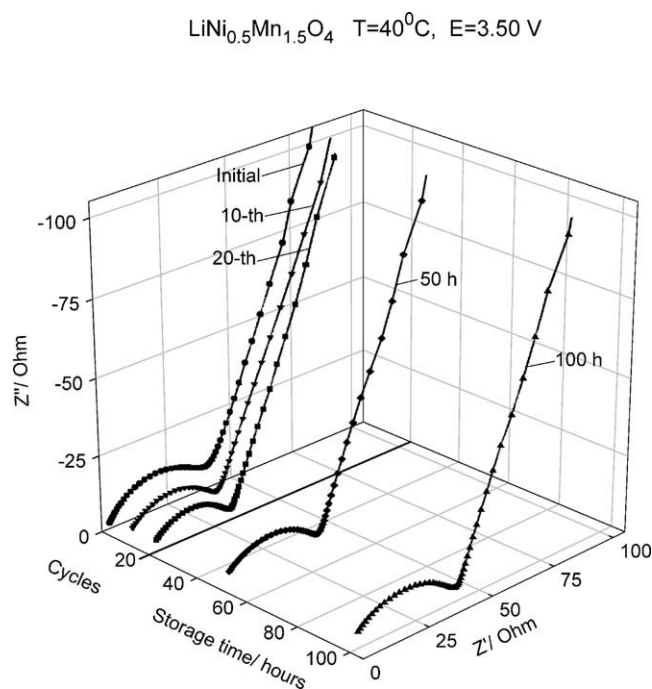


Fig. 3. A family of impedance spectra recorded at a fully intercalated state ($E=3.50\text{ V}$) from a pristine (initial) $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode (coin-type cell), after the 10th and 20th galvanostatic cycles (C/10 rate, potential range 3.50–4.90 V) and after storage. The electrolyte solution was DMC-EC (2:1)/1.5 M LiPF_6 , $T=40^\circ\text{C}$.

Table 2

The manganese and nickel contents (ppm) detected by the ICP method in DMC-EC (2:1)/1.5 M LiPF₆ solutions after cycling or storage of LiNi_{0.5}Mn_{1.5}O₄ electrodes at various conditions

Conditions	Mn content (ppm)	Ni content (ppm)	Mn losses from cathodes ^a (%)	Ni losses from cathodes ^a (%)
Storage 5 days at 30 °C	0.60	<0.03	0	0
Storage 15 days at 30 °C	0.69	<0.03	0	0
Storage 1 day at 60 °C	1.18	<0.03	0	0
Storage 7 days at 60 °C	8.10	1.51	1.3	0
Storage 45 days at 60 °C	11.4	137	1.3	50
Cycling at ^b 60 °C	150	40	4.7	4.0

The mother solution contained <0.03 ppm of Mn and <0.03 ppm of Ni. Each electrode sample was stored in 5 mL of the solution, in a polyethylene vial under argon atmosphere, in a thermostat.

^a The error in these calculations is around 10%.

^b Flooded cell, volume of solution was 3 mL. LiNi_{0.5}Mn_{1.5}O₄ electrode (free of binder and carbon black additives) was prepared by pressing the powder on an Al-foil (see Section 2).

solvent molecules [12]. Once the LiNi_{0.5}Mn_{1.5}O₄ electrodes are stabilized, they show minor changes in the impedance upon cycling and storage (Fig. 3).

In general, storage of these electrodes after their cycling with cut-off potentials varying from 4.70 to 4.82 V, results in small capacity losses. The capacity decreased significantly if the electrodes were stored and cycled with higher charging cut-off voltages of 4.90–4.92 V. One can conclude that capacity losses during storage are dependent on the electrodes' history, particularly on cycling rate (slow or fast) and on the charging cut-off potential. We measured larger capacity losses when the cut-off potentials were higher than 4.85 V. Such losses can be related, in part, to oxidation of the electrolyte solution at high potentials. Oxidation of solution species may generate species, which are expected to be acidic in nature (e.g. protons), which may accelerate manganese and nickel dissolution from the LiNi_{0.5}Mn_{1.5}O₄ lattice at high temperature and thus cause a capacity loss of the electrode [13]. We have found that storage of LiNi_{0.5}Mn_{1.5}O₄ electrodes at elevated temperatures in DMC-EC (2:1)/1.5 M LiPF₆ solutions led to both manganese and nickel dissolution (Table 2). In regard to nickel dissolution, the electrodes' stoichiometry did not change upon storage at 30 and 60 °C for 15 and 7 days, respectively. It was also established that storage at 30 °C and short-time storage at 60 °C in DMC-EC (2:1)/1.5 M LiPF₆ solutions (under argon atmosphere) resulted in minor if any Mn and Ni dissolution from the electrodes. On the other hand, prolonged storage at elevated temperature may lead to more pronounced metals dissolution and hence may cause significant changes in electrodes' composition, as demonstrated in Table 2.

The manganese and nickel dissolution from LiNi_{0.5}Mn_{1.5}O₄ electrodes was confirmed by spectroscopic studies. In Fig. 4, we compare Raman spectra of the pristine LiNi_{0.5}Mn_{1.5}O₄ electrode, of an electrode stored at $T=30^{\circ}\text{C}$ for 15 days, and of an electrode stored for 45 days at $T=60^{\circ}\text{C}$ in DMC-EC (2:1)/1.5 M LiPF₆ solutions. While storage at 30 °C led to minor changes of the Raman spectrum, storage at the elevated temperature resulted in the following major changes, which correlate well with the

element analysis studies related to the Mn and Ni dissolution: (i) the peak at 407 cm⁻¹ corresponding to nickel–oxygen stretching mode [9] almost disappeared and (ii) the intensity of the peak at 500 cm⁻¹ (Ni–O bond) decreased significantly in the case of the stored electrode. Besides, a new peak at 575–580 cm⁻¹ emerges, which can be attributed to the formation of λ -MnO₂ on the surface of the stored electrode. The results obtained are consistent with the data reported by McLarnon and co-workers [14], where these authors have shown conversion of a LiMn₂O₄ electrode to λ -MnO₂ upon storage at 70 °C in EC-DMC/LiPF₆ solution. It should be noted that a detailed spectroscopic study of the stored LiNi_{0.5}Mn_{1.5}O₄ electrode has shown that Raman spectra collected from some other locations on this electrode exhibited a decrease of the intensity of the 407 cm⁻¹ peak (indication of partial Ni dissolution) and did not exhibit a new peak of λ -MnO₂. In this respect, we suppose that metals (Mn and Ni) dissolve locally from LiNi_{0.5}Mn_{1.5}O₄ electrodes by the following mechanism due to an exchange

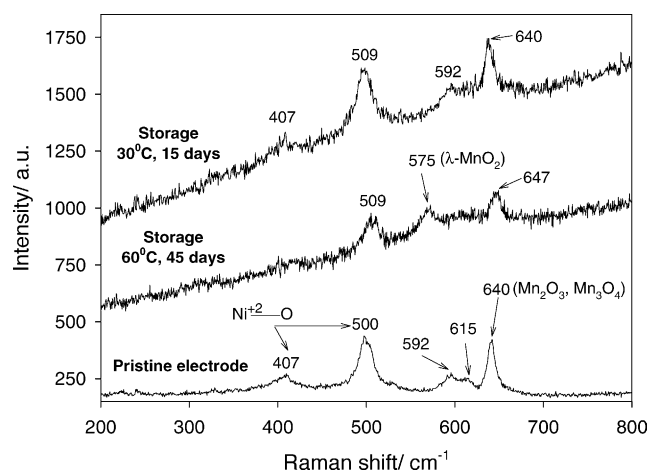


Fig. 4. Raman spectra obtained ex situ from a pristine LiNi_{0.5}Mn_{1.5}O₄ electrode, from an electrode stored at 30 °C for 15 days, and from an electrode stored at 60 °C for 45 days in DMC-EC (2:1)/1.5 M LiPF₆ solutions. After storage, the electrodes were rinsed with ethyl–methyl carbonate in a glove box, dried in vacuum and transferred to the Raman spectrometer in sealed cells containing the optical window (glass, 150 μm thick). On each electrode, Raman spectra were collected at least from three different points.

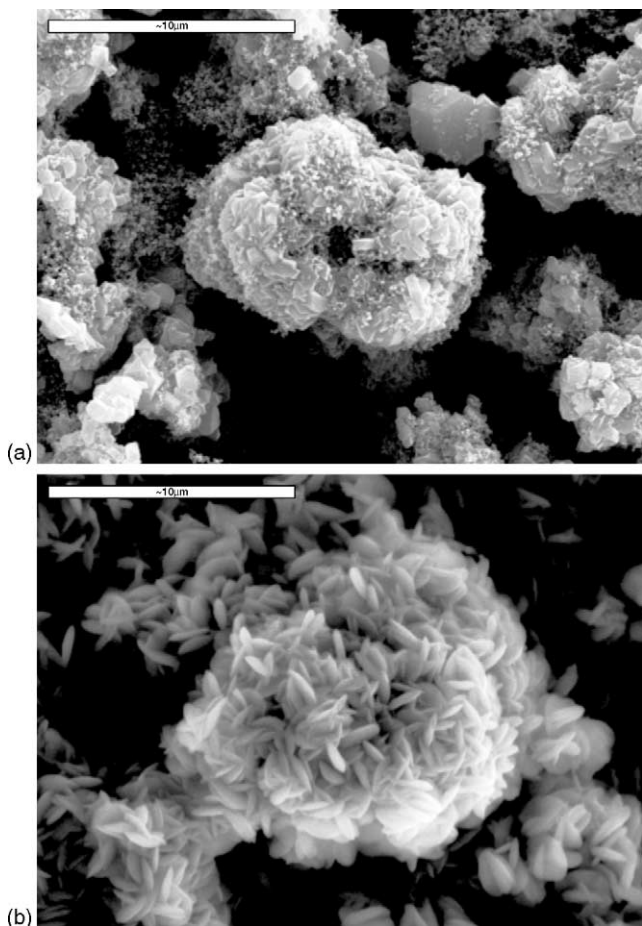
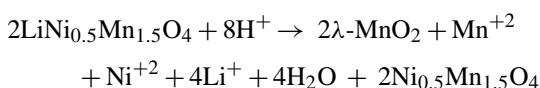


Fig. 5. SEM micrographs of (a) a pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode and (b) an electrode stored at 60°C for 45 days in a DMC-EC (2:1)/1.5 M LiPF_6 solution (same electrodes as in Fig. 4).

with protons (HF):



The formation of the surface $\lambda\text{-MnO}_2$ (and/or other manganese oxides, like $\gamma\text{-MnO}_2$) was revealed also by comparative XRD study of pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes and electrodes after storage. Some additional reflection peaks at two-theta angles of 17.0, 20.5, 26.0, 30.0, and 41.0 in the XRD pattern of the stored electrodes (not shown here) are related to $\lambda\text{-MnO}_2$.

Fig. 5 compares SEM images obtained from (a) a pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode and (b) of an electrode stored at 60°C for 45 days in solution (same electrodes as in Fig. 4). Pronounced morphological changes of the stored electrode are observed: small particles in agglomerates seen in the image of the pristine electrode became thinner, round-shaped and disintegrated. These changes may result from interparticle tension upon prolonged storage at elevated temperature, surface films formation [14] and their rearrangements, swelling polymeric binder by solvents molecules, and manganese and nickel dissolution, which leads to

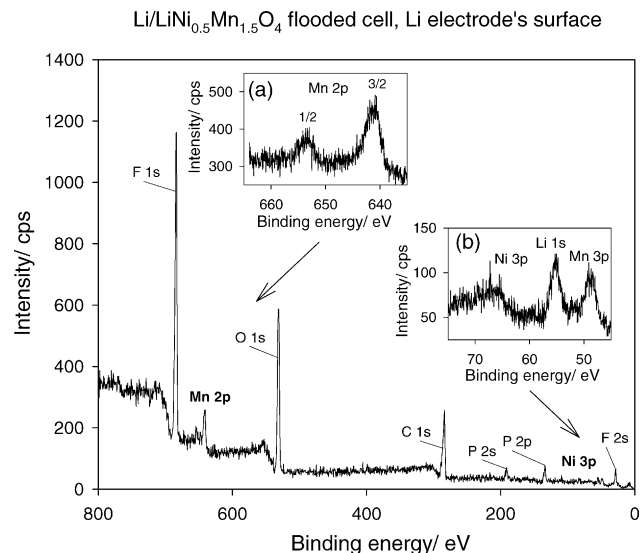


Fig. 6. XPS spectra measured from a lithium counter electrode of a flooded cell $\text{Li/LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ that underwent several voltammetric cycles at 60°C . The working electrode was prepared by pressing the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powder onto both sides of an Al-current collector and did not contain PVdF and carbon black additives. The electrolyte solution was DMC-EC (2:1)/1.5 M LiPF_6 .

changes in the nature of the active mass (at least, near its surface).

It was found that after storage at 60°C for 25 days, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes (particles embedded in Al current collector, free of binder and carbon black) did not show any electrochemical activity when cycled in a fresh DMC-EC (2:1)/1.5 M LiPF_6 solution. However, these electrodes were still active in solution, in which they were stored (this solution contained dissolved Mn^{2+} and Ni^{2+}). A similar positive influence of the dissolved transition metals (M^{2+}) on the cycling behavior of LiMO_2 electrodes in Li-ion cells was reported recently for LiCoO_2 electrodes [15]. This phenomenon deserves of course further studies.

Upon cycling, in $\text{Li/LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cells, at high temperatures the dissolved Mn^{2+} and Ni^{2+} ions are reduced on the lithium counter electrode, as was unambiguously established by the XPS measurements (Fig. 6). The multi-element spectrum and the insets *a* and *b*, related to the domains of Mn and Ni peaks (respectively) in Fig. 6 clearly indicate the presence of manganese and nickel compounds (probably oxides or carbonates) on the lithium electrode. A similar phenomenon of transition metals ions reduction (deposition) on the counter electrode in Li-ion cells is described in Refs. [15–17].

4. Conclusions

Using fast and slow potential scan rate cyclic voltammetry and impedance spectroscopy, it was shown that substituted spinel–nickel electrodes demonstrated quite stable electrochemical behavior at 60°C upon repeated charge–discharge

cycling and storage both at fully intercalated and partially deintercalated states. An important finding is that electrodes' capacity losses during storage are dependent on their history: rate of cycling (prior to storage) and the charging cut-off potential. We have established that cycling and/or storage of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes at elevated temperatures resulted in local Mn and Ni dissolution (due to reactions with acidic species in solution phase), and formation of $\lambda\text{-MnO}_2$ and maybe other types of manganese oxides on these electrodes. It is supposed that the above phenomena relate mostly to surface rather than bulk changes occurring during electrodes' cycling and storage. In fully intercalated state (OCV around 3.5 V), surface changes may be accompanied by pronounced morphological transformations of electrodes upon prolonged storage at 60°C due to films formation and their rearrangement, disintegration of particles agglomerates, metals dissolution etc.

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