



## Short communication

# Characterization of interphases appearing on $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ using $^7\text{Li}$ MAS NMR

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## ABSTRACT

$^7\text{Li}$  MAS NMR, usually a bulk characterization technique, is used here to analyze the positive electrode/electrolyte interphase. The sharpening of the NMR spectra line shape as the amount of surface species increases shows that the observed signal is clearly the sum of signals due to the distribution of lithium ions in the interphase in terms of distance from the bulk of electrode active material. This technique is then used to compare characteristics of the interphase coming from the contact with  $\text{LiPF}_6$ -based electrolyte in the case of storage or electrochemical cycling. A clear influence of the change of potential on the interphase configuration and in particular on its intimacy with the bulk of active material is deduced from the change in NMR spectra lineshape. This information is hardly obtained by other characterization technique, making NMR a powerful tool for the study of interphases and passivation layers in lithium batteries materials.

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## 1. Introduction

The so-called solid electrolyte interphase (SEI) between the negative electrode and the electrolyte of a Li-ion battery is known to monitor the overall battery behavior in terms of irreversible capacity loss, charge transfer kinetics and storage properties [1–4]. More than 10 years of research in this field have led to excellent control and optimization of the SEI layer. Interfacial reactions and the growth of a passivation layer at the positive electrode have been identified of paramount importance because they can lead to performance degradation of the battery upon aging and cycling [5,6]. However, the chemical, physical and structural properties of the interfacial layer at positive electrode, and its modification upon cycling, are still poorly known.

MAS NMR, as a local probe, is a useful tool to obtain informations on the chemical and structural local environment of the nucleus under observation ( $^6\text{Li}$ ,  $^7\text{Li}$ ,  $^1\text{H}$ , etc.), complementary to EIS measurements, to long range probe such as X-ray diffraction and surface probes such as XPS. This technique has been recently successfully applied to the observation of interphase layers on lithium nickel oxide based positive electrodes of lithium-ion batteries [7–9].

The main goal of the present work is to shed light on the formation and evolution of electrode/electrolyte interphase. The layered  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ , which is a promising candidate for lithium battery cathode [10–13] has been studied in this context. We show in this study that  $^7\text{Li}$  MAS NMR is an appropriate characterization tool, able to describe subtle changes in the electrode/electrolyte interphase configuration. This technique is then used to discuss the influence of the electrochemical cycling on the interphase compared to a simple storage in electrolyte.

## 2. Experimental

The  $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$  samples used for this study have been obtained through the classical coprecipitation method described elsewhere [12,13]. A series of four samples was made by mixing manually lithium carbonate with  $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ , with a 1/2, 1/4, 1/8, 1/16  $\text{Li}_2\text{CO}_3/\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$  weight ratio, using pestle and mortar. A second series of two samples were obtained by simply soaking one sample in  $\text{LiPF}_6$  (1 M EC/DMC 1:1) electrolyte for 10 h and achieving an electrochemical galvanostatic cycle in 10 h between 2.5 and 4.5 V for the second one. The two samples had a comparable time of contact with the electrolyte. Samples were stored in argon. Galvanostatic cycling was performed using Swagelok cells and MacPile system at a C/20 rate. A slurry of the electrode powder in n-methyl-pyrrolidinone (NMP) was deposited on a 1-cm<sup>2</sup>

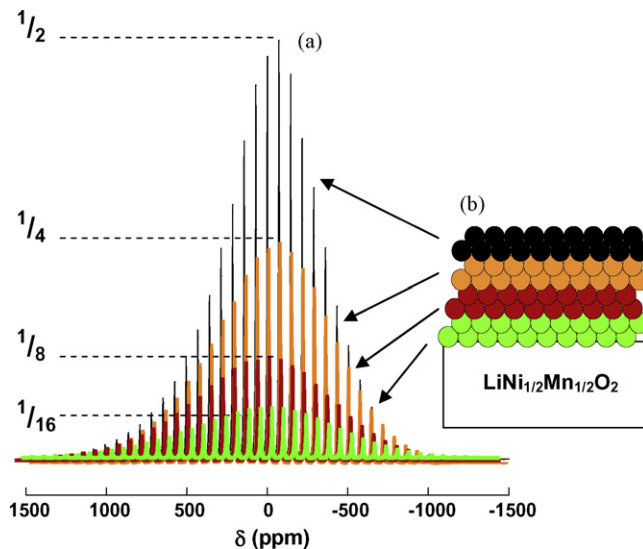
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aluminum disk and then dried under vacuum at 100 °C for 24 h. Electrodes were constituted of 75 w% of active material, 20 w% of ketjenblack carbon and 5 w% poly-vinylidene di-fluoride (PVdF).  $^7\text{Li}$  NMR measurements were carried out at room temperature on a Bruker Avance-500 spectrometer ( $B_0 = 11.8$  T, Larmor frequency  $\nu_0 = 194.369$  MHz in  $^7\text{Li}$  resonance). Single-pulse MAS spectra were obtained by using a Bruker MAS probe with a cylindrical 4-mm o.d. zirconia rotor. Spinning frequencies up to 14 kHz were used. A short single-pulse length of 1  $\mu\text{s}$  corresponding to a non-selective  $\pi/2$  pulse was applied. Recycle time was in the 0.5–60 s range and a spectrometer dead time (preacquisition delay) of 4.5  $\mu\text{s}$  was used before each acquisition. The isotropic shifts, reported in parts per million (ppm), are relative to an external powder sample of LiCl set at 0 ppm. In order to perform a quantitative analysis, the different spectra have been analyzed considering the total integrated intensity of the signal for each sample. Of course, all parameters were kept as constant as possible for each series of NMR measurements: number of scans, probe tuning process, spinning frequency, etc. The spectra displayed in this work were normalized taking into account the number of scans and the mass of sample.

### 3. Results and discussion

Like most of electrode materials used in lithium batteries,  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  is paramagnetic and contains transition metal ions, with unpaired electrons ( $\text{Ni}^{\text{II}}$ ,  $t_{2g}^6 e_g^2$  and  $\text{Mn}^{\text{IV}}$ ,  $t_{2g}^3 e_g^0$ ). In this case, the NMR signal corresponding to lithium ions within the host matrix will be dominated mainly by two extremely large interactions, with unpaired electrons [14]: the Fermi-contact interaction and a nucleus–electron dipolar interaction. The Fermi-contact interaction, as a measure of the unpaired electron spin density transferred from the paramagnet to the nucleus through overlapping orbitals [14,15], contains information about chemical bonding involving the paramagnetic transition metals and thus, concerns mostly lithium ions intercalated within the electrode active material. No Fermi-contact interaction is observed for lithium contained in the surface species as there is no chemical bonding with the active material. On the other hand, the dipolar interaction is caused by the local magnetic field in the vicinity of the nucleus under observation and then, is not necessarily linked to chemical bonds. This interaction is then dominating the signal observed for lithium detected in the species that form the electrode/electrolyte interphase [9]. In addition, this interaction will be responsible for the very large set of spinning sidebands [7,9] containing information about the interaction between lithium in the interphase and the electrode active material. The dipolar interaction has a  $(1/r)^3$  dependency where  $r$  is the distance between the two dipoles involved [16]. Then, a large dipolar interaction, leading to a broad NMR spectra lineshape will correspond to a small distance between the nucleus under observation (Li) and the paramagnetic centres of the electrode active material.

Because the gyromagnetic ratio of the unpaired electrons is several orders of magnitude larger than nuclear ones, an extremely strong dipolar interaction is observed between lithium nuclear spins and electronic spins of nearby localized unpaired electrons. It usually lead to a very broad and unresolved signal, corresponding to lithium ions within the structure of the host matrix and can mask the signal rising from lithium in the passivation layer/interphase. Therefore, a method allowing the observation of the interphase alone becomes necessary. The interphase can be considered as a secondary phase surrounding grains of electrode material and thus, further away from the paramagnetic Ni and Mn of the electrode material. Due to smaller distance from the paramagnetic centers, the dipolar interaction will be stronger for lithium within



**Fig. 1.** (a) Normalized  $^7\text{Li}$  MAS NMR spectra for  $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$  mixed with various  $\text{Li}_2\text{CO}_3/\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$  weight ratios: 1/16 (red), 1/8 (green), 1/4 (orange) and 1/2 (black). (b) Scheme showing the stacking of lithium species on the surface of active material corresponding to the previous ratios. The white rectangle represents an idealized section of the surface of one particle of active material and the disks represent particles or aggregates of diamagnetic lithium-containing species.

the electrode material and the corresponding NMR signal will have a much shorter relaxation time causing a faster decay compared to lithium in the interphase. Therefore, using a single pulse with a long preacquisition delay suppresses the fast decaying signal from lithium within the intercalation compound which makes the signal assigned to the surface lithium much more pronounced and easier to analyze [7,9].

As opposed to lithium ions within the electrode active material, surrounded by paramagnetic centers, on well-defined crystallographic positions, in the case of interphases or passivation layers, we will observe mostly intrinsically diamagnetic species that are usually found on the surface of these paramagnetic electrode materials. According to previously published works, compounds such as  $\text{Li}_2\text{CO}_3$  (in the case of atmosphere exposure) or LiF,  $\text{Li}_x\text{PO}_y\text{F}_z$ , lithiated polycarbonates and polymeric hydrocarbons coming from the decomposition of the electrolyte can be simultaneously observed [17–20]. XPS analysis of our samples were consistent with previously published data [21]. It is clearly a much more disordered and complex system and the thickness of the interphase has to be considered since a distribution of distance between lithium in the interphase and paramagnetic centers can be expected. These different lithiated species in the interphase are intrinsically diamagnetic and considering the small range of diamagnetic lithium in NMR, it is not possible to discriminate them.

In a previous paper, we have demonstrated that the progressive broadening of the lineshape of single-pulse NMR spectra reflects the strength of the nucleus/electron dipolar interaction between lithium in the interphase and paramagnetic electrode material and gives extremely useful structural information about the intimacy between the diamagnetic surface species and the bulk of paramagnetic electrode material [8,9]. Here,  $^7\text{Li}$  MAS NMR experiments have been performed on a model system made of  $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$  mixed with various  $\text{Li}_2\text{CO}_3/\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$  ratios. The  $\text{Li}_2\text{CO}_3$  secondary phase has been mixed using the same protocol for all ratios investigated and therefore, it is assumed that the intimacy between the first atomic layers of  $\text{Li}_2\text{CO}_3$  and the surface of  $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$  is similar for all samples. Therefore, the amount of surface lithium is the only changing parameter. Fig. 1a displays the superimposition

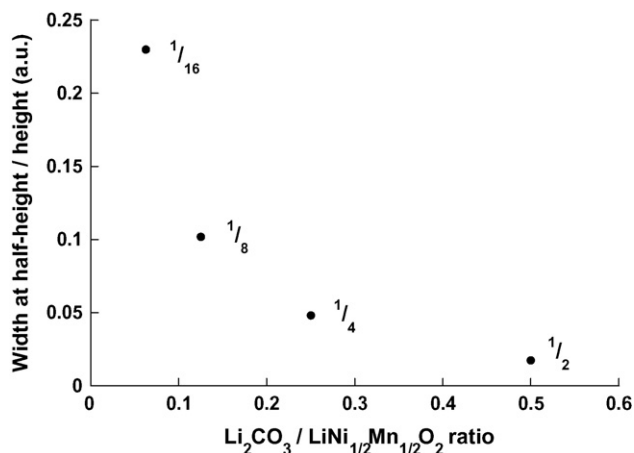


Fig. 2. Half-height width of  ${}^7\text{Li}$  NMR spectra normalized to the height as a function of  $\text{Li}_2\text{CO}_3/\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$  ratio.

of the normalized  ${}^7\text{Li}$  MAS NMR spectra obtained for the four different ratios. The spectra have been plotted with the same baseline to show the change in the NMR signal line shape with the amount of diamagnetic phase surrounding the electrode paramagnetic phase. The four spectra have a similar span ranging approx. from 1500 to  $-1200$  ppm and sideband intensities increase only in the central part and not in the external part of the spectrum when the amount of lithium increases.

In Fig. 2 is reported the width at half-height normalized to the height as a function of the  $\text{Li}_2\text{CO}_3/\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$  for each  ${}^7\text{Li}$  MAS NMR spectrum. The clear progressive decrease confirms that the spectra line shape become thinner for larger  $\text{Li}_2\text{CO}_3/\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$  ratio and thus more relative intensity is found in the central part of the spectrum as the amount of lithium carbonate increases. The observed evolution is well described by the stacking of  $\text{Li}_2\text{CO}_3$  particles submitted to a progressively weaker dipolar interaction with the paramagnetic bulk of active material, leading to a sharper signal as the ratio of  $\text{Li}_2\text{CO}_3$  increases, as shown in Fig. 1b.

These results show that the observed  ${}^7\text{Li}$  NMR signal do not rise from only one type of lithium, as it is usually the case for the electrode active material, but has to be considered as the superimposition of signals coming from a distribution of lithium with respect to the distance with the surface of the paramagnetic electrode material as schematized in Fig. 1b. Moreover it shows that  ${}^7\text{Li}$  NMR is a technique sensitive not only to the intimacy between the first atomic layers of the lithium-containing interphase and the bulk of paramagnetic material but also to the thickness of the interphase, information hardly obtained by other techniques such as XPS and IR.

It has to be noted that mixed  $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2/\text{Li}_2\text{CO}_3$  samples must be considered as a model system and they neither directly represent the chemical composition nor the built-up of layers formed in batteries due to charge and discharge processes. The mixed  $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2/\text{Li}_2\text{CO}_3$  samples are in fact intimate dilutions. Nevertheless, when deposits of salt-based  $\text{LiF}$  or  $\text{Li}_x\text{PO}_y\text{F}_z$ , for instance, appears from the decomposition of the electrolyte, the same definition can be applied: intrinsically diamagnetic  $\text{Li}_2\text{CO}_3$  or  $\text{LiF}$  are found on, or around, the surface of the paramagnetic materials [17]. The mixed  $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2/\text{Li}_2\text{CO}_3$  samples can then be considered as realistic representations, from the point of view of NMR, describing the evolution of the interaction between two phases (one being the diamagnetic surface phase and the other being the paramagnetic  $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ ) when the intimacy/proximity between them evolve with the amount of surface diamagnetic phase.

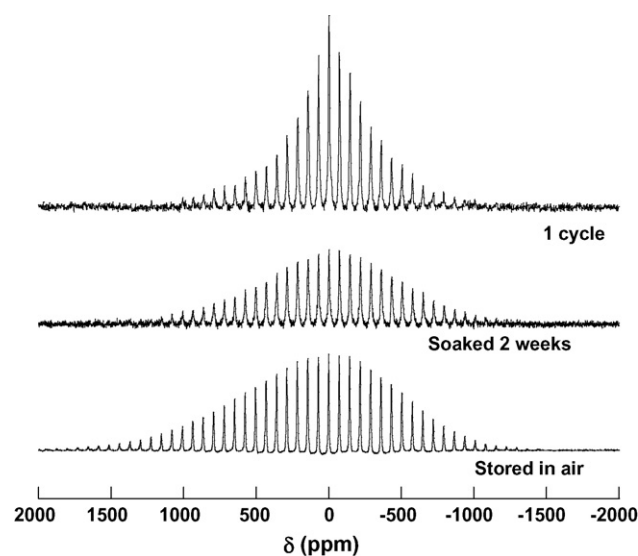


Fig. 3. Normalized  ${}^7\text{Li}$  MAS NMR spectra for  $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$  samples soaked in  $\text{LiPF}_6$  (1 M EC/DMC) electrolyte for 2 weeks, recovered at the end of discharge after one charge–discharge cycle and pristine  $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$  stored in ambient atmosphere.

This technique appears therefore, particularly appropriate to follow the evolution of the interphase coming from the contact with  $\text{LiPF}_6$  (1 M EC/DMC) electrolyte along the aging and cycling process. Fig. 3 compares the  ${}^7\text{Li}$  NMR spectra for a  $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$  sample simply soaked in electrolyte and another one cycled once (one charge followed by one discharge) between 2.5 and 4.5 V. These two samples spent approximatively the same amount of time exposed to the electrolyte. The line shape of the two spectra are clearly different. The spectrum obtained for the soaked sample displays a broad and featureless signal characteristics of an extremely important interaction between the bulk and the diamagnetic lithium species of the interphase grown from the contact with the electrolyte. It is very similar to the spectrum acquired after exposition to the ambient atmosphere [9], a confirmation that the line shape is related to the physical interactions existing at the interface but not to the chemical nature of the species found in the interphase. The higher relative intensity in the central part of the spectrum of the cycled sample indicates that part of the interphase is submitted to weaker interactions. It can be explained by a partial removal of the interphase leading to an increased separation from the bulk of active material, and thus a weaker interaction between the interphase and the active material. Another explanation would involve the stacking of additional species on the top of the firstly formed interphase from simple electrolyte contact. Most probably both phenomena can occur simultaneously as surface species removed during the cycling can be deposited again with a different configuration. Nevertheless, these results support the “layered” or “stacked” architecture of the interphase proposed by Edström et al. [17] and show that this stacked architecture can be observed directly using MAS NMR. Moreover, these results demonstrate clearly the strong influence of the potential on the interaction/intimacy of the interphase with the bulk of active material and the change in the configuration of species contained in the interphase on the surface of the electrode active material along the electrochemical cycling.

#### 4. Conclusions

${}^7\text{Li}$  MAS NMR has been used to observe the diamagnetic species forming the electrode/electrolyte interphase on the surface of paramagnetic electrode materials. Experiments performed

on a model system made of  $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$  mixed with various  $\text{Li}_2\text{CO}_3/\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$  ratios show clearly that the species forming the interphase correspond to a complex system and the thickness of the interphase has to be considered. New lithium-containing species stacked on the pre-existing layer result in lithium nuclei further away from the paramagnetic material and therefore, submitted to a weaker dipolar interaction leading to a sharper  $^7\text{Li}$  MAS NMR signal.

$^7\text{Li}$  MAS NMR experiments performed on samples stored in  $\text{LiPF}_6$  electrolyte and after one electrochemical cycle demonstrate the strong influence of the variation of potential on the interaction/intimacy of the electrode/electrolyte interphase with the bulk of active material and the evolution of the configuration of stacked species contained in the interphase on the surface of the electrode active material. These results show that  $^7\text{Li}$  MAS NMR is very promising tool to describe subtle changes in the electrode/electrolyte interphase.

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