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Residual Li₂O degrades PVdF during the preparation of NMC811 slurries for Li-ion batteries

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⁷Li MAS NMR quantification of lithiated species at the surface of aged NMC811 industrial powders and slurries shows that the electrode preparation process exacerbates Li extraction. A combination of ⁷Li MAS NMR and XPS suggest a new reaction for the PVdF binder degradation, involving in fact Li₂O as the reagent and the formation of LiF.

The slurry instability is a serious and well-known issue affecting the industrial production of lithium ion batteries and is caused by residual lithium compounds present at the surface of the cathode material (Li(Ni_xMn_yCo_{1-x-y})O₂ or NMC). Although the problem is recognized by the battery industry, the scarce communication between academia and industry and the limited access to industrial information lead to an important disparity in the knowledge of this issue between the two realities.¹ The often observed “slurry gelation” is most likely due to the PVdF instability and leads to catastrophic issues in the mass production line. An optimal viscosity of the slurry is actually essential to obtain high quality slurries and thence high performance batteries.

Residual lithium species are usually considered as limited to LiOH and Li₂CO₃.¹ Consequently, a surface reaction between the more basic LiOH and PVdF is frequently suggested in the literature as a possible cause of the widely observed slurry gelation.¹⁻⁶ Such a phenomenon was indeed found to occur more likely for high Ni compositions —more affected by the formation of lithiated surface species— than during the preparation of electrodes based on NMCs with lower Ni content. According to this explanation, the PVdF would undergo dehydrofluorination following the simplified reaction (CH₂-CF₂)_n + LiOH → (CH=CF)_n + LiF + H₂O proposed by G.J. Ross et al.⁷ However, as highlighted by Seong et al., this topic has not been critically considered in the literature yet and a proper method to confirm the suggested reaction and to accurately characterise the residual lithium species has never been used to this end.

In this communication, we show how a detailed description of the relevant compounds, and their quantification, can be obtained by using a combination of ⁷Li MAS-NMR and XPS. The analysis of industrial powder and slurry samples was conducted to suggest a new reaction for the PVdF binder degradation, involving Li₂O as the reagent.

Three industrial NMC811 powders (UMICORE) with different amounts of surface lithiated species and the corresponding dried slurries (mixtures of active material (AM), conductive

carbon, PVdF and NMP) were analysed (Table 1). The powders were obtained placing the pristine industrial powder under three controlled atmospheres, allowing to attain different surfaces and reactivities, as highlighted in a previous study.⁸ Sample 1 and Sample 2 powders were obtained after aging in air under relative humidity RH=30% for 15 minutes and 2 days, respectively. On the other hand, the pristine powder was left in synthetic air atmosphere with RH \approx 70% and without any carbon dioxide for 2 days to prepare Sample 3. Dried slurries were then made at Umicore's production plant using these three powders as AM, in typical fabrication conditions. The analysis of dried slurries instead of electrodes coated on the current collector was performed to avoid energetic processes inducing further degradation of the polymer. ⁷Li MAS-NMR was used to estimate the amount of surface diamagnetic lithium, as described in our previous article.⁸ Results are reported in Table 1. The extraction of lithium from the AM to form the considered surface species increases in all the samples during the slurry preparation step, demonstrating that additional changes affect the NMC811 surface upon this procedure.

	Amount ($\mu\text{mol/g}_{\text{AM}}$)		Aging conditions
	Powder	Slurry	
Sample 1			
Total Li	115.6	162	RH=30%, 15 minutes
Li ₂ O	46	59	
Li ₂ SO ₄	10	19	
LiOH	3	2	
Li ₂ CO ₃	0.3	1	
LiF	---	2	
Sample 2			
Total Li	160	198	RH=30%, 2 days
Li ₂ O	63	76	
Li ₂ SO ₄	15	18	
LiOH	2	3	
Li ₂ CO ₃	1	2	
LiF	---	3	
Sample 3			
Total Li	98.5	163	RH \approx 70%, without CO ₂ , 2 days
Li ₂ O	43	46	
Li ₂ SO ₄	6	22	
LiOH	0.3	6	
Li ₂ CO ₃	0.1	4	
LiF	---	13	

Table 1. Samples description. Surface diamagnetic lithium amounts evaluated by ⁷Li MAS-NMR given in $\mu\text{mol}_{\text{Li}}/\text{g}_{\text{AM}}$ with an error of $\pm 10\%$

The analysis of XPS spectra evidences the presence of LiF in all the analysed slurries. This compound, obviously absent in the powders, is characterised by a peak around 684.5 eV; this component is visible in the typical F 1s spectrum, obtained for these samples, reported in Figure 1a. ¹⁹F MAS-NMR was also performed to confirm the presence of LiF in the dried slurries independently of the X-Ray exposure, which was proven to be energetic enough to break C-F bonds in too harsh conditions.⁹ Figure 1b represents a typical spectrum obtained for slurries, showing the peak around -205 ppm, corresponding to the LiF contribution, indicated by straight orange arrows (see the inset of Figure 1b). Its relative spinning sidebands (dashed orange arrows in Figure 1b) are also marked. Since the slurry is not exposed to any energetic source during MAS-NMR analysis, the hypothesis of a PVdF degradation coming from X-rays

exposure can definitely be excluded and new hypotheses to explain the appearance of an LiF signal are needed.

The identification of LiF allowed us fully deconvoluting the isotropic resonance of the ^7Li MAS-NMR spectra by including a contribution at -1 ppm (Fig.2, complete spectra and deconvolutions in Fig. S1) in addition to the four contributions (Li_2CO_3 , LiOH , Li_2SO_4 , Li_2O) already confirmed for the pristine powder as detailed in our previous work.⁸ The method combining NMR and XPS data is explained in Reference⁸. It was thence possible to estimate the amount of each species (in $\mu\text{mol/g}_{\text{AM}}$) found in the six (powders and slurries) samples (also collected in Table S1 in SI together with the parameters used for the fit). Before proceeding to the interpretation of these results, some preliminary observations are needed:

- i- Slurries are prepared in an industrial dry room. The relative humidity of this environment (typically controlled to be between 0.7 and 1.5%) is sensibly lower than that of the climatic chamber samples were aged in. Reactions with H_2O (if there is any occurring) will be therefore ignored when analysing the effect of the electrode preparation step. Conversely, the presence of elevated amounts of CO_2 in the dry room suggests that reactions with the carbon dioxide should be considered.
- ii- Li_2SO_4 coming from the synthesis (residue from the sulphate precursors) is considered to be inhomogeneous in the analysed samples. Any increase or decrease in its quantity is thus not taken into account.
- iii- In all cases, the following order is found for the ^7Li NMR FWHMs: $\text{Li}_2\text{O} > \text{LiOH} > \text{Li}_2\text{CO}_3$, suggesting that, overall, Li_2O is closest to the active material while Li_2CO_3 is mostly located in the outermost part of the surface contamination layer.¹⁰ After the slurry preparation step, the LiF FWHM is always larger than those for LiOH and Li_2CO_3 (with exception of Sample 1 in which $\text{FWHM}_{\text{LiF}} = \text{FWHM}_{\text{LiOH}}$), suggesting a stronger interaction with the paramagnetic AM. Hence, the formation of LiF would occur at the interface between Li_2O (very close to the AM) and LiOH (closer to the material than Li_2CO_3).

Taking into account these arguments and the quantities reported in Table S1, we suggest that the degradation of the PVdF binder to form the observed LiF is induced by Li_2O , and not LiOH , as previously proposed in the literature, according to the reaction $(\text{CH}_2-\text{CF}_2)_n + \text{Li}_2\text{O} \rightarrow (\text{CH}=\text{CF})_n + \text{LiOH} + \text{LiF}$ (Reaction 1). Moreover, considering that Li_2O is detected in a considerably higher amount than LiOH by ^7Li MAS-NMR, its involvement in the degradation of the polymer binder appears to be most reasonable.

As a matter of fact, the LiOH quantity increases in both Sample 2 and 3 slurries, in apparent contradiction with its consumption upon reaction with the PVdF to give LiF. Moreover, Li_2O (or lithia) is an extremely basic species, which could thence react with the PVdF more easily than LiOH , due to its higher basicity.¹¹ In addition, it is particularly convincing to compare the F 1s XPS spectra acquired by Im et al. on pristine electrodes based on pure lithia, and those presented by Grissa et al. for NMC532 PVdF based electrodes.^{4,6} NMC electrodes appear significantly less affected by PVdF degradation than lithia ones, even after heavy calendaring of the former.^{4,6}

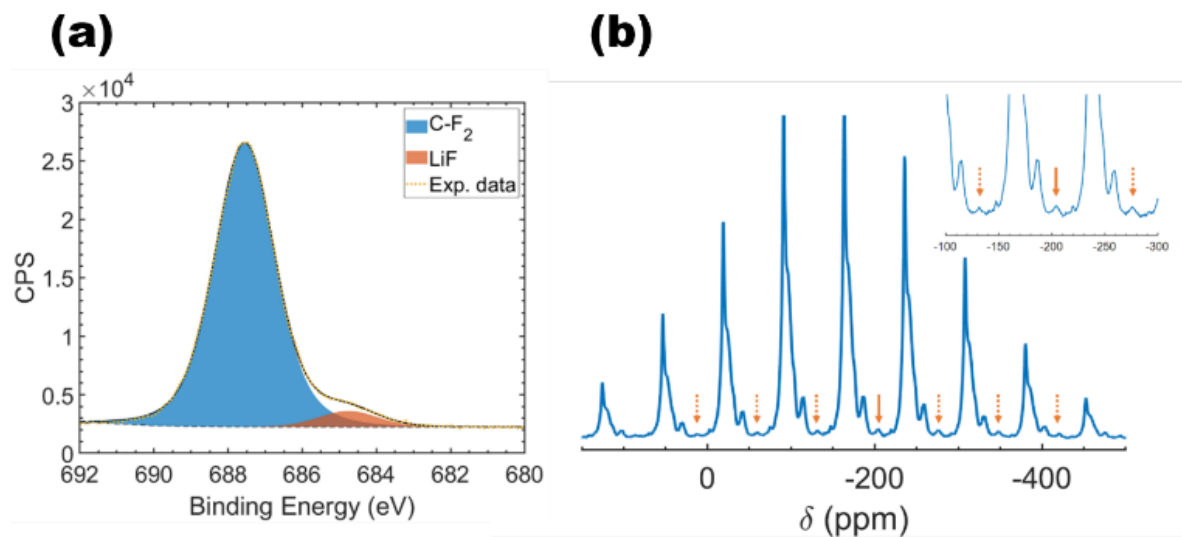


Figure 1. Experimental proof of the occurrence of LiF (in orange) at NMC811 dried slurry surfaces by XPS (a) and ¹⁹F MAS-NMR (b).

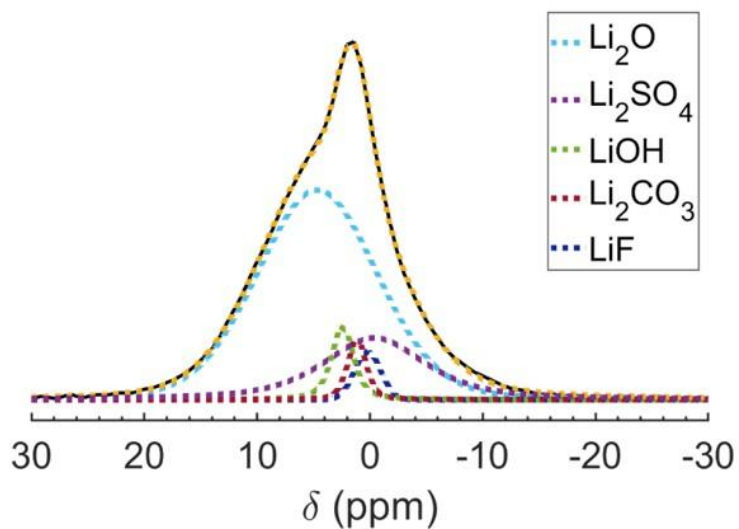
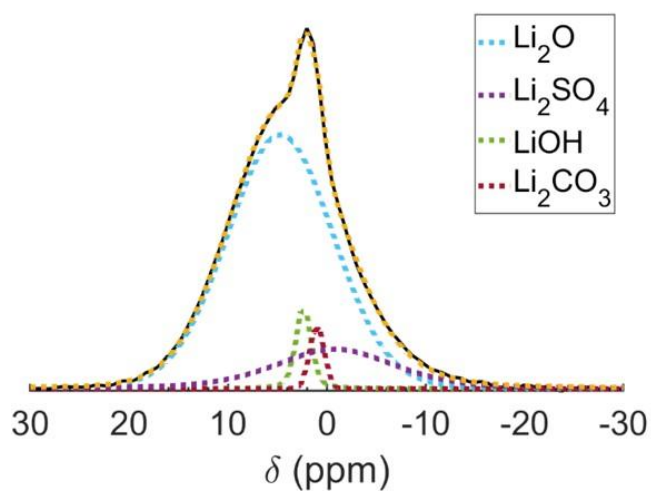


Figure 2. Deconvolution of ^7Li MAS NMR spectra of NMC811 pristine powder (a) and dried slurry (b)

A quantitative examination of the NMR data can help confirming the implication of lithia in the degradation process. We can now follow the evolution of the amount (in $\mu\text{mol/g}_{\text{AM}}$) of the species taking part in the suggested Reaction 1, as found by ^7Li MAS-NMR, and reported in Table S1. It should also be reminded that due to the constant presence of carbon dioxide, LiOH is consumed to form Li_2CO_3 via the reaction: $2\text{LiOH} + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{H}_2\text{O}$ (Reaction 2). Let us take Sample 2 as an example. During the electrode preparation (slurry), $3 \mu\text{mol/g}_{\text{AM}}$ of LiF are formed at the NMC811 surface. According to Reaction 1, this should be accompanied by the formation of the same quantity of LiOH. Similarly, $1 \mu\text{mol/g}_{\text{AM}}$ of Li_2CO_3 was formed during the process, as indicated in Table S1, meaning that $2 \mu\text{mol}$ of LiOH were consumed, according to Reaction 2. Consequently, the amount of LiOH should increase by $1 \mu\text{mol/g}_{\text{AM}}$ ($3 \mu\text{mol/g}_{\text{AM}}$ formed – $2 \mu\text{mol/g}_{\text{AM}}$ consumed), which is in line with the quantities found by ^7Li MAS-NMR. By using the same reasoning, the LiOH evolution upon electrode preparation of Sample 3 can be perfectly explained as well, confirming our hypothesis.

Concerning Sample 1, the evolution of lithiated species amounts is not completely in line with previous observations for Sample 2 and 3. Actually, following the above explained process, we found that $0.4 \mu\text{mol}$ of LiOH should have been consumed during the slurry preparation step, whilst $1 \mu\text{mol}$ are actually consumed according to results reported in Table S1. Since Sample 1 was aged only 15 minutes in the climatic chamber, the NMC811 surface had most likely not completely reacted with the humid atmosphere, making the assumption (i) above mentioned untrue for this sample. If the AM surface were not in equilibrium with water contained in the atmosphere, multiple reactions could still occur during the slurry preparation. Therefore, the identification of reactions taking place at the Sample 1 surface turns out to be more complicated than for Samples 2 and 3, emphasizing the complexity of reactions occurring at the surface and involving the surface of the active material, the surface species, and the surrounding media.

The reaction path by which Li_2O induces the PVdF degradation is hard to infer from our study, but it would be surely different from that relying on the high nucleophilic nature of OH^- ions, mainly proposed in aqueous solutions. We believe that the liquid media, be it water or minute H_2O quantities often present in NMP, are not essential to the occurring of the reaction. As a matter of fact, it was proven that positive electrodes calendaring (i.e. in dry state) greatly increases the LiF production; similarly, such effect is also observed by Im et al. in lithia based electrodes.⁴

In summary, we propose a new interpretation of LiF production in NMC811 slurries based on MAS-NMR and XPS results, induced by the presence of reactive Li_2O at the surface of the positive electrode material. Neither the quantity of LiOH at the AM surface nor the minute quantities of water in NMP would be decisive parameters in the degradation of the PVdF binder. Lithia quantity should thus be considered more carefully in order to preserve the mechanical properties of these high-energy Li-ion battery electrodes.

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