The Study of Surface Phenomena Related to Electrochemical Lithium Intercalation into Li$_x$MO$_y$ Host Materials (M = Ni, Mn)

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We report herein on the comparative study of LiNiO$_2$ and LiMn$_2$O$_4$ electrodes in three salt solutions, namely, LiAsF$_6$, LiPF$_6$, and LiC(SO$_2$CF$_3$)$_3$ in a mixture of the commonly used ethylene and dimethyl carbonates. The surface chemistry of the electrodes in these solutions was studied by surface-sensitive Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, and energy-dispersive X-ray analysis, and their electrochemical behavior was studied by variable-scan-rate voltammetry and impedance spectroscopy. It was found that the electrochemical behavior of these electrodes is strongly dependent on their surface chemistry. Complicated reactions between the active mass and solution components, which include the solvents, the salt anions, and unavoidable contaminants such as HF and perhaps, HSO$_3$CF$_3$, lead to the precipitation of surface films through which the Li ion has to migrate in order to reach the active mass. The impedance spectroscopy of these electrodes clearly reflects their surface chemistry. It demonstrates the serial nature of the Li insertion-deinsertion processes, which includes, in addition to solid-state diffusion and accumulation of Li ion migration through surface films and their charge transfer across the surface film/active mass interface, which strongly depends on the chemical composition of the surface films and hence, the solution chosen. LiNiO$_2$ is considerably more reactive with these solutions than LiMn$_2$O$_4$ probably due to its stronger nucleophilic nature. In addition, in LiPF$_6$ solutions, the electrodes’ impedance is higher due to precipitation of films comprising LiF, which is highly resistive to Li ion transport (probably produced by reactions of the Li$_x$MO$_y$ active mass with trace HF).

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Experimental

Composite thin electrodes consisted of LiNiO$_2$ or LiMn$_2$O$_4$ powder (obtained from Merck), synthetic graphite KS-6 (Timcal, Inc.), and polyvinylidene difluoride (PVDF) binder (Aldrich) in 60%:30%:10% ratio by weight, with aluminum foil as the current collector. (Standard electrodes had geometric area and electrode mass of 1.5 cm$^2$ and 2 to 3 mg, respectively). The preparation of the electrodes has been described elsewhere.$^{11-15}$ The oxide powders have a specific surface area of 3 m$^2$/g [Brunauer-Emmett-Teller (BET) method, Gemini 2375 from Micromeritics, multipoint mode] and an average particle size of 1 μm, evaluated by SEM measurements performed with a JEOL JSM-840 microscope. We used electrochemical tests of EC and DMC (1:1 by volume) that contained three different salts: LiAsF$_6$ 1 M, LiPF$_6$ 1 M, or LiC(SO$_2$CF$_3$)$_3$ 0.75 M. The latter two solutions were battery-grade, ready-to-use solutions that could be used as received (obtained from Merck KGaA). The LiAsF$_6$ solution was prepared from Merck’s battery-grade solvents (could be used as received) and a salt from FMC, Inc. The initial water content in the solution was around 20 ppm [Karl Fischer titration with a Metrohm 562 trace water analyzer], and the initial HF content in the LiPF$_6$ solutions is estimated as a few tens of parts per million (Merck’s analytical information). We used a three-electrode electrochemical cell comprised of lithium counter and reference electrodes assembled together with the Li$_x$MO$_y$ composite working electrode in a polyethylene rectangular container (parallel-plate configuration, highly uniform current distribution). For the electrochemical measurements, the instrumentation included a computerized multichannel battery cycler (Arbin) and EG&G potentiostats (models 273 or 283) driven by Echem software (EG&G). The electrochemical impedance spectroscopy (EIS) studies covered a frequency range from 100 kHz to 5 mHz and were performed at 25°C ($\pm$0.5°C) using a Schlumberger (Solartron) 1286 electrochemical interface and a 1255 frequency-response analyzer driver by the Zplot software (Scribner). It should be emphasized that the use of three-electrode cells, the fact that no current flows between the working and the reference electrodes, and the use of the Schlumberger equipment (the reference electrode is connected to a very high impedance) all ensure that what is measured by EIS is only the response of the working electrode. Hence, the status of the lithium electrodes in the

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LiNiO$_2$ and LiMn$_2$O$_4$ are among the most important compounds used as cathode materials in rechargeable lithium batteries.$^{1,2}$ During recent years we have seen an increasing number of publications and patents dealing with these two compounds$^{3-5}$ and their derivatives (e.g., LiNi$_{1-x}$Co$_x$O$_2$. $^{6,7}$ LiMn$_{2-x}$M$_x$O$_4$, M = Cr, Ni, Cu, Al, etc.$^{8-10}$). Reviewing the relevant literature, it appears that most of the papers currently published are devoted to synthesis routes, performance analysis, capacity fading mechanisms, etc. During the last couple of years, we have published several papers dealing with the electroanalytical behavior of LiMO$_y$ (M = transition metal) and Li insertion electrodes in which we addressed some interesting surface phenomena related to these electrodes.$^{11-15}$ We found that the active mass of these electrodes is always covered by surface films, which are related to interactions between the electrodes and solution species. These surface films strongly affect the impedance and kinetic mechanisms of these electrodes. It can be definitely said that the overall Li insertion and deinsertion processes, and other phenomena that may explain capacity-fading mechanisms of LiNiO$_2$ and LiMn$_2$O$_4$ cathodes in practical Li-ion batteries. The connection between the experiments and the results described herein and phenomena observed in real battery systems is discussed.
various solutions (i.e., their different impedance in each solution) does not affect the impedance spectra of the composite electrodes presented herein. For FTIR spectroscopic measurements in diffuse reflectance mode, we used the Magna 860 spectrometer (Nicollet) equipped with a DRIFT accessory (Harrick) placed in a homemade glove box under CO₂- and H₂O-free atmosphere. EDAX measurements were performed using the Link, Inc., system attached to the SEM. XPS measurements were performed using the AXIS-HS XPS system from Kratos Analytical, Inc. (England). All these measurements were performed ex situ. The electrodes were prepared for the spectroscopic measurements in a VAC, Inc., glove box under highly pure argon atmosphere. In addition to the usual removal of trace O₂ and H₂O by this system, the glove box’s atmosphere was circulated through a trap with liquid nitrogen before treating the samples for the spectroscopic measurements. The samples were washed by highly pure (Tomiyama, Inc.) 2Me-THF or DMC (Selectipur Series from Merck KGaA) in order to remove residual salts and were then dried in vacuum. (All the glove boxes are equipped with separate vacuum lines.) The samples were then transferred to the various spectrometers (SEM, EDAX, FTIR, XPS) under highly pure argon atmosphere in hermetically sealed vessels. Our transfer procedures ensure that what we measure is indeed the authentic state of the electrodes’ surfaces as they leave the glove box (i.e., covered by the surface films formed in solutions) and not products of secondary reactions of the surface species with active atmospheric components such as H₂O and CO₂, which are eliminated from the atmosphere of the glove box of the FTIR spectrometer and are practically absent in the SEM (EDAX) or XPS systems that operate at high vacuum. It should be noted that the other atmospheric components O₂ and N₂ are not reactive with the surface species formed on these electrodes. A typical description of these transfer procedures (and transfer vessels) appears in Ref. 19.

Results and Discussion

The surface chemistry of LiNiO₂ and LiMn₂O₄ spinel electrodes in three solutions.—We collected information on the surface chemistry of these systems by surface-sensitive FTIR spectroscopy, EDAX, and XPS. In spite of the fact that the results thus obtained are coherent and meaningful, it should be noted that it is impossible to obtain an unambiguous picture on the surface chemistry of these systems, because it is too complicated. With the means available to date, it was possible to address some surface functional groups, the obvious impact of the presence of some solution species, and the direction of some processes, all of which clearly have an impact on the electrochemical behavior. Figure 1 shows three typical FTIR spectra of LiNiO₂ electrodes after being cycled in the three salt solutions, as indicated, together with a typical spectrum of the pristine electrode before any contact with the solution. Figure 2 provides FTIR spectra of LiNiO₂ electrodes after being stored at open circuit [open circuit potential (OCV) ~3 V vs. Li/Li⁺] in an EC-DMC mixture during 0.5 and 20 h, as indicated. Some peak assignments to functional groups based on Ref. 20-27 also appear in these figures. From these spectra, it can be clearly seen that the pristine active mass is covered by a Li₂CO₃ film. (In the DRIFT mode, the IR beam is reflected from the outer side of the particles.) Upon storage in the pure solvent mixture, this film remains persistent and stable, and probably protective. The spectra in Fig. 2 may also reflect some possible interactions with the solvents to form surface alkoxide groups (peak around 1100 cm⁻¹ related to ν(OCO)₂[Li]).

However, upon cycling, the surface chemistry of these electrodes changes considerably, as reflected by the spectra of Fig. 1. It seems that the pristine Li₂CO₃ film is replaced by surface layers comprised of a variety of species formed by interactions between the active mass and solution species, mainly the solvents. We see a variety of peaks related to organic C=C, C≡O, and C=O bonds, as indicated. The C≡O peaks appear 1800-1700 cm⁻¹ may indicate the formation of polycarbonate species, and the system of peaks around 1650 cm⁻¹ (ν(C=O)), 1450-1350 cm⁻¹ (δ(CCH₂CH₂)), 1350-1300 cm⁻¹ (ν(C≡O)), 1200-1100 ν(C−O), and 850 cm⁻¹ (δ(OCO)₂[Li]) resemble the spectra of ROCO₂Li species, as already discussed. The species with C≡O bonds around 1800-1700 cm⁻¹ (polycarbonates?) can be formed by polymerization of EC initiated by EC oxidation. ROCO₂Li, as well as the ROLi species, may be formed on the active surface due to possible (speculated) surface nucleophilic reactions between LiNiO₂ and EC or DMC, as follows

$$\text{LiNiO}_2 + (\text{CH}_3\text{O})_2\text{C}=\text{O} \rightarrow \text{NiO}_2 - \text{CH}_3\text{CH}_2\text{OCO}_2\text{Li}$$

[1]$$\text{LiNiO}_2 + \text{CH}_3\text{OCO}_2\text{CH}_3 \rightarrow \text{NiO}_2 - \text{CH}_3 + \text{CH}_2\text{OCO}_2\text{Li}$$

[2]$$\text{LiNiO}_2 + \text{CH}_3\text{OCO}_2\text{CH}_3 \rightarrow \text{NiO}_2 - \text{CO}_2\text{Li} + \text{CH}_3\text{OLi}$$

[3]$$\text{EC} \rightarrow \text{ROCH}_2\text{CH}_2\text{OCO}_2\text{CH}_2\text{CH}_2\text{OCO}_2 \rightarrow \text{EC}$$

[4]$$\text{RO}^- + \text{EC} \rightarrow \text{ROCH}_2\text{CH}_2\text{OCO}_2\text{CH}_2\text{CH}_2\text{OCO}_2$$

These suggested reactions may explain the functionalization of the electrode surfaces in these systems, as reflected by the wealth of
the IR peaks in the spectra of the cycled electrodes. This surface chemistry, as evident from these studies, is developed during cycling and not during storage at OCP. It seems that cycling helps to remove the pristine Li$_2$CO$_3$ film, thus enabling further massive reaction of the active mass with solution species.

EDAX and XPS studies of the electrode surface chemistry revealed clearly that in all three solutions, the salt anion or related impurities are also heavily involved in the electrode’s surface chemistry. EDAX measurements of cycled electrodes clearly showed a pronounced increase in the content of fluorine on their surface due to charge-discharge cycling in all three solutions. In addition, appreciable amounts of As, P, and S are also present in the surface films on electrodes cycled in LiAsF$_6$, LiPF$_6$, and LiC(SO$_2$CF$_3$)$_3$ solutions, respectively.

Figure 3 shows the results of a typical XPS element analysis of LiNiO$_2$ powder, stored for 2 days in the three solutions. The XPS spectra of the pristine powder reflect the presence of a carbonate film (C 1S peak around 290 eV). It appears from these studies that storing the powder in Li salt solutions leads to considerable changes in the surface chemistry, which is in contrast to storage in the Li salt-free solvent mixtures, which basically retain the pristine surface chemistry (Li$_2$CO$_3$ film, Fig. 2). We can speculate that acidic impurities in the salt solution, such as HF, AsF$_3$ or AsF$_5$, HSO$_3$CF$_3$, etc., react with the pristine surface film, leading to its breakdown and dissolution; thus, reactions of the active mass with solution species can take place.

The carbon spectra in Fig. 3, which contain several peaks, correlate well with the FTIR spectra of Fig. 1, which reflect the formation of a wealth of surface species. The group of peaks around 285 and 290 eV are in line with the formation of surface organic and inorganic carbonates, as well as alkoxydes (see discussion in Ref. 31 and 32). The peak around 294 eV, which relates to carbon at a high oxidative state, correlates with the 1800-1700 cm$^{-1}$ peaks in Fig. 1, and to our suggestions that polycarbonate species are formed. The presence of residual solvents in the samples should be excluded due to the ultra-high vacuum achieved during the XPS measurements (0.14 mPa).

It is very interesting that the C spectrum related to the LiPF$_6$ solution lacks the pronounced peak around 290 eV (carbonate carbons). This obviously reflects the presence of a considerable amount of HF contamination, which is sufficient to react with the carbonate species, solubilize them, and replace them with surface LiF, as already discussed. This is also reflected by the F spectra in Fig. 3, which show a pronounced LiF peak (685 eV) for the sample stored in the LiPF$_6$ solution. A small LiF peak also appears in the F spectrum of the sample stored in the LiAsF$_6$ solution.

The F spectra of the three samples clearly reflect the formation of other fluorine-containing surface species as well. The F peaks between 687 and 690 appearing in the F spectra of the three samples probably indicate the precipitation of As-F, P-F, and C-F containing species in the LiAsF$_6$, LiPF$_6$, and LiC(SO$_2$CF$_3$)$_3$ solutions, respectively. This is strongly evident from the fact that the spectra of these samples also contain As, P, and S peaks, respectively (Fig. 3). The spectra in Fig. 3 also reflect a wealth of oxidation states for the nickel atoms in the samples. This correlates with the description of the rich surface chemistry of the active mass in these solutions, in which LiNiO$_2$ participates as a nucleophilic agent, as suggested previously (Eq. 1-3). Prolonged cycling or storage seems to intensify the surface film formation on these electrodes in all three solutions. This is clearly seen in the SEM micrographs obtained from cycled electrodes as compared with the pristine ones (Fig. 4).

Figure 5 shows FTIR spectra of electrodes stored for prolonged periods of time after being cycled (a few charge-discharge galvano-
In contrast to the LiNiO$_2$ electrodes discussed, the surface chemistry of LiMn$_2$O$_4$ electrodes seems to be much more moderate. It can be said that the lithiated MnO$_2$ spinel is considerably less reactive than LiNiO$_2$. This is reflected by EDAX studies of cycled LiMn$_2$O$_4$ electrodes in the three solutions that do not show As, P, or S peaks.

Figure 6 shows FTIR spectra measured from LiMn$_2$O$_4$ electrodes after being cycled in the three solutions compared with a spectrum of a pristine electrode. In fact, this figure presents results from experiments and measurements which are quite similar to those carried out with the LiNiO$_2$ electrodes and presented in Fig. 1. The pristine LiMn$_2$O$_4$ seems to contain some surface Li$_2$CO$_3$ (indicated), and the cycled electrodes obviously reflect changes in the surface structure due to cycling and contact with the solutions. However, the spectra of Fig. 6 are much less rich in peaks than the parallel spectra of the LiNiO$_2$ electrodes. Similar conclusions were drawn from XPS spectra measured from Li$_x$Mn$_2$O$_4$ powder after being stored in the three solutions. The carbon spectrum of pristine LiMn$_2$O$_4$ has a major peak at 285 eV which belongs to elementary carbon, and only minor peaks at higher binding energy (e.g., a carbonate C peak around 290 eV). We suspect that this elementary carbon XPS peak may not result from a unique surface chemistry of these compounds but rather reflects a carbonaceous contaminant resulting from the production process. The XPS spectra of Li$_x$Mn$_2$O$_4$ powders stored in solutions contain peaks of elements (e.g., F, As, P, S) whose source is the electrolyte used. However, comparing the atomic ratios between the elements and Mn on the active mass surface with the atomic ratios between these elements and Ni in the spectra related to LiNiO$_2$ (Fig. 3) indicates that the relative amount of elements such as F, As, P, S, etc. resulting from possible reactions of the active mass with the electrolytes on the surface of the LiMn$_2$O$_4$ is much smaller compared with the case of LiNiO$_2$, as discussed above.

Figure 7 shows SEM micrographs of cycled LiMn$_2$O$_4$ electrodes in the three solutions compared with the micrograph of the pristine one. These pictures show some minor morphological changes of the electrode surfaces due to cycling. However, it is striking that the difference in morphology between the pristine and cycled electrodes in this case is much less pronounced compared with the LiNiO$_2$ electrodes (Fig. 4). The spectroscopic studies described in this section seem to indicate that the spectral and morphological features in Fig. 1-7 reflect the formation of surface films on these electrodes, mostly due to their intrinsic reactions with solution components. We should not rule out the possibility that the surface chemistry of these electrodes can also be influenced by the anode side, i.e., surface species such as Rocco$_2$Li, Li$_2$CO$_3$, LiF, etc., formed on the Li

Figure 5. FTIR spectra (diffuse reflectance mode) of electrode material scraped from LiNiO$_2$ electrodes after a few galvanostatic charge-discharge cycles (3.2-4.2 V vs. Li/Li$^+$) in (b) LiPF$_6$, (c) LiAsF$_6$, and (d) LiC(SO$_2$CF$_3$)$_3$ EC-DMC (1:1) solutions. A dimension scale (50 μm) appears in each picture.

Figure 6. FTIR spectra of LiMn$_2$O$_4$ electrodes after a few galvanostatic charge-discharge cycles (3.2-4.2 V vs. Li/Li$^+$) in LiAsF$_6$ 1 M, LiPF$_6$ 1 M, and LiC(SO$_2$CF$_3$)$_3$ 0.75 M solutions in EC-DMC 1:1 (as indicated). A spectrum of the pristine electrode is also presented. Composite electrode material containing LiMn$_2$O$_4$, graphite, and PVDF binder was scraped from each electrode and measured by diffuse reflectance mode.

Figure 7. SEM micrographs of (a) a pristine composite LiNiO$_2$ electrode and electrodes after a few galvanostatic charge-discharge cycles (3.2-4.2 V vs. Li/Li$^+$) in (b) LiPF$_6$, (c) LiAsF$_6$, and (d) LiC(SO$_2$CF$_3$)$_3$ EC-DMC (1:1) solutions. A dimension scale (50 μm) appears in each picture.
counter electrodes,19,26-32 obviously saturate the solution and thus precipitate on the cathode surfaces. However, such anode-cathode impacts are not the dominant surface processes, as we see a pronounced difference in the behavior of LiNiO₂ and LiMn₂O₄ electrodes, although the experiments with them were almost identical. If the major surface species formed on the cathodes would originate from the anode side, the surface chemistry of LiNiO₂ and LiMn₂O₄ (as reflected by FTIR and XPS measurements) should be similar.

Further evidence for continuous and organized surface film formation on these electrodes (rather than sporadic precipitation of surface species coming from the anodes) is obtained by the impedance measurements of these electrodes, to be described later in this paper.

Figure 7. SEM micrographs (a) of a pristine LiMn₂O₄ composite electrode and those LiMn₂O₄ after a few galvanostatic charge-discharge cycles (3.2-4.2 V vs. Li/Li⁺) in the three EC-DMC salt solutions: (b) LiPF₆, (c) LiAsF₆, and (d) LiC(SO₂CF₃)₃. A dimension scale (50 μm) appears on each picture.

The voltammetric response of LiₓMO₅ (M = Ni, Mn) electrodes as a function of the solution used.—Figure 8 shows the first three cyclic voltammograms of pristine LiNiO₂ electrodes in LiAsF₆, LiPF₆, and LiC(SO₂CF₃)₃ solutions (a-c, respectively) at 0.5 mV/s. As already discussed in previous papers, this scan rate can be considered fast for Li intercalation into host materials such as graphite and LiMO₅ (M = Co, Ni, Mn).11-18 The fine features related to intercalation stages and phase transitions, i.e., probing of the basic thermodynamics of these processes, requires much slower scan rates (in the order of tens of microvolts per second and below). Hence, cyclic voltammetry with scan rates in the order of hundreds of microvolts per second probes kinetic limitations, such as Rct, and the resistance to Li ion migration through the surface films. It should also be noted that solid-state Li⁺ ion diffusion into these host materials can be probed by intermediate scan rates between tens and hundreds of microvolts per second, depending on the material used and the diffusion length (i.e., particle size).17 Hence, the cyclic voltammograms (CVs) of Fig. 8 reflect kinetic limitations of these electrodes. It is significant that in each solution different first and second cycle voltammetric behavior is observed, although the electrodes were almost identical in these experiments. The first cycle for all three electrodes reflects some kinetic limitation as the current response is obtained at higher potentials compared with the steady-state voltammograms. Steady-state voltammograms, in which the basic Li insertion and deinsertion processes are reflected, are achieved in a LiAsF₆ solution in a second consecutive cycle, for a LiPF₆ solution in a third consecutive cycle, and for the LiC(SO₂CF₃)₃ solution, at least four consecutive cycles are required until a steady-state CV behavior can be observed. After the steady-state voltammogram of the LiNiO₂ electrodes is obtained in the three solutions, lowering the scan rate leads to the well-known slow-potential-scan-rate CV picture which shows four basic reversible Li insertion-deinsertion processes, as already presented.11-15

This voltammetric picture and the strong salt effect observed correlate with the surface chemical studies of these electrodes described in the previous section, which clearly showed that in each solution different surface chemistries are developed. During the first cycles of a pristine electrode, the initial Li₂CO₃ film is replaced by other surface species related to the solution components. Hence, the first few CV cycles reflect the replacement and rearrangement of the surface films which are specific to each solution. The order in the number of cycles needed for an electrode to reach steady state in each solution, LiAsF₆ < LiPF₆ < LiC(SO₂CF₃)₃, is very significant because it seems to reflect the order of the complexity in the surface chemistry developed in each solution.

In the case of LiAsF₆ solutions, the surface chemistry relates mostly to solvent reactions. Since solvent molecules are the major-
ty in the solution species, stabilization is expected to be obtained relatively quickly. In the other two solutions, the surface chemistry is strongly affected by contaminants and by the salt anions, whose concentration is smaller, and thereby, reaching steady state on the electrode surfaces takes longer and/or more CV cycles.

Figure 9 summarizes quite similar voltammetric studies with the LiMn$_2$O$_4$ electrodes. Figure 9a-c shows two consecutive CVs of pristine electrodes at 0.5 mV/s in the three solutions. Decreasing potential scan rate, 0.5 mV/s $\rightarrow$ 10 $\mu$V/s, leads to the normal, expected (slow-scan-rate) voltammetric behavior of the LiMn$_2$O$_4$ spinel electrodes in the potential domain from 3.2 to 4.2 V vs. Li/Li$^+$ with all three solutions.\textsuperscript{11-14,34} It is very significant that the CVs of the electrodes in the three solutions are very similar. In all three solutions a nearly steady-state voltammetric behavior is achieved in the second cycle, and the differences between the first and second consecutive CV cycles are minor (Fig. 9). This correlates with the surface chemical studies of these electrodes (previous section) which revealed that these electrodes are much less reactive toward solution components compared with the LiNiO$_2$ electrodes, and also that the difference in their surface chemistry in the three solutions is relatively small.

Impedance spectroscopic studies.—Figure 10 shows typical families of Nyquist plots obtained from LiNiO$_2$ electrodes at equilibri-
um at different potentials (indicated) in the three solutions. Figure 10a-c relates to the LiAsF$_6$ solutions, while Fig. 10d and e relates to the LiPF$_6$ and LiC(SO$_2$CF$_3$)$_3$ solutions, respectively. These series of measurements were conducted after the electrodes were washed potentiodynamically (CV), and hence, their surface chemistry reached a steady state. In fact, impedance spectra measured from these electrodes in these solutions were modeled and discussed in depth in previous papers.$^{11-15}$ In brief, they reflect three major time constants: a high-frequency semicircle related to the surface films ($R_{Li-ion migration} \ \text{coupled with}\ \text{film capacitance}$), a medium-to-low-frequency semicircle related to $R_{ct}$ coupled with some interfacial capacitance, and a “Warburg-type element” which relates to the solid-state Li ion diffusion in the bulk of the active mass. When the electrodes are thin enough and reach potentials in which $R_{ct}$ is low, at the very low frequencies (mHz region), the Nyquist plot becomes a steep line that reflects a nearly capacitive behavior and in fact reflects the bulk electrode’s differential capacitance, $C_{int}$ (i.e., accumulation of Li ion in the active mass). Hence, in this case $C_{int} = 1/Z^\prime \prime_{aq}$.$^{17}$ The calculation of $C_{int}$ vs. $E$ from EIS according to this formula should give a plot very similar to that obtained by the slow-scan-rate CV. ($I$ vs. $E$ translated to $C_{int}$ vs. $E$ by division of $k(E)$ by the potential scan rate $v$.). It seems that when these electrodes are thin enough and there are no detrimental destructive interactions between the active mass and the solution species, their impedance spectra reflect very nicely the serial nature of the overall Li-insertion process: Li ion migration through surface film–charge transfer across the surface film–active mass interface/solid-state, Li ion diffusion in the bulk, and finally, accumulation of Li in the bulk of the active mass. The time constants attributed to $R_{ct}$ (low-to-medium frequencies) and diffusion are strongly potential dependent,$^{11-15}$ as seen also in Fig. 10.

The spectra of Fig. 10a-c (LiAsF$_6$ solution), which reflect quite a good resolution and a reasonable separation of the contributions of the major time constants and processes which contribute to the electrode impedance, show that in terms of depending on the electrodes, solutions, and experimental setup, impedance spectroscopy can serve as a meaningful complementary tool for studying the effect of solution composition on the behavior of these electrodes. It is very significant that the spectra in Fig. 10a-c and 10e related to the LiAsF$_6$ and the LiC(SO$_2$CF$_3$)$_3$ solutions are very similar in their basic structure, while the spectra in Fig. 10 (LiPF$_6$ solution) are completely different. The Nyquist plots of Fig. 10d contain one big semicircle related to most of the frequency range of interest (high-to-low frequencies) instead of the separation to different features, as described previously appearing in the spectra of Fig. 10a-c and e. This difference in behavior is well understood in light of the surface chemical studies (section above). The studies of these electrodes by XPS clearly showed that in the LiPF$_6$ solution LiF is a major constituent on the LiNiO$_2$ electrode surfaces, probably due to the reaction of the active surface with unavoidably present trace HF.

Our previous extensive studies of lithium and lithiumated carbon electrodes in similar solutions$^{35}$ clearly showed that whenever LiF films are formed on these electrodes, their impedance is very high because of the relatively high resistivity of thin LiF films for Li ion transport.$^{36}$ Hence, the big semicircle in the plots of Fig. 10d reflects the formation of highly resistive surface films on LiNiO$_2$ electrodes in a LiPF$_6$ solution, whose impedance response masks contributions of other time constants related to charge transfer and solid-state diffusion.

Figure 11 shows a finer comparison between the impedance responses of the LiNiO$_2$ electrodes in LiAsF$_6$ and LiC(SO$_2$CF$_3$)$_3$ solutions. It compares $C_{int}$ vs. $E$ calculated from $Z^\prime$ at the lowest frequency used (which is the closest to the $\omega \rightarrow 0$ condition) as explained previously, for the electrode in the LiAsF$_6$ solution (Fig. 11a), and $R_{film}$ and $R_{ct}$ calculated from the diameters of the high-frequency and the medium-to-low frequency semicircles in the Nyquist plots for electrodes in both solutions (Fig. 11b). The more well resolved the spectra, e.g., when the surface film’s resistance is sufficiently low, the more $C_{int}$ vs. $E$ calculated from EIS should resemble the slow scan rate cyclic voltammetry (SSCV) curve ($I$ vs. $E$ or $I/v = C_{int} \ \text{vs.}\ \ E$). It should be noted, however, that the resolution of $C_{int}$ vs. $E$ calculated from EIS depends strongly on how low is the lowest $\omega$ in the experiment. Due to practical reasons (e.g., experiment duration), the lowest frequency in our experiments was 5 mHz, which is not low enough to obtain the best resolution in the $C_{int}$ vs. $E$ curve.

A reasonable resolution of $C_{int}$ vs. $E$ was obtained only for the electrode treated in the LiAsF$_6$ solution. (The plot in Fig. 11a should also be compared with the SSCV plots related to the very low scan rates appearing in Ref. 11, 12, and 15.) Following the determination of the various $R$ values on the potential in Fig. 11b shows that for both electrodes $R_{film}$ is potential invariant, while $R_{ct}$ strongly depends on the potential and is a function with a minimum at potentials from 3.8 to 4 V (vs. Li/Li$^{+}$), as already discussed in a previous paper.$^{11}$ It is significant that $R_{ct} (\text{LiAsF$_6$}) > R_{ct} (\text{LiC(SO$_2$CF$_3$)$_3$})$ and $R_{film} (\text{LiC(SO$_2$CF$_3$)$_3$}) > R_{film} (\text{LiAsF$_6$})$ in most of the potential range of interest. This reflects the fact that the surface chemistry of LiNiO$_2$ in these solutions strongly depends on the electrolyte used, as demonstrated in the section on surface chemistry. Thus, in each solution the transport properties of the surface films developed on the electrodes should be different. We attribute $R_{ct}$ to Li ion transport across the surface film–active mass interface. Hence, it is expected that a different chemical structure of the surface films in these two cases leads to the difference in $R_{ct}$ shown in Fig. 11b. We also studied the impact...
of storage of these electrodes in electrochemical cells, which complements the study of the effect of storage on the electrodes’ surface chemistry shown in Fig. 5.

Figure 12 shows sets of Nyquist plots measured with a LiNiO$_2$ electrodes after being stored for 25 and for 120 days in a cell with an EC-DMC/LiC(SO$_2$CF$_3$)$_3$ solution (lithiated state). When comparing these plots with those in Fig. 10, it is clear that storage of LiNiO$_2$ electrodes in these solutions considerably increases their impedance, as a function of storage time. Both $R_{\text{film}}$ and $R_{\text{ct}}$ increase. Hence, these results further show that the LiNiO$_2$ electrode can be highly reactive with commonly used solution species. It is interesting to note that lithiated graphite electrodes in the same solution exhibit much higher stability during storage. Once a steady state is achieved after formation of stable surface films, the impedance of lithiated graphite electrodes in these solutions is basically stable upon storage with no cycling. We tend to attribute this difference in stability to the fact that on the LiNiO$_2$ electrode’s surface there are conditions for polymerization of solvent molecules (EC). This seems to be evident from the spectra of Fig. 5, which indicate the formation of polycarbonate (1800-1700 cm$^{-1}$ IR bands). Such polymerization is not blocked by the growth of the surface film because it does not propagate by electron transfer from the active mass, but rather is due to surface reactions of partially polymerized species with solvent molecules, probably catalyzed by acidic contaminants coming with the salt.

In contrast, on lithiated carbons, the surface films relate to solvent and salt reduction, which form relatively small molecules such as carbonates, Li halides, etc. These relatively small ionic molecules passivate the electrode and block it for electron transfer to solution species (which is the major route for surface film formation). Therefore, a steady state for these Li-carbon electrodes is achieved only when the surface films are sufficiently thick.

Figure 13a-f shows families of Nyquist plots measured from LiMn$_2$O$_4$ spinel electrodes in the three solutions at different potentials, as indicated.
In general, the impedance behavior of the LiMn$_2$O$_4$ electrodes in the three solutions is very similar, in contrast to the pronounced differences among the impedance of the LiNiO$_2$ electrodes. These spectra were also discussed in previous papers, and their various features were assigned to the time constants of the serial Li insertion-deinsertion processes$^{11-14}$. In brief, all the spectra contain a potential-invariant, high-frequency semicircle related to Li ion migration through surface films, a medium-to-low frequency semicircle which is strongly potential dependent, attributed to charge transfer across the surface film/active mass interface, a very pronounced and well separated "Warburg"-type element (low frequencies) related to the solid-state Li ion diffusion, and finally, at the lowest frequencies the $Z''$ vs. $Z'$ plots become steeper lines. ($C_{"\text{int}}$ can be calculated from $Z''$ at $\omega \rightarrow 0$).

Figure 14 shows $C_{\text{int}}$ vs. $E$ calculated from EIS for LiMn$_2$O$_4$ electrodes and LiC(SO$_2$CF$_3$)$_3$ solutions. In contrast to the case of LiNiO$_2$ electrodes, whose $C_{\text{int}}$ could not be calculated at a reasonable resolution from EIS measured in these two solutions (because of the high resistivity of the surface films), EIS of LiMn$_2$O$_4$ electrodes in these solutions allowed the calculation of $C_{\text{int}}$ vs. $E$ in both solutions at an impressive resolution. (The curves in Figure 14 should be compared with the typical SSCV curves of these electrodes previously presented.$^{11-14}$)

Figure 15 shows $R_{\text{film}}$ and $R_{\text{ct}}$ vs. $E$ (calculated from the diameters of the relevant semicircles) for the LiMn$_2$O$_4$ electrodes in the two solutions. As expected and already discussed$^{11}$, $R_t$ is nearly potential invariant, while $R_{\text{ct}}$ is high at the low and high potentials and minimal at middle potentials (in the range from 3.9 to 4.15 V) for both electrodes. It is significant, however, that the values of both $R_t$ and $R_{\text{ct}}$ in the LiPF$_6$ solution are higher than in the LiC(SO$_2$CF$_3$)$_3$ solution. We attribute this to the formation of more resistive surface films due to LiF precipitation on the electrode's surface via reaction of HF unavoidably present in LiPF$_6$ solutions with the active mass (as indicated by the XPS studies).

It is significant that for all three solutions the LiMn$_2$O$_4$ electrode's impedance was lower and the spectral features better resolved (e.g., $R$ and $C_{\text{int}}$ vs. $E$) compared with LiNiO$_2$ electrodes. Hence, these results complete the evidence that the LiNiO$_2$ material is more reactive with solution components than LiMn$_2$O$_4$.

**Conclusion**

This paper further demonstrates that the electrochemical behavior of commonly used cathode materials for Li-ion batteries (LiNiO$_2$ and LiMn$_2$O$_4$) to some extent strongly depends on their surface chemistry in solutions, in a similar way as was found for the electrochemical response of the lithiated carbonaceous anodes in the same solutions. It appears from the spectroscopic studies (XPS, EDAX, FTIR) that the active mass particles (both LiNiO$_2$ and LiMn$_2$O$_4$) are covered initially by pristine surface films comprised of Li$_2$CO$_3$ as a major component. Upon storage in solution, this film is replaced by solution-related surface species comprised of a variety of possible compounds, including ROLi, ROCO$_2$Li, polycarbonates, and salt-reduction products (which can include LiF, moieties containing As–F and P–F bonds, and reaction products of the SO$_2$CF$_3$ group containing sulfur, etc.).

At present we cannot draw exact mechanisms for the formation of these surface films. We assume that one source could be possible nucleophilic reactions of the LiMO$_2$ species with the alkyl carbonate solvents which are strong electrophiles. Acidic contaminants coming from the salts (HF, AsF$_5$, AsF$_3$, HSO$_3$CF$_3$, etc.) may also play an important role in the surface chemistry, reacting with the active mass in acid-based reactions. Such acidic species can catalyze polymerization of the alkyl carbonate solvents to surface polycarbonate species detected by the FTIR and XPS spectroscopic studies. LiNiO$_2$ was found to be much more reactive toward solution species than LiMn$_2$O$_4$. The surface chemistry strongly influences the impedance behavior of these electrodes and their kinetics. In general, the impedance of the LiNiO$_2$ electrodes is higher than that of LiMn$_2$O$_4$, probably because the former material is more nucleophilic and basic.

In general, it seems that in LiAsF$_6$ solutions the surface chemistry is the most stable and solvent related in the three salt solutions examined, and hence, the electrode impedance in LiAsF$_6$ solutions is the lowest. In LiPF$_6$ solutions, HF seems to play an important role, and thus, the electrode impedance is relatively high due to the precipitation of surface LiF. In the case of Li(C(SO$_2$CF)$_3$)$_3$, we cannot decide at the moment if the anion reacts directly on the cathode material or whether traces such as HSO$_2$CF$_3$ play a major role. Prolonged storage or cycling allows continuous surface reactions to proceed further (especially when acidic contaminants are involved), leading to the increase of the electrodes' impedance. However, it should be noted that all the surface chemistry discussed affects only the surface of the active mass and not its bulk. Hence, the significance of the above-described phenomena in practical battery systems may not be as pronounced as described in this paper due to the high ratio between the electrode surface area and solution volume in practical battery systems, which makes the effect of reactive contaminants relatively smaller than in laboratory testing cells, which usually contain an excess of solution.

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