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^7Li and ^1H MAS NMR observation of interphase layers on lithium nickel oxide based positive electrodes of lithium-ion batteries

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^7Li and ^1H magic-angle spinning (MAS) NMR spectra were recorded for $\text{Li}(\text{Ni}_x\text{Co}_y\text{Al}_z)\text{O}_2$ samples. The ^7Li MAS NMR signal of the layer on the pristine material is close to that of Li_2CO_3 in close contact with it. Its lineshape, due to dipolar interaction with electron spins of the material, is drastically different from that of pure Li_2CO_3 . Upon hydration, this layer grows, while ^1H NMR suggests that some lithium in the material is replaced by protons. Upon electrochemical cycling, the original layer is replaced by a different one, the solid electrolyte interphase, with distinct ^7Li and ^1H NMR signatures, showing its largely organic nature.

The so-called solid electrolyte interphase (SEI) layer on carbon-based negative electrodes of Li-ion batteries is of paramount importance, and its characterization has been widely discussed using various techniques. Among them, ^7Li NMR is able to detect the signal corresponding to the SEI, although it does not allow one to analyze its nature.¹⁻³

On the positive electrode side, the presence of an SEI is an issue more recently addressed, but of equal importance with the underlying evidence that it plays a key role in the mechanisms leading to performance degradation of the batteries upon aging.⁴ To our knowledge, a single ^7Li static NMR characterization of such layers by Wang and co-workers has been reported so far, showing that, similar to the negative electrode, the SEI is observed as a featureless signal, not so clearly separated from that of Li in the active material, which nevertheless allows its amount to be determined.⁵ This, however, does not allow its nature to be discussed.

^7Li magic angle spinning (MAS) NMR is increasingly used to study the local structure of positive electrode materials for Li-ion batteries.^{6,7} In Ni-based materials, the presence of low-spin (LS) Ni^{3+} ions with a $t_{2g}^6 e_g^1$ electronic configuration leads to strong paramagnetic interactions of two kinds. First, the dipolar interaction between the nuclear spins of the probed Li ions and the electronic spins in their environment leads to a very strong broadening of the NMR signals. It is, at least partly, averaged out by fast spinning of the sample at the magic angle. Second, if the local structure offers the possibility for some density of electron spins to be transferred from the Ni ions to the Li ones, a Fermi contact interaction arises, which shifts the resonance line away from normal chemical shift values for Li^+ . These interactions have been widely discussed,⁸ although the contact shift mechanisms have only recently been addressed using theoretical calculations.⁹

Using ^7Li MAS NMR, Tucker *et al.* showed evidence of the formation of Li-containing SEI species on substituted LiMn_2O_4 spinel-type materials upon moisture contamination.¹⁰

In this paper, we report a ^7Li and ^1H MAS NMR observation of the surface layer on $\text{Li}(\text{Ni}_x\text{Co}_y\text{Al}_z)\text{O}_2$ materials. We discuss the lineshape of the signal observed, as well as its changes upon hydration, and preliminary results on the SEI of electrochemically aged materials.

Experimental

Two samples (called S1 and S2) with the same $\text{Li}(\text{Ni}_{1-y-z}\text{Co}_y\text{Al}_z)\text{O}_2$ composition but with variants in the preparation conditions have been studied.

X-ray diffraction (XRD) patterns were recorded with a scan step of 0.02° ($2\theta_{\text{Cu}}$) for 40 s on a Siemens D5000 diffractometer, equipped with a copper anticathode (Cu K α) and a diffracted beam monochromator. They showed no evidence of impurity phase in the pristine materials.

A series of mixtures of lithium carbonate with sample S1 was prepared, with increasing degree of intimacy: (i) S1 powder was mixed with 2 wt % Li_2CO_3 using a pestle and mortar for 15 min. (ii) S1 powder was mixed with 2 wt % Li_2CO_3 using a planetary grinder (Fritsch) for 15 min. A tendency of preferential aggregation of the Li_2CO_3 powder was observed on the agate balls, so that the actual mixture may be poorer in Li_2CO_3 . (iii) S1 powder was mixed with 2 wt % Li_2CO_3 using a pestle and mortar for 15 min, and heated to 750°C under oxygen for 12 h.

XRD showed that the material remained unchanged and showed evidence of Li_2CO_3 in all three cases.

Hydrated samples were prepared from S1 as follows: the S1 powder was placed in a stove containing water-saturated air at 60°C for one and four days. XRD showed the presence of Li_2CO_3 on the hydrated samples.

S1 was used as active material in the positive electrode of a battery with a carbon negative electrode and 1 M LiPF_6 in propylene carbonate, ethylene carbonate, and 3 vol dimethyl carbonate (PC/EC/3DMC) as electrolyte, which underwent an accelerated aging test as follows. The cell was cycled once between 4.1 and 3.0 V, then charged to 4.0 V and kept at this voltage for one month at 40°C . After a discharge down to 3.0 V, the cell was dismantled and the positive electrode washed with DMC.

^7Li NMR spectra were recorded using Bruker Avance 500 (194.4 MHz) and 300 (116.6 MHz) spectrometers. Standard Bruker MAS probes were used with 4 mm o.d. zirconia rotors, the material being mixed with dry silica (typically 50 wt %). The spinning speed used was 15 kHz for the experiments at 194.4 MHz, whereas 10 kHz spinning allowed a comparable separation of the spinning sidebands at 116.6 MHz. Single pulse (preacquisition delay 14 μs) and Hahn echo sequences were used, with a 90° pulse duration of 2.4 μs . The echo delay was equal to one rotor period, to synchronize the rotational and spin echoes. The recycle delay varied in the 2-500 s range. Approximate T1 longitudinal relaxation times were measured by the inversion-recovery method, using the duration for which a zero intensity signal was recorded, as equal to $T1 \times \ln 2$. All spectra are referred to a 1 M aqueous solution of LiCl, set at 0 ppm.

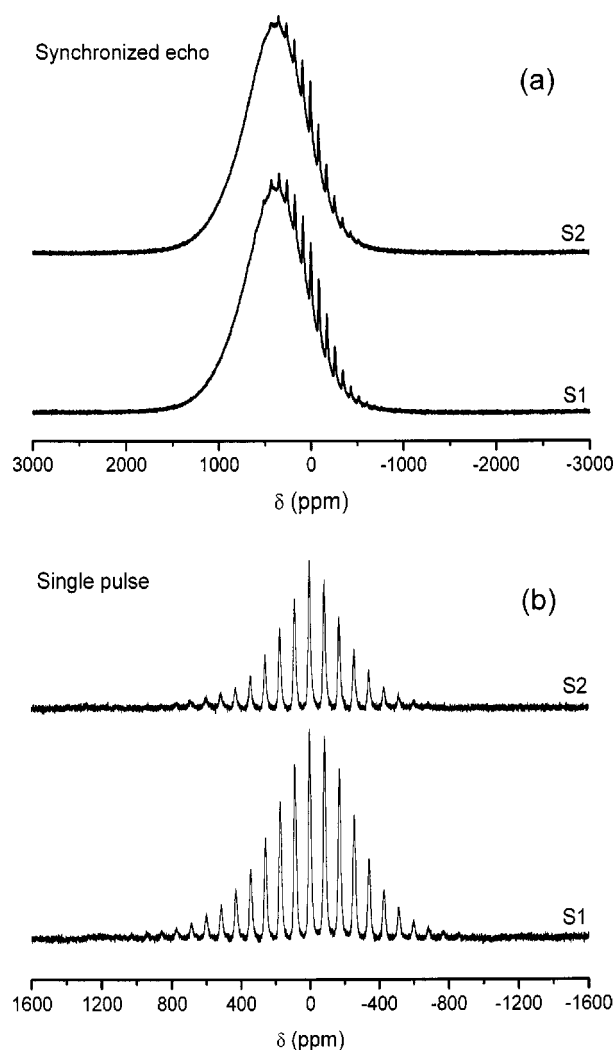


Figure 1. ^7Li MAS NMR spectra of two different $\text{Li}(\text{Ni}_{1-y-z}\text{Co}_y\text{Al}_z)\text{O}_2$ samples in (a) echo and (b) single pulse conditions (116.6 MHz, spinning 10 kHz, recycle delay 2 s). Spectra are plotted with an absolute intensity scale.

The “absolute scale” spectra for sets of identical NMR experiments are plotted taking into account the number of scans and mass of sample.

^1H NMR spectra were recorded on a Bruker Avance 300 spectrometer, with the same MAS probe and rotors as for ^7Li . To avoid parasitic signals from the probe, due to the relatively small amount of protons in the samples, a Hahn echo sequence was used with a 100 μs delay (10 kHz spinning speed), the 90° pulse was 2.4 μs , and the recycle time was 30 s. The spectra are referred to tetramethylsilane (TMS) (0 ppm).

Results and Discussion

Figure 1 shows the ^7Li MAS NMR spectra of two different $\text{Li}(\text{Ni}_{1-y-z}\text{Co}_y\text{Al}_z)\text{O}_2$ compounds (with the same composition) in the echo and single pulse conditions. One observes a very broad and shifted signal (*ca.* 400 ppm) in echo conditions. It arises from those lithium ions present in the active material, due to the dipolar and contact shift interactions discussed in the Introduction. That, even under relatively fast MAS conditions, the line is not separated into spinning sidebands is due to the magnitude of the dipolar interaction, and to the existence of a wide distribution of possible environments for Li in terms of number of Ni ions as first and second neighbor, leading to a distribution of overlapping signals. This signal is so broad that it cannot be observed in single pulse conditions,

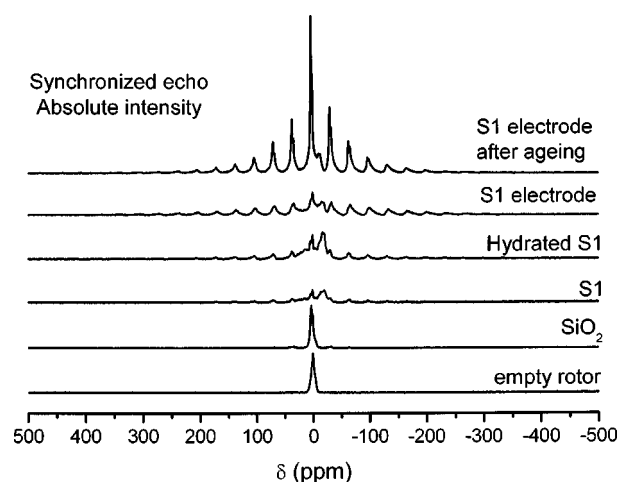


Figure 2. ^1H MAS NMR spectra of (a) the empty rotor, (b) silica, (c) pristine $\text{Li}(\text{Ni}_{1-y-z}\text{Co}_y\text{Al}_z)\text{O}_2$ (S1) material, (d) hydrated S1, (e) pristine electrode based on S1, and (f) the aged electrode based on S1 (300 MHz, synchronized echo, spinning 10 kHz, recycle delay 30 s). The spectra are plotted with an absolute intensity scale.

because the corresponding short free induction decay detection (FID) is lost in the dead time of the spectrometer (10–12 μs).

In addition to this broad signal, a much narrower one is also observed, both in single pulse and echo conditions. Its isotropic position is close to 2 ppm, and it includes a large number of well-separated spinning sidebands. That the broad signal is not observed in single pulse condition, using a preacquisition delay of 14 μs , makes the narrow signal easier to analyze in such condition. Because it exhibits no Fermi contact shift, it must result from Li ions not bonded, either directly or via oxygen, to the paramagnetic ions. Considering the amount of Ni ions present in the material, this can correspond only to Li ions not present in the active material; this is therefore an evidence for an interphase layer present on its surface. The magnitude of this signal, and therefore the amount of the layer, is different for the two samples studied (Fig. 1b), whereas the signals corresponding to Li in the two samples are identical (Fig. 1a). This is expected, considering the preparation detail (that we cannot comment here) in which the two samples differ, and that they have identical bulk compositions.

The ^1H MAS NMR spectrum of S1 is shown in Fig. 2; it exhibits a very weak signal in the 0 to 10 ppm region, broader (*i.e.*, with more spinning sidebands) than that recorded for the residual protons found in any sample, like, for example, silica, or even the empty rotor, but not significantly more intense. It therefore seems that the signal from the few residual protons in the probe is broadened by the strong hyperfine interactions with the paramagnetic compound. More important, another set of weak signals is also observed in the -10 to -20 ppm region. This is an unusual chemical shift range for protons, and may correspond to species inserted in the active material, in substitution for Li^+ ions, which are submitted to a Fermi contact interaction from the electron spins of the material (Ni^{3+}). The other spectra shown in Fig. 2 are discussed in the following.

Lithium carbonate-active material mixtures.—To try to understand the lineshape of the narrow signal described in Fig. 1, we investigated the ^7Li MAS NMR spectra of a series of mixtures of lithium carbonate with the active material, prepared as described in the Experimental section. Figure 3 thus shows the corresponding single pulse spectra, in comparison with those of Li_2CO_3 and of S1; the approximate T1 of each signal is also given. The spectrum of Li_2CO_3 exhibits a lineshape (envelope of the spinning sidebands) characteristic of a first-order quadrupolar interaction. ^7Li is a spin 3/2 nucleus so that, when present in a crystallographic site around which the electrical field gradient does not present a strictly spheri-

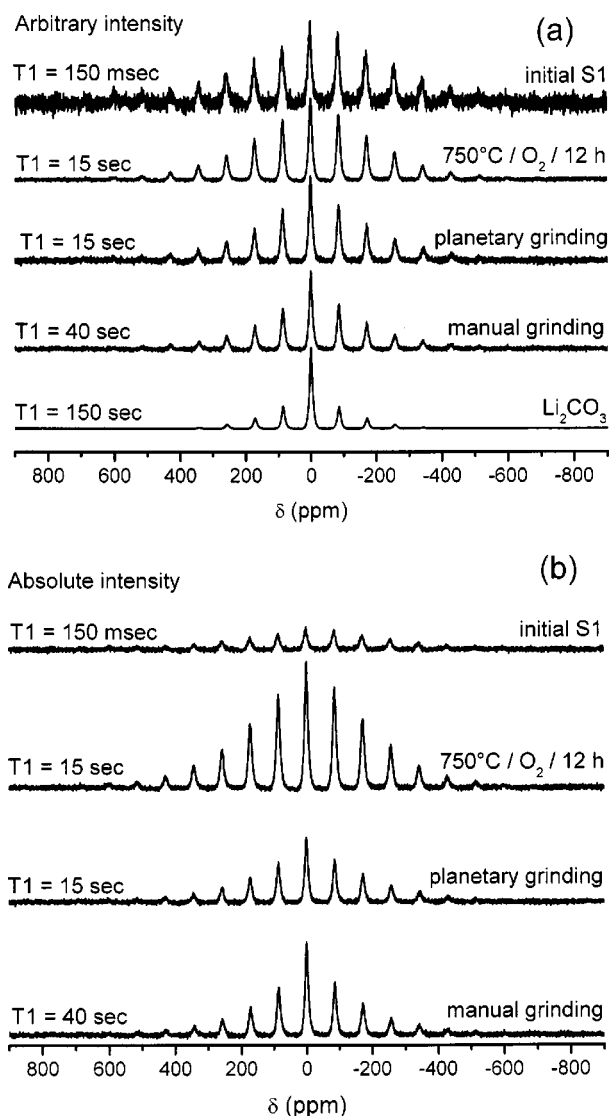


Figure 3. ^7Li MAS NMR spectra of Li_2CO_3 and various mixtures with the $\text{Li}(\text{Ni}_{1-y-z}\text{Co}_y\text{Al}_z)\text{O}_2$ active material S1 (single pulse, 116.6 MHz, spinning 10 kHz) plotted with (a) an arbitrary and (b) an absolute intensity scales. The T1 values (inversion-recovery) are indicated.

cal symmetry, the three NMR transitions do not occur at the same frequency, and do not exhibit the same lineshape, leading to the MAS spectrum shown in Fig. 3. In this spectrum, the isotropic signal results essentially from the central transition ($-1/2, 1/2$), while the spinning sidebands result essentially from the two satellite transitions ($-3/2, -1/2$ and $1/2, 3/2$). The T1 of ^7Li in this material is long, showing that no specific interaction is able to induce the longitudinal relaxation of the magnetization.

When the mixture of Li_2CO_3 becomes more and more intimate with the $\text{Li}(\text{Ni}, \text{Co}, \text{Al})$ material, the lineshape clearly evolves from the quadrupolar one of Li_2CO_3 to a broad and featureless one for the original layer on the material. Figure 3b shows the same set of spectra in an absolute scale, showing that the spectra of the mixtures are clearly not a mere superposition of that of pure lithium carbonate and that of the original layer on S1 (the amount of Li_2CO_3 detected by NMR in the planetary ground mixture is smaller; this is due to some loss of Li_2CO_3 on the agate balls as described in the Experimental section). The ^7Li MAS NMR lineshape of lithium carbonate, which is clearly detected by XRD in the mixtures, is therefore strongly affected by its proximity with the active material. Obvi-

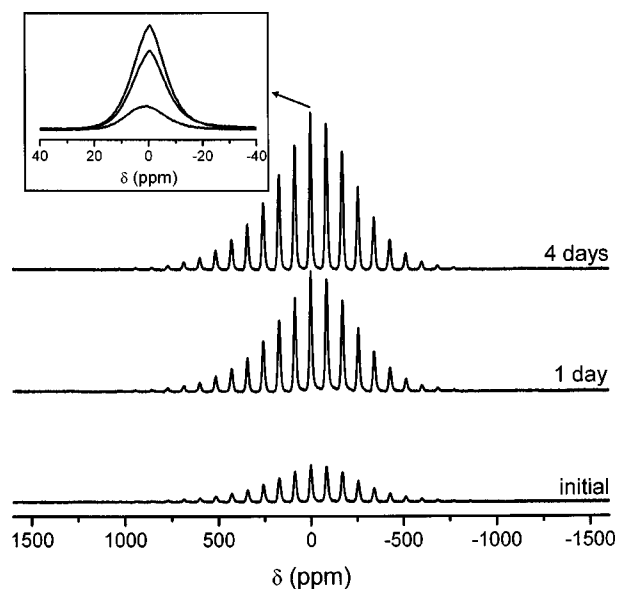


Figure 4. ^7Li MAS NMR spectra of the active material before and after a one day and a four day hydration process (116.6 MHz, spinning 10 kHz, single pulse, recycle delay 30 s). The spectra are plotted with an absolute intensity scale.

ously, this is due to a strong dipolar interaction with the electron spins present in the compound. Exerting through space, with a $1/r^3$ dependence on the distance, this interaction can take place between two different materials, contrarily to the Fermi contact shift one, which requires some orbital overlap between Li and the paramagnet. This clearly does not happen for this signal, which remains at the position of pure Li_2CO_3 .

Another consequence of the proximity of lithium carbonate with the paramagnetic material is the drastic shortening of T1, which is a classical effect in NMR.

Thus, according to the NMR observation, the lithium-containing layer present on the pristine material is fully compatible with lithium carbonate in intimate contact with the active material. However, it is difficult to discriminate between lithium carbonate and lithium hydroxide in such conditions.

Evolution of the layer upon hydration.—Figure 4 shows single pulse MAS NMR spectra of the pristine S1 material and after one and 4 days of hydration. The lineshape of the signal is hardly changed for the hydrated samples, although its magnitude is considerably larger. Besides, the T1 of Li in the layer of the hydrated samples is longer than that on the pristine material since the full signal intensity is not obtained with a recycling delay of 2 s, contrarily to the pristine material. Expansion of the isotropic line (inset) shows a very slight change in the signal, with an additional contribution slightly shifted to the low part-per-million values. We believe this suggests the presence of lithium hydroxide on the growing layer, converting into lithium carbonate, which is detected by XRD on the hydrated samples (and is not on the pristine material due to its much smaller amount).

The ^1H NMR spectrum of the hydrated sample (Fig. 2) shows a signal similar in shape to that of the pristine material, but slightly more intense, both for the positively shifted signals (corresponding to residual protons from the probe as discussed above plus protons from the surface layer of the material) and for the negatively shifted one (corresponding to intercalated protons, as discussed above). This suggests that the Li-containing layer is created by the replacement of some Li^+ ions in the material by protons, while the proton content of the surface layer is low, in particular when compared to the electrochemically aged material, as discussed in the following.

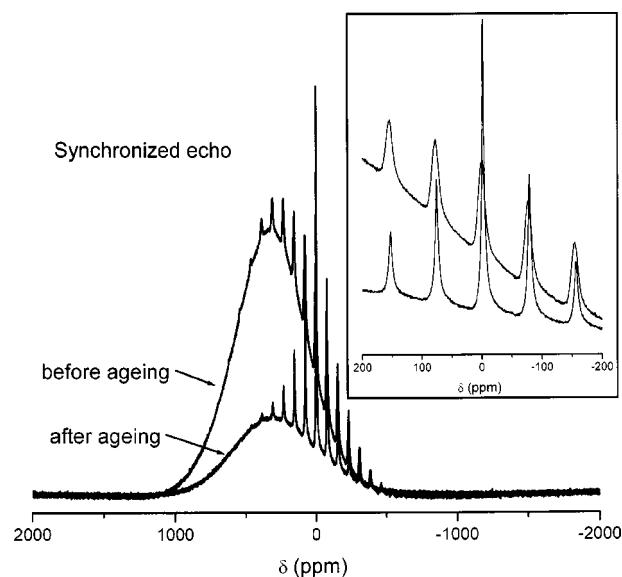


Figure 5. ^7Li MAS NMR spectra of the S1 based electrode before and after an accelerated aging test (194.4 MHz, synchronized echo, spinning 15 kHz, recycle delay 2 s).

It therefore seems that hydration essentially leads to the growth of the initial Li-containing layer, with only a small change in its nature. It is likely that the part of the layer further apart from the paramagnetic material exhibits a longer T1, like that observed for the mixtures in Fig. 3. Ionic mobility properties may also influence T1, so that the T1 issue is probably much more complex than just a signature of the proximity with the paramagnet.

Effect of electrochemical aging.—Figure 5 shows the ^7Li MAS NMR echo signals for the electrode based on the S1 material before and after the aging test. Both the signal of the material and that of the surface layer are considerably altered.

The change in the signal of Li in the active material resides mostly in its magnitude. This is most probably because the material is not fully reintercalated with Li during the discharge. The presence of Li vacancies must allow for a significant ionic mobility, which affects the spin refocusing process, and consequently decreases the magnitude of the echo signal.⁸ The necessary rotor synchronization prevents one from using shorter refocusing delays in the echo sequence.

As to the signal of Li in the interphase layer, its lineshape and magnitude are clearly different from the pristine electrode case. As shown by the expansion in the inset, it seems that the original signal has partly disappeared, and is partly replaced by a signal with a different lineshape, less influenced by proximity with the active material. This signal also exhibits significantly narrower spinning sidebands than the original layer, as well as a slightly different chemical shift. The nature of this signal is unclear at the present stage, and its identification requires further investigation.

The ^1H MAS NMR spectra of the pristine and aged electrodes are shown in Fig. 2, together with those of the pristine and hydrated materials. The presence of organic binder in the pristine electrode leads to a series of signals in the 0 to 10 ppm region, again with a large number of spinning sidebands probably due to the dipolar interaction with the paramagnetic active material. Upon aging, much more intense signals in this region appear, mainly at 4 and 1.5 ppm, with a set of spinning sidebands apparently narrower than for the

pristine electrode. This clearly shows that the layer in the aged electrode (SEI) is mostly organic in nature, contrary to that of the pristine compound. Note also that the position of the smaller negatively shifted signal is altered in the aged electrode, which we believe is due to the difference in the actual oxidation state of the cations in the cycled material, leading to a different contact shift interaction on the intercalated protons.

Conclusion

We have observed the interphase layer present at the surface of $\text{Li}(\text{Ni}_{1-y-z}\text{Co}_y\text{Al}_z)\text{O}_2$ using ^7Li MAS NMR, with a combination of single pulse and echo experiments, as well as ^1H MAS NMR. In the presence of the paramagnetic active material, the signal of Li in the layer is dominated by a very strong dipolar interaction with the electron spins of the material, which renders its lineshape very different from that of the same compound in the absence of paramagnetic material. Its chemical shift is nevertheless not affected. However, the narrow chemical shift range of solid mineral or organic compounds possibly present in the layer does not allow any *a priori* discrimination. Therefore, it is difficult to deduce readily the nature of the layer from its MAS NMR signal. However, we show that, for the pristine material, this signal is similar to that observed for lithium carbonate in close contact with the paramagnetic compound, and that this layer grows upon hydration of the material. ^1H MAS NMR shows a very weak proton signal in the surface layer of both the pristine and hydrated compounds, confirming that this layer is inorganic in nature. It also suggests the presence of protons intercalated in the material, whose amount increases upon hydration, thus releasing lithium ions that form the growing layer. After an aging test, the layer is partly replaced by a different one, the SEI with a distinct ^7Li NMR lineshape, while ^1H MAS NMR clearly shows that the layer of the aged material is mostly organic in nature, contrary to that on the pristine compound. We therefore believe that a systematic investigation using the NMR characterization described here should allow some understanding of the surface layer present on the pristine positive electrode materials of Li-ion batteries, as well as of the SEI formed during battery operation.

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