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Study of the $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ /Electrolyte Interface at Room Temperature and 60°C

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The surface layer (Cathode-Electrolyte Interface; CEI) on $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, a promising, high voltage positive electrode for Li-ion batteries, was studied by XPS, AC impedance spectroscopy and FTIR spectroscopy. Half cells and full cells with $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ as positive electrode material and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as a negative electrode material were assembled in conventional carbonate-based electrolytes with LiPF_6 or LiBF_4 as the salt, and the effect of cycling at different operating conditions (short and long storage time, state of charge and temperature) on the surface layer composition was assessed. Capacities reaching near the theoretical value of 140 mAh g^{-1} were obtained in half cells cycled at C/2 and room temperature, with 85% of the capacity being retained after 100 cycles. Cycling at 60°C leads to a decrease in capacity and coulombic efficiency. The surface analysis by XPS revealed that the CEI is composed of inorganic species such as LiF and $\text{Li}_x\text{PF}_y\text{O}_z$ or $\text{Li}_x\text{BF}_y\text{O}_z$ as well as organic species such as polyethers and carbonates. Generally, it was found that cycling or storing the material at 60°C with an electrolyte using LiPF_6 as a salt yield more organic species and less LiF at the surface than the one with LiBF_4 .

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There is an increasing demand for lithium-ion batteries with high energy and power density for mobile and stationary applications with most of the efforts are being focused on electric vehicles (EV, HEV, PHEV) and large scale storage related to the electric grid. This requires the development of new electrode and electrolyte materials able to meet the stringent requirements to render the batteries safer, cheaper and more durable. Research and development within this area is focused on: high voltage/capacity cathode materials; low voltage/high capacity anode materials; and electrolytes with improved electrochemical and thermal stability. Among the most promising cathode materials in this regard is the family of substituted spinels $\text{LiMn}_{2-x}\text{M}_x\text{O}_4$ (where $\text{M} = \text{Cr, Co, Fe, Ni, Cu}$), which possess an electrochemical voltage plateau above 4.5 V vs Li/Li^+ .^{1–6} $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (LMNO), in particular, exhibits a plateau at 4.7 V vs Li/Li^+ with a capacity of 148 mAh g^{-1} .¹ It shows excellent capacity retention and cycling stabilities in a broad range of charge/discharge rates,⁷ and unlike its parent counterpart LiMn_2O_4 which shows extensive capacity fade at 55°C ,⁸ its capacity is better retained at a similar temperature (60°C).^{9,10} The lower performance of batteries at elevated temperatures can be attributed to several factors¹¹ including: the decomposition of the electrolyte; the dissolution of cathode materials induced by HF; the dissolution of the SEI at the anode; and direct reactions between the cathode material and the electrolyte. Another cause of capacity fade is prolonged cycling, which is attributed to a rise in the impedance of the electrode. The impedance rise can be related to the formation of surface species on the cathode. This film is known as the cathode-electrolyte interface (CEI) and results in a loss of contact between cathode particles¹² that is exacerbated at more elevated temperatures. Consequently, there has been interest in identifying the species that form on the cathode surface leading to the observed fade in capacity.^{13,14} The study of this CEI is of particular interest in the case of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ since the 4.7 V operating range is near the oxidation potential of the electrolyte. The formation of a solid electrolyte interphase (SEI) on lithium in non-aqueous solution was proposed for the first time by Peled in 1979,¹⁵ and since then most of the studies on the surface layer have focused on the anode side, and graphite in particular.^{16,17} Unfortunately, little is known about the formation and nature of the CEI. Strauss et al.¹⁹ reported the formation of a cathode SEI (or CEI) on an FeS_2 cathode by overdischarging the cell to 0.7 V, composed of Li_2CO_3 , Li_2O and polymers species which lead to an improvement in cycle life. Aurbach et al.¹³ and Edström et al.¹⁴ reported on the presence of polycarbonates $[-\text{OCO}_2-]_x^-$, alkyl

carbonates (ROCO_2Li), alkoxides (ROLi) and the inorganic salts LiF and $\text{Li}_x\text{PF}_y\text{O}_z$ on the surface of LiCoO_2 , LiNiO_2 , LiMn_2O_4 and $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$. Similar species along with fluoride species, such as MF_x or $\text{Li}_x\text{MO}_y\text{F}_z$, were reported to form on particles of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ aged in a carbonate-based electrolyte at 30 and 70°C .²⁰ In a recent paper,²¹ we studied the cathode-electrolyte interface of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ stored and cycled at room temperature. It was discovered that a layer consisting of polyethers, polycarbonates, $\text{Li}_x\text{PF}_y\text{O}_z$ and LiF forms at the surface during cycling but does not grow during storage at room temperature. In a more recent paper Yang et al.²² studied the surface of charged $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ using a fluorine-free binder instead of PVDF and identified the components of the CEI to be mainly the oxidation product of ethylene carbonate; poly(ethylene carbonate) along with small amounts of $\text{Li}_x\text{PF}_y\text{O}_z$ and Li_xPF_y , originating from non-electrochemical reactions.²² Dedryvère²³ studied the interface of $\text{LiMn}_{1.6}\text{Ni}_{0.4}\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$ full cells and also observed carbonate and ethers species although very little lithiated species and LiF . It is expected that the storage and cycling at elevated temperature, 40 to 60°C , will influence the composition of the CEI and the performance of the material. In this work, we have studied the formation and composition of the surface layer on $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ in half cells, either stored or cycled at room temperature and 60°C in EC:DEC 3:7 with 1M (LiPF_6 or LiBF_4) electrolyte, or full cells using $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) as the negative electrode. The composition of the CEI was studied by X-ray photoelectron spectroscopy (XPS), AC impedance spectroscopy and Fourier-transform spectroscopy (FTIR) on the cathode material after storage and cycling.

Experimental

$\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ was synthesized using a modified sol-gel method described in Ref. 21. Briefly, stoichiometric amounts of lithium nitrate, manganese acetate and nickel acetate were dissolved in ethylene glycol in a “glycol : total-metal-content” molar ratio of 4:1. The mixture was fired in a stainless steel beaker, then ground in a mortar followed by sintering at 400°C for 4 h then at 800°C for 14 h in air. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was synthesized following the method of Ref. 24. Briefly, titanium butoxide was added dropwise to a solution of lithium acetate in ethanol. The resultant gel was dried at 60°C for 24 h and sintered at 800°C for 24 h. The material was characterized by scanning electron microscopy (SEM), using a JEOL 840A microscope. TEM micrographs were taken with a Philips CM 20 microscope operating at a voltage of 200 kV. XRD was performed using a Bruker-AXS D8 diffractometer using $\text{Cu K}\alpha$ ($\lambda = 1.54 \text{ \AA}$) from 15 to $90^\circ 2\theta$ with a step size of 0.03° and a step time of 0.5 s. The patterns were

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Figure 1. (Color online) XRD pattern of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode material.

analyzed by the Rietveld refinement method²⁵ using TOPAS 4 beta software from Bruker AXS.

The material was tested in 2325-type coin cells which were assembled in an argon-filled dry box. A mixture consisting of 75% active material, 7.5% KS-4 graphite, 7.5% Super S and 10% PVDF (3 wt% in NMP) binder was casted on an aluminum foil and dried overnight in a vacuum oven at 80°C. Punches of 12.7 mm in diameter were made from the film and these were pressed at 0.5 ton before being assembled into cells. Li metal was used as the anode and 1M (LiPF_6 or LiBF_4) in EC:DEC (3:7) was used as the electrolyte. For tests using full lithium-ion cells were assembled, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was used as the negative electrode material. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was casted on an aluminum foil in the same proportions as in $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ casts. Prior to the cell assembly the capacities of the two electrode punches were carefully balanced. A Celgard 3501 separator was used to isolate the cathode and anode active materials. The cells were cycled on an Arbin Instruments cycler. The coin cells were cycled at a C/2 rate (74 mA g^{-1}) using voltage limits between 3.5 and 4.9 V for half cells and between 2 and 3.4 V for the full lithium-ion cells. AC Impedance spectroscopy was carried on the two electrode coin cells with a Princeton Applied Research PAR 263A potentiostat coupled with Solartron 1260 Frequency Response Analyzer in the frequency range 10 kHz–10 mHz with an amplitude of 10 mV. XPS measurements were made with a Kratos Axis spectrometer using an Al K α radiation. CasaXPS[®] software was used to process the data and C 1s peak (284.7 eV) was used as a reference. Cells were opened in the glove box and washed with fresh dimethyl carbonate (DMC). They were transferred in air-tight container and mounted on the XPS sample holder and transferred to the XPS apparatus with a minimal exposure to air (30 s). Ex situ characterization

was done by FTIR in attenuated total reflectance (ATR) mode with a Bruker Tensor IFS 66/S using a ZnSe crystal plate. The coin cells were disassembled in a glove box, and the electrode was pressed against the ATR crystal. This was placed into an air-tight ATR cell and taken out of the glove box and the FTIR spectrum measured immediately.

Results and Discussion

Electrochemical cycling.— $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ was synthesized using a simple sol-gel method at a sintering temperature of 800°C, which gave the best capacities upon cycling according to a previous publication.²¹ The XRD pattern of the as-synthesized material was subjected to a Rietveld analysis as shown in Fig. 1. The main component was found to be a disordered spinel $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ with the space group Fd-3m. The lattice parameter was $8.1803(1) \text{ \AA}$ and the crystallite size was found to be $196 \pm 29 \text{ nm}$, all in agreement with those reported in Ref. 21. Similar to what was reported in Ref. 21, minor impurities that account for 4.7 wt % of the total material but are assigned to Ni_6MnO_8 rather than NiO. Ni_6MnO_8 has a similar structure to NiO (Fm-3m) but was better indexed due to the smaller lattice parameter observed as a result of Mn^{4+} in the structure which fit better the diffractogram. SEM micrographs of the $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ obtained are shown in Fig. 2. It can be seen from the micrographs that the material is formed of aggregates of several microns consisting of 200 nm crystallites with a flower-like microstructure.

$\text{Li}/\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cells were assembled and cycled at a rate of C/2 (74 mA g^{-1}). The charge and discharge capacities for an electrode with 2 mg cm^{-2} loading at room temperature and 60°C are shown in Fig. 3. At room temperature, the maximum capacity is obtained after 6–8 cycles, depending on the sample; while the efficiency (ratio of charge capacity to discharge capacity) of these cycles is typically low, 77–90%, increasing to 94–98% after 10 cycles. The results at 60°C demonstrate even lower capacity and efficiency. The efficiency is 77% after 5 cycles and increases to 90% after 100 cycles at 60°C. The maximal discharge capacity of 100 mAh g^{-1} is obtained immediately but fades to 82 mAh g^{-1} after 100 cycles. The capacities obtained at room temperature and 60°C are comparable to those obtained by Hagh et al.¹⁰ More notably, the lower capacity (by 30%) and coulombic efficiency (90%) at 60°C compared to room temperature suggests the formation of a more resistive layer on the surface of the particles. To further investigate the behavior at 60°C, we stored for 60 days uncycled cells at 100% state of charge (SOC) and 0% SOC and then cycled them at room temperature, and their capacities are shown in Fig. 4. In all cases, the capacities are lower than in the case of cells cycled immediately after assembly or storage at room temperature.²¹ The cells stored for 24 h at 0% SOC and 100% SOC both gave capacities of 95 mAh g^{-1} after 100 cycles. However, there is a difference in the initial capacities, as while the cell stored at 0% SOC quickly reached a stable capacity, the one stored at 100% SOC took 20 cycles to reach its maximal capacity. In the case of the cell stored at 100% SOC for 60

Figure 2. Scanning electron micrographs of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ at different magnifications.

Figure 3. (Color online) Comparison of charge (filled symbol) and discharge (open symbols) capacity of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ at room temperature and 60°C . Electrolyte is EC:DEC 3:7 + 1M LiPF_6 ; Counter electrode is Li foil, cycled at C/2.

days, the discharge capacity is low but increases rapidly to 90 mAh g^{-1} . The cell stored at 0% SOC for 60 days provided higher initial discharge capacities, but lower values after prolonged cycling. The lower capacity for cells stored at 60°C compared to cells cycled immediately after assembly suggests the formation of a more resistive layer at the surface of the electrode during storage. This layer is probably partially dissolved, as indicated by the increase in capacity with cycling, but storage at an elevated temperature adversely affects the electrochemical performance of the cell. However, storage at 100% SOC yields improved capacity recovery and more stable capacity regardless of storage times. The effect of storage on capacity could be further understood by AC impedance spectroscopy. We obtained scans before and after storage at 60°C for 10 days in the discharged state (4 V) (Fig. 5). The spectra exhibit a sim-

Figure 4. (Color online) Capacity of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cycled at room temperature after 24 h storage at 100% SOC (green triangles) and 0% SOC (diamonds) and 60d storage at 60°C at 100% SOC (orange triangles) and 0% SOC (red triangles). The capacity of a fresh $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ is shown as a comparison. Electrolyte is EC:DEC 3:7 + 1M LiPF_6 ; Counter electrode is Li foil, cycled at C/2.

Figure 5. (Color online) Impedance spectra of a LMNO/Li cell at 4 V before and after storage at 60°C .

ilar behavior of two semicircles. It can be seen that after storage at 60°C , a slight decrease in the high frequency semicircle and an increase in the lower frequency semicircle is observed. More importantly, it can be said that storage at 60°C causes an increase in the overall cell impedance, from $2810 \Omega \text{ cm}^2$ before storage to $3750 \Omega \text{ cm}^2$ after storage. Hagh et al.¹⁰ Performed similar measurements on $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ as cathode material and Li as anode material at room temperature and 60°C and observed a similar trend. They found that the cell impedance increased when it was stored at 60°C , especially when stored at 100% SOC, and that both the anode and cathode contributed to the rise of the cell impedance.

LiBF_4 was also used as a salt in conventional carbonate-based electrolytes to compare to the LiPF_6 results above. Electrolytes composed of LiBF_4 have been shown to provide interfaces with low charge transfer resistance.^{11,26} We assembled cells using EC:DEC 3:7 with 1M LiBF_4 in Li and Li-ion cells with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) as a negative electrode material. As seen in Fig. 6, although the initial discharge capacity with LiBF_4 based electrolyte is comparable to that of an electrolyte with LiPF_6 , the efficiency is quite low and becomes worse with cycling. After 5 cycles, the charge and discharge capacities are 155 and 135 mAh g^{-1} , respectively, while after 100 cycles they reach 180 and 100 mAh g^{-1} , respectively. This increase in capacity could be attributed to electrolyte oxidation during the charging process. On the other hand, when full cells were tested with LiBF_4 -based electrolyte, the efficiency is substantially higher which suggests that the poor efficiency of LiBF_4 electrolyte

Figure 6. (Color online) Comparison of the charge and discharge capacity of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ with EC:DEC 3:7 + 1M LiPF_6 or LiBF_4 as electrolyte with Li or $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) as negative electrode, cycled at C/2.

with $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ could be due to the use of Li metal as negative electrode. The high irreversible capacity might be due to the reduction of the electrolyte on the lithium surface that leads to the formation of an SEI that, although composed of similar species as in the case of LiPF_6 or LiBF_4 salts, is quite different in morphology.²⁷ It is known that using LiBF_4 leads to the formation of a porous out-layer on the surface of the SEI while LiPF_6 produces a dense film that is more thermally stable.²⁸ The initial charge and discharge capacity for the full cells using the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as negative electrode and $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ as positive electrode with LiBF_4 electrolyte at a C/2 rate were 123 and 81 mAh g^{-1} , respectively, and after 100 cycles the capacities reached 48 and 39 mAh g^{-1} . The capacity for the full cell using 1M LiPF_6 in EC:DEC (3:7) as electrolyte was initially similar to an initial discharge capacity of 91 and 78 mAh g^{-1} after 100 cycles. Since the cells were balanced with a slight excess of LMNO, the capacities are expressed as capacity per gram of the limiting electrode, LTO. The cells were balanced with an excess of LMNO since it has been shown that they give the best capacity retention^{29,30} because of the fact that with LMNO-limited cells the potential vs. the lithium electrode never goes over 4.9 V and thus electrolyte oxidation is avoided.³⁰ Values around 107 mAh g^{-1} have been reported for LTO/LMNO full cells with 1.2 M LiPF_6 in EC:EMC (3:7) electrolyte,²⁹ slightly higher than what we obtained.

XPS.—In order to identify the species formed on the surface of the cathode, an XPS analysis was performed on cells opened after different storage and cycling times. Cells were opened after being stored for 24 h or 60 days at 60°C at either a 0% SOC or 100% SOC. Cells cycled 100 times at C/2 for 100 cycles at room temperature and at 60°C were also opened. XPS spectra for all samples were taken for Li 1s, C 1s, O 1s, F 1s, B 1s and P (2p_{1/2} and 2p_{3/2} but only 2p_{3/2} will be discussed). For clarification, a review of the surface of a pristine electrode ($\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ casted on an Al foil with PVDF as binder) will be provided initially and a more detailed analysis can be found in Ref. 21. The O 1s peak at 529.5 eV was

assigned to $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$. There was some Li_2CO_3 present, evidenced by a Li 1s peak at 54.5 eV, an O 1s peak at 531.5 eV and a C 1s peak at 289 eV. PVDF was visible via a C 1s peaks at 290.7 eV (-CF-) and 285.6 eV (-CH-) and the F 1s peak at 687.5 eV. In addition, the reaction of PVDF with the cathode material³¹ led to a small amount of LiF, as indicated by the F 1s peak at 684 eV. XPS spectra taken on pure PVDF, Li_2CO_3 and LiF confirm our assignment.

The O 1s, C 1s and Li 1s spectra for cells stored at 60°C for 24 h at 0% SOC, 60 d at 0% SOC and 60 d at 100% SOC are shown in Figs. 7a–7c, respectively. The F 1s and P 2p_{3/2} spectra for the corresponding cells are shown in Figs. 8a–8c, respectively. The O 1s peak at 529–530 eV observed in all stored cells originates from $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ indicating that its surface is partially covered by a layer that forms during storage. Peaks assigned to PVDF are also visible for these three samples (see Figs. 7 and 8). The electrode stored for 24 h showed the presence of some LiF on the surface, as shown by the Li 1s peak at 55.76 eV and the F 1s peak at 684.5 eV. This differs from the cell stored at room temperature for 24 h and 60 days reported in our previous study²¹ which only showed the presence of LiF after extended cycling (100 cycles). This is not surprising however, as LiPF_6 is known to decompose to PF_5 and LiF. PF_5 in turn reacts with residual water to form HF and PF_3O . The latter can then form Li_xPF_y and $\text{Li}_x\text{PF}_y\text{O}_z$ species.³² This process was found to be thermodynamically favored both at room temperature and 60°C.³² In contrast, cells stored for 60 days exhibited a broad Li 1s peak with a maximum at 54.7 eV which indicates the presence of ROCO_2Li species along with the O 1s peak at 532 eV and the C1s peak at 288.8 eV. However, these peaks could also be attributed to Li_2CO_3 that results from the decomposition of these carbonate species³³ at elevated temperatures. Moreover, LiF seems to be also present in stored cells since there is a F 1s peaks at 683.3 eV and its peak could be masked by the broad Li 1s peak. All stored samples showed two P 2p_{3/2} peaks, one at 133.7 eV, indicative of $\text{Li}_x\text{PF}_y\text{O}_z$ and another one at 136.5 eV, indicative of Li_xPF_y . Since the electrodes were rinsed thoroughly with DMC, one can assume that the

Figure 7. (Color online) O 1s, C 1s and Li 1s spectra of as-synthesized $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ a) stored 24h at 60°C b) stored at 0% SOC for 60 days at 60°C, c) stored at 100% SOC for 60 days at 60°C d) cycled 100 times at room temperature e) cycled 100 times at 60°C f) cycled 100 times at room temperature, LTO negative electrode.

Figure 8. (Color online) F 1s and P 2p spectra of as-synthesized $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, EC:DEC 3:7 + 1M LiPF_6 electrolyte, a) stored 24 h at 60°C b) stored at 0% SOC for 60 days at 60°C, c) stored at 100% SOC for 60 days at 60°C d) cycled 100 times at room temperature e) cycled 100 times at 60°C f) cycled 100 times at room temperature, LTO negative electrode.

observed Li_xPF_y species are bound to the surface and not just residual LiPF_6 from the electrolyte; LiPF_6 is very soluble in DMC and should be washed away during the rinsing step. Other species were identified on the surface of all stored samples; they could be polyethers ($-\text{CH}_2\text{O}-$) (O 1s peak at 532.2 eV and C 1s peak at 284.86 eV) or carbonates (ROCO_2M) (O 1s peaks at 531.7 and 532.2 eV and C 1s peaks at 286 and 288.5 eV). For the cell stored at 60°C for 60 d, an additional O 1s peak at 533.5 eV is observed and coupled with C 1s peak 290 eV, could indicate the presence of polycarbonates produced by the polymerization of EC which was observed at 60°C on LiMn_2O_4 by Edström et al.¹⁴ Storing at elevated temperature clearly produces additional organic species compared to room temperature storage, as noted previously²¹ and as in the case of LiMn_2O_4 .¹⁴ As previously mentioned, a third cell was stored at 60°C for 60 days at 100% SOC; this was done in order to check if there were differences in the species formed at the surface (see Figs. 7c and 8c). The main differences between the cells stored at 60°C for 60 days at 0% SOC and 100% SOC are as follow: (i) a more complicated C 1s spectrum with two additional peaks, one at 287 eV and another one at 288.7 eV, ii) an additional O 1s peak at 531 eV

and iii) a higher proportion of $\text{Li}_x\text{PF}_y\text{O}_z$ compared to Li_xPF_y for the cell stored at 100% SOC (see peaks P 2p Fig. 8c). All in all, the XPS spectra infer that the lower specific capacity observed for the cells that were stored before they were cycled seems to be caused in part by the growth of the organic and inorganic salt layers mostly during the storage period. When the storage of the cells was at 60°C, there was an evidence for the formation of more of the inorganic species that are less porous than the organic ones and also less conducting to Li ions which all led to a further decrease in the observed capacities.

Two batteries cycled 100 times at room temperature and 60°C were also opened. Figures 7d and 7e shows the Li 1s, C 1s and O 1s XPS spectra of these batteries while Figs. 8d and 8e shows the F 1s and P 2p_{3/2} XPS spectra. As expected, the O 1s spectrum does not show any peaks at 529.5 eV ($\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$), indicating that cycling will cause the surface of the electrode to be fully covered with the CEI. The C 1s spectra show additional peaks when the battery was cycled at 60°C (Fig. 7e), besides the graphite peaks at 284.7 eV, peaks at 286.4, 288.9 and 290.3 eV cannot be attributed to PVDF since the electrode surface is fully covered. In addition to the

Figure 9. (Color online) C 1s, O 1s and Li 1s spectra of LiMn_{1.5}Ni_{0.5}O₄, EC:DEC 3:7 + 1M LiBF₄ electrolyte with 100 cycles a) Li negative electrode and b) LTO negative electrode.

absence of O 1s peak at 529.5 eV and F 1s peak at 688 eV, corresponding to PVDF, and the absence of Mn 3p peak (seen on the Li 1s spectra for the other cells also indicate that the CEI fully covers the electrode surface. Both electrodes also exhibit C 1s peaks at 286.6 and 288.46 eV (see Fig. 7d) that can be assigned to carbonates or ROCO₂Li, along with O 1s peaks at 531 and 532.3 eV. For the cell cycled at 60°C, the O 1s peak at 534.3 eV and C 1s at 290.3 eV (which cannot be attributed to PVDF as discussed above) could be assigned to polycarbonates as in the case of the cells stored for an extended period at 60°C, as explained previously. As in the case of stored cells, cells cycled 100 times exhibit two different phosphorus species, with one P 2p_{3/2} peak at 134 eV, indicative of Li_xPF_yO_z and another one at 136 eV indicative of Li_xPF_y. Also, two F 1s peaks are observed at 686 eV (Li_xPF_yO_z and Li_xPF_y) and a smaller at 684 eV (LiF). In summary, the effect of temperature is that it enhances reactivity at 60°C which produces species not observed at room temperature such as polycarbonates, as in the case of LiMn₂O₄.¹⁴ However, in contrast with LiMn₂O₄, there are also significant amounts of organic species formed on the surface after cycling or storage at room temperature on LiMn_{1.5}Ni_{0.5}O₄. This is consistent with the impedance measurements³⁴ which showed an increase in the impedance with cycling at 60°C.

A full cell using 1M LiPF₆ in EC:DEC (3:7) as electrolyte was also opened after 100 cycles. Figs. 7f and 8f show the XPS spectra of the cathode. The spectra exhibits C 1s peaks at 285.1, 286.8 and 290 eV and O 1s peaks at 531.3 and 533.1 eV that can be attributed to carbonate and polyether species at the surface (see Figs. 7f), and some LiMn_{1.5}Ni_{0.5}O₄ that is still visible at the surface (529 eV O 1s peak), unlike half cells where this peak is absent for cycled cells. In addition, there is no evidence for any LiF at the surface (absence of Li 1s at 55 eV and F 1s at 684 eV peaks); all of the F containing spe-

cies being Li_xPF_y or Li_xPF_yO_z. This agrees with the studies conducted by Dedryvère et al.²³ on LiMn_{1.6}Ni_{0.4}O₄/Li₄Ti₅O₁₂ full cells who also observed that the surface of the electrode is not entirely covered with organic species and reported the presence of low amounts of LiF. This discrepancy between half cells and full cells seem to indicate that some species that cover the positive electrode actually come from the positive electrode and migrate during cycling.

Two other cells using 1M LiBF₄ in EC:DEC (3:7) as electrolyte and having either Li or LTO as a negative electrode were also opened after 100 cycles at RT. Figs. 9a, 9b, 10a, and 10b show the XPS spectra of these cathode materials. In both cases, LiF is present on the surface, as evidenced by the Li 1s peaks at 55 eV and F 1s peak at 684 eV. The B 1s spectra show peaks at 191 eV and 194 eV in the case of Li/LMNO cell and 192 eV in the case of LTO/LMNO cell. These 191-192 eV peaks could be assigned to Li_xBF_yO_z (Ref. 17) species and the peak at 194 eV could be assigned to Li_xBF_y.¹⁴ Both batteries showed a F 1s peak at 687 eV that could also be assigned to Li_xBF_yO_z/Li_xBF_y species. The mechanism for the formation of Li_xBF_yO_z/Li_xBF_y is similar to the one with LiPF₆ salt; LiBF₄ reacts with H₂O to form LiF and BOF which in turn forms Li_xBF_yO_z.¹⁶ The Li/LMNO cell seems to have relatively more organic species at the surface (O 1s peaks at 528, 530, 531, and 532 eV, C 1s peaks at 284.7, 286, 288.7, and 290 eV) compared to the LTO/LMNO cell (O 1s 529 and 532 eV and C 1s 284.7, 285.6, and 289 eV). The relatively more complicated spectra and increased presence of surface species seems consistent with BF₃ being a stronger initiator of polymerization than PF₅.¹⁴ It was previously reported³² that LiBF₄ electrolyte leads to a more substantial presence of polycarbonate and alkyl carbonate species on the surface. The negative electrode also affects electrochemical performance; the Li metal electrode leads to a

Figure 10. (Color online) F 1s and B 1s spectra of LiMn_{1.5}Ni_{0.5}O₄, EC:DEC 3:7 + 1M LiBF₄ electrolyte with 100 cycles a) Li negative electrode and b) LTO negative electrode.

Table I. Composition of the surface of opened cells.

Cell	Salt	Condition	F 1s	O 1s	C 1s	P 2p	B 1s
Li/LMNO	1 M LiPF ₆	24 h/0% SOC/60°C	18.6	9.8	70.2	1.4	—
Li/LMNO	1 M LiPF ₆	60d/0% SOC/60°C	16.8	16.4	64.2	2.6	—
Li/LMNO	1 M LiPF ₆	60d/100% SOC/60°C	14.2	13.4	70.5	1.9	—
Li/LMNO	1 M LiPF ₆	100 cycles/RT	7.7	22.1	68.0	2.2	—
Li/LMNO	1 M LiPF ₆	100 cycles/60°C	7.6	22.0	66.9	3.5	—
LTO/LMNO	1 M LiPF ₆	100 cycles/RT	17.0	20.7	59.8	2.5	—
Li/LMNO	1 M LiBF ₄	100 cycles/RT	22.2	25.4	49.2	—	3.3
LTO/LMNO	1 M LiBF ₄	100 cycles/RT	15.35	21.9	60.6	—	2.1

Figure 11. FTIR spectra of LiMn_{1.5}Ni_{0.5}O₄ a) stored 24 h at 60°C, b) stored at 0% SOC for 60 days at 60°C, c) stored at 100% SOC for 60 days, d) cycled 100 times at room temperature, e) cycled 100 times at 60°C. Li counter electrode, EC:DEC 3:7 + 1M LiPF₆ electrolyte.

larger amount of organic species on its surface than LTO. It is likely that species formed at the surface of Li could migrate from the cathode during cycling, especially at elevated temperatures.

In order to get insight into the changes on the surface induced by different storage and cycling procedures, the percentage of F, O, C and P at the surface of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ was determined using XPS and the amounts are shown in Table I. The Li was not quantified due to the overlap of the Li 1s peak with the Mn 3p peak and only the relative abundance of F, O, C and P and not the entire amount of species on the surface is compared. When using Li as a negative electrode and LiPF_6 as a salt, the percentage of F is 18.6% for 24 h storage, 16.8% for 60 days storage at 0% SOC and 14.2% for 60 days storage at 100% SOC. For both batteries after 100 cycles (at RT and 60°C) the percentage decreases to 7.7%. On the other hand, the amount of P increases from 1.41% for 24 h storage to 2.6 and 1.9% for 60 days storage at 0 and 100% SOC, respectively and 2.2 and 3.53% for the batteries cycled 100 times at room temperature and 60°C, respectively. Further studies could include Ar sputtering on the surface while monitoring the relative abundance of species which could give an insight on whether cycling at elevated temperature yield a thicker layer of organic and inorganic species. Our measurements only indicate that at 60°C there is additional organic layer (species) visible at the surface but the relative composition of the layer is relatively similar to that of cell cycled at room temperature. In the case of uncycled cells, the electrode surface is still visible and thus PVDF will contribute to a proportion of F found on the surface. The lower amount of F in cycled cells is likely due to the surface of the electrode being covered by organic and inorganic layers, which masks the PVDF. Moreover, an increase in the amount of P suggests that the main F-containing species on the surface is $\text{Li}_x\text{PF}_y\text{O}_z$, rather than Li_xPF_y since the main P component at 134 eV is assigned to $\text{Li}_x\text{PF}_y\text{O}_z$. The amount of $\text{Li}_x\text{PF}_y\text{O}_z$ increases after cycling at 60°C compared to room temperature. The amount of C remains relatively stable between 64 and 70% for all storage and cycling conditions, but the amount of O does increase upon storage and cycling. After 24 h, O makes up 9.8% of the surface, 16 and 13.4% after 60 days of storage at 0 and 100% SOC, respectively, while cycling at room temperature and 60°C increases the percentage of O to 22%. This increase can be attributed to an increase in the organic species at the surface such as polyethers, polycarbonates and ROCO_2M as well as $\text{Li}_x\text{PF}_y\text{O}_z$. When using LTO as negative electrode, the amount of F is 17%; O is 20.7%, C is 59.8% and P is 2.5%, in line with the amounts observed with other cells cycled 100 times. When using LiBF_4 salt, the surface composition changed depending on the type of the negative electrode. With a Li negative electrode, the amount of F was 22.2%, compared to 15.35% with LTO, while the amount of B decreased from 3.3% with Li to 2.1% with LTO. This indicates that the presence of LiF and $\text{Li}_x\text{BF}_y\text{O}_z$ species is more important when Li was used as negative electrode, although it is not clear why. On the other hand, the amount of C is relatively low (49.2%) compared to other cells made using LiPF_6 , which varied between and 70% while the amount of O is slightly higher at 25.4% than for the other cells cycled for 100 times, at 20–22%.

FTIR.—Similar to XPS measurements, cells were opened after storage and cycling at 60°C and their FTIR spectra were taken. The spectra are shown in Fig. 11 for cells stored for 24 h at 60°C, stored 60 days at 60°C and at 0% SOC or 100% SOC and after 100 cycles at room temperature and 60°C. All cells were opened in the glovebox and transferred to an ATR cell without exposure to air. Since the electrodes were not washed, bands corresponding to ethylene carbonate (EC) and LiPF_6 are expected. These bands are: P-F at 845 cm^{-1} ; C-O bands between 1050 and 1200 cm^{-1} , C-H bands between 1350 and 1600 cm^{-1} and carbonyl ($\text{C}=\text{O}$) bands between 1700 and 1800 cm^{-1} . Diethyl carbonate (DEC) evaporates after opening the cell and does not appear on the spectra. However, new bands were observed at 1367 and 1351 cm^{-1} , probably due to polyether species. A shoulder appeared at 1730 cm^{-1} that could be attributed to carbonate species, ROCO_2M (20). This is clearer for the cell cycled for 100

times at 60°C, but can be seen as a weak shoulder for other storage and cycling times. In addition, a broad peak is present at 1250 to 1280 cm^{-1} which was attributed to $\text{Li}_x\text{PF}_y\text{O}_z$.³⁵ It is quite small for samples stored at 60°C and cycled at room temperature but it is prominent for the cell cycled at 60°C, suggesting a thicker layer is formed under these conditions. Finally, a shoulder appeared at 1200 cm^{-1} that could originate either from alkoxides, ROM, or $\text{Li}_x\text{PF}_y\text{O}_z$ species. The species identified by FTIR are in agreement with those found during XPS measurements. The presence of $\text{Li}_x\text{PF}_y\text{O}_z$, polyether and carbonate species could be verified and the major difference between the spectra was an apparent increase in the peak attributed to $\text{Li}_x\text{PF}_y\text{O}_z$ for the cell cycled at 60°C.

Conclusion

In this paper, a thorough study on the nature and function of the cathode electrolyte interface of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ in half and full cells configuration using conventional carbonate electrolytes with LiPF_6 or LiBF_4 as salt was presented. The following conclusions can be drawn:

1. With LiPF_6 containing electrolyte, $\text{Li}/\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cells cycled at almost theoretical capacity at room temperature while those with LiBF_4 electrolyte showed large irreversible capacities.
2. The cycling at 60°C yield lower capacities and efficiencies. Storage at 60°C and subsequent cycling at room temperature is deleterious to the capacity.
3. XPS and FTIR measurements extracted from cells post-cycling show that all electrodes are covered with salt and organic species. The organic layer is composed of alkyl carbonates (ROCO_2Li) and polyethers. Li_2CO_3 was observed in the case of electrodes stored at 60°C and never cycled, but not in cycled cells, and polycarbonates, $[-\text{OCO}_2-]_x$, on cells stored or cycled at 60°C.
4. The salt layer is composed of $\text{Li}_x\text{PF}_y\text{O}_z$ or $\text{Li}_x\text{BF}_y\text{O}_z$ depending on the electrolyte used as well as LiF that is present on all cells. The quantity of LiF is substantial for cycled electrodes in half cells, but not full cells in presence of LiPF_6 electrolyte.

Future work would involve cycling and examination of the surface of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ after cycling in full cells at 60°C and determination of the variation of the thickness of the CEI as a function of cycling and/or storage.

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References

1. Q. Zhong, A. Bonakdarpour, M. Zhang, Y. Gao, and J. R. Dahn, *J. Electrochem. Soc.*, **144**, 205 (1997).
2. K. Amine, H. Tukamoto, H. Yasuda, and Y. Fujita, *J. Power Sources*, **68**, 604 (1997).
3. H. Kawai, M. Nagata, M. Tabuchi, H. Tukamoto, and A. R. West, *Chem. Mater.*, **10**, 3266 (1998).
4. H. Shigemura, H. Sakaebae, H. Kageyama, H. Kobayashi, A. R. West, R. Kanno, S. Morimoto, S. Nasu, and M. Tabuchi, *J. Electrochem. Soc.*, **148**, A730 (2001).
5. A. Eftekhari, *J. Power Sources*, **124**, 182 (2003).
6. T. Ohzuku, S. Takeda, and M. Iwanaga, *J. Power Sources*, **81–82**, 90 (1999).
7. S. Niketic, P. Whitfield, and I. Davidson, Meeting Abstracts, 213th ECS Meeting, Phoenix, AZ, **801**, 155 (2008).
8. Y. Shin and A. Manthiram, *Electrochem. Solid-State Lett.*, **6**, A34 (2003).
9. B. Markovsky, Y. Talyossef, G. Salitra, D. Aurbach, H.-J. Kim, and S. Choi, *Electrochem. Commun.*, **6**, 821 (2004).
10. N. M. Hagih, F. Cosandey, S. Rangan, R. Bartynski, and G. G. Amatucci, *J. Electrochem. Soc.*, **157**, A305 (2010).
11. S. S. Zhang, K. Xu, and T. R. Jow, *J. Solid State Electrochem.*, **7**, 147 (2003).
12. D. Aurbach, B. Markovsky, A. Rodkin, M. Cojocaru, E. Levi, and H.-J. Kim, *Electrochim. Acta*, **47**, 1899 (2002).

13. D. Aurbach, B. Markovsky, G. Salitra, E. Markevich, Y. Talyossef, M. Koltypin, L. Nazar, B. Ellis, and D. Kovacheva, *J. Power Sources*, **165**, 491 (2007).
14. K. Edström, T. Gustafsson, and J. O. Thomas, *Electrochim. Acta*, **50**, 397 (2004).
15. E. Peled, *J. Electrochem. Soc.*, **126**, 2047 (1979).
16. A. M. Andersson, K. Edström, N. Rao, and Å. Wendsjö, *J. Power Sources*, **81–82**, 286 (1999).
17. A. M. Andersson, A. Henningson, H. Siegbahn, U. Jansson, and K. Edström, *J. Power Sources*, **119–121**, 522 (2003).
18. D. Aurbach, *J. Power Sources*, **89**, 206 (2000).
19. E. Strauss, D. Golodnitsky, and E. Peled, *Electrochem. Solid-State Lett.*, **2**, 115 (1999).
20. Y. Talyossef, B. Markovsky, R. Lavi, G. Salitra, D. Aurbach, D. Kovacheva, M. Gorova, E. Zhecheva, and R. Stoyanova, *J. Electrochem. Soc.*, **154**, A682 (2007).
21. H. Duncan, Y. Abu-Lebdeh, and I. J. Davidson, *J. Electrochem. Soc.*, **157**, A528 (2010).
22. L. Yang, B. Ravdel, and B. L. Lucht, *Electrochem. Solid-State Lett.*, **13**, A95 (2010).
23. R. Dedryvere, D. Foix, S. Franger, S. Patoux, L. Daniel, and D. Gonbeau, *J. Phys. Chem. C*, **114**, 10999 (2010).
24. C.-M. Shen, X.-G. Zhang, Y.-K. Zhou, and H.-L. Li, *Mater. Chem. Phys.*, **78**, 437 (2003).
25. H. Rietveld, *Acta Crystallogr.*, **22**, 151 (1967).
26. S. S. Zhang, K. Xu, and T. R. Jow, *Electrochem. Commun.*, **4**, 928 (2002).
27. K. Kanamura, S. Shiraishi, H. Tamura, and Z.-i. Takehara, *J. Electrochem. Soc.*, **141**, 2379 (1994).
28. *Lithium Batteries Science and Technology*, G.-A. Nazri and G. Pistoia, Editors, Kluwer, Boston (2003).
29. H. M. Wu, I. Belharouak, H. Deng, A. Abouimrane, Y. K. Sun, and K. Amine, *J. Electrochem. Soc.*, **156**, A1047 (2009).
30. H. F. Xiang, X. Zhang, Q. Y. Jin, C. P. Zhang, C. H. Chen, and X. W. Ge, *J. Power Sources*, **183**, 355 (2008).
31. A. M. Andersson, D. P. Abraham, R. Haasch, S. MacLaren, J. Liu, and K. Amine, *J. Electrochem. Soc.*, **149**, A1358 (2002).
32. T. Eriksson, A. M. Andersson, A. G. Bishop, C. Gejke, T. Gustafsson, and J. O. Thomas, *J. Electrochem. Soc.*, **149**, A69 (2002).
33. M. N. Richard and J. R. Dahn, *J. Electrochem. Soc.*, **146**, 2068 (1999).
34. D. Aurbach, B. Markovsky, Y. Talyossef, G. Salitra, H.-J. Kim, and S. Choi, *J. Power Sources*, **162**, 780 (2006).
35. D. Ostrovskii, F. Ronci, B. Scrosati, and P. Jacobsson, *J. Power Sources*, **94**, 183 (2001).