***Operando* NMR and XRD study of chemically synthesized LiC_x oxidation in a dry room environment**

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ABSTRACT: We test the stability of pre-lithiated graphite anodes for Li-ion batteries in a dry room battery processing room. The reaction between LiC_x and laboratory air was followed using *operando* NMR and x-ray diffraction, as these methods are sensitive to change in Li stoichiometry in graphite. There is minimal reactivity between LiC_6 and N_2 , CO_2 or O_2 ; however, LiC_6 reacts with moisture to form lithium (hydr)oxide. The reaction rate follows zero-order kinetics with respects to intercalated lithium suggesting that lithium transport through the graphite is fast. The reaction occurs by sequential formation of higher stages— LiC_{12} , then LiC_{18} , and then LiC_{24} —as the hydrolysis proceeds to the formation of Li_xOH_y and graphite end products. Slowing down the formation rate of the Li_xOH_y passivation layer stabilizes of the higher stages.

INTRODUCTION:

Increasing the amount of Li is a known strategy for increasing performance and cycle life of rechargeable Li-ion batteries. The excess lithium is used in preparation and maintenance of the solid electrolyte interphase (SEI) formed primarily at the anode surface during cycling. Industry typically accomplishes this by increasing the amount of cathode material or using lithium-rich materials. This strategy results in a significant amount of wasted cathode material, which decreases the energy density of the battery. FMC Inc. has proposed a strategy to increase the lithium content in batteries by producing pre-lithiated anode materials. (1) However, pre-lithiation presents inherent difficulties: 1) pre-lithiated materials are only 0.1–0.2 V more positive than Li metal and therefore are highly reductive; 2) they spontaneously react with both the battery electrolyte and $\text{O}_2/\text{H}_2\text{O}$ exothermically (2); and 3) they produce a passivation layer of lithium carbonate and oxide may inhibit Li-transport. (3) Confronting processing prob-

lems of reactive pre-lithiated anodes is important for providing alternate means to improve battery performance by increasing Li loading or allowing for SEI synthesis.

Here we assess the stability of LiC_x in dry room battery processing conditions by following the reaction of LiC_x with ambient air using *operando* nuclear magnetic resonance (NMR) and x-ray diffraction (XRD). During processing, LiC_x may react with trace amounts of moisture present within the environment and the electrolyte to form an oxide-rich SEI as illustrated in Figure 1. This work shows that while LiC_6 can be readily made, it is a moisture getter and will rapidly delithiate. The kinetics of delithiation is zero-order with respect to the Li within the graphite host; the rate-limiting step being the permeation of H_2O throughout the anode material. We also show that the slow chemical delithiation proceeds in similar fashion to electrochemical delithiation, although it is irreversible. A passivating layer of lithium (hydr)oxide forms during the reaction which protects higher stages of lithiated graphite for over 24 h. Therefore, controlled exposure to moisture or organic solvents after synthesis may allow for safe handling of pre-lithiated anode materials for Li-ion battery processing.

This system is also a model for the study of chemical delithiation. We show that rapid reordering of the high stages of intercalated Li proceeds through mobile layers, *i.e.* defects or lacunar layers. Therefore the classic model of Daumas and Herold (4) is in agreement with our XRD and NMR data and recent *operando* electrochemical transmission electron microscopy (ec-TEM) results from Regan et al. (5). Lastly, we discuss delithiation mechanism and suggest possible reasons for the chemical stability of higher stage LiC_x .

EXPERIMENTAL SECTION:

Synthesis of Li_xC_6 . The carbon source was a mesophase graphite (MGP-A, Pred Materials) annealed under Ar(g) for 3 h at 500 °C and immediately transferred into an Ar atmosphere glovebox. Stabilized lithium metal powder (SLMP[®], FMC Lithium) was stored in the same glovebox and used as received. The MGP-A (3 g) and desired molar ratio of SMLP were added to a gas-tight high-density polyethylene container along with 10 g of dried ZrO_2 milling media (5 mm dia.). The container was then placed

into a stainless steel bomb, sealed, locked into a SPEX 8000M mixer/mill, and shook vigorously for 1.5 h. Afterward, the container was brought back into the glovebox for further use.

Characterization. The graphite particles were imaged using a Hitachi-S4800 scanning electron microscope (SEM) operating at 2 kV with a probing current of 10 μ A. N₂ Brunauer, Emmet, and Teller (BET) surface area measurements were performed with an Autosorb-1-C (Quantachrome Instruments) at 77 K. X-ray diffraction (XRD) samples were prepared in the glovebox by sealing powders between two 25 μ m-thick Kapton[®] sheets using Torseal[®]. Measurements were made using an X'pert Pro diffractometer (PANalytic, Inc.) with Cu-K α x-ray source operating at 45 kV and 40 mA. Scattering angles 10–100° (10–30° for time-resolved spectra) were collected in 0.02° steps with a count time of 0.4 s per step. The spectra were indexed with powder diffraction files (HighScore Plus, ICDD and COD) 96-101-1061 for graphite, 04-002-4997 for LiC₆, and 35-1046 for LiC₁₂.

⁷Li NMR spectra were recorded on a 9.4T Bruker 400 Avance III NMR spectrometer operating at a ⁷Li resonance frequency of 155.57 MHz. Lithium mobility is high enough at room temperature in lithiated graphites so that motional narrowing of the resonance produces ⁷Li line widths on the order of 1 kHz in these nominal solids, sufficient to resolve several Knight-shifted LiC_x stages in static samples (6). Spectra typically were acquired at room temperature (295 K) using a one pulse experiment with minimum dead times delay (5 μ s), a recycle delay of 10 s, and a 90° pulse optimized for the material. Conductive samples detune the probe; therefore, careful electrical optimization of the NMR coil is required for these samples. Highly conductive materials (LiC₆₋₁₂) required on-resonance pulse times of 14-15 μ s to achieve a 90° pulse; products (LiC₁₈₋₂₄ and LiOH) required a shorter 90° pulse, typically 10 μ s. Chemical shifts were measured on samples whose height exceeds the NMR coil length by at least 1 cm and are reported with respect to an external 1 M LiCl(aq) solution: $\delta = 0$.

NMR samples were prepared in an argon-filled glovebox by sealing 0.3 g of sample in a standard 5 mm NMR tube using Torseal[®]. Samples sealed in this way are stable over a period of weeks. Continuous hydrolysis reactions were initiated by drilling a 1.2 mm hole through the seal and inserting the open sam-

ple tube into the bore of the NMR magnet, which could be flushed with either dry N₂ or ambient (wet) air. Step hydrolysis reactions were performed by introducing aliquots of selected gases by syringe injection into the NMR tube, displacing the argon cover gas. For these experiments the NMR tube was resealed with a tight-fitting plastic NMR cap that makes a gas-tight seal that protects the integrity of the sample over the time duration of the measurements up to several hours.

RESULTS AND DISCUSSION:

Particle morphology. The mechanical reactor used to synthesize Li_xC₆ from lithium and graphite has been discussed previously (2). The schematic and SEM images in Fig. 1 show that milling crushes the spherical particles (20 μ m dia) into disks (10 μ m dia. x 1 μ m thick). Milling also increases the BET specific surface area from 1 m² g⁻¹ to 90 m² g⁻¹, which increases the concentration of reactive sites for delithiation. The N₂ isotherm also showed hysteresis at P/P₀ = 0.45 confirming the presence mesoscale pores in the milled samples. The crystallite size judged by the (002) peak (related to the scattering peak's full width half maximum of the XRD peaks by the Scherrer equation) (7) in all the milled products—regardless of Li content—were near 180 Å.

XRD of Prepared Graphites. The NMR and XRD spectra of the milled LiC₆ and LiC₁₂ shown in Figure 2 match recorded spectra of electrochemically synthesized Li-graphites (8,9,10,11,12). The accepted structure of LiC₆, shown in Figure 3, involves Li atoms occupying each gallery between graphite layers, which increases the (002) and (004) lattice spacing from 3.33 Å (26.7°) to 3.68 Å (24.2°), and from 1.67 Å (54.8°) to 1.84 Å (49.4°), respectively, when fully lithiated to LiC₆ (13). The prepared LiC₁₂ was determined to be 98% phase pure. Unlike other Li-graphite stoichiometries, LiC₁₂ has an appreciable (001) scattering peak at 7.08 Å (12.5°) and the (002) spacing is between LiC₆ and graphite, 3.53 Å (25.2°). The accepted structure of this phase has every other gallery filled with Li (Figure 3), however the stacking of the graphite sheets has not been fully solved. Lastly, the XRD of the excess lithiated product (>25 wt.%) was added to the LiC₆ preparation showed no diffraction peaks from Li metal and therefore is identical to LiC₆. Assuming that the excess lithium is evenly spread out on the surface of the LiC₆ par-

ticles, the Li layer thickness is estimated at 5–10 nm. The small scattering length density of Li ($3.92 \times 10^{-6} \text{ Å}^{-2}$) and the thinness of the layer rationalize the absence of metallic Li in the XRD.

NMR of Prepared Graphites. The chemical shifts of LiC_x stages reported in the literature vary considerably and therefore care should be taken when comparing results between laboratories (6,14,15,16,17). A spread in chemical shift values can be due to sample geometry and container; small samples, less than the rf detection coil length, packed in conventional 5 mm NMR tubes display chemical shifts ca. 1 ppm lower in chemical shift value than equivalent samples that extend beyond the coil dimensions. This effect can be greatly exaggerated (up to 10 ppm!) by analyzing small samples in Shigemi tubes that are not susceptibility matched. Since there is no effective loss of resolution in the ^7Li spectra from samples that extend beyond coil length, we suggest that magnetic susceptibility contributions to the chemical shift reported by other laboratories can be made uniform by using samples whose column height is greater than the coil length, as reported herein.

In the ^7Li NMR spectra (Figure 2a), LiC_6 shows a center band resonance corresponding to the $\pm 1/2$ transition at 47.9 ppm with the lower intensity outer transitions $\pm(3/2, 1/2)$ of this spin 3/2 nucleus. The spacing between the prominent horns of the $\pm(3/2, 1/2)$ outer transitions is the quadrupole frequency (ω) and is equal to half the quadrupole coupling constant (see Fig. 2a) (6,14). The outer transitions are apparent because the Li atoms are well-ordered in the graphite, maintaining axially symmetry with respect to the adjacent carbon p-orbitals (14). The quadrupole frequency of LiC_6 is measured to be 23 kHz. LiC_{12} has a chemical shift of 50.8 ppm and quadrupole frequency of 17 kHz. As mentioned, in this stage Li fills every other graphite gallery. The NMR chemical shift reported for LiC_{12} derives from a 4:1 mixture of LiC_{12} and LiC_{18} obtained by direct synthesis. It has been speculated that there are lacunar Li layers in LiC_{12} (14). That is, LiC_{12} is not an entirely stable stoichiometry; rather, there is a slight disproportionation to give rise to trace amounts of LiC_6 and "liquid-like" LiC_{12-18} , shown in Fig. 3 (8,18,19,20). In this mixture the LiC_{18} chemical shift is 19.7 ppm, the same value found in pure stage LiC_{18} (Figure 2a). The pure stage LiC_{18} , which is thermodynamically stable, has a quadrupole frequency of 19 kHz, agreeing with

previous reports (6,14,15,20). Lastly, when an excess amount of Li (>25 wt.%) was added to the LiC₆ preparation, the Li metal resonance is observed at 270 ppm along with the inner and outer transitions from LiC₆.

Characterization of Reacted Graphites. Before we discuss the *operando* experiments, we will characterize the end product. When lithiated graphite is exposed to moisture it spontaneously reacts to form a passivation layer. During this reaction intercalated lithium leaves the graphite galleries towards reactive edge site. While NMR is sensitive to the chemical nature of the intercalated Li, it is insensitive to the chemical nature of the Li-salt product. The product shows a broad resonance peak around 0 ppm in Figure 2a, typical of a hydrated Li salt, along with a peak at 11 ppm. The latter peak seems to correspond to LiC₂₄ and contains faint outer transitions, which confirm the presence of intercalated Li.

The product contains broad diffraction peaks in Figure 2b matching those from LiOH or LiOH•H₂O, along with Bragg reflections of graphite and a high stage Li-C₆ compound, presumably LiC₂₄. Rietveld refinement gave mass fraction composition of 0.19, 0.28, and 0.63, corresponding to LiC₂₄, LiOH(•H₂O), and graphite. Assuming that 14/15th of the intercalated Li reacts forming LiOH and leaving behind LiC₂₄, the mass fraction of LiC₂₄, LiOH, and graphite would be 0.19, 0.24, and 0.57, respectively, in good agreement with the spectral fitting. The overall mass balanced equation can be written as

Operando NMR (discussed in detail later) obtained throughout the hydrolysis support this equation. The loss of LiC₆ is initially accompanied by signal growth at 20 ppm (LiC₁₈). As the reaction proceeds to ca. 80-90% completion the peak maxima of the product shifts to 11 ppm, the expected position for higher stages—LiC₂₄. Sparks caused by the addition of water to this final product further support the presence of a reactive LiC₂₄ stage. This final stage is stable for days.

Stability with Select Gases: Figure 4 shows the evolution of the ⁷Li NMR spectrum upon addition of selective gases, recording the disappearance of the LiC₆ peak at 47 ppm and the growth of the product's peak at 11 ppm. There was minimal change caused by replacing the Ar(g) in the NMR tube with ambient

air that was stored over calcium sulfate (Drierite) which removed the moisture. The addition of a small aliquot of ~ 1000 ppm H_2O in $\text{N}_2(\text{g})$ instantly triggered delithiation. The reaction stopped when all of the H_2O was consumed, i.e., the extent of delithiation relates to the amount of $\text{H}_2\text{O}(\text{g})$ added. When the sample was exposed to ambient air, the remaining LiC_6 was rapidly consumed. Surface products derived from XPS analysis (2) include the presence of a few oxo-species: LiCO_3 , Li_2O , LiOH , and alkyloxides. There were no observed diffraction peaks from crystalline Li_2CO_3 . Since XPS probes only a nanometer into the surface and Li_xOH_y is a known CO_2 getter, it is possible that the surface Li_2CO_3 was due to the hydroxide's reaction with $\text{CO}_2(\text{g})$. Therefore, LiC_6 is very sensitive to moisture but it is stable in a well-dried environment (<1 ppm H_2O) provided that airflow is minimized.

Deintercalation Kinetics: The reaction of LiC_6 with ambient air was followed using ^7Li NMR and XRD (focusing on the (002) scattering); the results are shown in Figure 5. Both the NMR tube and XRD pouch were sealed under $\text{Ar}(\text{g})$ to delay the reaction's initiation. Controlling access of ambient air into the NMR tube can modify the rate of hydrolysis. By varying the NMR probe purge gas (either dry N_2 or humid air), the hole size through the NMR tube seal, or by varying the sample packing density, the rate of reaction was systematically varied from 5–60 min. With the addition of ambient air, the peak corresponding to LiC_6 in both the NMR and XRD decrease. In the NMR spectra, Fig. 5a, a peak at 18 ppm increases and shifts to 11 ppm as the reaction progresses. We identify the initial peak as LiC_{18} and associate the shift with further delithiation to high stage LiC_{24} . The NMR does not distinguish easily between LiC_6 and LiC_{12} during the course of the reaction because the peaks are only 3 ppm apart. Thus the NMR spectra follow the disappearance of the LiC_{6-12} signals and the emergence of LiC_{18-24} and Li-salt.

The XRD spectra resolve the individual stages and detect the raw graphite (Fig. 5b). Here, laboratory air enters the sample holder by permeating through the Kapton film, i.e. mass transport of H_2O is orders of magnitude slower than for the NMR sample. The (002) peak from LiC_6 (24.2°) decreases as LiC_{12} peak increases (25.2°). After a few hours, the peaks associated with LiC_{18} (25.8°) and LiC_{24} (26.3°) appear along with graphite (26.9°). The fact the higher stages appear with raw graphite suggests that delithi-

ation of LiC_{18} forms not only LiC_{24} but also raw graphite. In other words, delithiation proceeds through sequential stages— LiC_{12} , then LiC_{18} , and then LiC_{24} —before resulting in graphite as the final product. This is in excellent agreement with the slow electrochemically-driven delithiation followed by *operando* XRD from Reynier *et al.* (10).

A representative fitting of the NMR spectra is given in Fig. 6a. The resonances from the lithiated graphites, LiC_6 and LiC_{18-24} , both central and outer transitions, were fitted in addition to the broad signal from $\text{LiOH}(\bullet\text{H}_2\text{O})$ for each spectrum. The integrated peak intensities from the deconvolution of each spectrum were used to provide molar ratios of the Li species. Plotting the results against time (Fig. 6b) shows that the signal from $\text{LiC}_{6/12}$ decreases linearly while those of the salt and higher stages increase linearly. There is little loss of total Li signal, *i.e.* all the Li species are accounted for. These facts suggest that the reaction rate is zero-order with respect to intercalated Li (LiC_{6-12}). Likewise, we fitted the (002) XRD scattering signals and plotted their area in Figure 7. The signal from LiC_{6-12} decreases linearly as that of LiC_{18-24} increase in the same manner thus confirming the zero-order kinetics with regard to Li. Given this, we speculate that the reaction is surface-limited or that the rate at which H_2O enters the cell is rate determining. The latter is most likely since: 1) the specific surface area of the material is relatively large, $90 \text{ m}^2 \text{ g}^{-1}$; 2) Li transport is fast in graphite (19); 3) the two cells had different H_2O transport rates and the rate of the reaction in the cells reflected this—the NMR tube allowed a higher flux of ambient air to displace the Ar(g) . Therefore, the overall pseudo-rate expression can be written as

$$r = kp_{\text{H}_2\text{O}}^n \quad (2)$$

where $p_{\text{H}_2\text{O}}$ is the water vapor pressure and n is the reaction order with respect to $\text{H}_2\text{O(g)}$.

Modeling. We modeled the reaction assuming that Li discharge followed a Langmuir-type host isotherm. However, Levi and Aurbach (21,22) clearly demonstrated that electrochemical Li intercalation and concordantly delithiation more closely follows a Frumkin isotherm. That is to say, Li insertion occurs near occupied host sites. Their model is similar to the classic model of Daumas and Herold (4), who explained the staging in terms of an island-growth model where 2D-Li clusters formed within the galleries

and diffused throughout the graphite as islands, see Fig. 3. The near-neighbor-type attraction is reserved within a particular gallery while electrostatic repulsion functions to suppress intercalation into adjacent galleries. Monte Carlo simulations of Kirczenow (23) showed that Daumas-Herold domains form thermodynamically stable structures and that deintercalation proceeds through a Stage 2 (LiC_{12}) intermediate that propagates throughout the material as a wave. The simulated transition kinetics between Stage 1 and 2 was found to be pseudo-zero order at high over-potentials as was the Stage 2 to 3 transitions. Stage 4 was the longest-lived stage having a small amount of Stage 3 present. The stability seemed to originate from the large energy barrier required for the islands to diffuse past heavily populated intercalation domains at the edge. That is, the same repulsive interactions that facilitate the 2D islands growth and staging also facilitate the stability of Stage 3 and 4 islands during deintercalation.

Given that the milled particles are small, density of edge sites is large, and Li transport within the galleries is fast, a series of Langmuir-type rate expressions corresponding to Li insertion into particular stage galleries is fitting as an approximation. We take the reaction as proceeding through the following mass-balanced steps:

As written, the rate-determining step (rds) involves H_2O access to an active surface site (Eq. 2), but as a first approximation we couple mass transport and adsorption together in this step. This mechanism predicts zero-order kinetics with respect to Li in the graphite. Note, although the mechanism as written implies that LiC_{24} is air stable, this stability is likely aided by a surface (hydr)oxide passivation film and the aforementioned energy of activation barrier for deintercalation near edge sites.

A qualitative simulation of the kinetics given the above conditions is shown in Figure 8. The kinetic expressions assume the general irreversible mass-action form, *e.g.* for Eq. (4) the rate expression is

$$v_2 = k_2 (X_{\text{LiC}_6})^2 \theta_{\text{H}_2\text{O}} \quad (8)$$

The system of differential equations (DE) was solved using Maple (Maplesoft). Each DE was of the form, $\frac{dX_i}{dt} = r_i$, where r_i is the net rate of production of species i , *e.g.*, $r_{\text{LiC}_{12}} = v_2 - 3 v_3$. Adding together the calculated molar fraction, X_i , of LiC_6 and LiC_{12} , and those of LiC_{18} and LiC_{24} , we thus simulated the kinetic data from the NMR. The molar fractions of the individual stages—including raw graphite—were used to simulate the XRD data. The only difference between the two models is the flux of H_2O in the system (approximated by a change in $p_{\text{H}_2\text{O}}$). The simulations are in qualitative agreement with observed kinetics. This suggests that for sufficiently small graphite particles ($<10 \mu\text{m}$), Langmuir-host isotherms can be used to model Li intercalation kinetics.

As stated before, chemical delithiation occurs similarly to electrochemical lithiation and delithiation. Large scale reordering is required when every other gallery is filled (Stage 2, LiC_{12}) to where every third gallery is filled (Stage 3, LiC_{18}). Interestingly, recent *operando* electrochemical transmission electron microscopy (ec-TEM) shows that changes in staging of intercalated sulfate occur suddenly as a wave through the graphite flake (5). NMR spectra presented here and elsewhere (15,17,24) show that there are different Li environments in LiC_{12} , notably highly crystalline sites and more mobile sites. It is speculated that these mobile sites are due to the defect and lacunar layers within the graphite, Figure 3 (6,14). These sites may function to lower the energy required for rapid ordering the Li absorption sites (20,23).

CONCLUSIONS:

Pre-lithiation may allow for more control over the formation of the solid-electrolyte interphase, and possibly increase lithium loading and battery life. However, SPEX-milled pre-lithiated anode materials have high surface area and reactivity similar to Li metal, making its use in Li-ion battery manufacturing difficult. We found that the LiC_x exhibited high stability in moistureless air, showing little reaction with oxygen, nitrogen, and carbon dioxide gases. However, in the presence of moisture, delithiation spon-

taneously occurs and Li-(hydr)oxide forms at the surface, causing a change in Li-C stoichiometry from LiC_6 to LiC_{24} . Intermediate stages were formed during delithiation but LiC_{24} was the only stabilized stage, being stable in humid air for days since the (hydr)oxide layer inhibits further delithiation. The reaction is zero-order with respect to intercalated Li and is controlled by mass transport of H_2O throughout the powder sample. Our results are in close agreement with Monte Carlo simulations and first-principle calculations.

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8:

Figure 1: Schematic of experiments (left) and SEM images (right) of annealed **a)** MGPA; **b)** ball-milled lithiated-MGPA.

Figure 2: ^7Li NMR (**a**) and XRD (**b**) spectra of lithiated graphites and the end product of LiC_6 's reaction with ambient air. Vertical lines in the NMR spectra guide the eye with respect to peak position changes. Vertical lines in the XRD spectra mark refined peaks of the product, with the green marks corresponding to a Li_xOH_y phase. Legends displayed in plots.

Figure 3: A representative schematic of Daumas and Herold's classic model (4,22) for the evolution of staging during lithiation and delithiation of graphite. Lacunar layers function to lower the energy of activation for reordering of the stages, *i.e.* lithium mobility is high here.

Figure 4: *Operando* ^7Li NMR spectra following the loss of LiC_6 and the increase in $\text{LiC}_{18/24}$ and LiOH signal during reaction with various gasses. The contour plot shows the fitting the end product with peaks from LiC_6 , broad LiOH , and $\text{LiC}_{18/24}$.

Figure 5: **a)** *Operando* ^7Li NMR spectra following the loss of $\text{LiC}_{6/12}$ (48/51 ppm) and the increase in higher stages (19/11 ppm) and the broad Li-salt signal (0 ppm). **b)** *operando* XRD spectra of the (002) region following the loss of LiC_6 (24.1°) and the increase in higher stages and graphite ($25.3\text{--}26.7^\circ$).

Figure 6: **a)** Fitted end-product's NMR spectrum from LiC_6 hydrolysis with peaks for LiC_6 , broad LiOH , and $\text{LiC}_{18/24}$. **b)** Integrated areas of the fitted peaks (including the outer transitions) in the *operando* NMR spectra are given plotted vs. reaction time, with residuals calculated from the difference between the sum of the areas and the total area, *i.e.*, initial Li in sample.

Figure 7: **a)** Fitting of the product's XRD data of the (002) region to peaks indicative of major stages of lithiated graphite including raw graphite. **b)** Integrated intensities of the fitted peaks in the *operando* XRD spectra with linear fits to each species. Residual plot indicates change in the area, which is proportional to the total mass of the sample.

Figure 8: Simulation of the NMR (top) and XRD (bottom) experiments obtain from solving the mass-action differential equations for concentration of Li sites and C_6 sites, respectively. The rate of H_2O adsorption is the same in both plots.